

Atomic Structure & Chemical bonding



ATOMS are the basic units of **Matter**

They are made of a Nucleus of **neutrons** + **protons**, surrounded by a cloud of **electrons**

Atoms can **bind** to form **MOLECULES**

MATTER can be a **PURE SUBSTANCE** or **MIXTURE**

PURE SUBSTANCE can be **ELEMENTS** or **COMPOUNDS**

MIXTURES can be **HOMOGENEOUS** or **HETEROGENEOUS**

MATTER can exist in different **states**:

solid, liquid, gas, plasma, Bose-Einstein condensate, Fermi condensate

MATTER is also a sort of Energy and can be converted into **RADIATION**
(and vice-versa ;-)



The Atom & the Atomic Model(s)

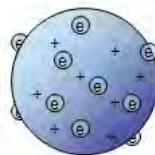
- ATOM is a very old concept ~2400 years old that means:
The smallest portion of Matter that still carries its properties

Models of the Atom

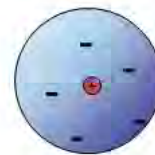
"In science, a wrong theory can be valuable and better than no theory at all."
- Sir William L. Bragg



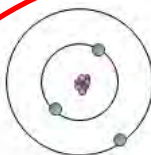
Greek model
(400 B.C.)



Thomson's plum-pudding
model (1897)



Rutherford's model
(1909)



Bohr's model
(1913)



Charge-cloud model
(present)

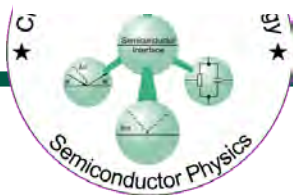




The Schrödinger equation and atomic orbitals ;-)

One of the most common operators in quantum mechanics is *the Hamiltonian operator* (or simply Hamiltonian, \hat{H}).

- **Hamiltonian** is an operator of total energy; i.e. the sum of kinetic (due to the electron motion) and potential (arising from the electrostatic field of the positively charged nucleus in which electron is located) energies.
- Its **eigenfunctions** are wave functions describing atomic orbitals while its **eigenvalue** is the total energy of the electron.





The Schrödinger equation and atomic orbitals ;-)

In other words, every wave function Ψ that satisfies the equation

$$\hat{H}\Psi = E\Psi$$

represents an atomic orbital with energy equal to E .

The Hamiltonian, with its two components, for one electron bound to a nucleus is:

$$\hat{H} = \underbrace{-\frac{\hbar}{2m_e} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)}_{\text{Kinetic energy}} - \underbrace{\frac{Ze^2}{4\pi\epsilon_0 r}}_{\text{Potential energy}}$$

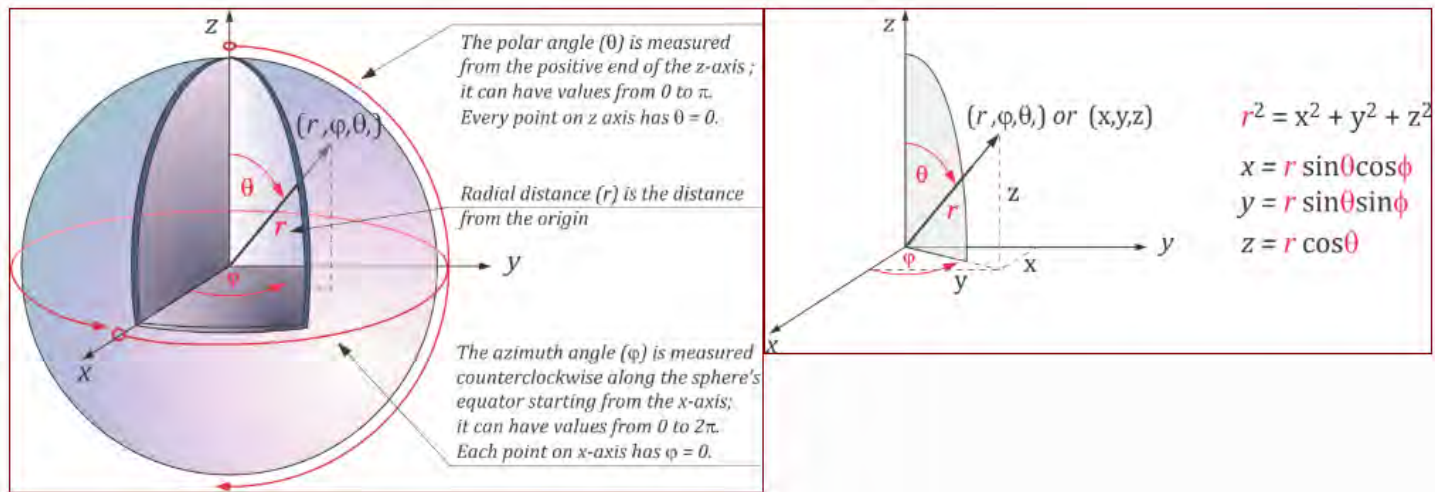
where: m_e is electron mass, \hbar is reduced Planck constant ($h/2\pi$), x , y and z are the coordinates, Z is the nuclear charge, e is the charge on one proton/electron, ϵ_0 is vacuum permittivity and r is the distance between the electron and nucleus. Note that the Hamiltonian contains the mass of electron and thus takes into account electron's particle character.



