CH-110 Chimie Générale Avancée I

Q & A

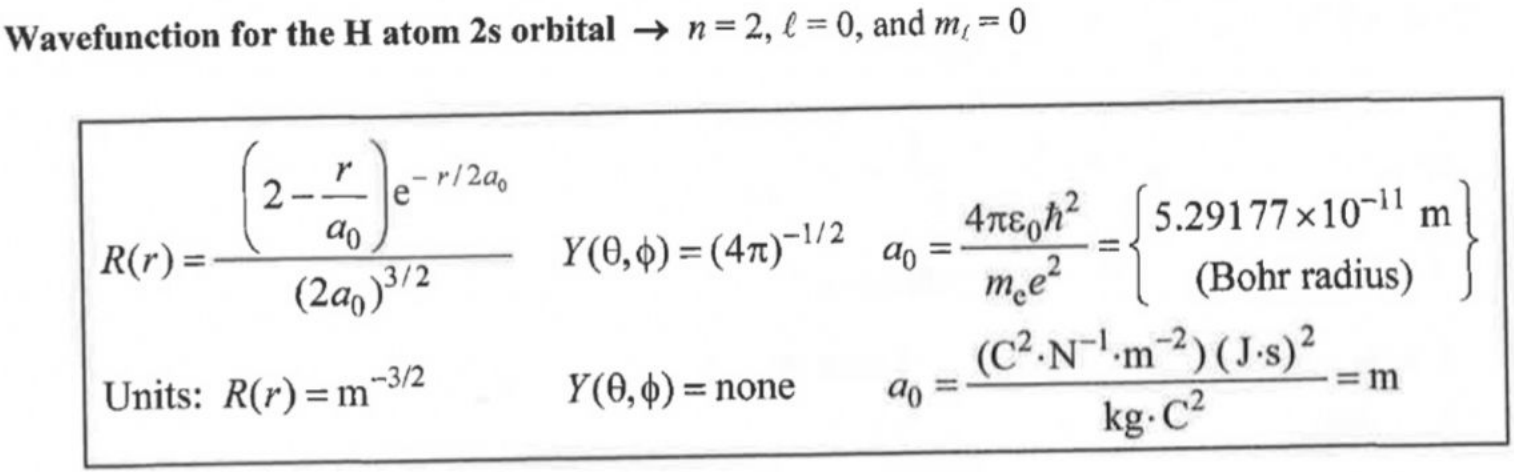
Prof. A. Steinauer

angela.steinauer@epfl.ch

Andrea/Angela

Wavefunction for H atom 2s orbital (Topic 1D)

Could you give an example of how to use this formula?



Wavefunction for the H atom 2s orbital → $n = 2$, $\ell = 0$, and $m_\ell = 0$

$$R(r) = \frac{\left(2 - \frac{r}{a_0}\right) \mathrm{e}^{-r/2a_0}}{(2a_0)^{3/2}} \qquad Y(\theta,\phi) = (4\pi)^{-1/2} \qquad a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_\mathrm{e}e^2} = \begin{Bmatrix} 5.29177\times10^{-11}\ \mathrm{m} \\ \text{(Bohr radius)} \end{Bmatrix}$$

$$\text{Units: } R(r) = \mathrm{m}^{-3/2} \qquad Y(\theta,\phi) = \text{none} \qquad a_0 = \frac{(\mathrm{C}^2\cdot\mathrm{N}^{-1}\cdot\mathrm{m}^{-2})\,(\mathrm{J}\cdot\mathrm{s})^2}{\mathrm{kg}\cdot\mathrm{C}^2} = \mathrm{m}$$

Andrea/Angela

Wavefunction for H atom 2s orbital (Topic 1D)

Answer:

The short answer is, you will not have to use this equation. This is beyond the scope of this class.

You should be aware that there are two different functions in the equation, R and Y, the radial and angular wavefunctions and be able to explain what they are referring to. In brief,

1. **The Schrödinger equation for hydrogen** can be solved by separating variables into radial (R) and angular (Y) components.
2. **Each component** corresponds to a different aspect of the orbital’s shape and size.
3. **Quantum numbers** n, l, m_l etc., stem from these solutions and characterize the orbitals.

TABLE 1.2 Hydrogenlike Wavefunctions* (Atomic Orbitals), $\psi = RY$

(a) Radial wavefunctions

n	l	$R_{nl}(r)$
1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} \mathrm{e}^{-Zr/a_0}$
2	0	$\frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2 - \frac{Zr}{a_0}\right)\mathrm{e}^{-Zr/2a_0}$
	1	$\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)\mathrm{e}^{-Zr/2a_0}$
3	0	$\frac{2}{9\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}\left(3 - \frac{2Zr}{a_0} + \frac{2Z^2r^2}{9a_0{}^2}\right)\mathrm{e}^{-Zr/3a_0}$
	1	$\frac{2}{9\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2 - \frac{Zr}{3a_0}\right)\mathrm{e}^{-Zr/3a_0}$
	2	$\frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^2\mathrm{e}^{-Zr/3a_0}$

(b) Angular wavefunctions

l	"m_l"†	$Y_{l,m_l}(\theta, \phi)$
0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
1	x	$\left(\frac{3}{4\pi}\right)^{1/2} \sin\theta \cos\phi$
	y	$\left(\frac{3}{4\pi}\right)^{1/2} \sin\theta \sin\phi$
	z	$\left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$
2	xy	$\left(\frac{15}{16\pi}\right)^{1/2} \sin^2\theta \sin 2\phi$
	yz	$\left(\frac{15}{4\pi}\right)^{1/2} \cos\theta \sin\theta \sin\phi$
	zx	$\left(\frac{15}{4\pi}\right)^{1/2} \cos\theta \sin\theta \cos\phi$
	$x^2 - y^2$	$\left(\frac{15}{16\pi}\right)^{1/2} \sin^2\theta \cos 2\phi$
	z^2	$\left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$

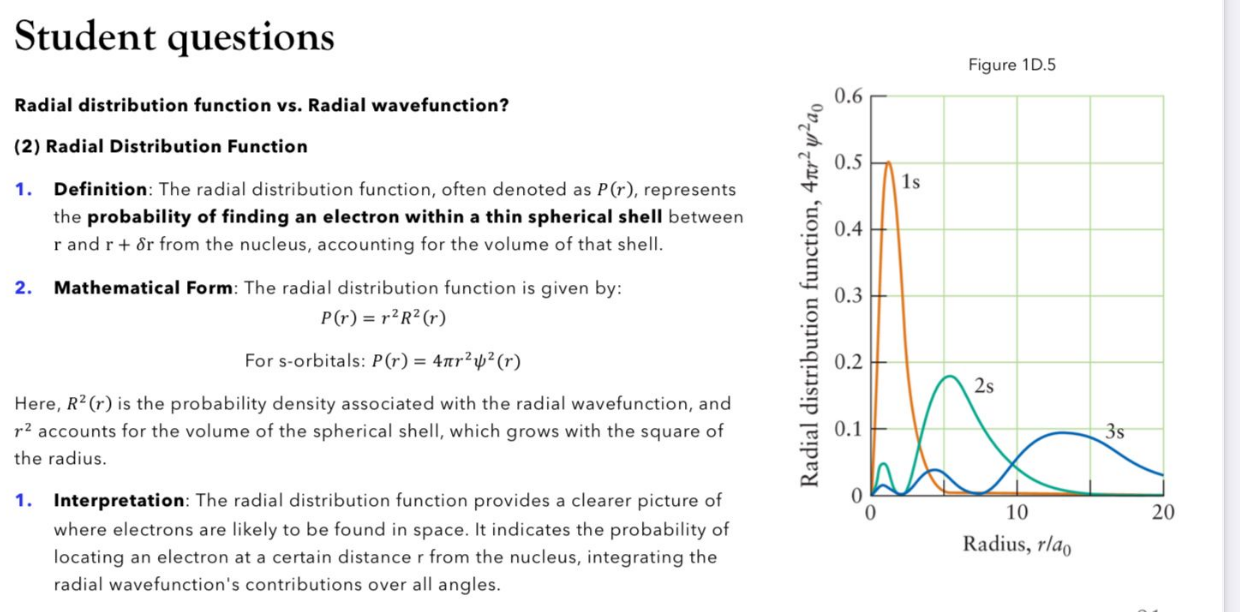
*Note: In each case, $a_0 = 4\pi\varepsilon_0{}^2/m_e e^2$, or close to 52.9 pm; for hydrogen itself, $Z = 1$.

