Tutorial 4

1 a) Define atom.
b) Why are they considered the basic units of matter?
c) What are their constituent particles and how are they spatially arranged?
d) How many models do we use nowadays to describe the atom; its physics and chemistry?
e) What are the orbitals in the Bohr's model?

Answers:

a) Atoms are the basic units of matter. Atoms are the smallest portion of matter that still retain its physical and chemical properties.

b) Because they still retain the physical and chemical properties of matter. If we decompose an atom into its constituent particles, we can no longer retrieve the original matter: electron, protons and neutrons alone tell us nothing about Matter.

c) Atoms are composed of a nucleus of neutrons and protons, surrounded by a cloud of electrons.

d) The most modern version of atomic model is orbital model or charged cloud; but to understand certain phenomena, we still use Bohr's model of orbits.

e) Orbitals are statistical functions that define regions of space around the nucleus where the probability of finding an electron is different from zero.

2 a) How many quantum numbers define/characterise an orbital?

b) How many quantum numbers characterise an electron in an orbital?

c) Identify and explain these quantum numbers.

Answers:

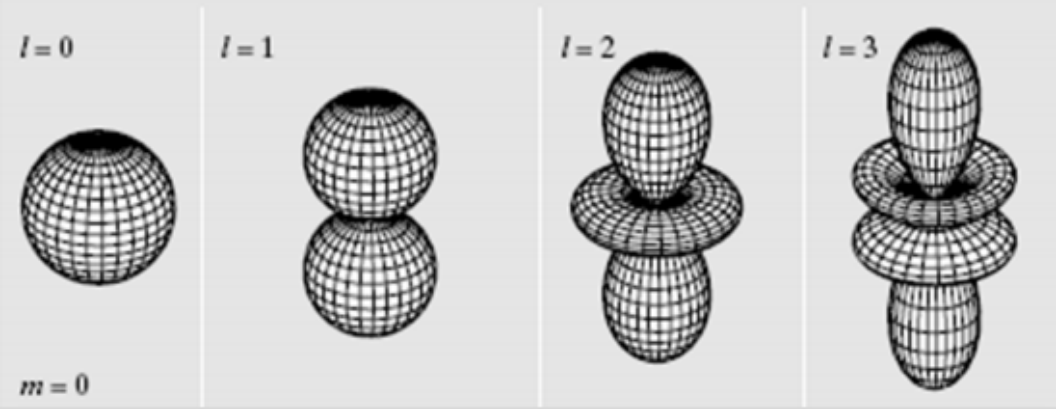
1. Principal quantum number: n. → Energy level
2. Azimuthal quantum number: l. → Shape of the orbital
3. Orbital magnetic quantum number: m_l → Polarity

Each orbital can accommodate up to **2 electrons maximum** with **opposite spins**.

Each electron in an orbital is characterised by the 3 above quantum numbers plus the **spin**.

Spin quantum number: m_s or s → $s = \pm \frac{1}{2}$

3 (a) Identify the following atomic orbitals?



(b) Why were they given such names?

(c) What is the relationship among the 3 orbital quantum numbers?

(d) How are these quantum numbers calculated?

(e) What are the 3 quantum mechanical rules to be applied if we want to understand the electronic distribution in an atom?

Answers:

a) From left to right: “s-Orbital”, “p-Orbital”, “d-Orbital”, “f-Orbital”.

b) The electronic transitions between the energy levels within the atom were first observed by X-ray spectroscopy and the specific transitions were named after the line shape in the spectra. When quantum mechanics became an accepted subject, these names eventually became associated with the spectroscopic observations and the names were retained. → S, $l = 0$ “sharp” | P, $l = 1$ “principal” | D, $l = 2$ “diffuse” | F, $l = 3$ “fundamental”

Answers:

(c) The 3 orbital quantum numbers: n, l, m_l have the following relations among each other:

$$n = 1,2,3 \dots,$$

$$l = 0,1,2,3, \dots, n-1,$$

$$m_l = -l, (-l+1), \dots 0, \dots, (l-1), l$$

(d) When spatial dimensions approach the atomic scale, they can not be understood in terms of classical laws. Physical behavior at the atomic and nanoscale is accurately predicted by quantum mechanics, as represented by the Schrödinger equation, allowing a quantitative understanding of the properties of low-dimensional structures.

