

**Example 2- L:***CO<sub>2</sub> and H<sub>2</sub>O, VSEPR theory*

We wish to predict the molecular geometries of a water molecule and a carbon dioxide molecule respectively. The VSEPR theory is our tool to solve this job and it tells us that the electron groups surrounding the central atom will be placed as far apart as possible.

The first step is to write the Lewis structure for the two molecules in order to be able to just count the number of electron groups surrounding the central atom. This is done in Figure 2- 14.

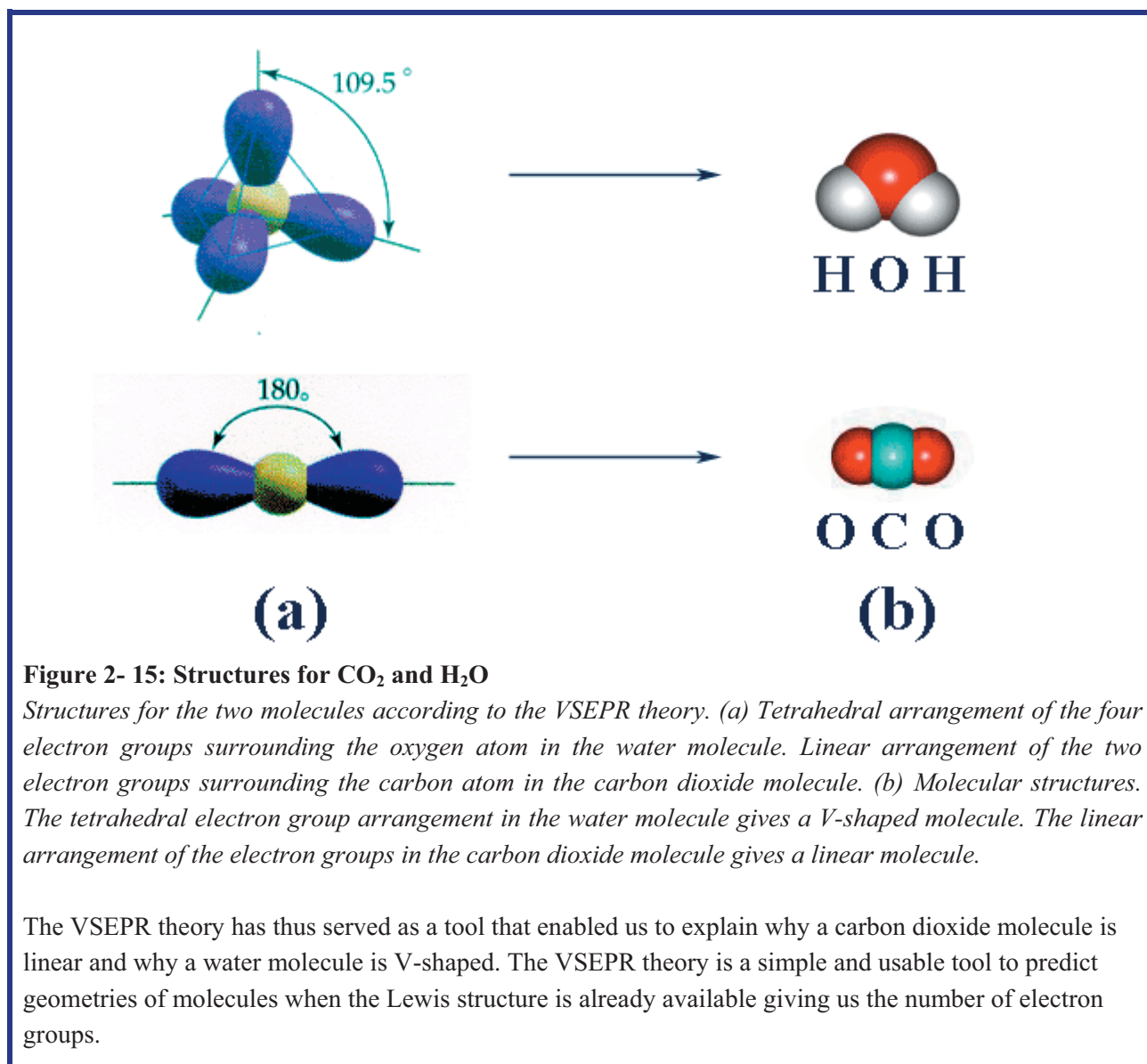
**Figure 2- 14: Electron groups in H<sub>2</sub>O and CO<sub>2</sub>**