What are the Eigenfunctions?

Ψ is the wave function describing an electron (in terms of its wave character and are functions of the distance between the electron and the nucleus (r) and two angles—the polar (θ) and azimuth (φ).

$$\Psi(r, \theta, \varphi) = R(r) \times \Theta(\theta) \times \Phi(\varphi) = R(r) \times Y(\theta, \varphi)$$



- the spherical coordinate system is more commonly used when working with the Schrödinger equation. In this coordinate system a position of any point in the three dimensional space is uniquely defined by the distance from the fixed origin (r), and the polar (θ) and azimuth (φ) angles.

The theory suggests that the real physical meaning of the wave function can be found in the function's square, Ψ^2 .

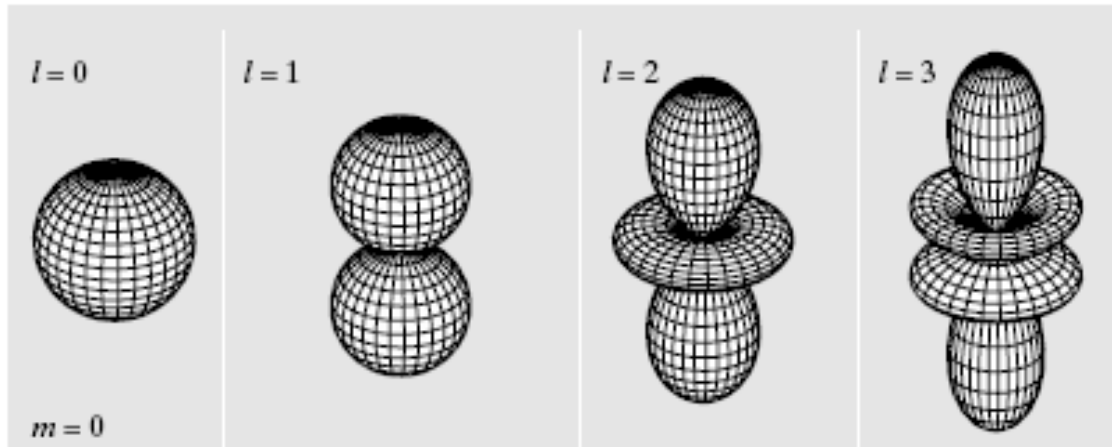
$$P_{space} = \int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} \Psi^*(r, \theta, \varphi) \times \Psi(r, \theta, \varphi) dr d\theta d\varphi$$

Commonly encountered is *the radial probability function*, $P(r)$, which provides the probability of finding an electron at a given distance from the nucleus summed over all angles:

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



Atomic orbitals



S, $l = 0$
“sharp”

P, $l = 1$
“principal”

D, $l = 2$
“diffuse”