Schrödinger's Equation

$$i\hbar \frac{\partial}{\partial t}\psi(\boldsymbol{r},t) = -\frac{\hbar^2}{2m}\nabla^2\psi(\boldsymbol{r},t) + V(\boldsymbol{r},t)\psi(\boldsymbol{r},t)$$

Schrödinger's Equation

$$i\hbar\frac{\partial}{\partial t}\psi(\boldsymbol{r},t) = -\frac{\hbar^2}{2m}\nabla^2\psi(\boldsymbol{r},t) + V(\boldsymbol{r},t)\psi(\boldsymbol{r},t)$$

i *is the imaginary number* $\sqrt{-1}$;

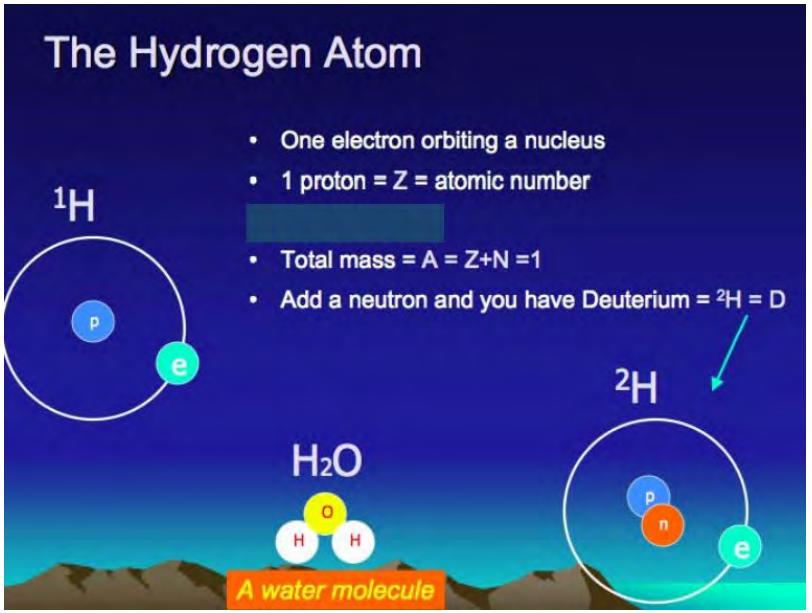
$\hbar$ *is Plack's constant diveded by* 2π: $1.05459 \times 10^{-34}\ j \cdot s$

$\psi(\boldsymbol{r},t)$ is the wave funcion, defined over space and time

m *is the mass of particle*

∇^2 *is the Laplacian operator,* $\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$

$V(\boldsymbol{r},t)$ is the potential energy influencing the particle



The orbitals are the eigenfunctions and their eigenvalues are calculated from the Schrödinger equation. Details of the calculation for the hydrogen atom can be found under the following link:

Solving Schrödinger's equation for the hydrogen atom :: Atomic Physics :: Rudi Winter's web space (aber.ac.uk)

Answers:

(e) The Pauli exclusion principle states that no two electrons in an atom may coincide in all four quantum numbers (n, l, m and s). It follows that an atomic orbital can hold a maximum of two electrons that differ in their spin quantum number. These two electrons are called paired. The different spin is represented by an arrow head pointing either up or down. In other words, the Pauli principle states that the probability for two electrons with parallel spin at the same location vanishes.

The Hund's rule: for the occupation of degenerate orbitals (orbitals with the same energy); degenerate orbitals are occupied in such a way that the largest possible number of unpaired electrons occur. That means, these orbitals are first simply occupied. The rule seems plausible if one considers that two electrons in the same orbital interact more strongly with each other than if they occupy different orbitals. When they occupy different orbitals. The electrostatic repulsion energy is therefore greater in the first case than in the second. To place two electrons in one orbital, the spin pairing energy must be applied; in the case of degenerate orbitals, this is avoided if possible.

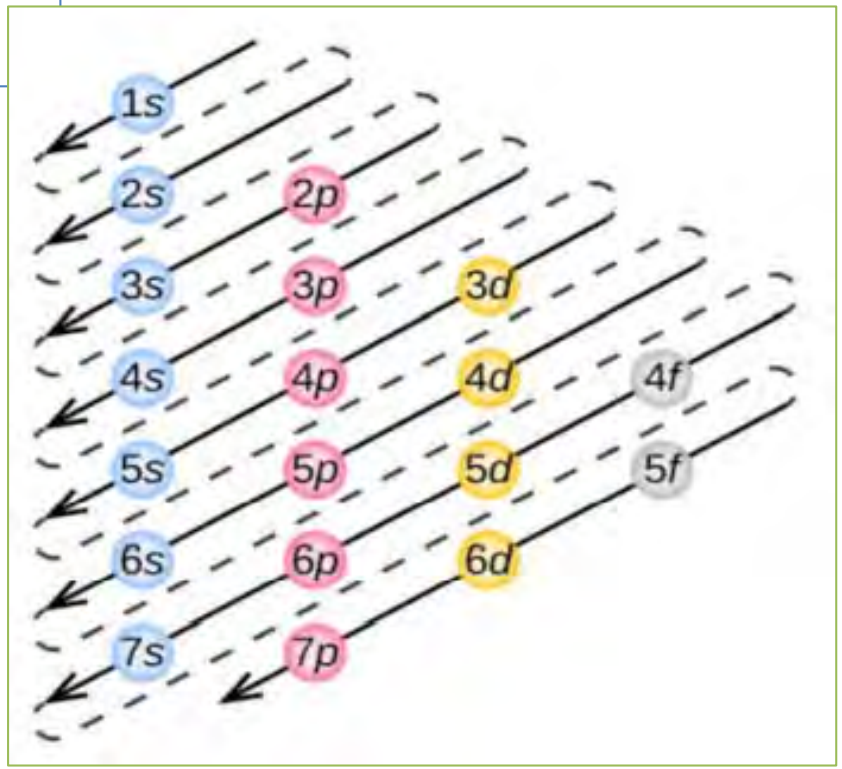
According to Hund's rule, half-occupied states of the same secondary quantum number are relatively favorable in terms of energy, similar to fully occupied states:

Tab.1 | **Voll- und halbbesetzte Energiezustände**

voll besetzt	s^2	p^6	d^{10}	f^{14}
halb besetzt		p^3	d^5	f^7

Answers:

(e) The Aufbau Principle / Energy principle: according to the build-up principle, the lowest energetically lowest orbitals are occupied first. According to the Pauli principle, an atomic orbital can hold a maximum of two electrons whose spin is opposite. According to Hund's rule, orbitals are first simply occupied so that the greatest possible number of unpaired electron occurs.



4. All known and predicted Elements are arranged in a diagram called the **Periodic Table of the Elements**.

a) How are the elements ordered according to quantum mechanics?

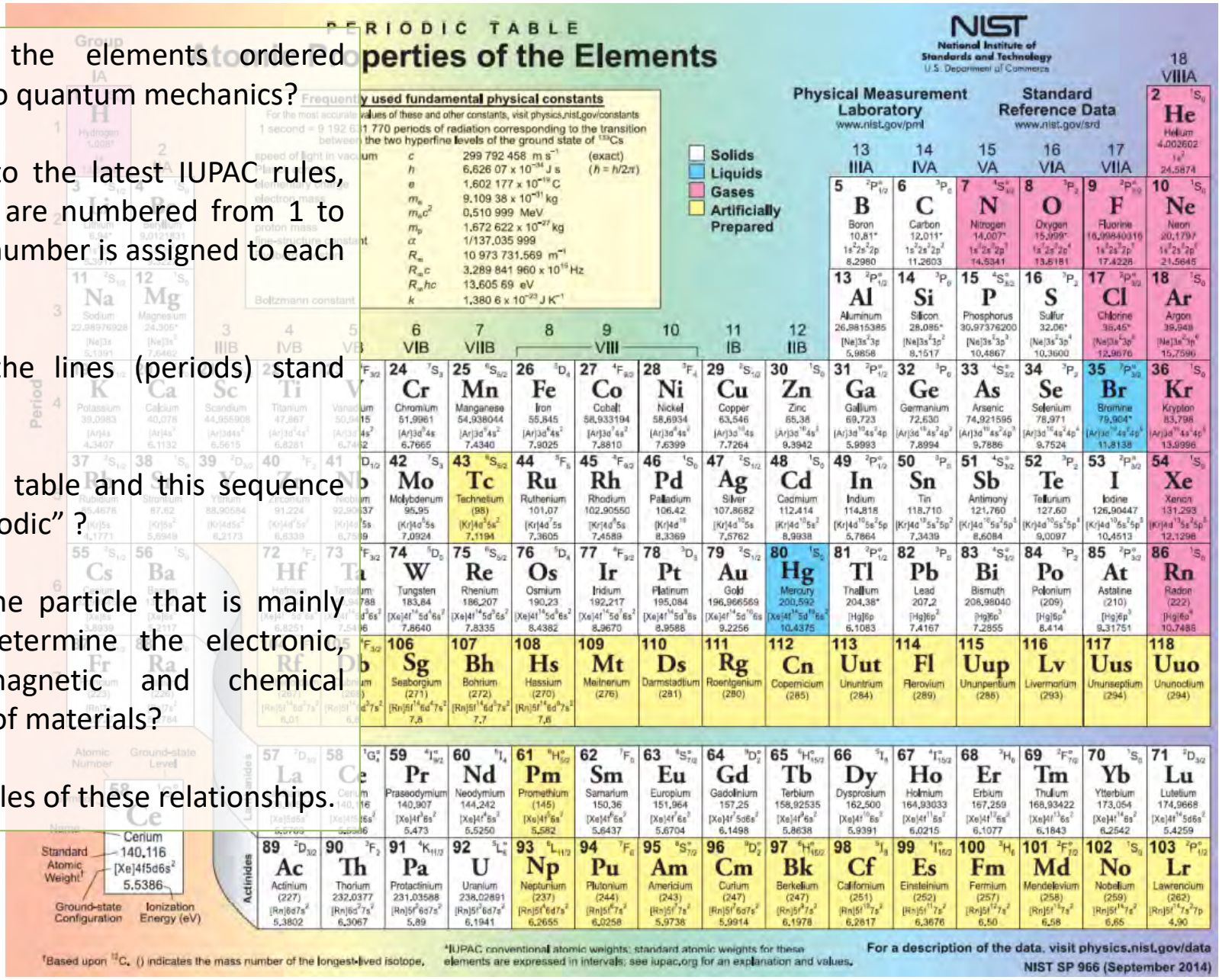
b) According to the latest IUPAC rules, the groups are numbered from 1 to 18. Which number is assigned to each group?

