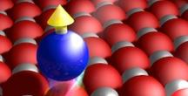


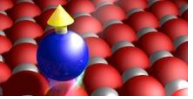
1.1 Mean radius of a 1s orbital

Calculate the mean radius $\langle r \rangle$ of a 1s orbital.

Evaluate it for the H atom.

Hints:

- Find $\langle r \rangle$ as expectation value, knowing that the angular part Y of the total wavefunction is normalized to 1.



1.1 Mean radius of a 1s orbital - Solution

$$\langle r \rangle = \langle \psi | r | \psi \rangle \int \psi^* r \, \psi \, dV = \int_0^\infty \int_0^\pi \int_0^{2\pi} r \, R_{n,l}^2 \, \left| Y_{l,m_l} \right|^2 r^2 \, dr \, \sin\theta \, d\theta \, d\phi = \int_0^\infty r^3 R_{n,l}^2 \, dr$$

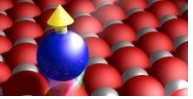
For the 1s orbital

$$R_{1,0}(r) = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

$$\langle r \rangle = \frac{4Z^3}{a_0^3} \int_0^\infty r^3 e^{-2Zr/a_0} \, dr = \frac{3a_0}{2Z}$$

For the H atom, $Z = 1 \rightarrow \langle r \rangle = \frac{3a_0}{2} = 79.3$ pm

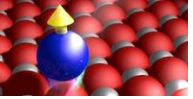
→



1.2 Most probable radius of 1s orbitals

Find the expression of $P(r)$ for 1s hydrogenic orbitals.

Calculate the most probable radius, r^*, at which an electron will be found when it occupies a 1s orbital of a hydrogenic atom of atomic number Z and tabulate the values for the one-electron species for H, He^{+}, C^{5+}, Ne^{9+}.



1.2 Most probable radius of 1s orbitals - Solution

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

For 1s orbitals: $$R(r) = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-2Zr/a_0}$$

$$P(r) = \frac{4Z^3}{a_0^3} r^2 e^{-2Zr/a_0}$$

To find the maximum probability, we look for the extrema of P

$$\frac{dP}{dr} = \frac{4Z^3}{a_0^3}\left(2r - \frac{2Zr^2}{a_0}\right) e^{-2Zr/a_0} = 0$$

This function is zero where the term in parentheses is zero, which (other than at $r = 0$) is at