*From the Lewis structure the number of electron groups surrounding the central atoms is counted. The oxygen atoms in the water molecule are surrounded by four electron groups (two lone pairs and two single bonds). The carbon atom in the carbon dioxide molecule is surrounded by two electron groups (two double bonds).*

The carbon atom in CO<sub>2</sub> is surrounded by two electrons groups (two double bonds) whereas the oxygen atom in H<sub>2</sub>O is surrounded by four electron groups (two single bonds and two lone pairs). According to the VSEPR theory these electron groups will be placed as far apart as possible. When there are only two electron groups these will be as far apart when they are placed 180° apart on a straight line with the central atom in the middle. Thus the atoms will be placed on a straight line which gives the linear structure of the carbon dioxide molecule. The four electron groups in the water molecule are placed as far apart as possible when they are placed in a so-called tetrahedron with angles of 109.5°. That way the two hydrogen atoms will be placed on two of the positions of the tetrahedron while the two lone pairs will occupy the two other positions. Thus the H-O-H bonds do not give a straight line but rather a V-shape. The angle of the H-O-H bonds is however slightly smaller than the tetrahedral angles of 109.5°. The H-O-H angle is actually just 104°. Thus an addition to the VSEPR theory is necessary in order to explain this “smaller” angle:

*Lone pairs occupy a larger volume around the central atom than bond electron pairs. Thus lone pairs will “press” the atomic bond together.*

This means that the two lone pairs around the oxygen atom in the water molecule will “press” the two single bonds together and therefore the H-O-H angle is smaller than the tetrahedral angle of 109.5°. The two geometries are sketched in Figure 2- 15.



It is (as mentioned earlier) the number of electron groups surrounding the central atom that determines the arrangement and geometry around the central atom. In Example 2- L we just saw that lone pairs occupy more space than bond electrons. For lone pairs the following rules apply:

Lone pairs occupy more space than bond electron groups

Lone pairs will be placed as far apart from other lone pairs as possible

Lone pairs will be placed as far apart from bond electron groups as possible

These guidelines can be used to predict the arrangement of bond electron groups and lone pairs relative to each other around the central atom when the total number of electron groups is known and when the number of lone pairs is known. In Table 2- 1 you can see how the geometry of a molecule depends on the number of electron groups and how many of these groups that are lone pairs.

**Table 2- 1: Geometries of molecules and composite ions**

The geometry depends on the number of electron groups surrounding the central atom of the molecule or composite ions and how many of these electron groups that are lone pairs.

Electron groups	Electron group arrangement	Bond electron pairs	Lone pairs	Geometry of molecule or composite ion	Example
2	Linear	2	0	Linear	CO <sub>2</sub>
3	Trigonal planar	3	0	Trigonal planar	NO <sub>3</sub> <sup>-</sup>
		2	1	V-shape	NO <sub>2</sub> <sup>-</sup>
4	Tetrahedral	4	0	Tetrahedral	CH <sub>4</sub>
		3	1	Trigonal pyramidal	PH <sub>3</sub>
		2	2	V-shape	H <sub>2</sub> O
5	Trigonal bipyramidal	5	0	Trigonal bipyramidal	PCl <sub>5</sub>
		4	1	Seesaw <sup>*</sup>	SF <sub>4</sub>
		3	2	T-shaped <sup>*</sup>	BrF <sub>3</sub>
		2	3	Linear	XeF <sub>2</sub>
6	Octahedral	6	0	Octahedral	SF <sub>6</sub>
		5	1	Square pyramidal	IF <sub>5</sub>
		4	2	Square planar	XeF <sub>4</sub>

<sup>\*</sup>These rather special geometries are not explained in this book. Educational textbooks describing orbital hybridization theory can explain why these specific geometries are observed for the particular molecules for that particular number of bond electron groups and lone pairs.

By use of VSEPR theory, in which the Lewis structures helped us determining the number of surrounding electron groups, we are now able to predict actual structures of molecules and composite ions. However from the VSEPR theory we know nothing about the chemical bond itself. Where are the bond electrons actually placed? Or more specific: In which types of orbitals are the bond electrons placed? The answer to this can be found in the orbital hybridization theory which is the topic in the next section.