c) What do the lines (periods) stand for?

d) Why is this table and this sequence called “periodic” ?

e) Which is the particle that is mainly used to determine the electronic, optical, magnetic and chemical properties of materials?

f) Give examples of these relationships.



Answers:

a) The elements are arranged from left to right and from top to bottom. The arrangement generally coincides with increasing atomic mass or after increasing atomic number, which is the number of protons in the nucleus in equilibrium with the number of electron around the nucleus.
   - Elements with the same number of electron shells are arranged in the same row, which is also called period.
   - Elements with the same number of electrons in the outer shell or orbital are arranged in the same column, which is also called a group.

b) The number of groups: 1-18, refers to the total number of electrons in the outer shells.

c) The number of periods: 1-7, refers to the maximum energy level occupied by the electrons.

d) Because the physical (optical, electronic, magnetic) and chemical properties of the elements are related in a "periodic" way to their atomic mass and total number of electrons; groups of elements with similar properties fall into vertical columns in this table. The elements of the same group usually have the same chemical properties.

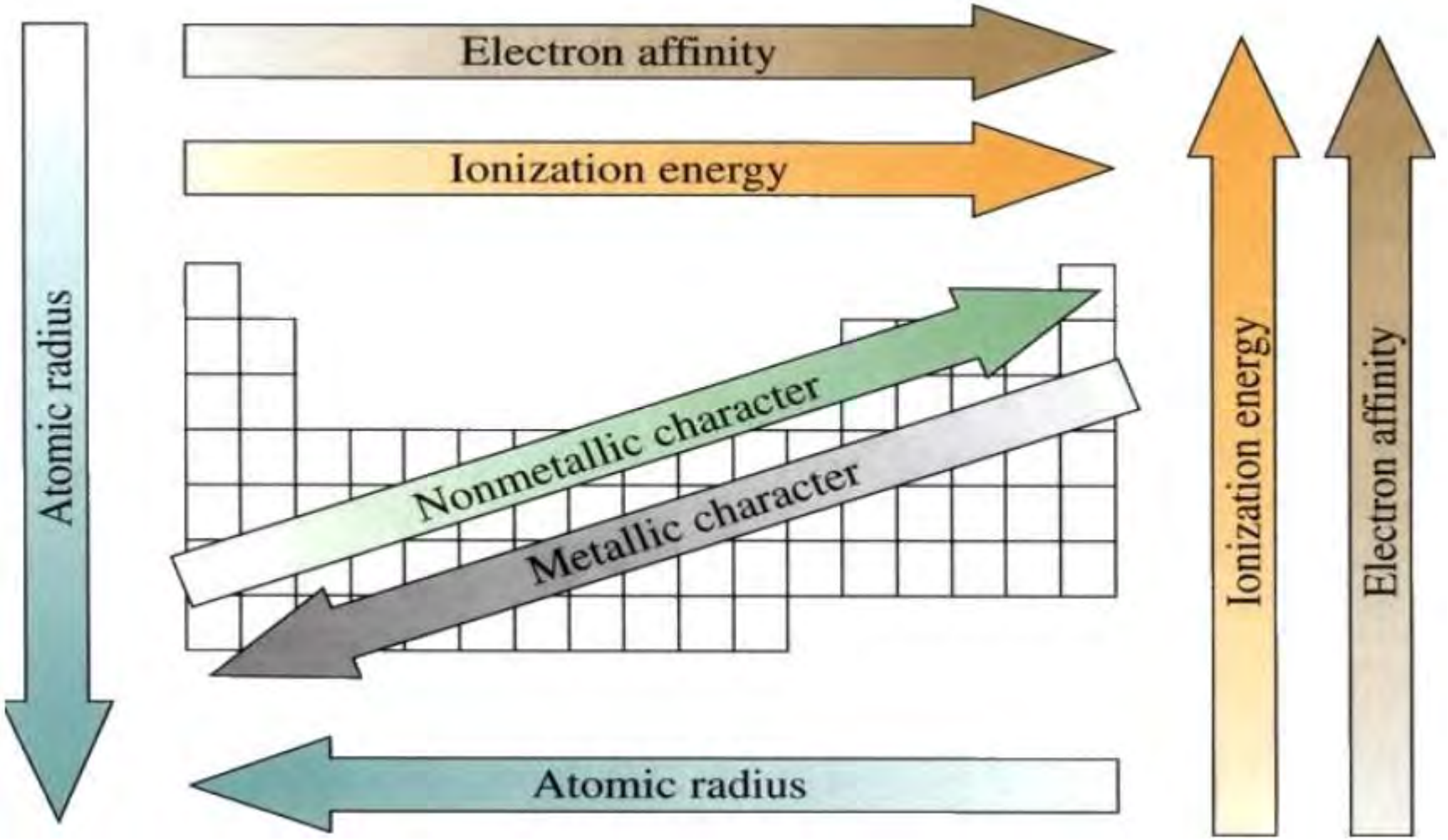
e) Electron!!!