$$r^* = \frac{a_0}{Z}$$

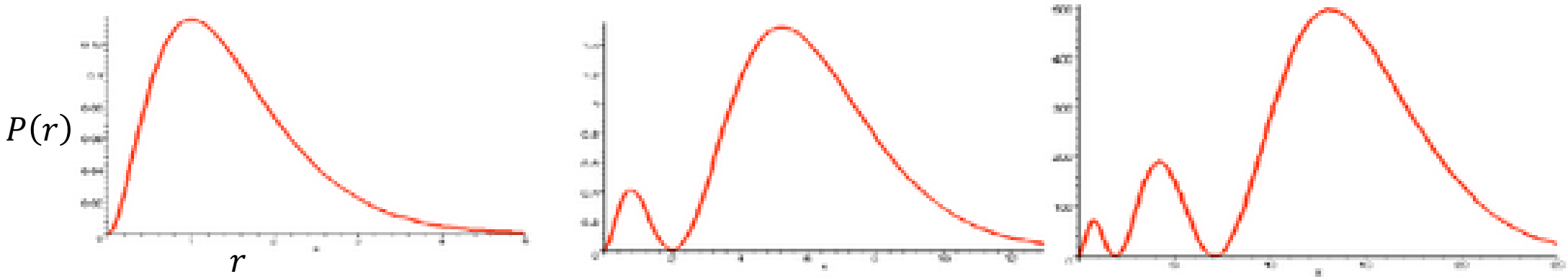
With $a_0 = 52.9$ pm, we find

	H	He^+	C^{5+}	Ne^{9+}
Z	1	2	6	10
r^* (pm)	52.9	25.5	8.8	5.3

The 1s orbital is drawn towards the nucleus as the nuclear charge increases

1.3 Radial distributions

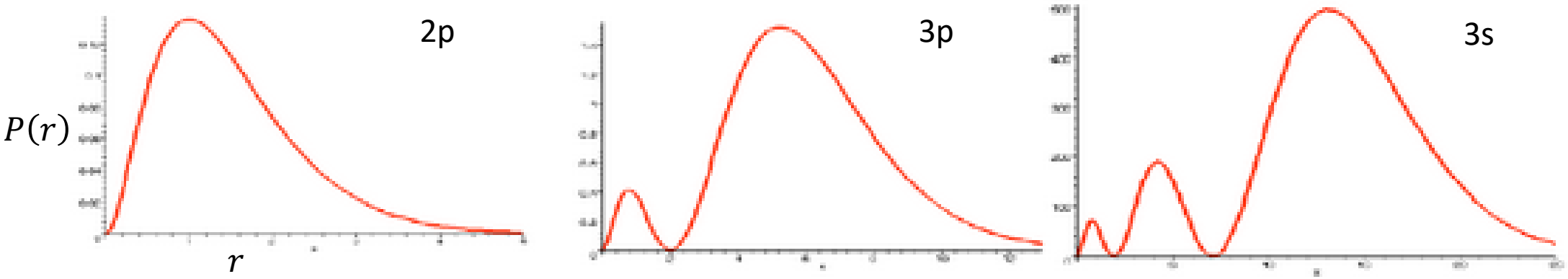
Match the following radial probability density distributions $P(r)$ with 3s, 2p, and 3p orbitals.
Make a reasoning based on the number of nodes and justify your answer.

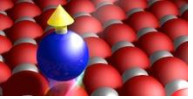


1.3 Radial distribution - Solution

s wavefunctions:
1s zero nodes
2s one node
3s two nodes

p wavefunctions start at $n = 2$:
2p zero nodes
3p two nodes



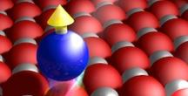


1.4 Spin-orbit-split levels

Consider one electron in the following orbitals

- 2p
- 3s
- 3d
- 4d
- 4f

For each case, find the values of j and their multiplicity.



1.4 Spin-orbit-split levels - Solution

- 2p

$l = 1$, $s = 1/2$, $j = l + s = 3/2$ (multiplicity 4 with $m_j = \pm 3/2, \pm 1/2$) and , $j = l - s = 1/2$ (multiplicity 2 with $m_j = \pm 1/2$)

- 3s

There is no spin-orbit coupling for s orbitals since the orbital angular momentum is zero, $j = l = 0$

- 3d

$l = 2$, $s = 1/2$, $j = 5/2$ (multiplicity 6 with $m_j = \pm 5/2, \pm 3/2, \pm 1/2$) and , $j = 3/2$ (multiplicity 4 with $m_j = \pm 3/2, \pm 1/2$)

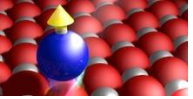
- 4d

$l = 2$, $s = 1/2$, $j = 5/2$ (multiplicity 6) and , $j = 3/2$ (multiplicity 4)

It does not depend on the principal quantum number n

- 4f

$l = 3$, $s = 1/2$, $j = 7/2$ (multiplicity 8 with $m_j = \pm 7/2, \pm 5/2, \pm 3/2, \pm 1/2$) and , $j = 5/2$ (multiplicity 6 with $m_j = \pm 5/2, \pm 3/2, \pm 1/2$)



1.5 Hund's rules

Use the Hund's rules to determine the ground state for the following atoms:

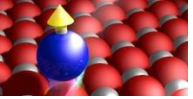
Carbon: $1s^2\ 2s^2\ 2p^2$

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

Vanadium: [Ar] $3d^3\ 4s^2$

Holmium: [Xe] $4f^{11}\ 5d^0\ 6s^2$

Write the ground state configuration as spectroscopic term.



1.5 Hund's rules - Solution

Carbon: $1s^2\ 2s^2\ 2p^2$
Only the 2p subshell is partially occupied

m_l	$+1$	0	-1
m_s	$\uparrow$	$\uparrow$	

Maximize $|M_S|$
$M_S = +1 \rightarrow S = 1$

Maximize $|M_L|$
$M_L = +1 \rightarrow L = 1$

subshell less than half-filled $\rightarrow J = L - S = 0$

$^3\mathrm{P}_0$

Oxygen: $1s^2\ 2s^2\ 2p^4$
Only the 2p subshell is partially occupied

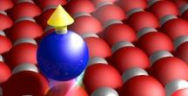
m_l	$+1$	0	-1
m_s	$\uparrow\downarrow$	$\uparrow$	$\uparrow$

Maximize $|M_S|$
$M_S = +1 \rightarrow S = 1$

Maximize $|M_L|$
$M_L = +1 \rightarrow L = 1$

subshell more than half-filled $\rightarrow J = L + S = 2$

$^3\mathrm{P}_2$



1.5 Hund's rules - Solution

Vanadium: [Ar] $3d^3\ 4s^2$
Only the 3d subshell is partially occupied

m_l	$+2$	$+1$	0	-1	-2
m_s	↑	↑	↑		

Maximize $|M_S|$
$M_S = 3/2 \rightarrow S = 3/2$

Maximize $|M_L|$
$M_L = 3 \rightarrow L = 3$

subshell less than half-filled $\rightarrow J = L - S = 3/2$

$^4\mathrm{F}_{3/2}$

Holmium: [Xe] $4f^{11}\ 5d^0\ 6s^2$
Only the 4f subshell is partially occupied

m_l	$+3$	$+2$	$+1$	0	-1	-2	-3
m_s	↑ ↓	↑ ↓	↑ ↓	↑ ↓	↑	↑	↑

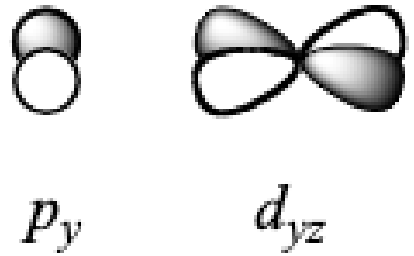
Maximize $|M_S|$
$M_S = 3/2 \rightarrow S = 3/2$