F, $l = 3$
“fundamental”

“s-Orbital” “p-Orbital” “d-Orbital” “f-Orbital”

The orbitals are characterised by 3 quantum nrs.:

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

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

$$m_\ell = -\ell, (-\ell + 1), \dots, 0, \dots, (\ell - 1), \ell$$

What are the Eigenvalues? : the 3 quantum numbers!

n is the Principal quantum nr. refers to the energy level

l is the Azimutal quantum nr and refers to the shape of the orbital

m_l is the orbital magnetic nr. And refers to its polarity

Each orbital can accomodate up to **2 electrons máx.** with **opposite spins.**

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

m_s (or just **s**) spin quantum nr; $s = \pm \frac{1}{2}$

- All orbitals with the same quantum number n form a **shell**.
- The shells are labeled simply by indicating the value of the principal quantum number, for example $n = 1$ is the first shell, the one closest to the nucleus. Somewhat older, but still frequently found symbols for shells, are **$K, L, M, N,$** etc. for shells with n values **1, 2, 3, 4,** etc. Shells can be composed of one or more subshells.
- Each **subshell** is defined with quantum number **ℓ** . Each subshell is designated with a letter depending on the value of ℓ :
 - s: for $\ell = 0$,
 - p: for $\ell = 1$,
 - d: for $\ell = 2$,
 - f : for $\ell = 3$ etc.
- The number of orbitals within each subshell is given by the number of possible values for the quantum number **m_ℓ** .