†In all cases except $m_l = 0$, the orbitals are sums and differences of orbitals with specific values of m_l.

Andrea/Angela

Radial distribution function vs Radial wavefunction (Topic 1D)

Hard to understanding these concepts



Student questions

Radial distribution function vs. Radial wavefunction?

(2) Radial Distribution Function

1. **Definition**: The radial distribution function, often denoted as $P(r)$, represents the **probability of finding an electron within a thin spherical shell** between r and r + δr from the nucleus, accounting for the volume of that shell.
2. **Mathematical Form**: The radial distribution function is given by:

$$P(r) = r^2R^2(r)$$

For s-orbitals: $P(r) = 4\pi r^2\psi^2(r)$

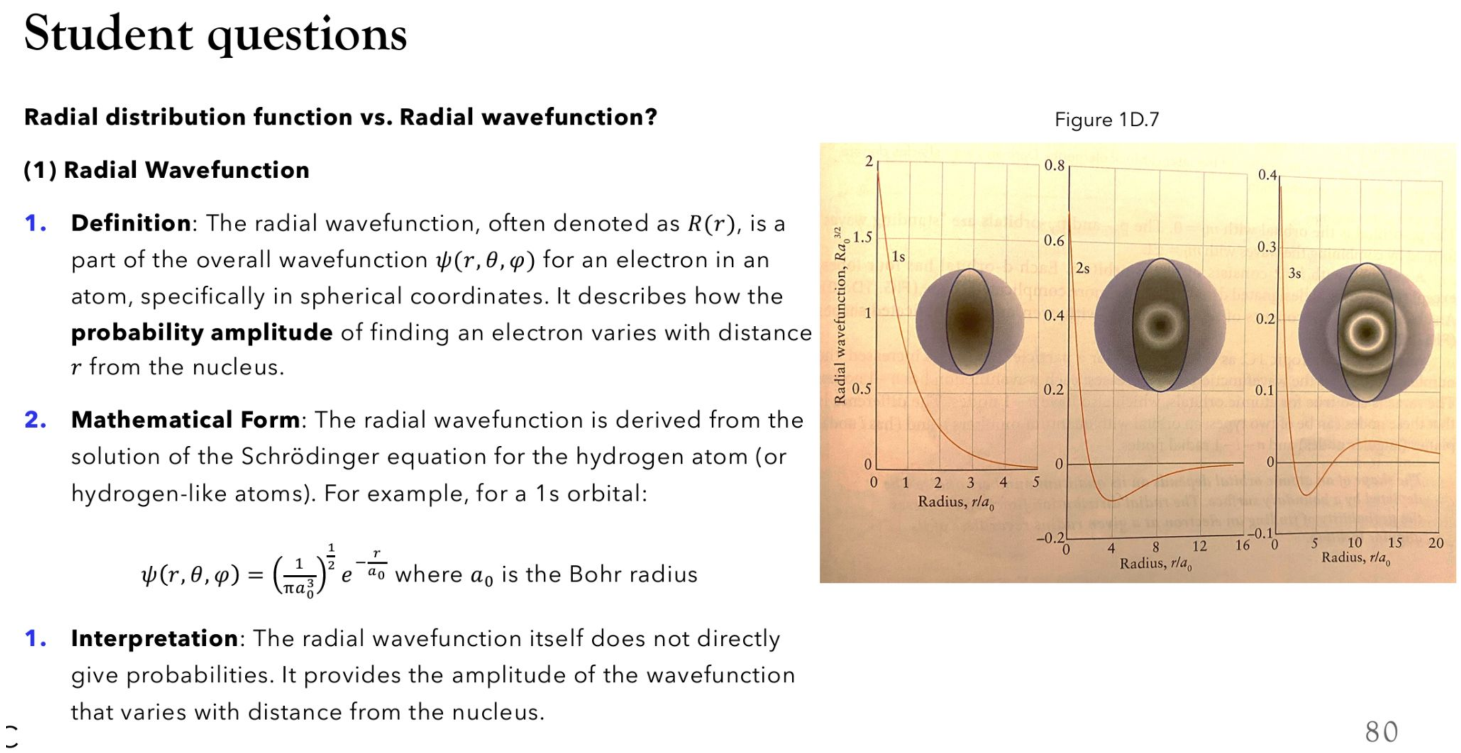
Here, $R^2(r)$ is the probability density associated with the radial wavefunction, and r^2 accounts for the volume of the spherical shell, which grows with the square of the radius.

1. **Interpretation**: The radial distribution function provides a clearer picture of where electrons are likely to be found in space. It indicates the probability of locating an electron at a certain distance r from the nucleus, integrating the radial wavefunction's contributions over all angles.

Figure 1D.5

Andrea/Angela

Radial distribution function vs Radial wavefunction (Topic 1D)



Student questions

Radial distribution function vs. Radial wavefunction?

(1) Radial Wavefunction

1. **Definition**: The radial wavefunction, often denoted as $R(r)$, is a part of the overall wavefunction $\psi(r,\theta,\varphi)$ for an electron in an atom, specifically in spherical coordinates. It describes how the **probability amplitude** of finding an electron varies with distance r from the nucleus.
2. **Mathematical Form**: The radial wavefunction is derived from the solution of the Schrödinger equation for the hydrogen atom (or hydrogen-like atoms). For example, for a 1s orbital:

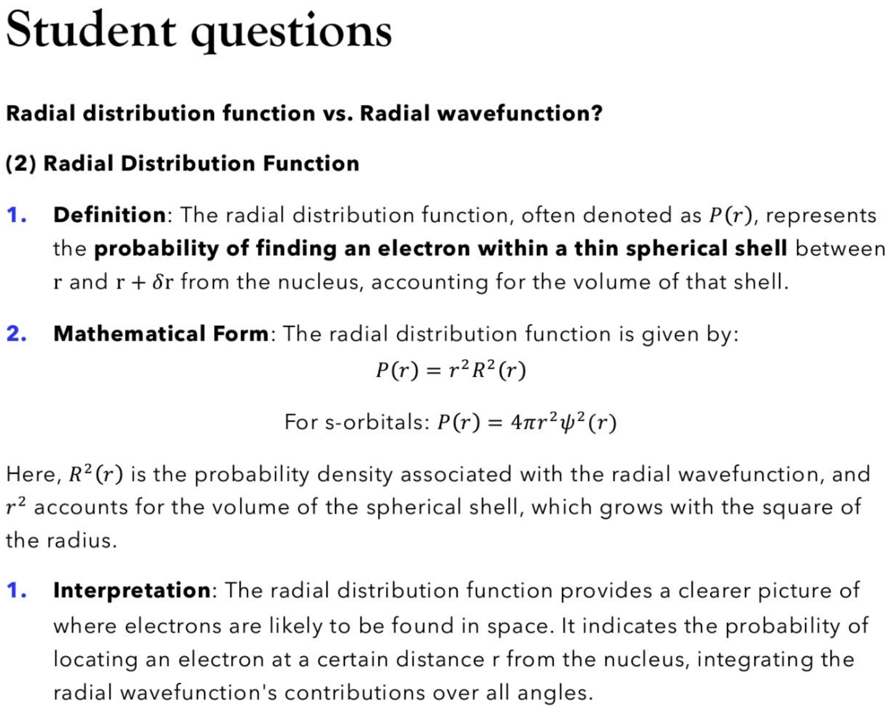
$$\psi(r,\theta,\varphi) = \left(\frac{1}{\pi a_0^3}\right)^{\frac{1}{2}} e^{-\frac{r}{a_0}} \text{ where } a_0 \text{ is the Bohr radius}$$

1. **Interpretation**: The radial wavefunction itself does not directly give probabilities. It provides the amplitude of the wavefunction that varies with distance from the nucleus.