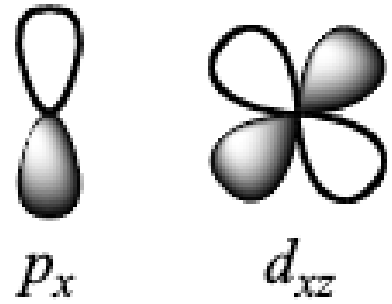
Maximize $|M_L|$
$M_L = 6 \rightarrow L = 6$

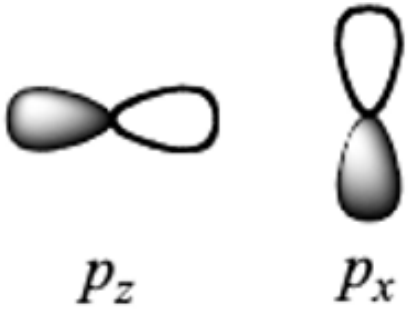
subshell more than half-filled $\rightarrow J = L + S = 15/2$

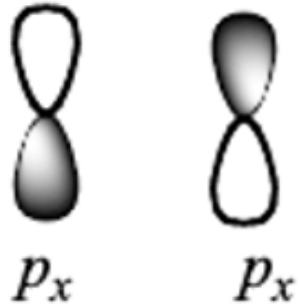
$^4\mathrm{I}_{15/2}$

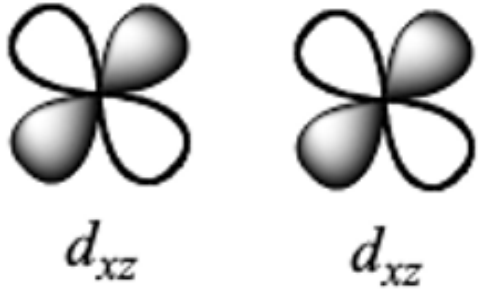
Predict what type (if any) of molecular orbital and bond can be formed by these pairs of atomic orbitals.
Specify if it is bonding or antibonding.









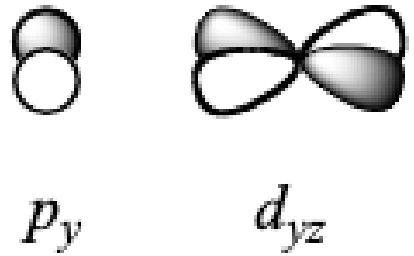


1.6 Molecular orbitals - Solution

Predict what type (if any) of molecular orbital and bond can be formed by these pairs of atomic orbitals.
Specify if it is bonding or antibonding.

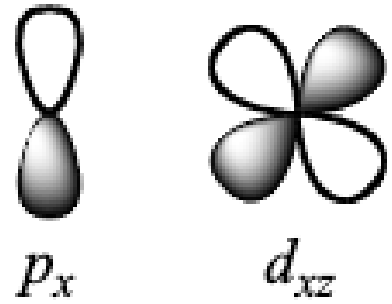
Along interatomic axis, in phase

σ



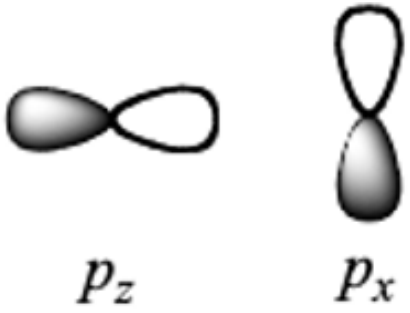
Normal to interatomic axis, in phase

π

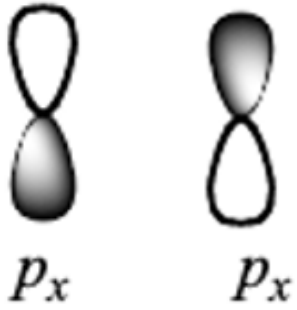


Normal to interatomic axis, in phase

π

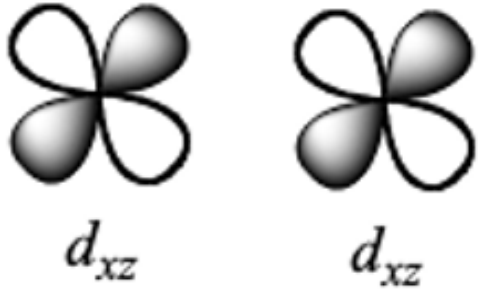


No defined geometry, no orbital



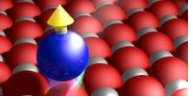
Normal to interatomic axis, out of phase