### 2.2.5 Orbital hybridization

In the previous section (2.2.4 VSEPR theory) we saw that the number of electron groups (bond electron pairs and lone pairs) around the central atom is determining the geometry of the molecule or composite ion. We have also been looking at the geometry of the atomic orbitals in the section 1.1.7 Orbital configuration.

However the orientations of the atomic orbitals in space do not fit the directions predicted by the VSEPR theory according to Table 2- 1 on page 70. For this reason other orbitals than the atomic orbitals must be present in the molecules and composite ions in order to “give” the right bond directions according to the VSEPR theory. These orbitals are a type of molecular orbitals (also mentioned in section 2.2.2 *Molecular orbital theory*) which are called *hybrid orbitals*. These hybrid orbitals thus host the valence electrons which constitutes the chemical bond between the atoms.

When atoms join and form molecules by creating covalent bonds, the atomic orbitals do not have the right directions and orientations which mean that they can not host the bond electrons. According to the theory of orbital hybridization the atoms solve this problem by making existing atomic orbitals into “new” hybrid orbitals. This is the same principle as for the molecular orbitals. These hybrid orbitals (which are molecular orbitals) then have the right orientation in space according the VSEPR theory. Thus the bond electrons and the lone pairs (the electron groups) surrounding the central atom can be placed as far apart as possible. The formation of the hybrid orbitals will be explained and sketched through the following examples.

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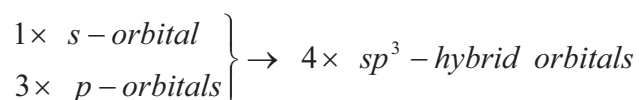
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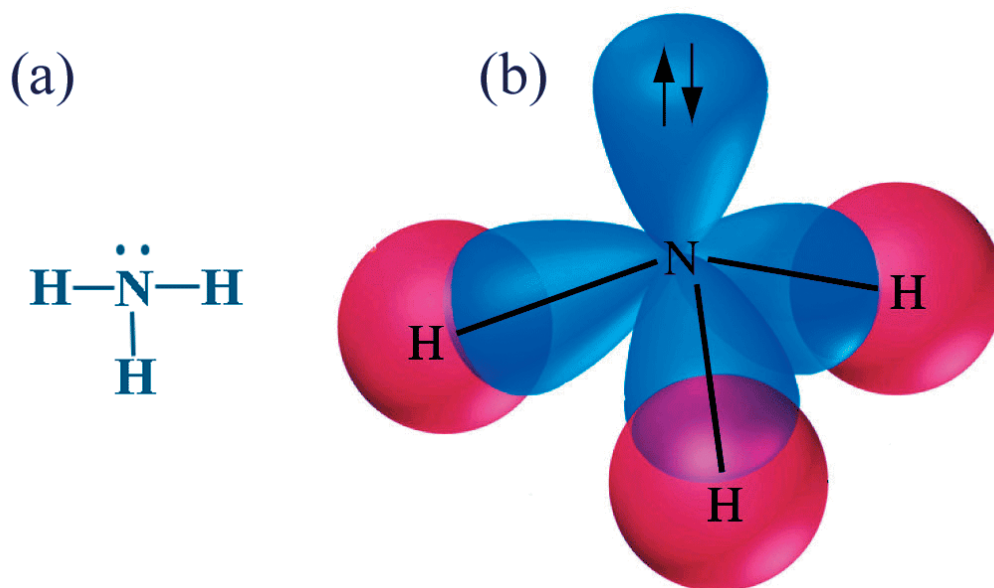
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**Example 2- M:***NH<sub>3</sub> molecule, sp<sup>3</sup>-hybridization*

Let us start by looking at a molecule of ammonia. First the Lewis structure of the molecule is written (done in Figure 2- 16a). The central nitrogen atom is surrounded by four electron groups (three single bonds and a lone pair). The question is in which orbitals these electron groups are hosted? The spherical atomic s-orbital and the three atomic p-orbitals are not arranged around the nitrogen atom in a tetrahedron as the VSEPR theory requires. The nitrogen atom solves this problem by transforming the four atomic orbitals into four “new” identical hybrid orbitals. These four orbitals are called *sp<sup>3</sup>* hybrid orbitals and they are arranged in a tetrahedral manner around the nitrogen atom.