Figure 1D.7

Andrea/Angela

Radial distribution function vs Radial wavefunction (Topic 1D)



Student questions

Radial distribution function vs. Radial wavefunction?

(2) Radial Distribution Function

1. **Definition**: The radial distribution function, often denoted as $P(r)$, represents the **probability of finding an electron within a thin spherical shell** between r and r + δr from the nucleus, accounting for the volume of that shell.
2. **Mathematical Form**: The radial distribution function is given by:

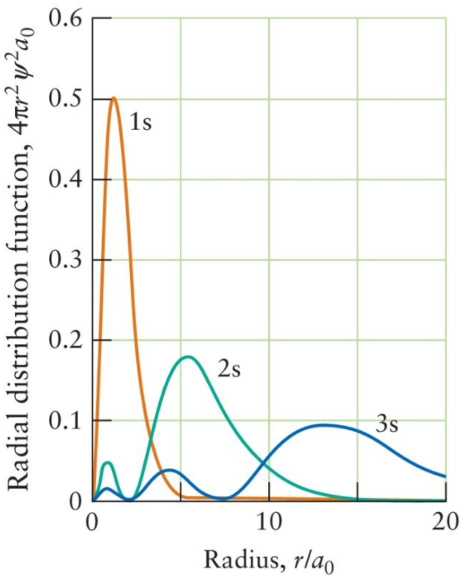
$$P(r) = r^2 R^2(r)$$

$$\text{For s-orbitals: } P(r) = 4\pi r^2 \psi^2(r)$$

Here, $R^2(r)$ is the probability density associated with the radial wavefunction, and r^2 accounts for the volume of the spherical shell, which grows with the square of the radius.

1. **Interpretation**: The radial distribution function provides a clearer picture of where electrons are likely to be found in space. It indicates the probability of locating an electron at a certain distance r from the nucleus, integrating the radial wavefunction's contributions over all angles.

Figure 1D.5



1C

Andrea/Angela

Radial distribution function vs Radial wavefunction (Topic 1D)

Well explained here:
https://www.youtube.com/watch?v=AI5ok-linwI&ab_channel=PatternsRemonstrator

Georges

Electron configuration (Topic 1E)

Which orbital to write first between the ns and the (n-1)d for the electron configuration?

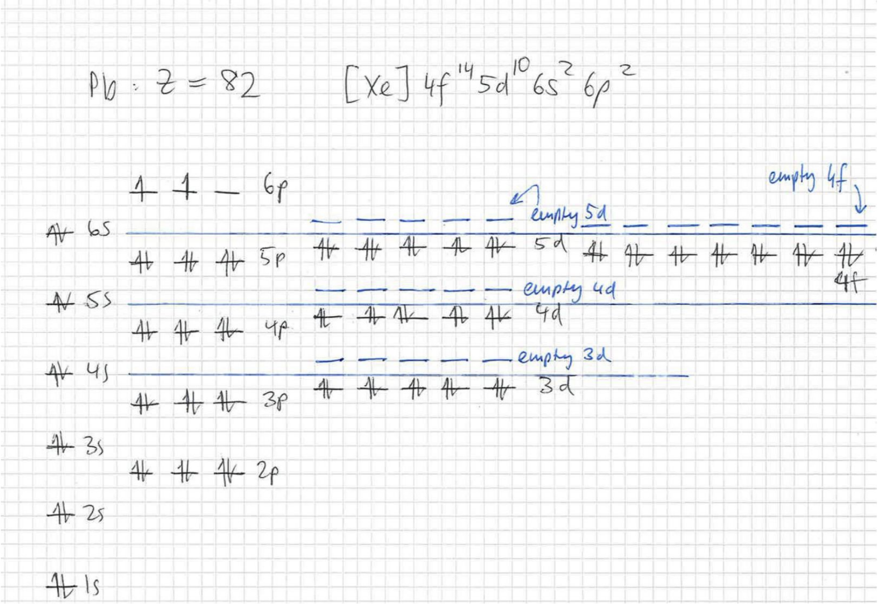
When occupied by at least one electron, the (n-1) d orbital becomes lower in energy compared to the n s orbital. The (n-1)d orbital should be written before the ns orbital

Georges

Orbital energies (Topic 1E)

Could you provide us with relative energies for filled orbitals instead of empty?

I read in the lesson that energies of orbitals are lowered when filled by a pair of electrons, does it also apply when 1 electron occupies the orbital?



Ans: When 1 electron occupies the orbital the energy will be lowered

Georges

Exercise 5 (Topic 2A)

1. I don’t understand how rule c was used in **exercice 5.1** for Cl- and Cs+, could you elaborate?

2. For **exercice 5.2** is the a general rule to determine the element closer in size, we find the one with the same electrons?

3. For **ex 5.10,** question c, why do we only consider the charge of the compounds and not the radius? How can we compare the radius of the two compounds ?

General trends

Those trends will help you to answer those questions

- Atomic radius: generally decreases from left to right across a period and increases down a group
- Cations are smaller than their parent atoms, whereas anions are larger.

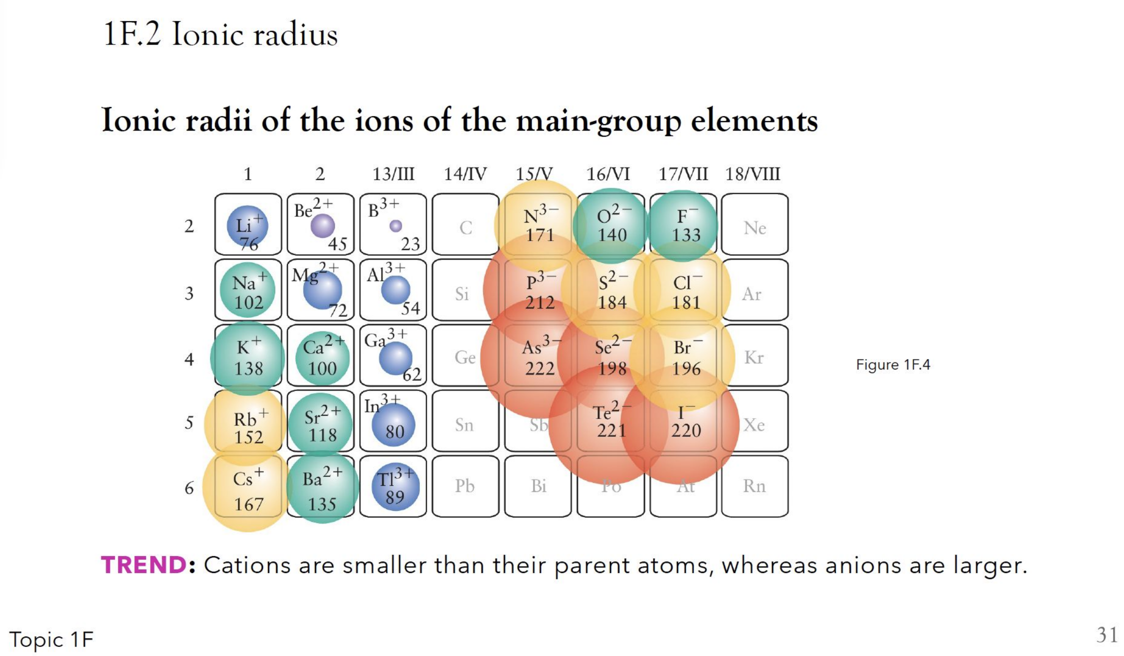
For ions:

For isoelectronic ions (e.g.O^{2-} and F^{-}): the smallest will be the one with the highest Z

Exercise 5 (Topic 2A)

I don’t understand how rule c was used in **exercice 5.1** for Cl- and Cs+, could you elaborate?