Answers (cont):

f) The refractive index is related to the dielectric constant of the materials in the following way:

- Polarization properties, colors are determined by the dielectric constant of materials and therefore we can use spectroscopic ellipsometry to measure optical constants and dielectric function and infer other physical properties.
- The magnetic properties are related to the spin arrangement of the electrons within the atoms of each material.
- Materials are conductors, semiconductors or insulators depending on how the electrons are arranged and distributed around the nucleus according to the quantum mechanical rules. (see the following exercise)
- Chemical reactions occur due to the sharing of electrons of the atomic outer shells.
- The semiconductor properties are mainly manipulated by doping, and doping is exchange of electronic charges between the dopant atoms/defects (donors **n** and acceptors **p**) and the atoms in the crystal structure.

Some of the periodic properties and how they develop along the table of elements (physical and chemical)

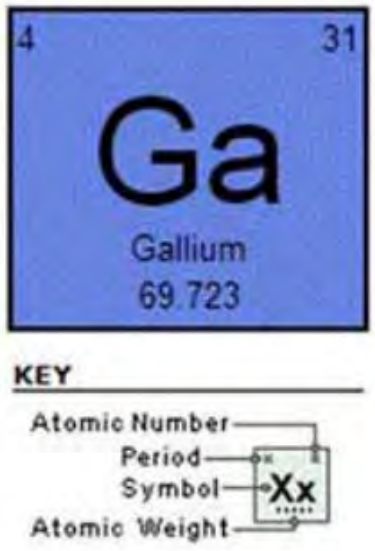


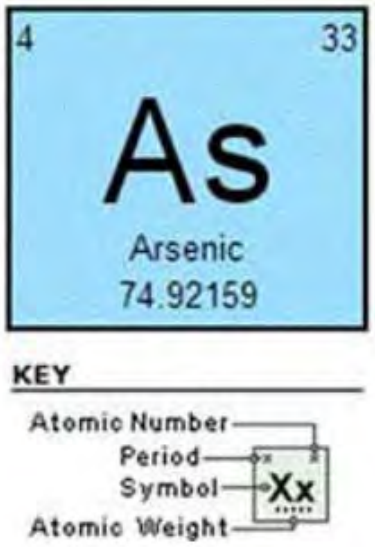
[Klick here for more information: Periodensystem - Ptable]

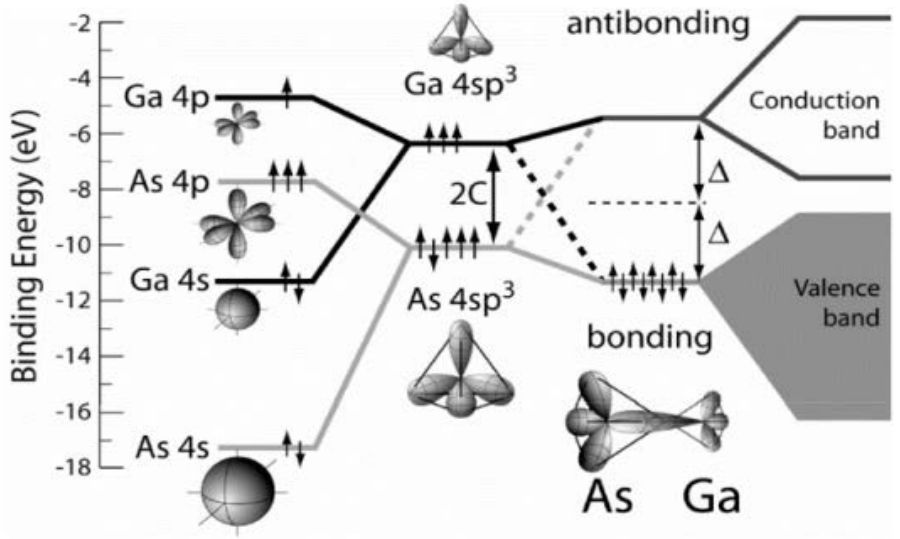
Application of the previous concepts and procedures to the following 2 case studies:

Si and GaAs

5. a) Write the electron configuration of the following atoms:







b) Which electrons and orbitals will contribute to the chemical bonding of these two materials? Use the Lewis dot diagram to illustrate the chemical bonding between them.

c) What type is the bonding between these two elements? Why?

d) What type of hybridization happens for each one of these elements and what type of molecular bond is established between them?

e) How do the bands and the bandgap appear or are generated?

f) What type of material results from these two elements? Why?

g) What type of molecular geometry? Why?

h) What type of crystal structure?