The name *sp<sup>3</sup>* indicates that we are talking about a transformation of *one* s-orbital and *three* p-orbitals. The new four hybrid orbitals are then used to host the four electron groups surrounding the nitrogen atom in the ammonia molecule which is sketched in Figure 2- 16b.



**Figure 2- 16: *sp<sup>3</sup>*-hybridization in NH<sub>3</sub>**

(a) Lewis structure for the ammonia molecule. (b) The central nitrogen atom is *sp<sup>3</sup>* hybridized. The four *sp<sup>3</sup>* orbitals are blue on the figure. The 1s-orbitals of the three hydrogen atoms are red on the figure. The lone pair (marked with two arrows) occupies more space than the bond electron pairs between the nitrogen atom and the three hydrogen atoms. Thus the lone pair “pushes” the angles between the N and H atoms so that these angles become less than the tetrahedral angle of 109.5°.

By using the hybrid orbitals to host the bond electron pairs and the lone pair, the tetrahedral structure predicted by the VSEPR theory is obtained. You can see an overlap between the s-orbitals of the hydrogen



atoms and the  $sp^3$  orbitals of the nitrogen atom and these overlaps constitute the single bonds. The lone pair occupies more space than the three bond electron pairs. This means that the lone pair “presses” the three bonds together so that the angles are only  $107^\circ$  rather than the tetrahedral angle of  $109.5^\circ$ .

Since only two electrons can be hosted in one orbital, the hybrid orbitals can only host one bond electron pair which correspond to the number of electrons in a single bond. Such a single bond is called an  $\sigma$ -bond which we also saw in the section 2.2.2 *Molecular orbital theory*. If we are dealing with a double bond (consisting of four electrons) one hybrid orbital is not enough for such a bond. In that case, already existing atomic p-orbitals are used for the creation of so-called  $\pi$ -bonds which together with  $\sigma$ -bonds constitute double bonds (and triple bonds). A molecule of ethene can be used as an example which we are going to look at now.

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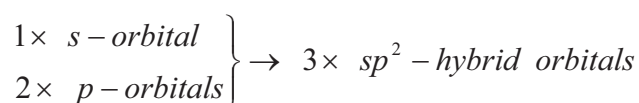


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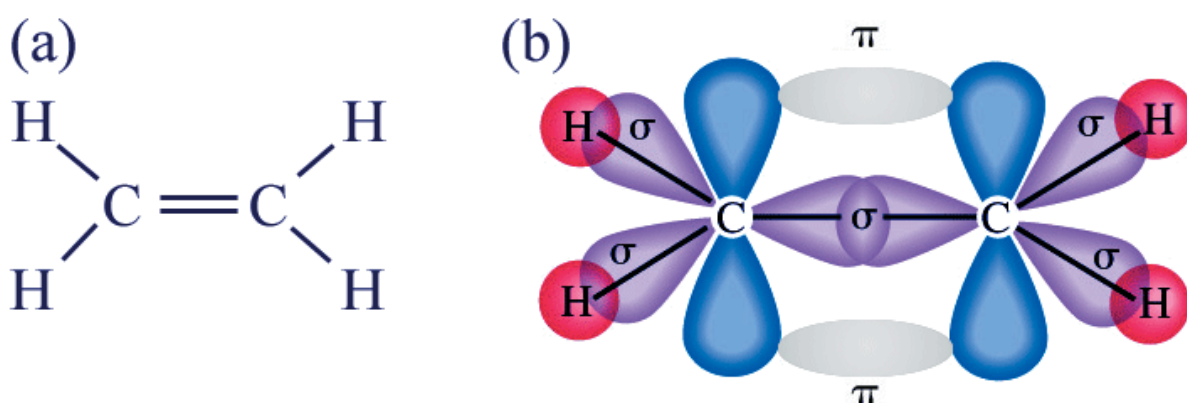
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**Example 2- N:***C<sub>2</sub>H<sub>4</sub> molecule, sp<sup>2</sup>-hybridization*

It is seen from the Lewis structure of C<sub>2</sub>H<sub>4</sub> (Figure 2- 17a) that the two central carbon atoms each are surrounded by three electron groups (1 double bond and 2 single bonds). Three such electron groups surrounding the central atom results in a trigonal planar arrangement according to Table 2- 1 on page 70 (from the VSEPR theory). Thus there is a need for three identical orbital with such a trigonal planar arrangement to host the electron groups. Each carbon atom then transforms *one* s-orbital and *two* p-orbitals into three identical sp<sup>2</sup>-hybrid orbitals. As the name sp<sup>2</sup> indicated, they are “made” from *one* s-orbital and *two* p-orbitals.