In general, anions are bigger than cations



1F.2 Ionic radius

Ionic radii of the ions of the main-group elements

	1	2	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
2	$\mathrm{Li^{+}}$ 76	$\mathrm{Be^{2+}}$ 45	$\mathrm{B^{3+}}$ 23	C	$\mathrm{N^{3-}}$ 171	$\mathrm{O^{2-}}$ 140	$\mathrm{F^{-}}$ 133	Ne
3	$\mathrm{Na^{+}}$ 102	$\mathrm{Mg^{2+}}$ 72	$\mathrm{Al^{3+}}$ 54	Si	$\mathrm{P^{3-}}$ 212	$\mathrm{S^{2-}}$ 184	$\mathrm{Cl^{-}}$ 181	Ar
4	$\mathrm{K^{+}}$ 138	$\mathrm{Ca^{2+}}$ 100	$\mathrm{Ga^{3+}}$ 62	Ge	$\mathrm{As^{3-}}$ 222	$\mathrm{Se^{2-}}$ 198	$\mathrm{Br^{-}}$ 196	Kr
5	$\mathrm{Rb^{+}}$ 152	$\mathrm{Sr^{2+}}$ 118	$\mathrm{In^{3+}}$ 80	Sn	Sb	$\mathrm{Te^{2-}}$ 221	$\mathrm{I^{-}}$ 220	Xe
6	$\mathrm{Cs^{+}}$ 167	$\mathrm{Ba^{2+}}$ 135	$\mathrm{Tl^{3+}}$ 89	Pb	Bi	Po	At	Rn

Figure 1F.4

TREND: Cations are smaller than their parent atoms, whereas anions are larger.

Topic 1F

31

Exercise 5 (Topic 2A)

For **exercice 5.2** is the a general rule to determine the element closer in size, we find the one with the same electrons?

Question 5.2: Is the size of the Cl− anion closer to the size of the Li+, Na+ or K+ cation ?

r(Li+) < r(Na+) < r(K+)

Cl- has the same number of electron as K+. For isoelectronic ion, the one with the highest number of proton (highest Z_{eff}) will be the smallest. [Z(K) = 19 > Z(Cl) = 17]. Hence r(K+) < r(Cl-)

Exercise 5 (Topic 2A)

For **ex 5.10,** question c, why do we only consider the charge of the compounds and not the radius? How can we compare the radius of the two compounds ?

5.10 Compare the magnitudes of the lattice energies of the following pairs of ionic compounds using the symbols '>' or '<'. c) LiF MgO

$$E_P \propto \frac{Z_1 \cdot Z_2}{r}$$

MgO has Z_{Mg++} x Z_{O--} = 4 compared to LiF Z_{Li+} x Z_{F-} = 1

O^{2-} and F^- are isoelectronic ions on the same period ($r(F^-) < r(O^{2-})$)

Gülsüm

Type of bond (Topic 2B)

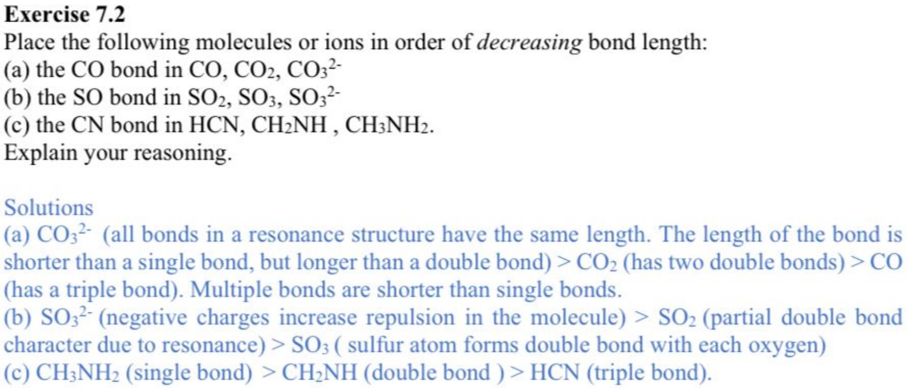
Is a metallic bond a type of covalent bond? If not, what is the distinction?

Metallic bonds form between metals. They share space with the electron on the neighbouring atom.

Covalent bonds form between nonmetals. They share pairs of electrons.

Gülsüm

Exercise 7.2 (Topic 2D)



Exercise 7.2

Place the following molecules or ions in order of *decreasing* bond length:

(a) the CO bond in CO, CO_2, CO_3^{2-}

(b) the SO bond in SO_2, SO_3, SO_3^{2-}

(c) the CN bond in HCN, CH_2NH , CH_3NH_2.

Explain your reasoning.

Solutions

(a) CO_3^{2-} (all bonds in a resonance structure have the same length. The length of the bond is shorter than a single bond, but longer than a double bond) > CO_2 (has two double bonds) > CO (has a triple bond). Multiple bonds are shorter than single bonds.

(b) SO_3^{2-} (negative charges increase repulsion in the molecule) > SO_2 (partial double bond character due to resonance) > SO_3 (sulfur atom forms double bond with each oxygen)

(c) CH_3NH_2 (single bond) > CH_2NH (double bond) > HCN (triple bond).

1. Why does SO3 not have resonance structures ?

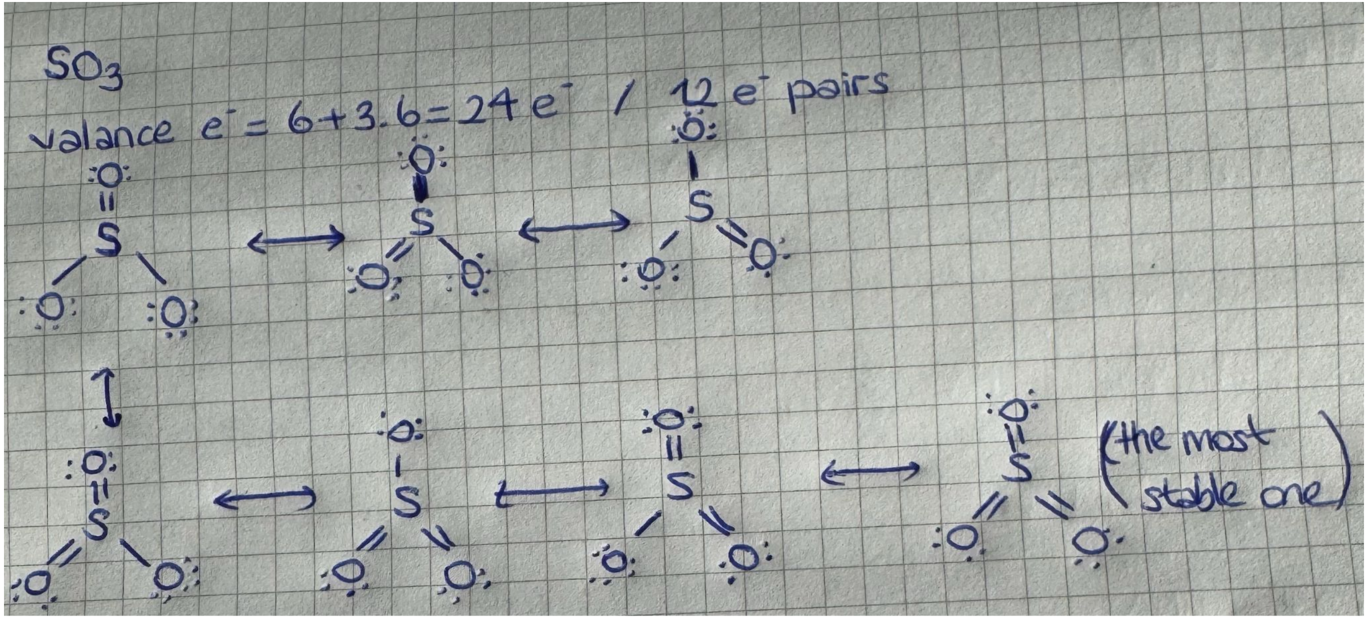
2. Could you please draw the resonance structures of SO2 ?