π^*



Normal to interatomic axis, out of phase

π^*



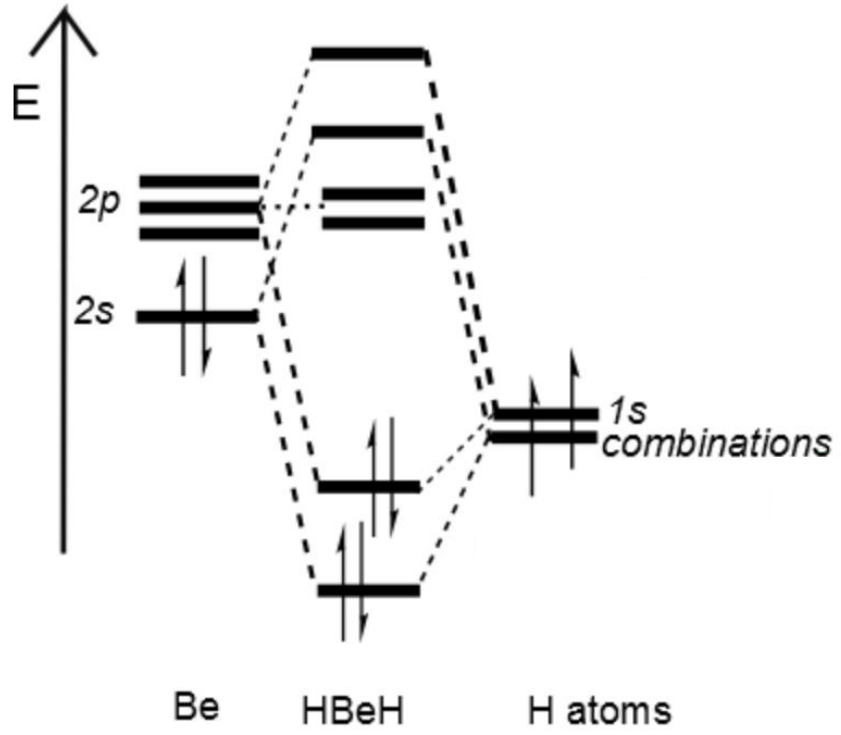
1.7 Molecules and orbitals

A) Consider the methane molecule: CH_4

- Considering the hybrid orbitals seen in the lecture, can you figure out its structure and geometry?
- Which bonds are formed?

B) Beryllium ($1s^2\ 2s^2$) and two hydrogen atoms form the linear BeH_2 molecule: HBeH.
The resulting scheme for the molecular orbitals is shown in the figure.

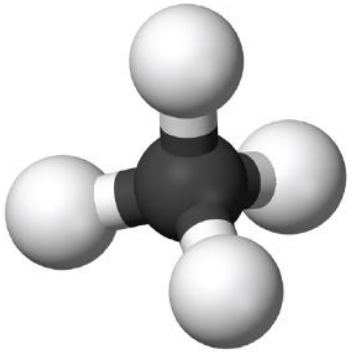
- Identify the levels of the σ and σ^* orbitals in the scheme.
- Draw the corresponding molecular orbitals.



A)

Methane has a tetrahedral structure, related to the formation of sp^3 hybrid orbitals.

