

Title: Term values of the electronic states of the molecule

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In the beginning of this module, we have learnt the formation of the molecule from atoms. We have also learnt the molecular orbital and the electronic states of the molecules.

In the last lecture we have seen the electronic transitions and the vibrational structure of these electronic transitions.

The nomenclature of these electronic states needs to be understood and the transition selection rules need to be evaluated so that the electronic transitions between the two electronic states of the molecule could be explained.

There are several ways to determine the term values of the electronic states. However, in this lecture we will focus only one procedure.

In lecture-26, when we solved the Schrödinger equation for the hydrogen molecule ion to understand the stability of the electronic states, we get a number of different potential energy curves. We refer to these states as the electronic states of the molecule.

The electronic state corresponding to the lowest energy is known as ground electronic state and the others are known as excited electronic states.

In analogy to the case for atomic electronic states, we will identify these states using molecular term symbols. The method for determining these molecular term symbols is somewhat more complicated than that for atomic term symbols.

The manifold of the electronic states can be obtained, as for atoms, by the successive bringing together of the parts. This building up of the atom can be done only in one way. But for the molecule there are three different ways.

Process-I: The molecule may be built up by bringing the atoms together. This means that the molecular states will be the result of the given states of separated atoms. Thus, when we carry out for all possible combinations of separated atomic states, we obtain the complete manifold of the states of the molecule.

Process-II: Instead of developing the molecular states from the separated atoms, we can start from the so called united atom and split them hypothetically.

Process-III: Since we have already learnt the electronic arrangements of molecules in lecture-27, we can start with the electronic configuration of the orbital of the molecule and then determine the molecular term values as we have done it in case of atoms. In this lecture we will determine the term values of the electronic states following this procedure.

The “*terms*” tell us the values of certain angular momenta. In the case of molecule, we have to define the angular momenta in terms of the orbital angular momentum L and the spin angular momentum S of the atoms.

As we know that in the atom L and S are the good quantum numbers when we determine the terms because the motion of the electrons in an atom takes place in a spherically symmetrical field of nuclear force.

In case of spin orbit coupling, L and S couple to give total angular momentum $J (= L + S)$. In case of linear molecule, the symmetry of the field in which the electrons move is reduced.

There is only axial symmetry about the internuclear axis (the cylindrical symmetry) created by the strong electric field of the nuclei. This destroys the relationship between J , L and S . Not only that even the L ceases to be the good quantum number. As a consequence, only the component of L along the inter-nuclear axis is a constant of motion or good quantum number.

In an electric field, unlike the magnetic field, reversing the directions of motion of electrons does not change the energy of the system. Which means that the energies of $M_L = +1$ and $M_L = -1$ will be degenerate. Therefore, it is convenient to classify the electronic states of diatomic molecules according to the values of $|M_L|$ not L .

Thus we define the projection of L along the inter-nuclear axis as Λ as shown in figure-34.1.

$$\text{So, } \Lambda = |M_L| \dots\dots\dots(34.1)$$

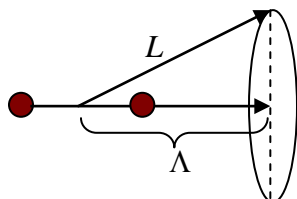


Figure-34.1

According to equation 34.1, for a given value of L , the quantum number Λ can take the values

$$\Lambda = 0, 1, 2, \dots, L$$

$$= \left| \sum_i \lambda_i \right| \dots \dots \dots (34.2)$$

Where λ is the projection of l of individual electrons along internuclear axis.

For example, $\lambda = 0$ for a σ electron, $\lambda = \pm 1$ for a π electron and so on.

Depending on the values of Λ , the electronic state is defined.

For $\Lambda = 0$, it is Σ state

For $\Lambda = 1$, it is Π state

For $\Lambda = 2$, it is Δ state

For $\Lambda = 3$, it is Φ state

Note here that the degenerate π molecular orbital is defined as π_+ and π_- , where $+$ and $-$ subscripts represent the clockwise and anticlockwise rotation.