3. When do molecules form resonance structures ?

Exercise 7.2 (Topic 2D)

1. Why does SO3 not have resonance structures ?

SO3 has resonance structures:



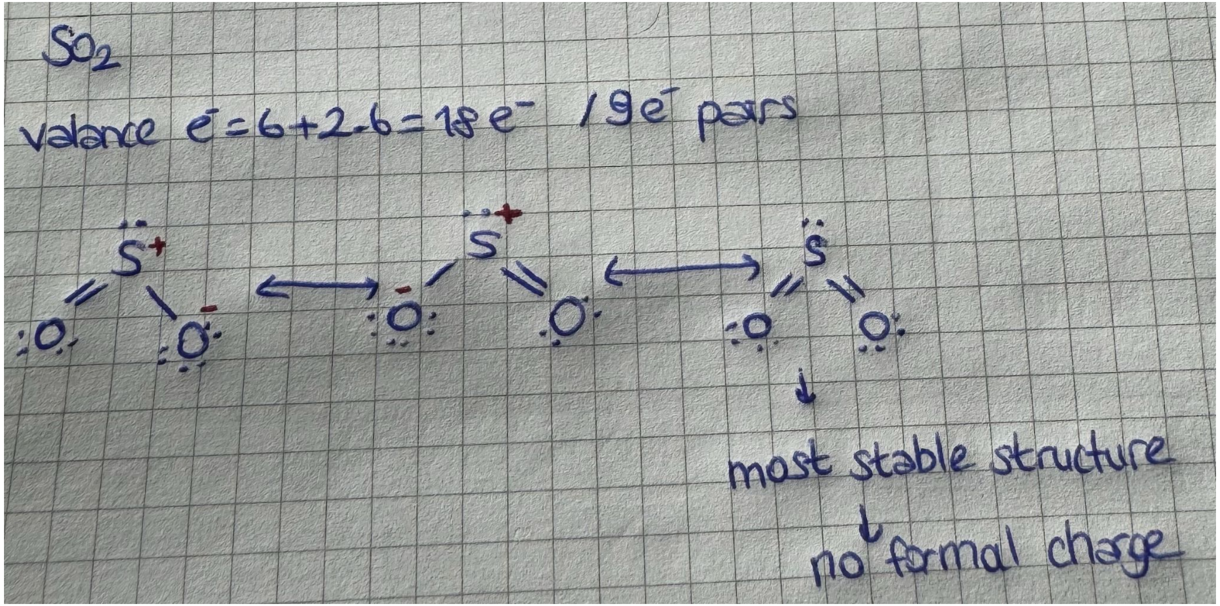
SO_3

valance $e^- = 6+3.6=24\ e^-$ / $12\ e^-$ pairs

Exercise 7.2 (Topic 2D)

2. Could you please draw the resonance structures of SO2 ?

There are three resonance structures of SO2:



SO_2

valance $e^- = 6 + 2 \cdot 6 = 18\,e^-$ / $9\,e^-$ pairs

most stable structure
↓
no formal charge

Exercise 7.2 (Topic 2D)

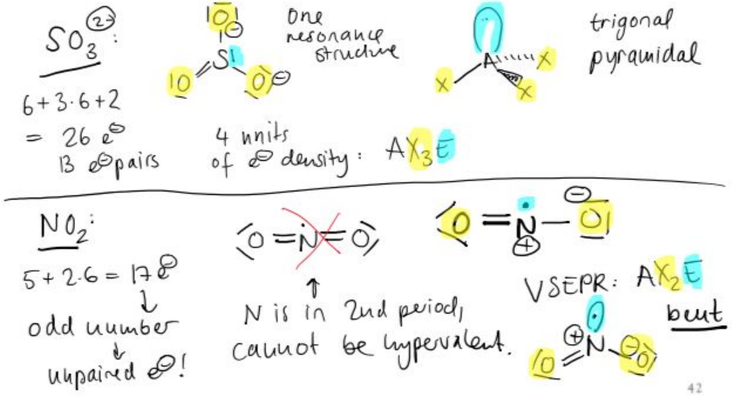
3. When do molecules form resonance structures?

The electronic structure of the molecules sometimes cannot be only explained by one Lewis structure. In the resonance structures, the position of the atoms are the same but the distribution of the electrons are different. In other words, resonance structures help explaining the electron delocalization.

Gülsüm

VSEPR and Resonance (Topic 2E)

If we had chosen this resonance for SO_3^{2-}, how could we have known that there is a lone pair and that the electron arrangement is AX3**E**?



SO_3^{2-}:

$6+3\cdot6+2$

$= 26\ e^-$

13 e^- pairs

one resonance structure

4 units of e^- density: AX_3E

trigonal pyramidal

NO_2:

$5+2\cdot6 = 17\ e^-$

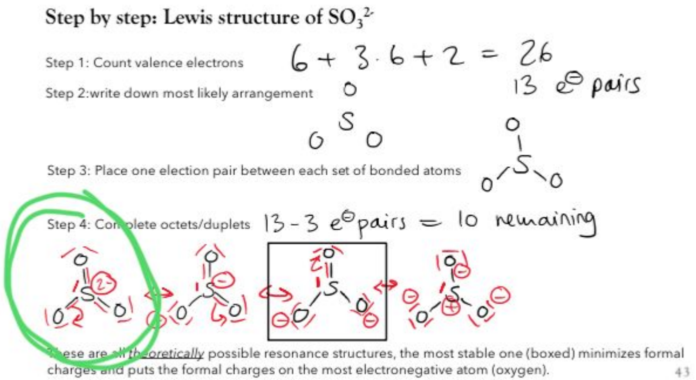
odd number

unpaired e^-!

N is in 2nd period, cannot be hypervalent.

VSEPR: AX_2E

bent



Step by step: Lewis structure of SO_3^{2-}

Step 1: Count valence electrons $6+3\cdot6+2 = 26$

13 e^- pairs

Step 2:write down most likely arrangement

Step 3: Place one election pair between each set of bonded atoms

Step 4: Complete octets/duplets $13-3$ e^-pairs = 10 remaining

These are all *theoretically* possible resonance structures, the most stable one (boxed) minimizes formal charges and puts the formal charges on the most electronegative atom (oxygen).

VSEPR and Resonance (Topic 2E)

If we had chosen this resonance for SO_3^{2-}, how could we have known that there is a lone pair and that the electron arrangement is AX3**E**?

In the AX3E notation the A represents the central atom (S) , X is bonded atom (O) and E is the lone pair electrons.

To determine if there's any lone pair electrons:

First step is to count the valence electrons and calculate number of electron pairs.

Second step is to distribute the electrons and complete the octet of the atoms (if applicable), i.e, drawing of Lewis structure.