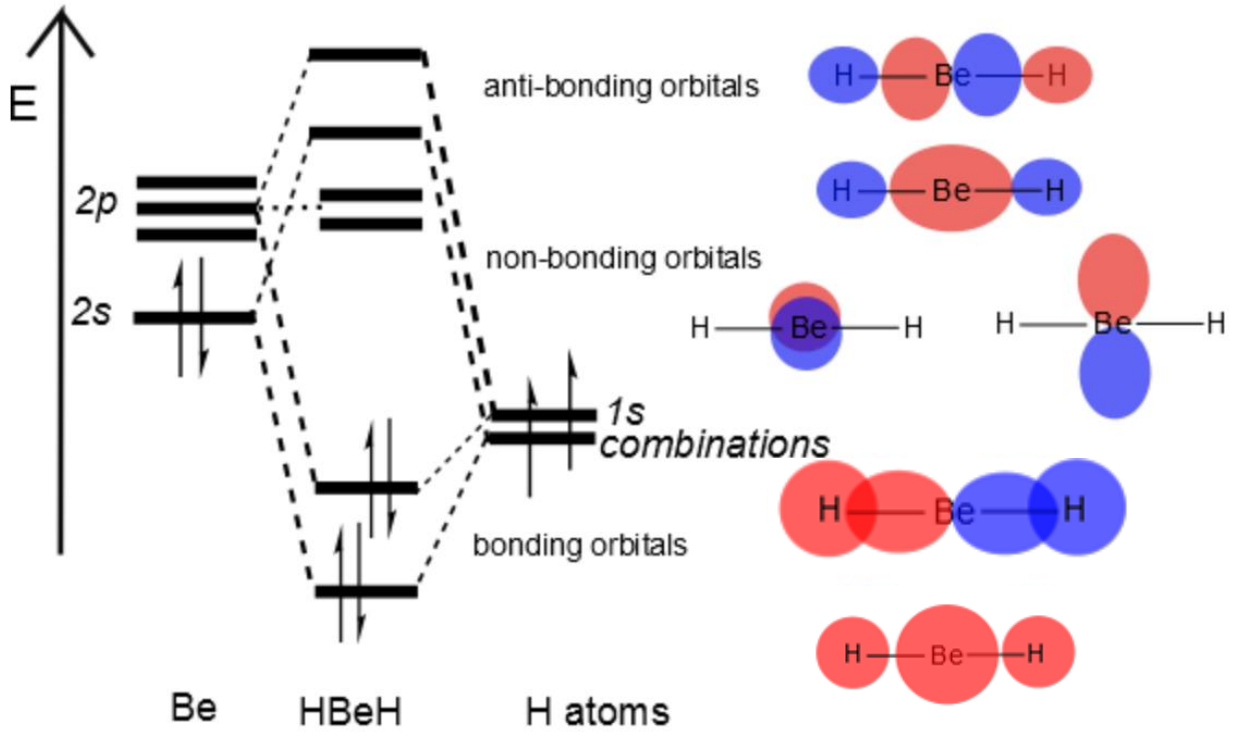
Bonds: four σ bonds between the sp^3 and the four H 1s



methane

B)

The s orbitals form σ bonds with the H 1s orbitals.
Note the increasing number of nodes for increasing energy.
(When condensed, the BeH_2 molecules form polymers.)



σ* orbitals formed by the two H 1s and 2s, 2p

degenerate p_x, p_y

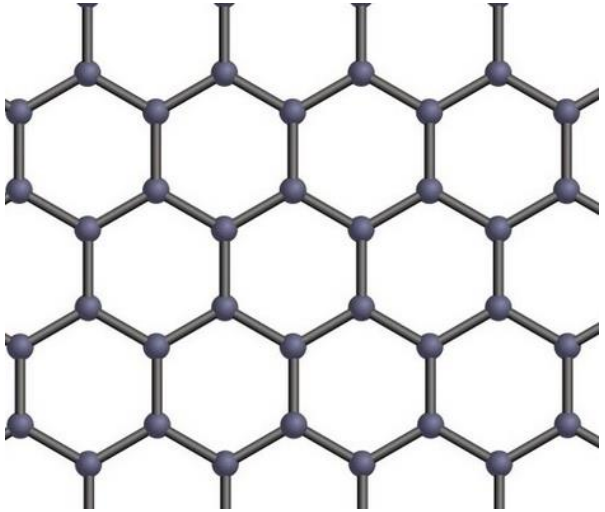
σ orbitals formed by the two H 1s and 2s, 2p

we can also introduce hybrid sp orbitals instead of the 2s and 2p

1.8 Graphene

Graphene is an allotrope of carbon consisting of a single layer of atoms arranged in a honeycomb structure.

- Which atomic orbitals participate into the bonding?
- What are the hybrid orbitals that are formed?
- Which types of bonds are formed and where?



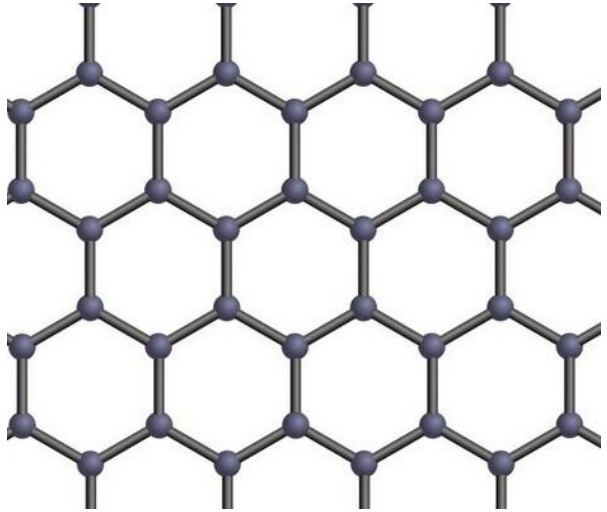
1.8 Graphene - Solution

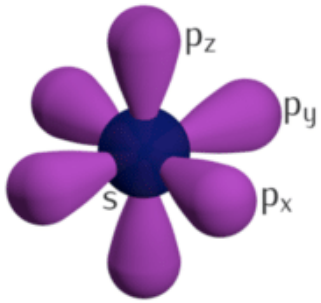
Carbon: $1s^2\ 2s^2\ 2p^2$

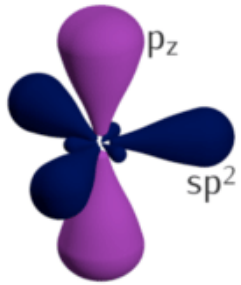
The orbitals 2s and 2p participate into the bonding