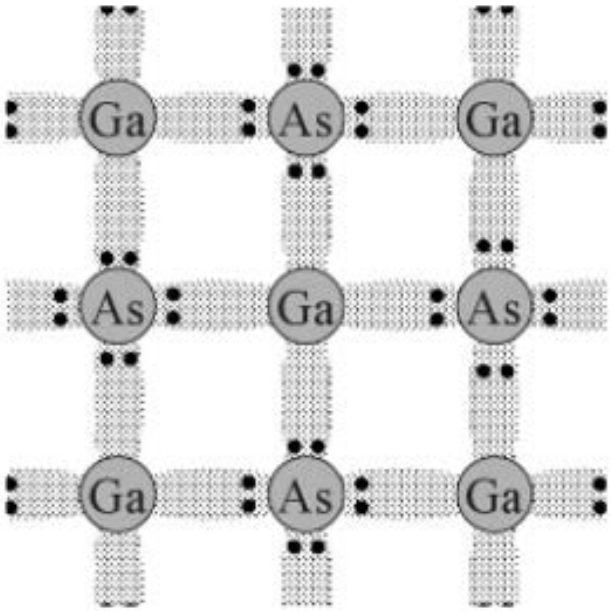
Answers:

a) Ga: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$ → electrons per energy level: 2,8,18,**3**

As: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^3$ → electrons per energy level: 2,8,18,**5**

b) Gallium has 3 electrons in the outer shell; Arsenic has 5. These are the valence electrons; they contribute to chemical bonding. Ga and As will share these electrons to complete their outer shell with 8 electrons, according to the octet rule.

c) Gallium Arsenide (GaAs) bonding is covalent type, and gallium arsenide is a covalent semiconductor. The outer shells of the gallium atoms contribute with three electrons, and those of the arsenic atoms contribute with five, providing the eight electrons needed for four covalent bonds. The centers of the bonds are not at the midpoint between the ions but are shifted slightly toward the arsenic because As is more electronegative than Ga (check table of elements in lecture 1). In this case we say that the covalent bond is polar. Actually, the electronegativity difference is high enough so that the bonding is almost ionic.



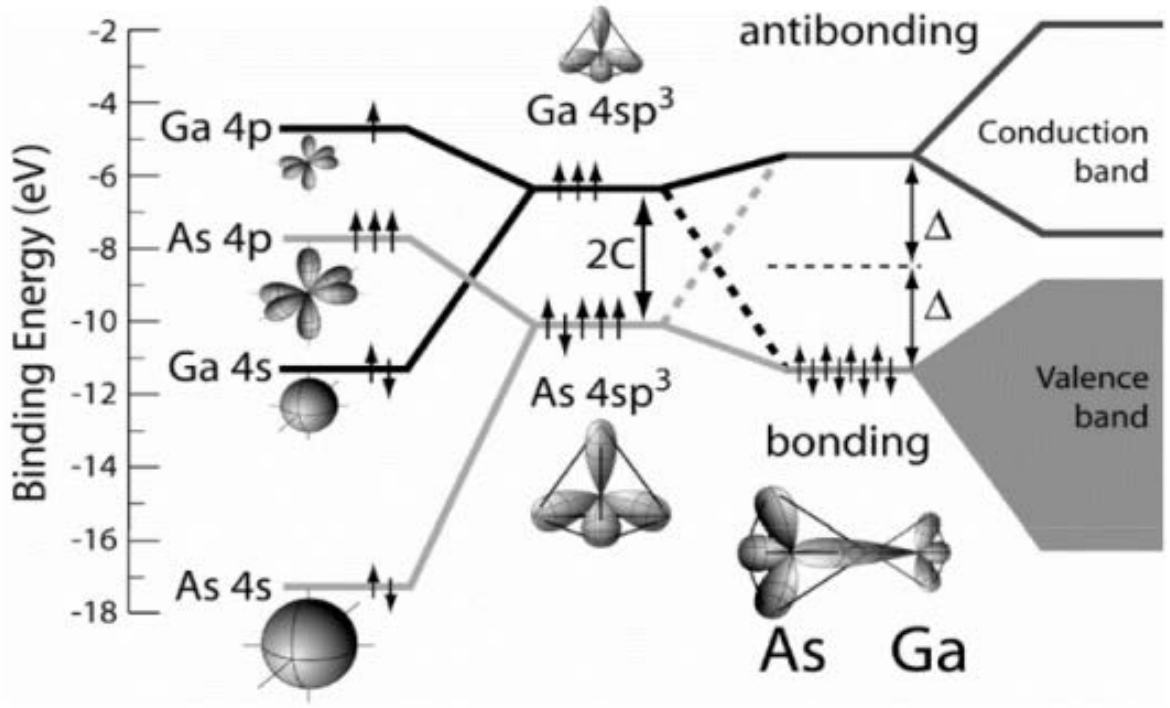
Answers:

d) sp3 hybridization / 4 sigma bonds

e) The figure must be read from left to right:

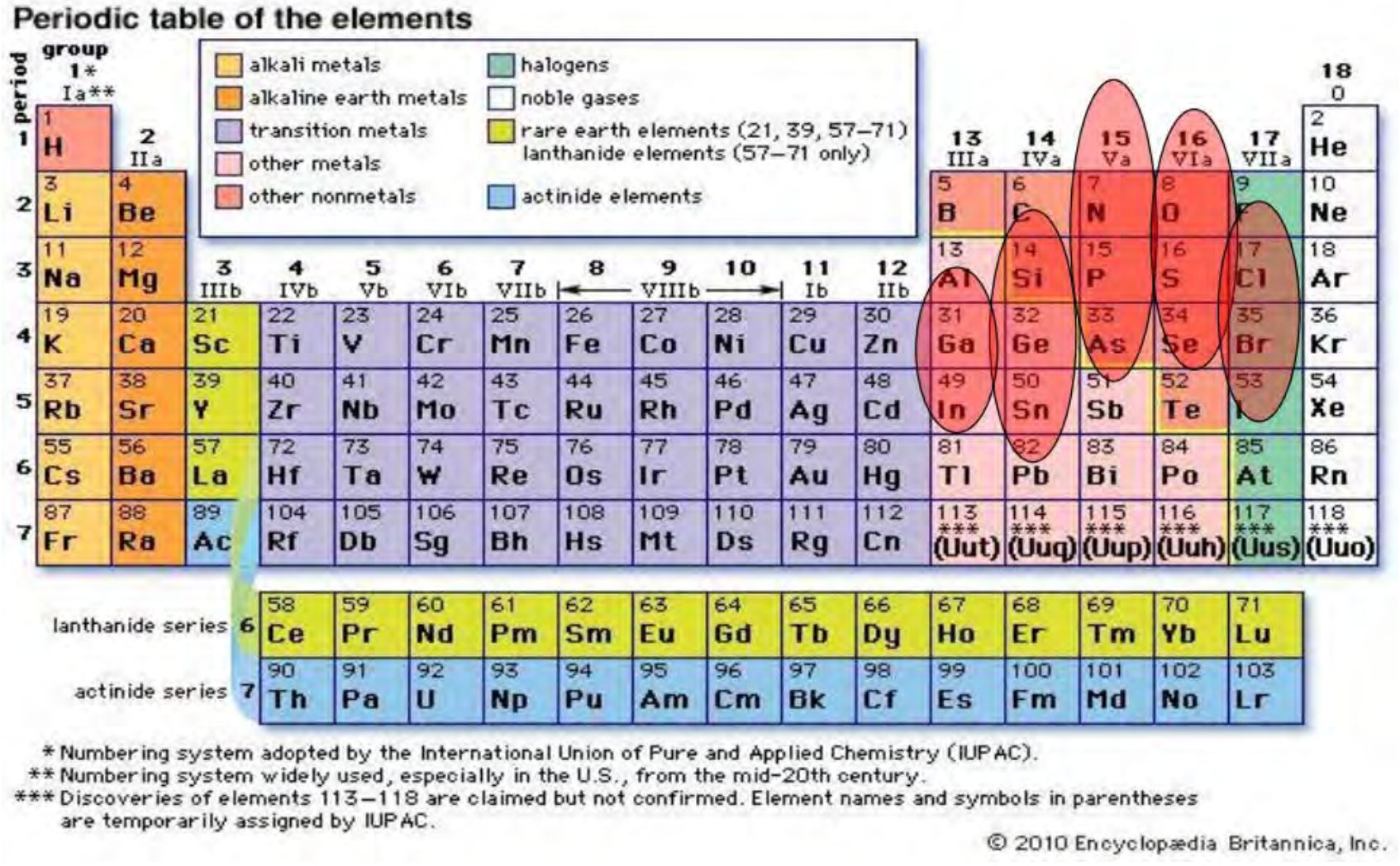
- The 4s orbitals of As and Ga with 2 electrons with opposite spins hybridize with the 4p orbitals (As: 3 electrons with same spin up, Ga: 1 electron spin up) giving rise to 4sp3 hybridized atomic orbitals (As 4sp3: 5 electrons; Ga 4sp3: 3 electrons, with the spin orientation according to the 3 QM rules).
- The hybrid sp3 orbitals of the two atoms come out at much different energies; the resultant energy of the hybridized orbitals is higher for Ga and lower for As.
- This energy difference is shown schematically in the figure that follows, and is twice the quantity termed the chemical splitting, C.
- Mathematically: $2C = Ec_{,sp3} - E_{a,sp3}$ with E_c and E_a refering to the energies of the cation and anion molecular orbitals.