An example of the two electrons is shown in figure-34.2.

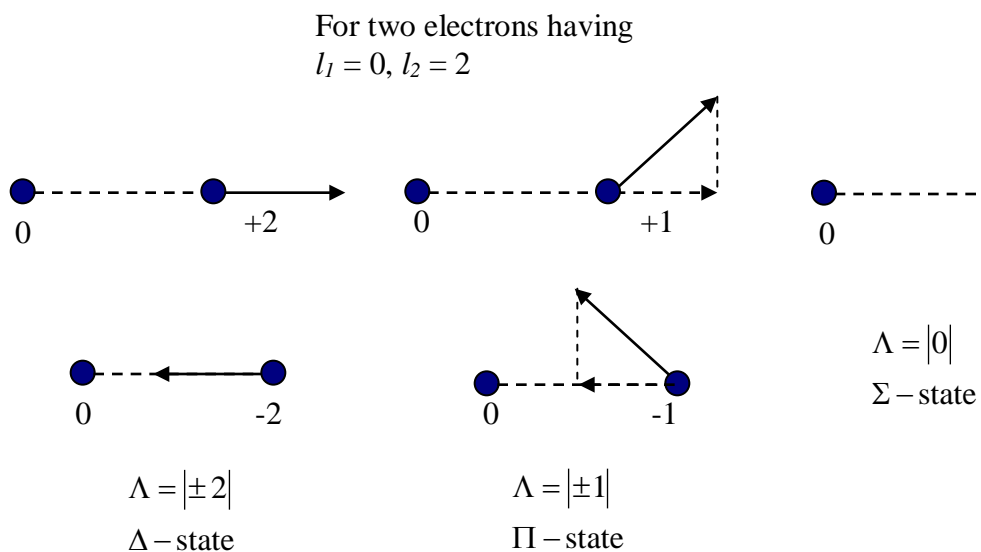


Figure-34.2

A molecular term symbol labels the molecular states and specifies the total spin and orbital angular momentum of the molecule, along with various other symmetries.

The term symbol is written as

$$^{2S+1} \Lambda_{(g/u)}^{(+/-)}$$

In the following we will understand the meaning of these notations.

1. As defined, Λ is the quantum number for the total orbital angular momentum L of the electrons about the inter-nuclear axis.
2. As defined, S is the total spin angular momentum quantum number, formed from the individual electron. Spin quantum number of single electron $s = 1/2$, and $m_s = \pm 1/2$.

For one unpaired electron, $S = s = 1/2$ (a doublet state with $2S + 1 = 2$).

For two unpaired electrons, the possible values are $S = 1$ and 0 . For $S = 1$, gives triplet ($2S + 1 = 3$) and for $S = 0$ gives singlet ($2S + 1 = 1$) states.

3. Symmetric molecules are having a centre of symmetry. The gerade (g) or ungerade (u) subscripts apply only to these molecules and labels the symmetry of the electronic wavefunction with respect to inversion through this centre. For the molecule, this can be thought of as simple multiplication of functions of even or odd symmetry of the individual electrons. In the following table provides the resultant symmetry of the molecule from two electrons.

Individual electrons	Molecular
gerade (g) \times gerade(g), even \times even	gerade, g
Gerade (g) \times ungerade (u), even \times odd	ungerade, u
ungerade (u) \times ungerade (u), odd \times odd	gerade, g

4. The $+/-$ superscript applies only to Σ state ($\Lambda = 0$), and labels the symmetry of the electronic wavefunction with respect to reflection in a plane containing the nuclei.

Now we will carry out some examples of diatomic molecules to find out the ground state from its electronic configuration.

Closed shell configuration:

For any closed shell molecular electronic configuration, for example $1s\sigma_g^2 1s\sigma_u^2 2s\sigma_g^2$, there is no net orbital and spin angular momentum. So, $\Lambda = 0$ and $S = 0$. The term will be always, $^1\Sigma_g^+$ state.