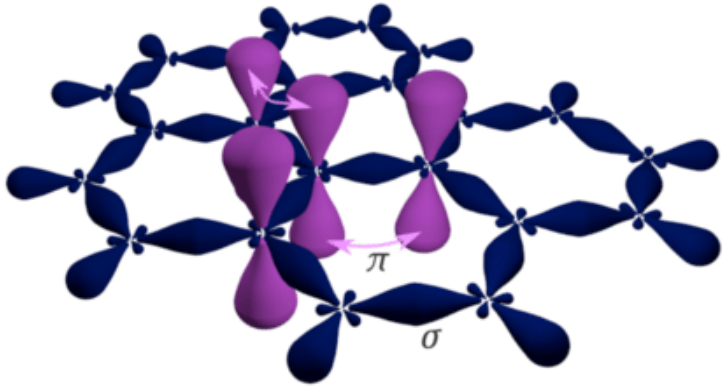
The planar structure is obtained thanks to the sp^2 hybridization

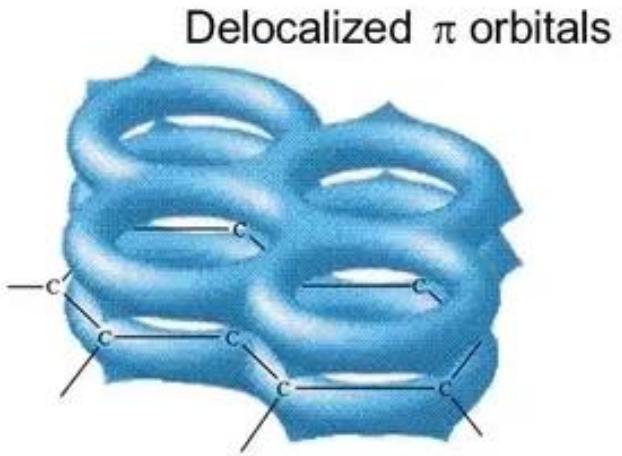
σ bonds between the sp^2 orbitals in the plane;
π bonds between the p_z orbitals perpendicular to the plane