Hence *one* atomic p-orbital remains unchanged in each carbon atom. The double bond consists in that the overlap between two sp<sup>2</sup> orbitals constitutes an σ-bond while a π-bond is formed in the space between the two remaining atomic p-orbitals of the carbon atoms. This is sketched in Figure 2- 17b.



**Figure 2- 17: sp<sup>2</sup>-hybridization in C<sub>2</sub>H<sub>4</sub>**

(a) Lewis structure of an ethene molecule. (b) Each carbon atom is sp<sup>2</sup> hybridized (the 2×3 sp<sup>2</sup> orbitals are purple on the figure). The double bond consists of an σ-bond (overlap of the two sp<sup>2</sup> orbitals) and a π-bond in the space between the two p-atomic orbitals. The two p-orbital are blue on the figure while the π-bond is grey on the figure. The bonds to the hydrogen atoms are σ-bonds.

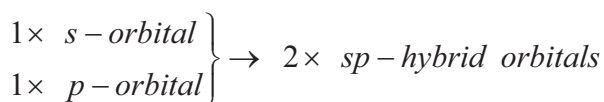
From the figure it is seen that rotation around the C=C double bond is not possible because the π-bond “locks” the possible of rotation. Thus double bonds are far less flexible compared to single bonds which only consist of σ-bonds.

In the previous example we have just seen how a double bond consists of *one*  $\sigma$ -bond and *one*  $\pi$ -bond. In the case with the linear carbon dioxide molecule, the central carbon atom is double bonded to each of the two oxygen atoms which we saw in Example 2- H on page 61. How is that possible? The answer is given in the following example.

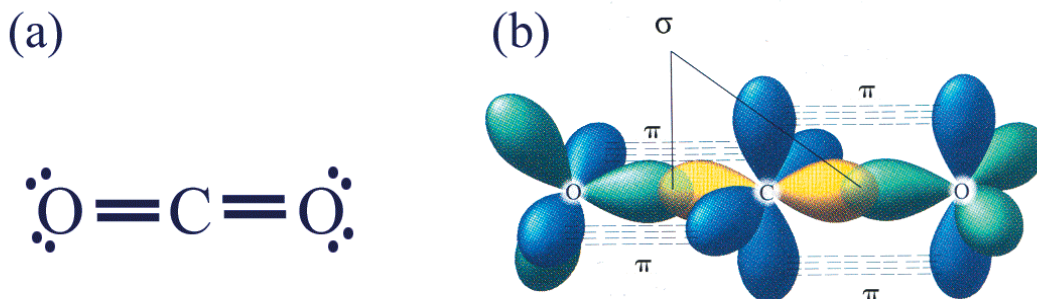
### Example 2- O:

*CO<sub>2</sub> molecule, sp-hybridization*

From the Lewis structure of the carbon dioxide molecule (Figure 2- 18a) it is seen that the carbon atom is surrounded by two electron groups (two double bonds). Two electron groups mean that there is a need for two identical orbitals 180° apart according to the VSEPR theory and Table 2- 1 on page 70. The carbon atom solves this problem by forming two identical so-called *sp*-hybrid orbital. As the name *sp* indicated these orbitals are made from *one* s-orbital and *one* p-orbital.



Hence *two* of the atomic p-orbitals in the carbon atom remain unchanged. From the Lewis structure it is also seen that each oxygen atom is surrounded by three electron groups (2 lone pairs and 1 double bond). In Example 2- N on page 74 we saw that three electron groups around an atom results in  $sp^2$  hybridization. Thus the carbon atom is *sp*-hybridized and the two oxygen atoms are each  $sp^2$  hybridized. This is sketched in Figure 2- 18b.