Atomic energy levels

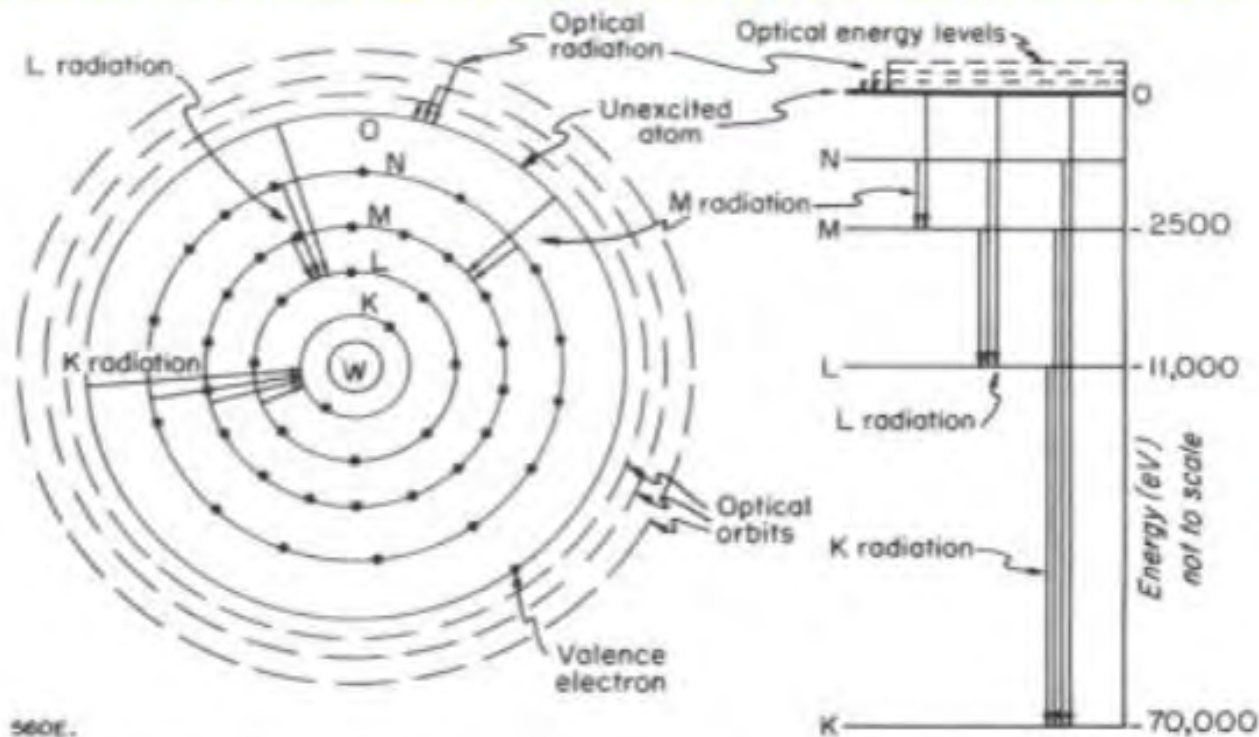


Figure 1-2. Schematic diagram of the tungsten atom showing the shells on the left and an energy level diagram on the right. The energy scale in eV is not drawn to scale. X-radiation arises through transitions of electrons to the K, L, and M shells. Optical radiation arises by transitions of the valence electron from optical orbits to the O shell.

X-rays arise from transitions to K, L, M levels (eV to keV energy range)

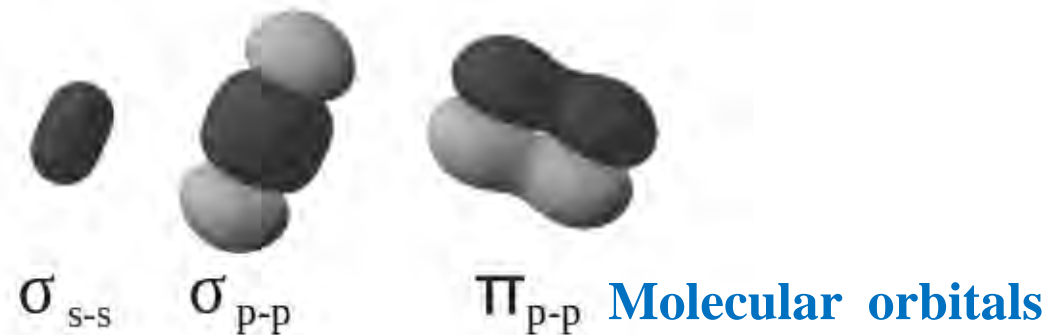
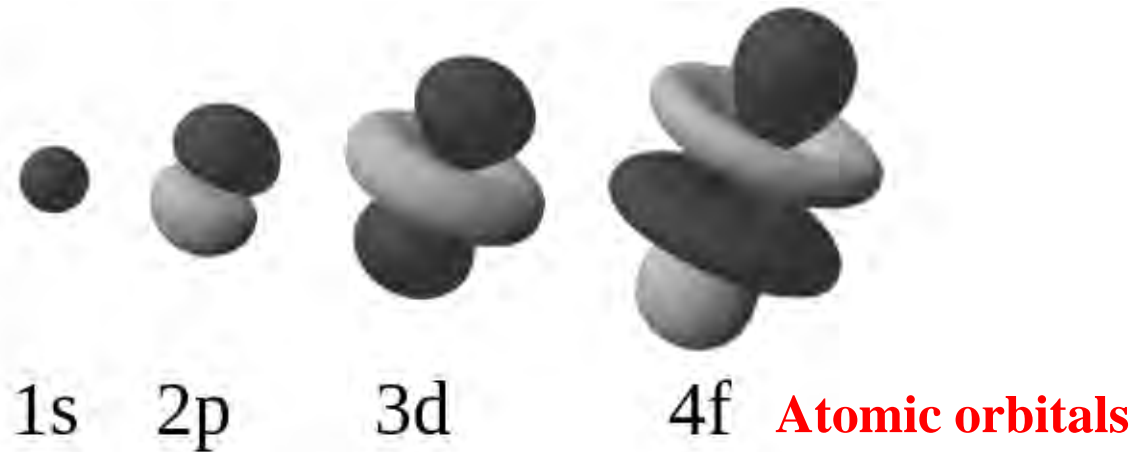
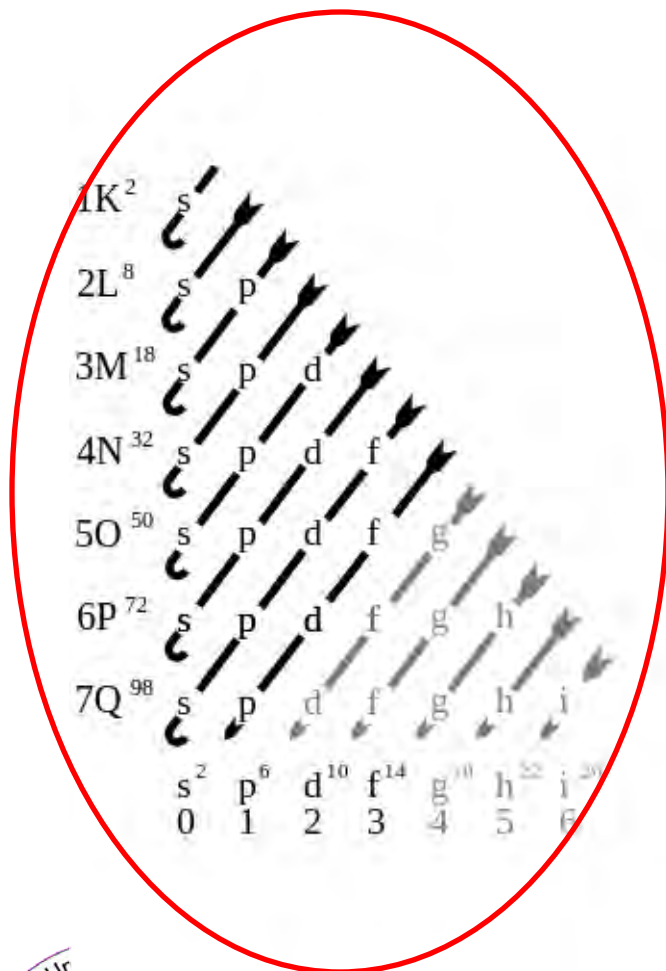
NOTE