One unpaired electron:

Let us take the case of hydrogen molecular ion H_2^+

The electronic configuration

$1s\sigma_g^1$ (figure-34.3).

$$M_L = 0$$

$$\Lambda = 0; \Sigma \text{ state}$$

$$S = 1/2$$

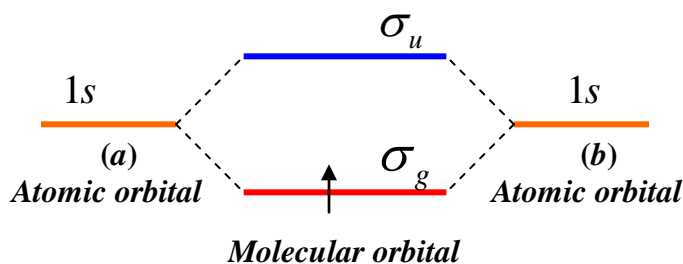


Figure-34.3

Bond order

$$= (\text{no. of electrons in bonding orbital} - \text{no. of electrons in anti-bonding orbital}) / 2$$

$$= (1-0) / 2 = 1/2 > 0. \text{ Molecular electronic state is stable.}$$

Molecular term for the ground state is $^2\Sigma_g^+$

$He_2^+ \quad 1s\sigma_g^2 1s\sigma_u^1$ (figure-34.4)

$$M_L = 0$$

$$\Lambda = 0; \Sigma \text{ state}$$

$$S = 0 + 1/2 = 1/2$$

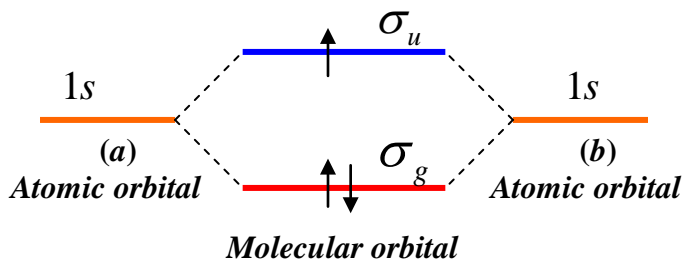


Figure-34.4

$$\text{Bond order} = 1/2 > 0.$$

Stable ground state will form.

Parity = $g \times g \times u = u$ Molecular term for the ground state is $^2\Sigma_u$

Two electrons system:

Hydrogen molecule H_2 . Molecular electronic configuration is $1s\sigma_g^2$ (figure-34.5).

Bond order = 1; molecule is stable in the ground electronic configuration.

$\Lambda = 0$; $S = 1$ or 0 ;

But due to Pauli exclusion principle, $S = 0$ for closed shell.

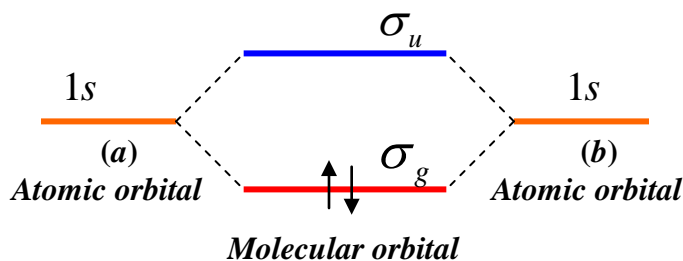


Figure-34.5

Parity = $g \times g = g$

Molecular term for the ground state

is $^1\Sigma_g^+$

Let us draw the Λ - M_S table as we have done in case of atoms. Here since $\Lambda = \left| \sum_i \lambda_i \right|$ we

will write as $(\lambda_1^{+/-}, \lambda_2^{+/-})$ where + and - represents $m_s = +1/2$ and $m_s = -1/2$, respectively.

For σ electrons $\lambda = 0$, so the Λ - M_S table for $1s\sigma_g^2$ configuration is

M_S Λ	0
0	$(0^+, 0^-)$

Now, we can write down the wavefunctions.