**Figure 2- 18: sp-hybridization in CO<sub>2</sub>**

(a) Lewis structure of a carbon dioxide molecule. (b) The carbon atom is *sp*-hybridized (two yellow *sp*-orbitals) while the two oxygen atoms are  $sp^2$  hybridized ( $2 \times 3$  green  $sp^2$ -orbitals). The double bonds each consist of an  $\sigma$ -bond (overlap of a *sp*-orbital and a  $sp^2$ -orbital) and a  $\pi$ -bond in the space between one p-orbital from the carbon atom and one from the oxygen atom. The p-orbitals are blue on the figure while the  $\pi$ -bonds are indicated with dotted lines.

Again we see that in double bonds we have  $\sigma$ -bonds in the overlap between hybrid orbitals and  $\pi$ -bonds in the space between atomic p-orbitals. Thus in the case of carbon dioxide the two  $\pi$ -bonds are rotated 90° relative to each other.



If the central atom is from the 3<sup>rd</sup> period and downwards we have seen (in the section 2.2.3 *Lewis structure*) that it is possible for the central atom to be surrounded by more than four electron groups (eight electrons). In Table 2- 1 on page 70 it is seen that when the central atom is surrounded by five electron groups these will be arranged as a trigonal bipyramide. This required five identical orbitals with such an arrangement and orientation. This is achieved if the central atom transforms five atomic orbitals (*one s-orbital, three p-orbitals and one d-orbital*) into *five* identical so-called  $dsp^3$ -hybrid orbitals. Again the name indicates that these hybrid orbitals are made from *one s-orbital, three p-orbitals and one d-orbital*. In a similar manner we know that when the central atom is surrounded by six electron groups these will be arranged like an octahedron around the central atom. This requires *six* identically orbitals with such an arrangement and therefore the central atom transforms *one s-orbital, three p-orbitals and two d-orbitals* into *six* identically  $d^2sp^3$ -hybrid orbitals which are arranged around the central atom like an octahedron.

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**Table 2- 2: Hybrid orbitals**

*The number of electron groups surrounding the central atom determines which types of hybridization orbital that surround the central atom and thus the orbital geometry around the central atom.*

Electron groups	Hybridization	Atomic Orbitals			Geometry around central atom
		s	p	d	
2	$sp$	1	1	0	Linear
3	$sp^2$	1	2	0	Trigonal planar
4	$sp^3$	1	3	0	Tetrahedral
5	$dsp^3$	1	3	1	Trigonal bipyramide
6	$d^2sp^3$	1	3	2	Octahedral

In Table 2-2 a survey of the different types of hybridization and hybrid orbitals is given. The type of hybridization depends on the number of electron groups that surround the central atom. In order to sketch the type of hybridization of a molecule you have to follow the following list:

Write down the Lewis structure (section 2.2.3 *Lewis structure*)

Count the number of electron groups that surround the central atom

The number of required hybrid orbitals equals the number of surrounding electron groups. Hybridization type is given in Table 2-2.

These three steps are followed in Example 2- M, Example 2- N and Example 2- O in this sub section. Till now we have been dealing with covalent bonds in single molecules. Now we are going to look at the bonds that exist in very large lattice structures between metal atoms. We are going into the world of metallic bonds.