The exact solutions of the Schrödinger equation are possible *only* for the systems that contain one electron around a nucleus.

These are systems such as the hydrogen atom, helium cation, He^+ , lithium with $2+$ charge, Li^{2+} , etc.

For systems with two and more electrons, the solutions are not exact—in these cases some approximations and assumptions have to be used in order to solve the Schrödinger equation.

In an Atom these orbitals overlap and the final result of such an overlap can be:



The same happens to molecular orbitals.



These results are governed by the following rules or principles

Aufbau Principle :

is basically a German word “Aufbauen” which means building up. According to this principle, the **electrons will first occupy the orbitals that have the lowest energy**. According to the following order:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p.... .

Hund's Rule:

every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied, and all electrons in singly occupied orbitals have the same spin.

Pauli exclusion principle:

an orbital can have maximum two electrons and these must have opposite spins.



The **octet rule** refers to the tendency of atoms to prefer to have eight electrons in the *valence shell* (outer orbital).

When atoms have fewer than eight electrons, they tend to react and form more stable compounds.

When discussing the octet rule, we do not consider d or f electrons. **Only the s and p electrons are involved in the octet rule**, making it useful for the *representative elements* (elements not in the transition metal or inner-transition metal blocks).

An octet corresponds to an electron configuration ending with s^2p^6 .



THE PERIODIC TABLE OF THE ELEMENTS

1 IA 1A	2 IIA 2A												13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
1 H Hydrogen 1.008													5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
3 Li Lithium 6.941	4 Be Beryllium 9.012												13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948
11 Na Sodium 22.990	12 Mg Magnesium 24.305																	
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.88	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.933	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.39		31 Ga Gallium 69.732	32 Ge Germanium 72.61	33 As Arsenic 74.922	34 Se Selenium 78.972	35 Br Bromine 79.904	36 Kr Krypton 84.80
37 Rb Rubidium 84.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411		49 In Indium 114.818	50 Sn Tin 118.71	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.29
55 Cs Cesium 132.905	56 Ba Barium 137.327	57-71 Lanthanide Series	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.85	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.967	80 Hg Mercury 200.59		81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [209]	85 At Astatine [209]	86 Rn Radon 222.018
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103 Actinide Series	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]		113 Uut Ununtrium unknown	114 Fl Flerovium [289]	115 Uup Ununpentium unknown	116 Lv Livermorium [293]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown

Lanthanide Series

Actinide Series

57 La Lanthanum 138.906	58 Ce Cerium 140.115	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.24	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.966	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.50	67 Ho Holmium 164.930	68 Er Erbium 167.26	69 Tm Thulium 168.934	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967
89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]

Alkali Metal

Alkaline Earth

Transition Metal

Basic Metal

Semimetal

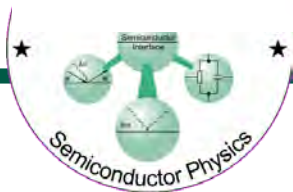
Nonmetal

Halogen

Noble Gas

Lanthanide

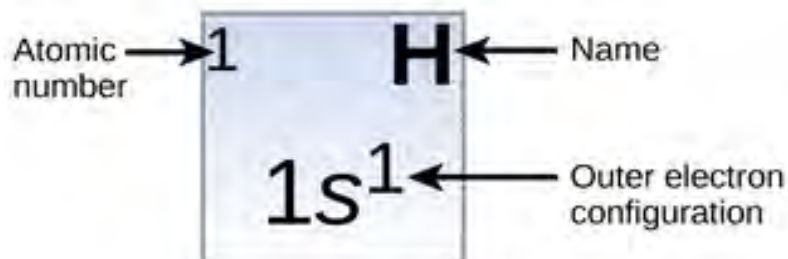
Actinide



Electron Configuration Table

In atomic physics and quantum chemistry, the **electron configuration** is the distribution of electrons of an atom or molecule (or other physical structure) in atomic or molecular **orbitals**.