The spatial wavefunction is $\phi_{spatial} = \sigma_g(1)\sigma_g(2)$

The spin wavefunction is $\chi_{spin}^{Antisymmetric} = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$

The total molecular wavefunction is

$$\Psi(^1\Sigma_g^+) = \frac{1}{\sqrt{2}}\sigma_g(1)\sigma_g(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

For He_2 molecule, the electronic configuration $1s\sigma_g^2 1s\sigma_u^2$

Bond order = 0; No bond forms, ground state is not stable.

For Li_2 molecule, the electronic configuration $1s\sigma_g^2 1s\sigma_u^2 2s\sigma_g^2$

Bond order = 1; Ground state is stable.

$\Lambda = 0$; $S = 1$ or 0 ; but due to Pauli exclusion principle, $S = 0$

So, the molecular term for the ground state is $^1\Sigma_g^+$

For O_2 molecule, Molecular electronic configuration is given in figure-34.6

$1s\sigma_g^2 1s\sigma_u^2 2s\sigma_g^2 2s\sigma_u^2 2p\sigma_g^2 2p\pi_u^4 2p\pi_g^2$ and Bond order = $(6-4)/2 = 1$, molecule is stable.

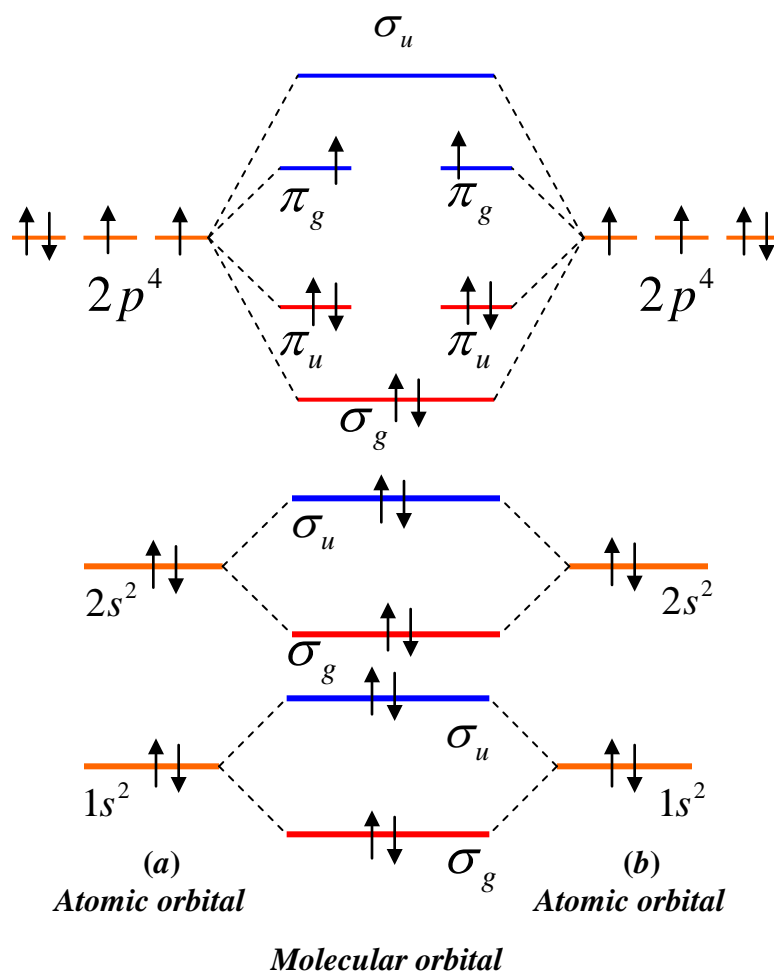


Figure-34.6

So the Λ - M_S table for the electronic configuration is given below.

For π electrons, $\lambda_1 = 1$ and -1 ; similarly $\lambda_2 = 1$ and -1 . For spin, $m_s = +1/2$ and $m_s = -1/2$.