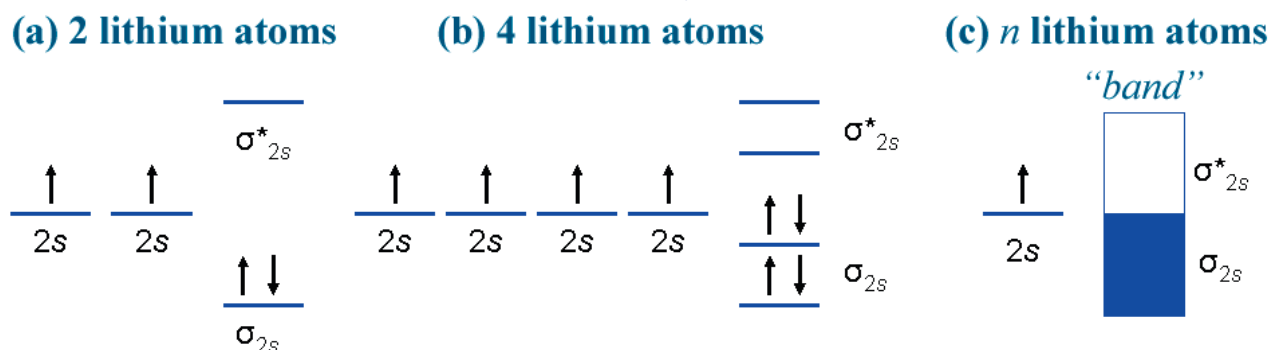
## 2.3 Metallic bonds

In the previous sub sections we learned that the bond electrons in the covalent bonds are placed in hybrid molecular orbitals with totally specific directions. This means that the valence electrons thus are more or less “locked” in the bonds in those hybrid orbitals. Because of this “locking” of the electrons, covalent bonds generally are very poor at conducting electricity. The very low electrical conductance of covalent bonds is the exact opposite of the case with metallic bonds. Metals have very high electrical conductance in all directions which thus implies that the metallic bonds are good at conducting electricity. Therefore metallic bonds and covalent bonds must be fundamentally different. We are going to look more into that in this section. We will also see how metal atoms are arranged in different *lattice structures*.

### 2.3.1 Band theory

A simple model to describe metallic bonds is the so-called *electron sea model*. Metals can be considered as metal cations surrounded by valence electrons that “swim” around in all directions like in a sea. In that way, metals have high electrical and thermal conductivity in all directions since the valence electrons freely can move around. In order to describe this in more details we have to introduce the so-called *band theory*. In the band theory the molecular orbitals (that we heard about in the section 2.2.2 *Molecular orbital theory*) are again included.

We will start with the metal lithium (Li) which is the first element of the 2<sup>nd</sup> period and thus has only one valence electron (placed in the 2s-orbital). If two lithium atoms approach each other the two atomic 2s-orbitals will be transformed into two molecular orbitals; a bond orbital ( $\sigma_{2s}$ ) and an anti-bond orbital ( $\sigma_{2s}^*$ ) according to the theory described in section 2.2.2 *Molecular orbital theory*. If we have four lithium atom, the four atomic orbitals (2s) will be transformed into four molecular orbitals; two bond orbitals ( $\sigma_{2s}$ ) and two anti-bond orbitals ( $\sigma_{2s}^*$ ). From quantum mechanical considerations, the bond orbitals and anti-bond orbitals can not be degenerated. This means that they can not be equal in energy level and thus they will each have its own level of energy. If we have  $n$  lithium atoms ( $n$  is a very large number – for example  $n = 6.023 \times 10^{23}$ ), the  $n$  atomic orbitals (2s) will be transformed into  $n$  molecular orbitals;  $\frac{1}{2}n$  bond orbitals ( $\sigma_{2s}$ ) and  $\frac{1}{2}n$  anti-bond orbitals ( $\sigma_{2s}^*$ ). Since those  $n$  molecular orbitals can not be degenerated they must all be different in energy levels. Thus those energy levels must be very close and in practice they constitute a continuous energy *band*. The described situations are shown in Figure 2- 19.



**Figure 2- 19: The energy levels for the molecular orbitals for lithium metal**

(a) Two lithium atoms together create two molecular orbitals. (b) Four lithium atoms together create four molecular orbitals. (c)  $n$  lithium atoms together create  $n$  molecular orbitals. When the number of atoms is large, the energy levels of the molecular orbitals create a continuous energy band.

The large amount of atomic orbitals constitutes in practice a continuous energy transition between the molecular orbitals. This is the energy *band*. The bond orbitals in lithium metal will be occupied each with one electron and the anti-bond orbitals are empty. Because the transition from bond orbital to anti-bond orbital is very small in terms of energy, the electrons can easily move from a bond orbital to an anti-bond orbital. Thus it is easy to get a current of electrons transported through the metallic structure because the electrons can easily move in the empty anti-bond orbitals. They can flow through the metal as an *electron sea*. This is thus an explanation of the high metallic electrical conductance in all directions from the very

simple *electron sea model* and the *band theory*. The high thermal conductivity follows in the aftermath of the high electrical conductance since the moving valence electrons transport heat as well.