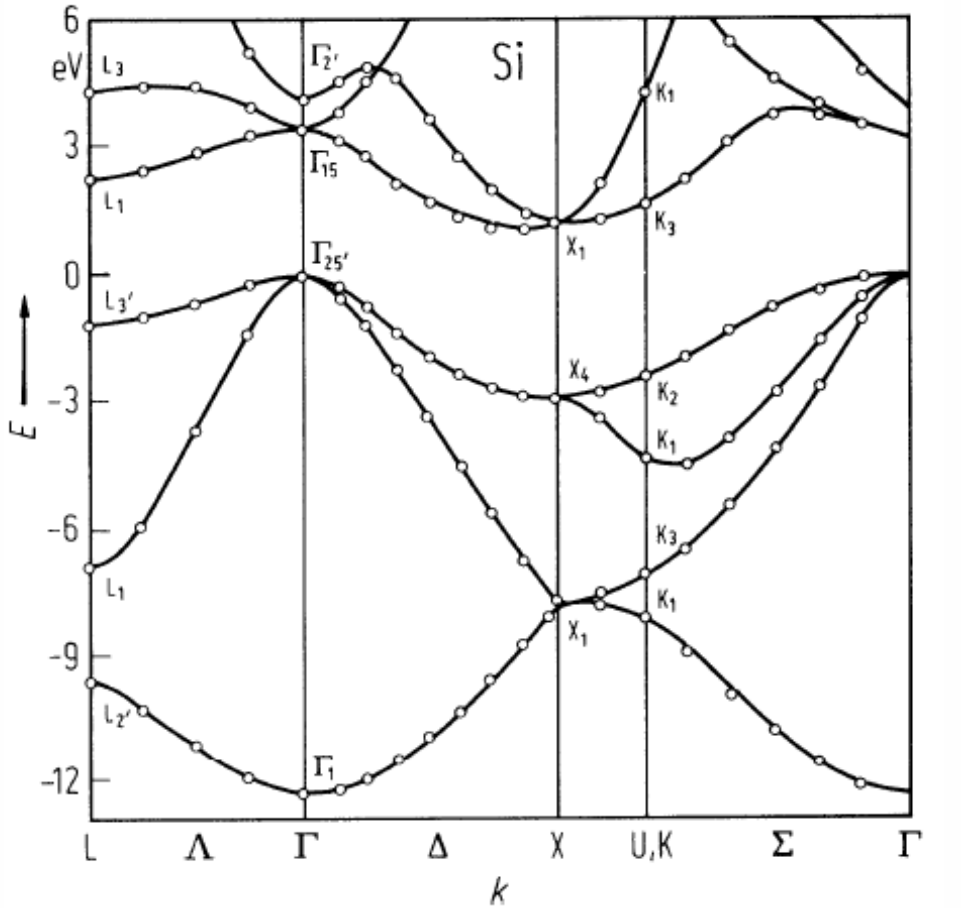






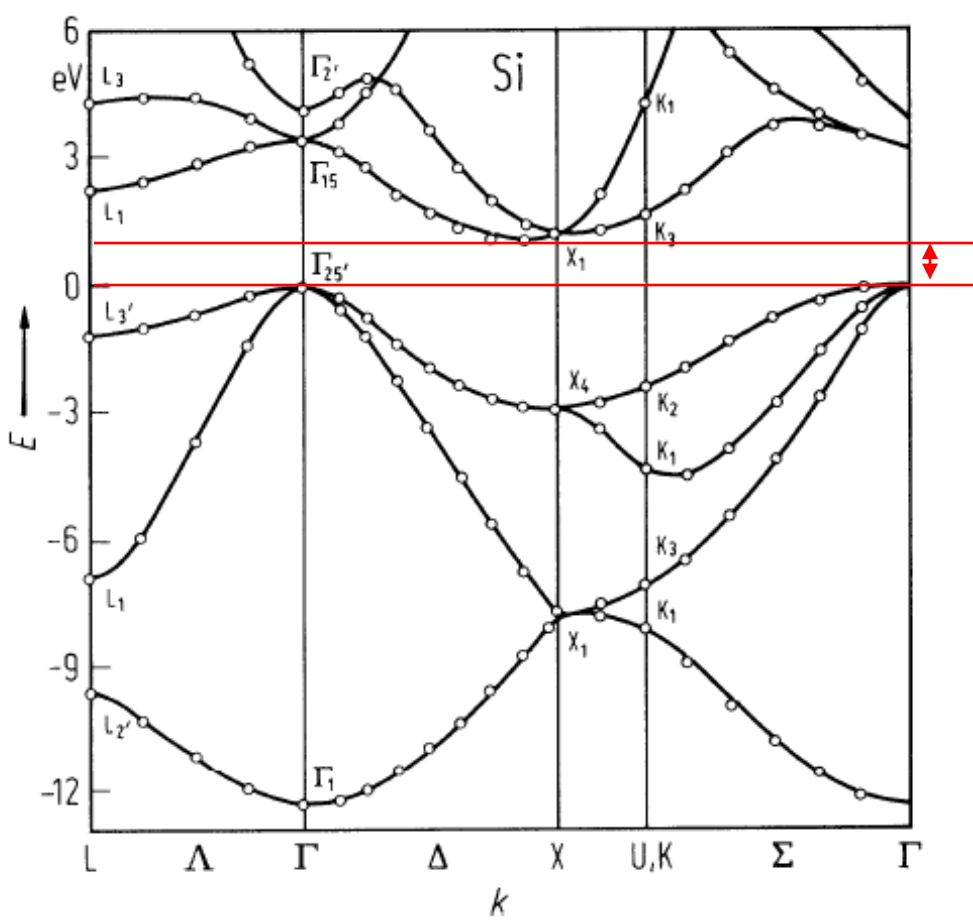
1.9 Band structure of Si

Consider the band structure of Si shown below.
Identify the gap and estimate its width.



1.9 Band structure of Si - Solution

The gap corresponds to the region in which there are no states, for any k-vector.