Final step is to count the electron pairs in the Lewis structure and distribute the lone pair electrons in any.

For example in the SO_3^{2-} structure the number total v.e is 26 electrons which result in 13 electron pairs. The drawing of right Lewis structure will give 12 electron pairs meaning that one of the electron pair is a lone pair which will be on S atom.

Andrea

Rydberg formula (Topic 1A)

1. **If the electron transitions from n=3 to n=2 for example, will n_1 be 2 or 3 ?**

Answer:

$$\nu = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Where :

- R = 3.29 x 10^{15} Hz (Rydberg constant - determined experimentally)
- $n_1 = 1,2,\ldots$
- $n_2 = n_1 + 1, n_1 + 2, \ldots$

In this particular case, n_1= 2 and n_2 = 3 . An example can be found in the slide CH-110_240913_Topic1A - Example A1.2

Andrea

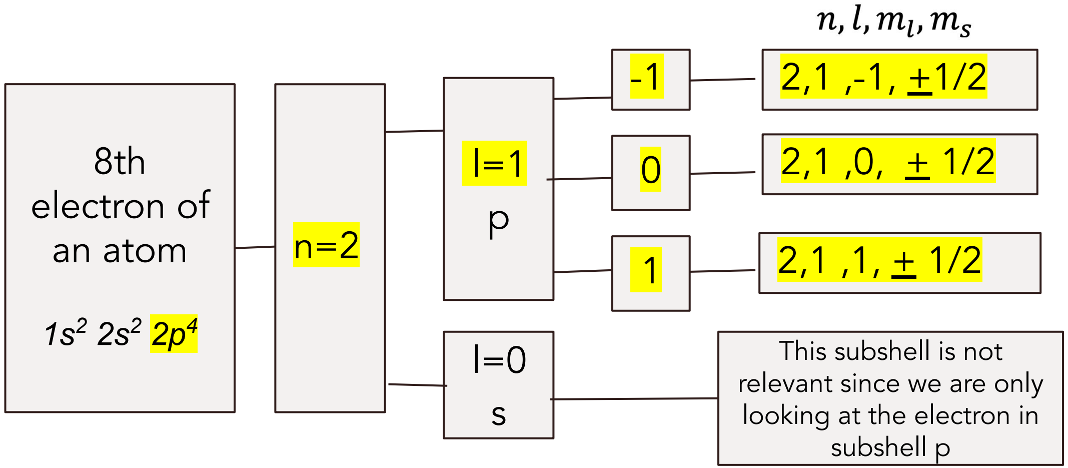
Exercise 4.10 (Topic 1D)

Exercise 4.10

Give all the possible combinations for the 4 quantum numbers of the 8th electron of an atom in its ground state in absence of a magnetic field.

Deconstructing the exercise into parts.

The **4 quantum numbers (** n, l, m_l, m_s **)** for the **8th electron** that goes according to the following electron configuration **(**$1s^2\ 2s^2\ 2p^4$) in its **ground state** (state of lowest energy) in the **absence of a magnetic field** (no preferred orientation in space).



8th electron of an atom

$1s^2\ 2s^2\ 2p^4$

n=2

l=1
p

l=0
s

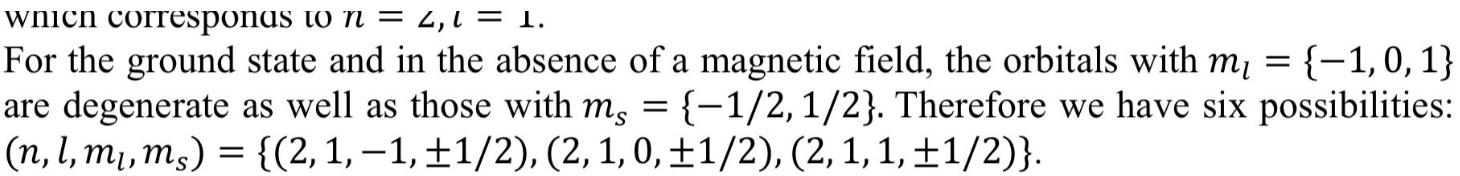
n, l, m_l, m_s

-1 — 2,1 ,-1, ±1/2

0 — 2,1 ,0, ± 1/2

1 — 2,1 ,1, ± 1/2

This subshell is not relevant since we are only looking at the electron in subshell p


which corresponds to $n = 2, l = 1$.
For the ground state and in the absence of a magnetic field, the orbitals with $m_l = \{-1, 0, 1\}$ are degenerate as well as those with $m_s = \{-1/2, 1/2\}$. Therefore we have six possibilities: $(n, l, m_l, m_s) = \{(2, 1, -1, \pm 1/2), (2, 1, 0, \pm 1/2), (2, 1, 1, \pm 1/2)\}$.

2. Why the absence of a magnetic field means that the orbitals are degenerate?

Recalling from the lectures, the orbitals of a given shell are said to be **degenerate** when they have the same energy.

Without the influence of the magnetic field, orbitals are exposed to a spherically symmetric potential. This arises because the Coulomb potential is spherically symmetric, meaning there is no spatial direction that is inherently special. When an external magnetic field is applied, it introduces a preferred direction in space, causing orbitals that were previously degenerate (e.g., the p_x, p_y, p_z orbitals) to split into different energy levels. This splitting due to the magnetic field is known as the Zeeman effect (NOT COVERED IN THIS CLASS).

3. Why can't we just say that ml = 0 because there is no magnetic field ?

m_l isn't the magnetic field. It is the magnetic quantum number! It determines the orientation of the orbital in space relative to an external magnetic field. In the absence of magnetic field, the energies of the orbitals are degenerate, therefore this quantum number can take all of the possible numbers corresponding to an orbital of the same energy in the ground state.

Paula

Surface and dipole moment (Topic 2E)

1. Are we expected to know how to draw these types of surfaces (topic 2E)? NO.
2. Can we use the normal convention for the dipoles, pointing towards the most electronegative atom? This is the chemical convention and we use this one in organic chemistry as well.

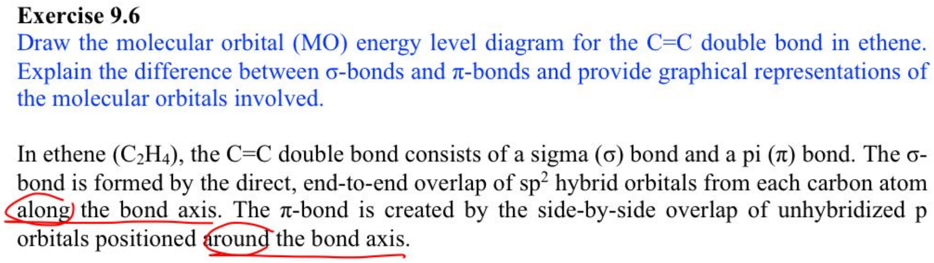
   Answer: you can use whichever convention you prefer, you just have to indicate the plus and minus partial charges.

Paula

Exercise 9.6 (Topic 2G)

1. Could you explain the difference between being along the bond axis and around the bond axis with a drawing ?

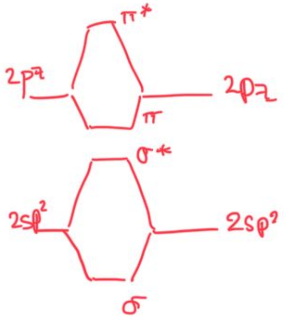
2. Can we draw the MO diagram as shown in red? If not, why? And how could we have predicted the energy levels with the pi bond and pi star being lower than sigma star?