$M_S \backslash \Lambda$	-1	0	1
2	----	$(1^+, 1^-)$	----
1	----	----	----
0	$(1^-, -1^-)$	$(1^+, -1^-), (1^-, -1^+)$	$(1^+, -1^+)$
-1	----	----	----
-2	----	$(-1^+, -1^-)$	----

Now, we will look at the wavefunctions.

The spatial wavefunction for $\Lambda = 2$

$$\phi_{spatial} = \pi_+(1)\pi_+(2)$$

Since this is symmetric, we have to multiply with the antisymmetric of spin wavefunction to make the total wavefunction antisymmetric.

The antisymmetric spin wavefunction is

$$\chi_{spin}^{Antisymmetric} = \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

And the total wavefunction is for ($\Lambda = 2$ and term is $^1\Delta_g$),

$$\Psi(^1\Delta_g) = \frac{1}{\sqrt{2}} \pi_+(1)\pi_+(2) [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

For $\Lambda = -2$, the spatial wavefunction is $\phi_{spatial} = \pi_-(1)\pi_-(2)$ and this will give rise to same term $^1\Delta_g$. So $^1\Delta_g$ is doubly degenerate.

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Now for $\Lambda = 0$, the spatial wavefunction is

$$\phi_{spatial} = \frac{1}{\sqrt{2}} [\pi_+(1)\pi_-(2) \pm \pi_-(1)\pi_+(2)]$$

The symmetric wavefunction is

$$\phi_{spatial}^{symmetric} = \frac{1}{\sqrt{2}} [\pi_+(1)\pi_-(2) + \pi_-(1)\pi_+(2)]$$

Because by exchanging the electrons, wavefunction does not change.

$$\phi_{spatial}^{symmetric}(2,1) = \frac{1}{\sqrt{2}} [\pi_+(2)\pi_-(1) + \pi_-(2)\pi_+(1)]$$

$$\phi_{spatial}^{symmetric}(1,2) = \phi_{spatial}^{symmetric}(2,1)$$

We have to multiply with the antisymmetric of spin wavefunction to make the total wavefunction antisymmetric.

Since $\Lambda = 0$, $M_S = 0$, it gives rise to $^1\Sigma_g^+$ and the total wavefunction is,

$$\Psi(^1\Sigma_g^+) = \frac{1}{2} [\pi_+(1)\pi_-(2) + \pi_-(1)\pi_+(2)] [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

The antisymmetric spatial wavefunction is

$$\phi_{spatial}^{Antisymmetric} = \frac{1}{\sqrt{2}} [\pi_+(1)\pi_-(2) - \pi_-(1)\pi_+(2)]$$

$$\phi_{spatial}^{Antisymmetric}(2,1) = \frac{1}{\sqrt{2}} [\pi_+(2)\pi_-(1) - \pi_-(2)\pi_+(1)]$$

$$\phi_{spatial}^{Antisymmetric}(1,2) = -\phi_{spatial}^{Antisymmetric}(2,1)$$

Since this is antisymmetric, we have to multiply with the symmetric of spin wavefunction to make the total wavefunction antisymmetric.

The symmetric spin wavefunctions are

$$\begin{aligned} \chi_{spin}^{Symmetric} &= \alpha(1)\alpha(2) \\ &= \beta(1)\beta(2) \\ &= \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)] \end{aligned}$$

Since $\Lambda = 0$, $M_S = 1$, it gives rise to $^3\Sigma_g^-$ and the total wavefunction is,

$$\begin{aligned}\Psi(^3\Sigma_g^-) &= \frac{1}{2}[\pi_+(1)\pi_-(2) - \pi_-(1)\pi_+(2)]\alpha(1)\alpha(2) \\ &= \frac{1}{2}[\pi_+(1)\pi_-(2) - \pi_-(1)\pi_+(2)]\beta(1)\beta(2) \\ &= \frac{1}{2}[\pi_+(1)\pi_-(2) - \pi_-(1)\pi_+(2)][\alpha(1)\beta(2) + \beta(1)\alpha(2)]\end{aligned}$$

So the ground state electronic configuration of oxygen gives three terms namely,

$$^3\Sigma_g^-, ^1\Delta_g \text{ and } ^1\Sigma_g^+.$$

For energy ordering, we will use the Hund's rule.