### 2.3.2 Lattice structures

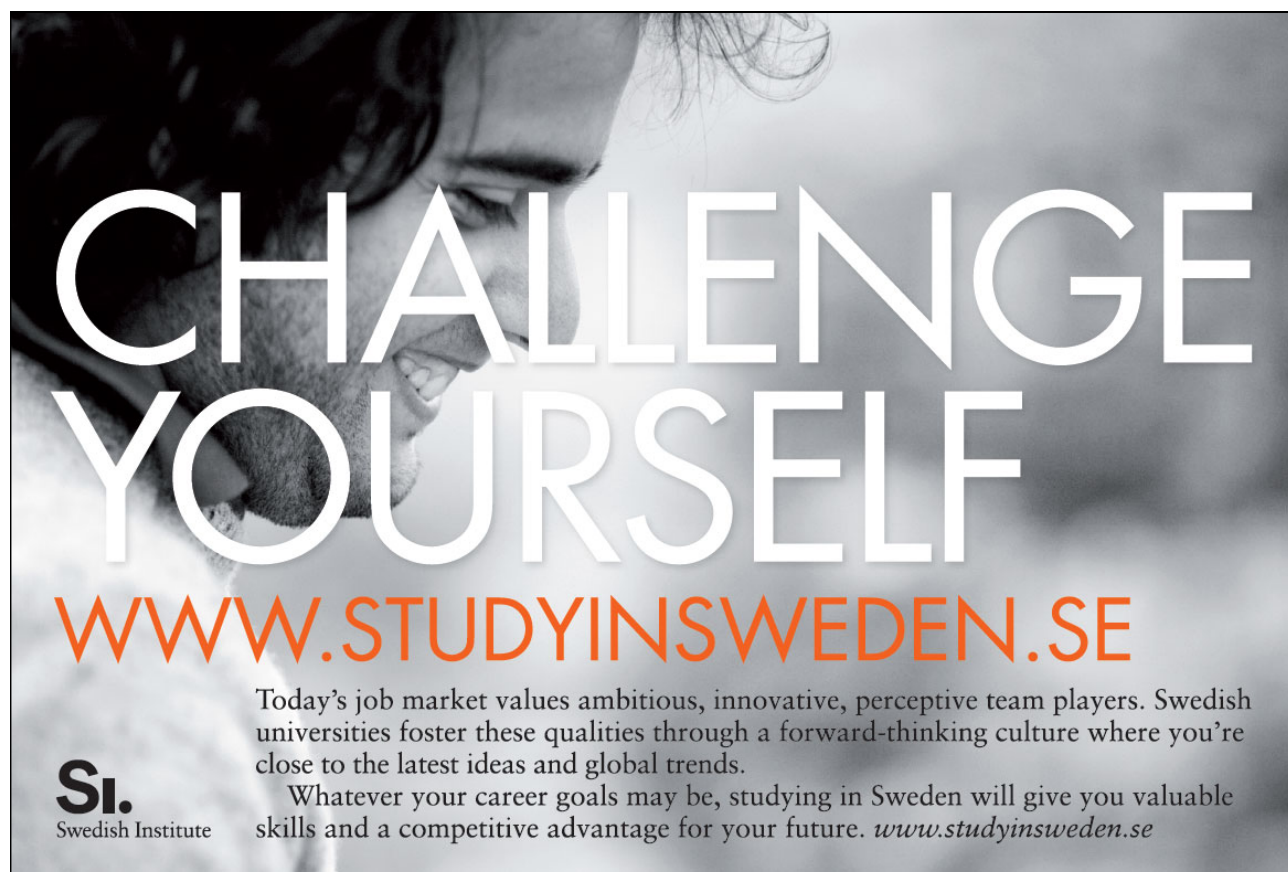
In the previous section we have seen how metal bond can be described according to the band theory. The valence electrons can freely move through the metal lattice in empty anti-bond orbitals. But how are the single atoms arranged relative to each other? We are going to look at the answer to this question in this section. Generally two types of structures in solid compounds can be distinguished:

Crystalline solid compounds

Amorphous solid compounds

In crystalline solid compounds there is a high order of systematism in the structure which is in contrast to amorphous solid compounds which are characterized by totally lack of order in the structure. Metals belong to the first category. Metal atoms are arranged in so-called *crystal lattices*. The atoms in such crystal lattices can be arranged in different manners which mans that different metals can have different types of crystal lattices. We are going to look at how these different crystal lattices are organized. Initially we assume that the metal atoms can be regarded as hard spheres that can be stacked so that they just touch each other.

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