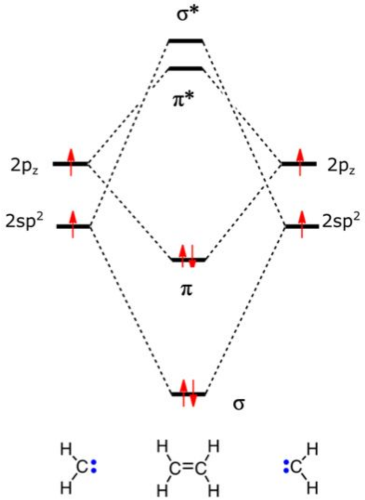


Exercise 9.6

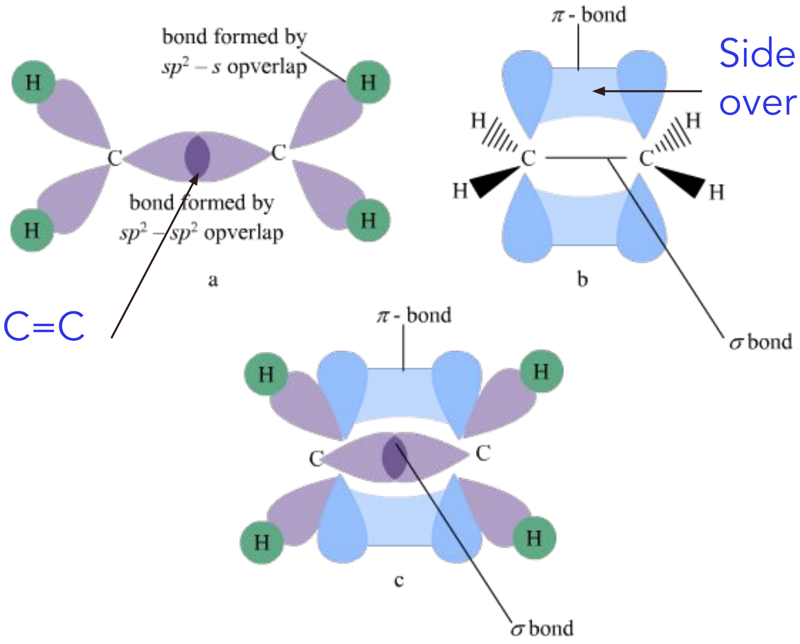
Draw the molecular orbital (MO) energy level diagram for the C=C double bond in ethene. Explain the difference between σ-bonds and π-bonds and provide graphical representations of the molecular orbitals involved.

In ethene (C_2H_4), the C=C double bond consists of a sigma (σ) bond and a pi (π) bond. The σ-bond is formed by the direct, end-to-end overlap of sp^2 hybrid orbitals from each carbon atom along the bond axis. The π-bond is created by the side-by-side overlap of unhybridized p orbitals positioned around the bond axis.





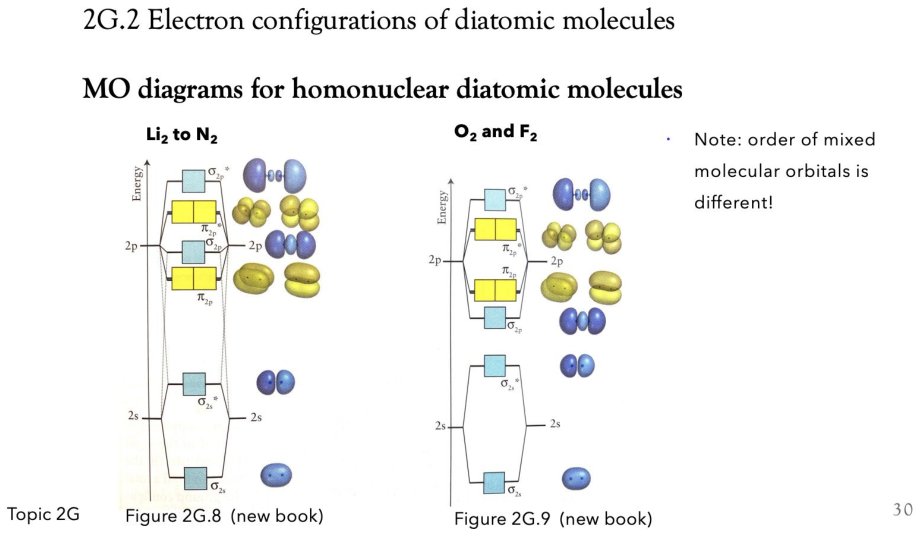
Answer



Side by side overlap

Along the C=C bond axis

The MO diagram can not be drawn as shown in red. The difference in energy of the p and sp orbitals is not big enough. According to the course we generally have the following type of diagrams for homo and hetero nuclear diatomic molecules.



2G.2 Electron configurations of diatomic molecules

MO diagrams for homonuclear diatomic molecules

Li_2 to N_2

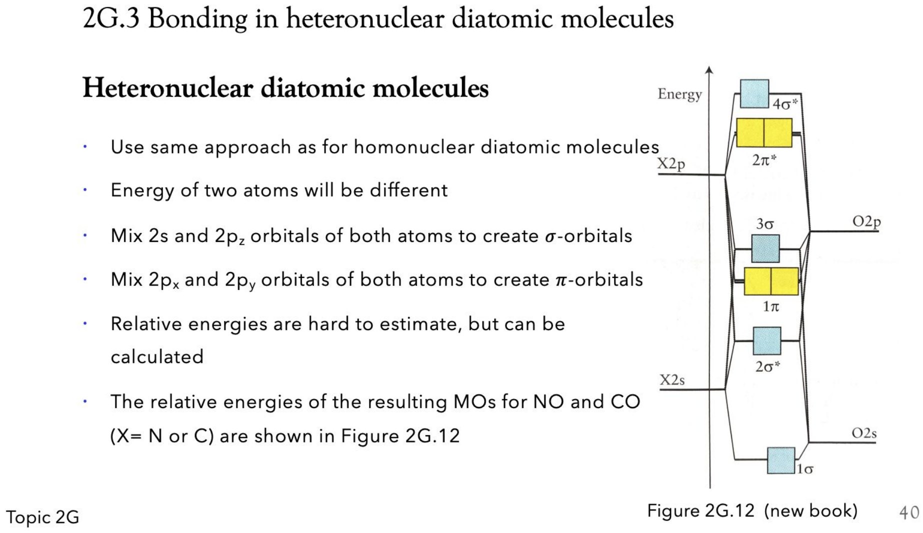
O_2 and F_2

- Note: order of mixed molecular orbitals is different!

Topic 2G

Figure 2G.8 (new book)

Figure 2G.9 (new book)



2G.3 Bonding in heteronuclear diatomic molecules

Heteronuclear diatomic molecules

- Use same approach as for homonuclear diatomic molecules
- Energy of two atoms will be different
- Mix 2s and $2p_z$ orbitals of both atoms to create σ-orbitals
- Mix $2p_x$ and $2p_y$ orbitals of both atoms to create π-orbitals
- Relative energies are hard to estimate, but can be calculated
- The relative energies of the resulting MOs for NO and CO (X= N or C) are shown in Figure 2G.12

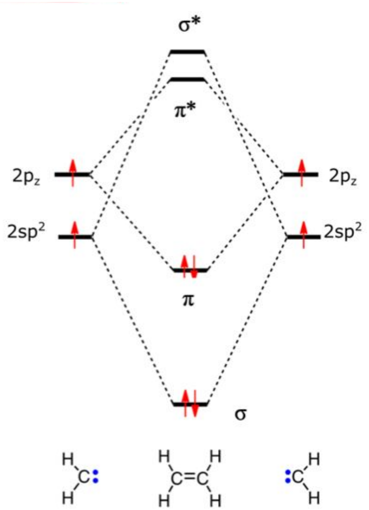
Topic 2G

Figure 2G.12 (new book)

In this case we don't have a diatomic molecule.

To more precisely calculate the MO energies to draw the correct MO diagram, the use of computer power is generally necessary.