Hund's rules are applied to determine the energy ordering of terms arising from the ground state electron configuration of a molecule:

1. The term with the highest spin multiplicity, $2S + 1$, is lowest in energy. This stems from the electron spin correlation: electrons with parallel spins have a tendency to spend more time further apart, on average, than those with paired spins.
2. For terms of the same multiplicity, the term with the largest orbital angular momentum, given by Λ , is lowest in energy.

According to Hund's rule, the terms arising from the ground state of O_2 lie in the order

$$^3\Sigma_g^- < ^1\Delta_g < ^1\Sigma_g^+.$$

For Be_2 molecule,

Atomic electronic configuration : $1s^2 2s^2$

Molecular electronic configuration: $1s\sigma_g^2 1s\sigma_u^2 2s\sigma_g^2 2s\sigma_u^2$

Bond order = 0: no bond formation: molecule is not formed with Be_2 .

The electric dipole selection rules for the electronic transitions for linear molecules can be determined from the following

1. Total angular momentum selection rule:

The total angular momentum change i.e $\Delta\Lambda = 0, \pm 1$. That means $\Sigma \rightarrow \Sigma$, $\Pi \rightarrow \Pi$, $\Delta \rightarrow \Delta$ will be allowed because $\Delta\Lambda = 0$. Similarly, $\Sigma \rightarrow \Pi$, $\Pi \rightarrow \Delta$, $\Pi \rightarrow \Sigma$, $\Delta \rightarrow \Pi$ will be allowed because $\Delta\Lambda = \pm 1$.

2. Since we are taking electric dipole transitions, the spin should be conserved. So the spin selection rule is $\Delta S = 0$. Please note that this is true in the absence of spin orbit mixing i.e. spin orbit coupling.
3. The selection rules for the plane of reflection symmetry, $\Sigma^+ \rightarrow \Sigma^+$ and $\Sigma^- \rightarrow \Sigma^-$
4. Since the electric dipole transition operator changes parity by one in the wavefunction, the transition selection rules for the parity are $g \rightarrow u$ and $u \rightarrow g$.

Total angular momentum of the electrons: Spin-orbit coupling

The total electronic angular momentum about the inter-nuclear axis, denoted by Ω , is determined by adding Λ and M_s , as we have done it in case of atom. So the total quantum number of the resultant angular momentum about inter-nuclear axis is

$$\Omega = |\Lambda + M_s|$$

For example, if the electronic term of a molecule is $^2\Pi$, then $S = 1/2$ and $\Lambda = \pm 1$. Then the projection of spin along the inter-nuclear axis $M_s = \pm 1/2$. So the total angular momentum is

$$\Omega = +1 + \frac{1}{2} = \frac{3}{2}$$

$$\Omega = +1 - \frac{1}{2} = \frac{1}{2}$$

$$\Omega = -1 + \frac{1}{2} = -\frac{1}{2}$$

$$\Omega = -1 - \frac{1}{2} = -\frac{3}{2}$$

Thus, the term $^2\Pi$ splits into two multiplets i.e. spin-orbit levels $\Omega = \pm 3/2$ and

$\Omega = \pm 1/2$. Both these levels are degenerate. The symbol for these multiplets are $^2\Pi_{3/2}$

and $^2\Pi_{1/2}$

Recap

In this lecture we have learnt that because of the strong inter-nuclear force, the individual quantum numbers of the electrons in a molecule do not remain good quantum numbers, instead the projections along the inter-nuclear axis need to be considered.

We have also learnt the procedure for determining the terms of the molecule from the electronic configuration.

As in case of atom, in the molecule also the spin orbit interaction takes place and the total quantum number of the electrons arise from their projection along the inter-nuclear axis.