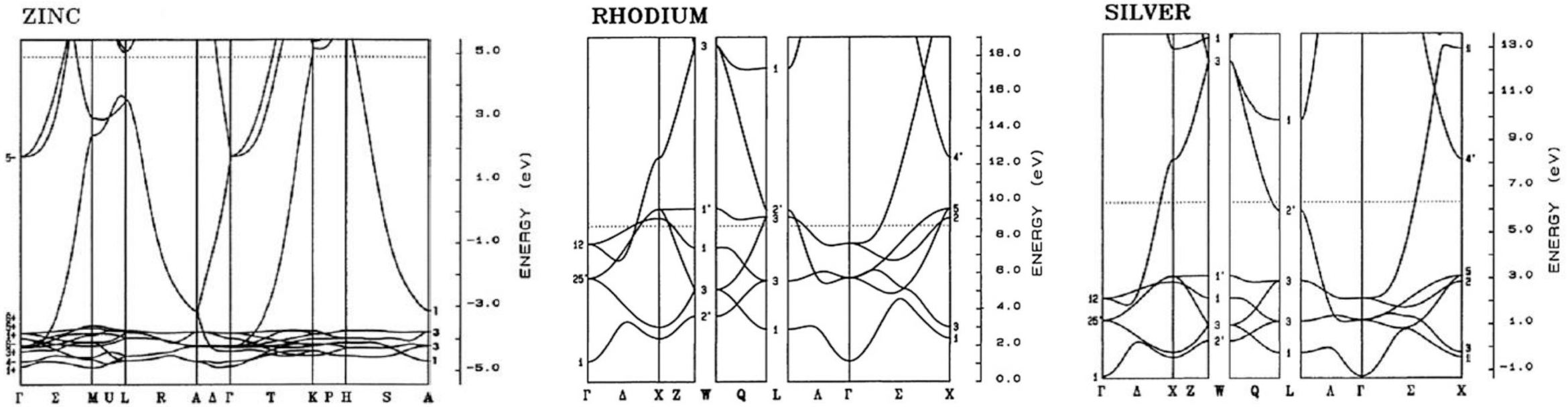


$E_{gap} \approx 1$ eV

1.10 Band structure and DOS

The calculated band structure of three metals is shown in the figures below.
The Fermi energy is indicated by the dotted line. For each of them:

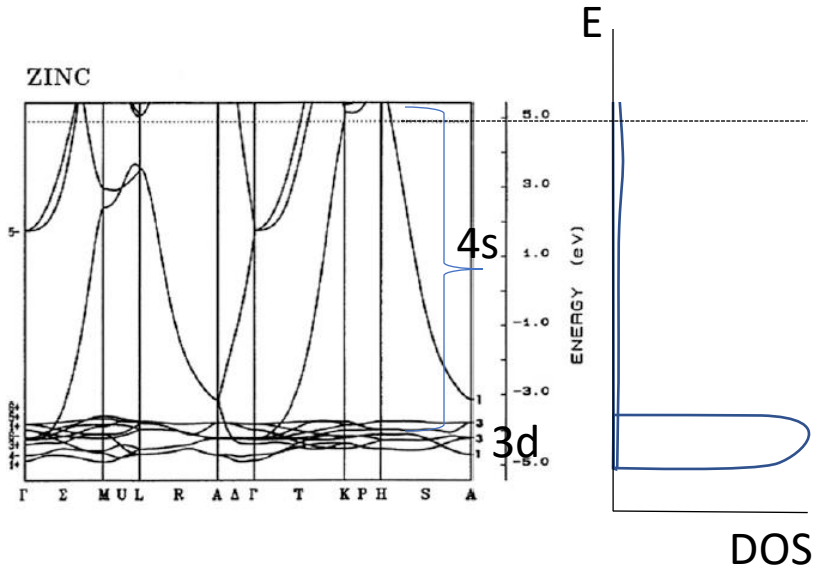
- use the periodic table to find the atomic electron configuration
- identify the atomic states that form the bands in the solid, and identify the bands in the band diagram
- sketch qualitatively the density of states (DOS)



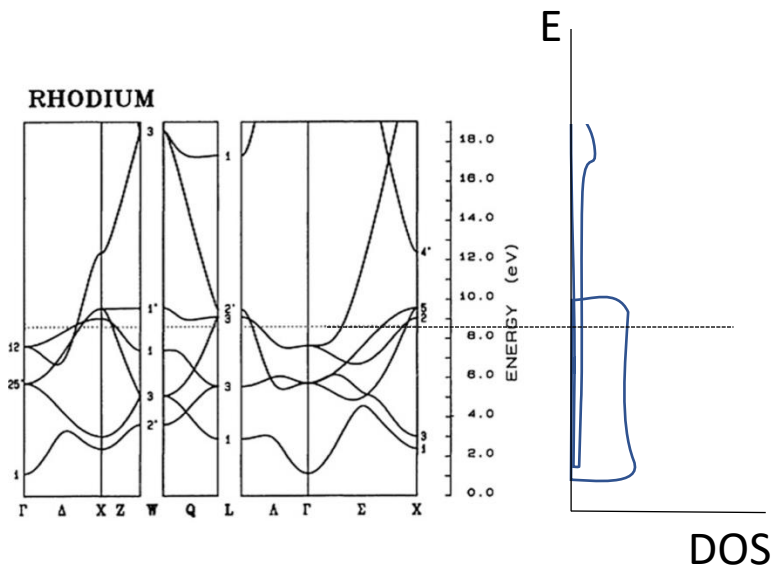
Handbook of the Band Structure of Elemental Solids, D. A. Papaconstantopoulos

1.10 Band structure and DOS - Solution

Zn: [Ar] $3d^{10}$ $4s^2$
3d and 4s



Rh: [Kr] $4d^8$ $5s^1$
4d and 5s



Ag: [Kr] $4d^{10}$ $5s^1$
4d and 5s