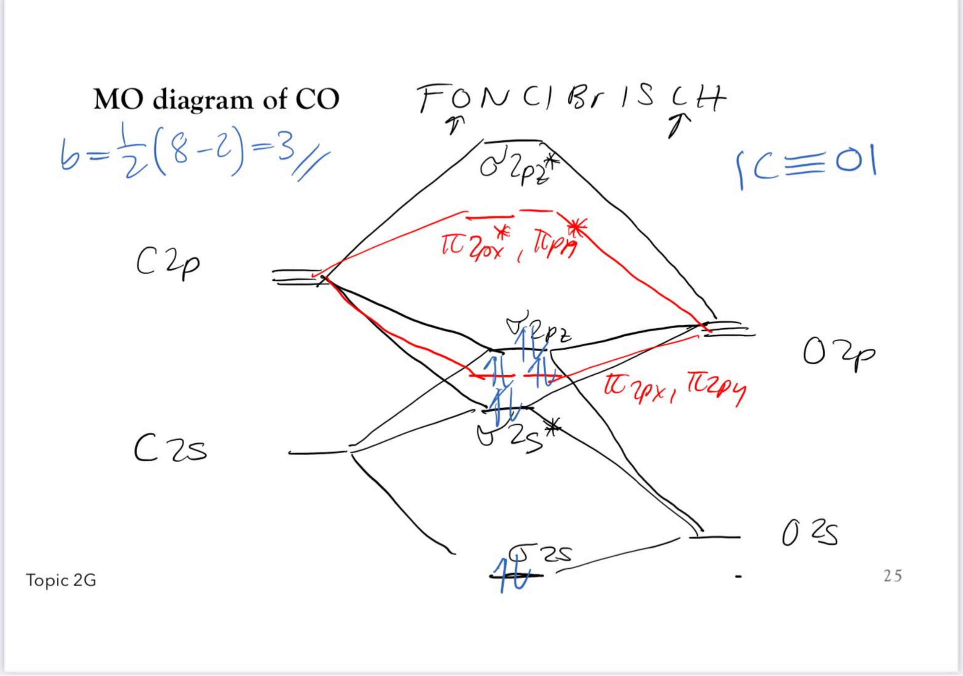
We will not go further than diatomic molecules in the exam.



Paula

Molecular orbitals (Topic 2G)

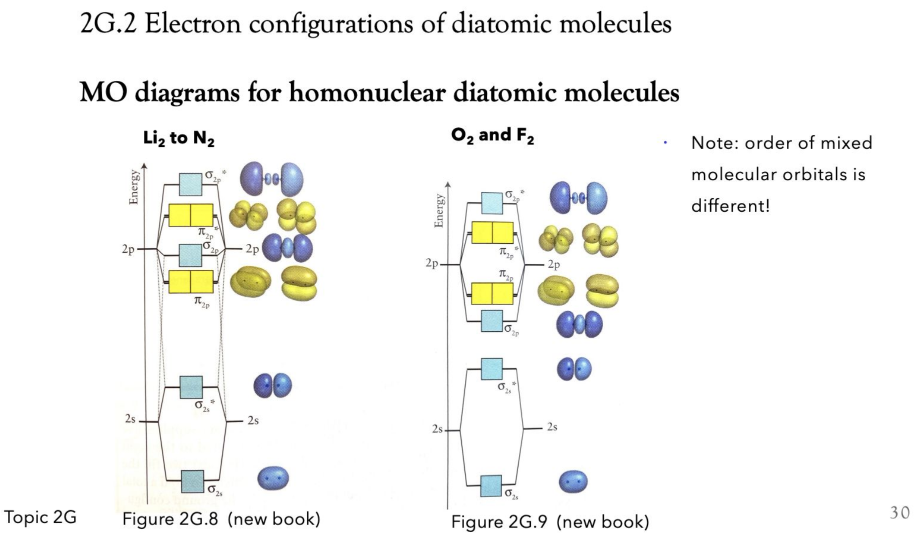
I don’t understand how to determine the order of filling of electrons and the relative energies of molecular orbitals…



MO diagram of CO

Answer

According to the course:



2G.2 Electron configurations of diatomic molecules

MO diagrams for homonuclear diatomic molecules

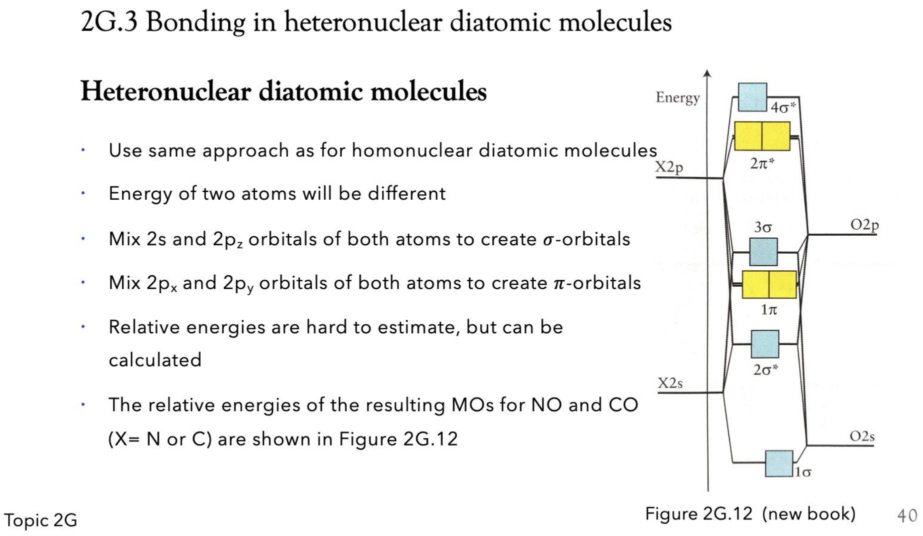
Li_2 to N_2

Figure 2G.8 (new book)

O_2 and F_2

Figure 2G.9 (new book)

- Note: order of mixed molecular orbitals is different!



2G.3 Bonding in heteronuclear diatomic molecules

Heteronuclear diatomic molecules

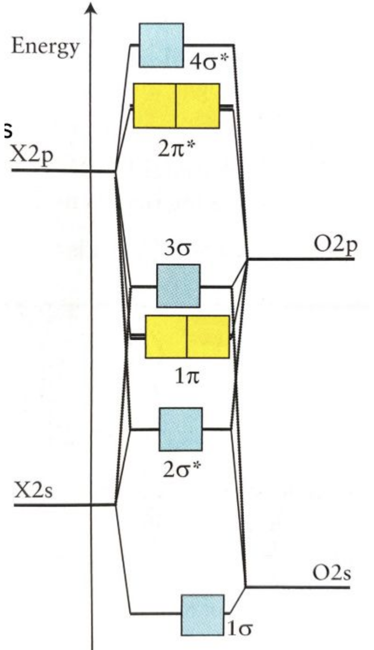
- Use same approach as for homonuclear diatomic molecules
- Energy of two atoms will be different
- Mix 2s and $2p_z$ orbitals of both atoms to create σ-orbitals
- Mix $2p_x$ and $2p_y$ orbitals of both atoms to create π-orbitals
- Relative energies are hard to estimate, but can be calculated
- The relative energies of the resulting MOs for NO and CO (X= N or C) are shown in Figure 2G.12

Figure 2G.12 (new book)

$Z<8$ $Z>=8$

There are not many cases with heteronuclear molecule with bonds. You are not expected to know more than the NO and CO MO order.

Here we have CO a heteronuclear molecule, so we have the following MO diagram.



To fill in the electrons we follow the 'Aufbau principle' and fill in the electrons in the increasing order of energy of the MO and starting with the positive spins for each MO.