Note: the values of chemical splitting increase as the atoms move further apart on the periodic table in a given row (larger difference in electronegativity). As the interatomic distance shrinks the chemical splitting increases.



- When the hybridized orbitals of the 2 atoms come together, they tend to share their valence electrons top-to-top giving rise to a sigma bond and an antisigma-bond. According to QM rules the electrons shared in this newly created molecular bond, will fill first the lower energy levels that corresponds to the valence band leaving the higher energy levels of the conduction band "empty". The region in between is the band gap and the energy difference between the two bands is the energy band gap of the semiconductor just formed.

f) Binary semiconductor Type III-V semiconductors, since Ga belongs to the 13th group (formerly IIIa) and As to the 15th group (formerly Va).



g) Tetrahedral, because it's imposed or is a result of the sp3 hybridization in fig 1.

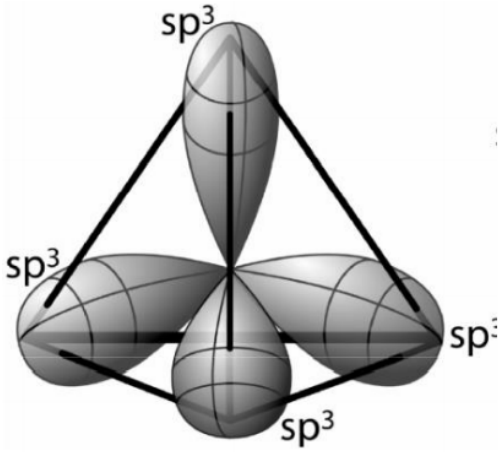


Fig 1

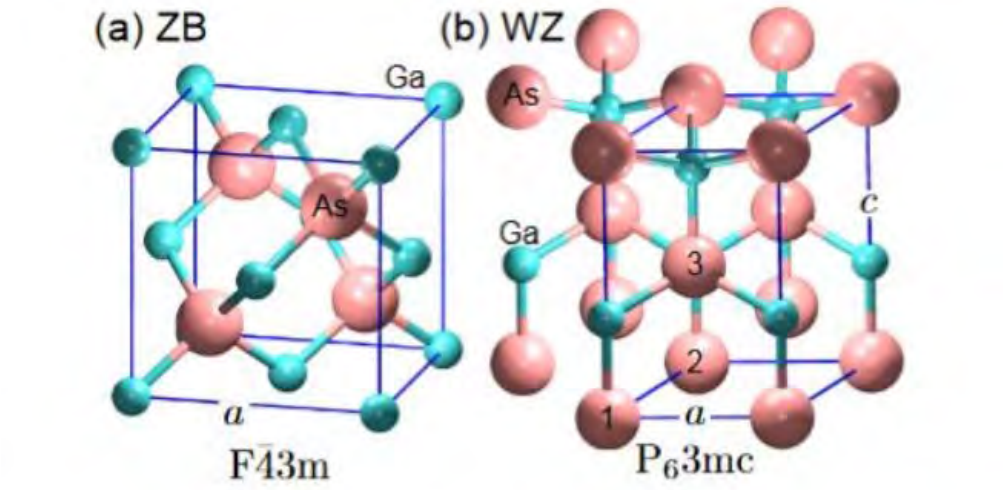


Fig 2: (Color online) The structure of ZB and WZ GaAs crystals. The conventional unit cell for a ZB and a WZ GaAs crystal is shown in (a) and (b), respectively. The As and Ga atoms are represented by large pink and small green spheres, respectively.

h) Typical Zincblende or Wurtzite structure with four neighbors per atom – why? (recall lecture 1): they are both 2 interpenetrating fcc lattices with two atoms in the base: atom A at $(0,0,0)$ and atom B at $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ for ZB structure and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ for WZ structure.

Homework

Repeat the same procedure as shown in question 5. for Silicon

a) Write the electron configuration of the atom Si.

b) Which electron and orbitals will contribute to the chemical bonding of these two materials? Use the Lewis dot diagram to illustrate the chemical bonding between them.

c) What type is the bonding between these two elements? Why?

d) What type of hybridization happens for these elements and what type of molecular bond?

e) How do the bands and the gap appear or are generated?

f) What type of material results from these two elements? Why?

g) What type of molecular geometry? Why?

h) What type of crystal structure?