Period	Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1		1 H 1s ¹																	2 He 1s ²
2		3 Li 2s ¹	4 Be 2s ²											5 B 2s ² 2p ¹	6 C 2s ² 2p ²	7 N 2s ² 2p ³	8 O 2s ² 2p ⁴	9 F 2s ² 2p ⁵	10 Ne 2s ² 2p ⁶
3		11 Na 3s ¹	12 Mg 3s ²											13 Al 3s ² 3p ¹	14 Si 3s ² 3p ²	15 P 3s ² 3p ³	16 S 3s ² 3p ⁴	17 Cl 3s ² 3p ⁵	18 Ar 3s ² 3p ⁶
4		19 K 4s ¹	20 Ca 4s ²	21 Sc 4s ² 3d ¹	22 Ti 4s ² 3d ²	23 V 4s ² 3d ³	24 Cr 4s ¹ 3d ⁵	25 Mn 4s ² 3d ⁵	26 Fe 4s ² 3d ⁶	27 Co 4s ² 3d ⁷	28 Ni 4s ² 3d ⁸	29 Cu 4s ¹ 3d ¹⁰	30 Zn 4s ² 3d ¹⁰	31 Ga 4s ² 3d ¹⁰ 4p ¹	32 Ge 4s ² 3d ¹⁰ 4p ²	33 As 4s ² 3d ¹⁰ 4p ³	34 Se 4s ² 3d ¹⁰ 4p ⁴	35 Br 4s ² 3d ¹⁰ 4p ⁵	36 Kr 4s ² 3d ¹⁰ 4p ⁶
5		37 Rb 5s ¹	38 Sr 5s ²	39 Y 5s ² 4d ¹	40 Zr 5s ² 4d ²	41 Nb 5s ¹ 4d ⁴	42 Mo 5s ¹ 4d ⁵	43 Tc 5s ¹ 4d ⁶	44 Ru 5s ¹ 4d ⁷	45 Rh 5s ¹ 4d ⁸	46 Pd 4d ¹⁰	47 Ag 5s ¹ 4d ¹⁰	48 Cd 5s ² 4d ¹⁰	49 In 5s ² 4d ¹⁰ 5p ¹	50 Sn 5s ² 4d ¹⁰ 5p ²	51 Sb 5s ² 4d ¹⁰ 5p ³	52 Te 5s ² 4d ¹⁰ 5p ⁴	53 I 5s ² 4d ¹⁰ 5p ⁵	54 Xe 5s ² 4d ¹⁰ 5p ⁶
6		55 Cs 6s ¹	56 Ba 6s ²	57 La 6s ² 5d ¹	72 Hf 6s ² 4f ¹⁴ 5d ²	73 Ta 6s ² 4f ¹⁴ 5d ³	74 W 6s ² 4f ¹⁴ 5d ⁴	75 Re 6s ² 4f ¹⁴ 5d ⁵	76 Os 6s ² 4f ¹⁴ 5d ⁶	77 Ir 6s ² 4f ¹⁴ 5d ⁷	78 Pt 6s ¹ 4f ¹⁴ 5d ⁹	79 Au 6s ¹ 4f ¹⁴ 5d ¹⁰	80 Hg 6s ² 4f ¹⁴ 5d ¹⁰	81 Tl 6s ² 4f ¹⁴ 5d ¹⁰ 6p ¹	82 Pb 6s ² 4f ¹⁴ 5d ¹⁰ 6p ²	83 Bi 6s ² 4f ¹⁴ 5d ¹⁰ 6p ³	84 Po 6s ² 4f ¹⁴ 5d ¹⁰ 6p ⁴	85 At 6s ² 4f ¹⁴ 5d ¹⁰ 6p ⁵	86 Rn 6s ² 4f ¹⁴ 5d ¹⁰ 6p ⁶
7		87 Fr 7s ¹	88 Ra 7s ²	89 Ac 7s ² 6d ¹	104 Rf 7s ² 5f ¹⁴ 6d ²	105 Db 7s ² 5f ¹⁴ 6d ³	106 Sg 7s ² 5f ¹⁴ 6d ⁴	107 Bh 7s ² 5f ¹⁴ 6d ⁵	108 Hs 7s ² 5f ¹⁴ 6d ⁶	109 Mt 7s ² 5f ¹⁴ 6d ⁷	110 Ds 7s ² 5f ¹⁴ 6d ⁸	111 Rg 7s ² 5f ¹⁴ 6d ⁹	112 Cn 7s ² 5f ¹⁴ 6d ¹⁰	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
				* 58 Ce 6s ² 4f ²	59 Pr 6s ² 4f ³	60 Nd 6s ² 4f ⁴	61 Pm 6s ² 4f ⁵	62 Sm 6s ² 4f ⁶	63 Eu 6s ² 4f ⁷	64 Gd 6s ² 4f ⁷ 5d ¹	65 Tb 6s ² 4f ⁹	66 Dy 6s ² 4f ¹⁰	67 Ho 6s ² 4f ¹¹	68 Er 6s ² 4f ¹²	69 Tm 6s ² 4f ¹³	70 Yb 6s ² 4f ¹⁴	71 Lu 6s ² 4f ¹⁴ 5d ¹		
				** 90 Th 7s ² 6d ²	91 Pa 7s ² 5f ² 6d ¹	92 U 7s ² 5f ³ 6d ¹	93 Np 7s ² 5f ⁴ 6d ¹	94 Pu 7s ² 5f ⁶	95 Am 7s ² 5f ⁷	96 Cm 7s ² 5f ⁷ 6d ¹	97 Bk 7s ² 5f ⁹ 6d ¹	98 Cf 7s ² 5f ¹⁰	99 Es 7s ² 5f ¹¹	100 Fm 7s ² 5f ¹²	101 Md 7s ² 5f ¹³	102 No 7s ² 5f ¹⁴	103 Lr 7s ² 5f ¹⁴ 6d ¹		



The **element's** position in the periodic **table** is related to its **electron configuration** i.e how the electrons are organized around the nucleus.

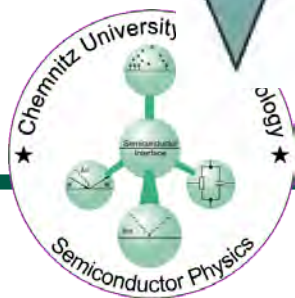
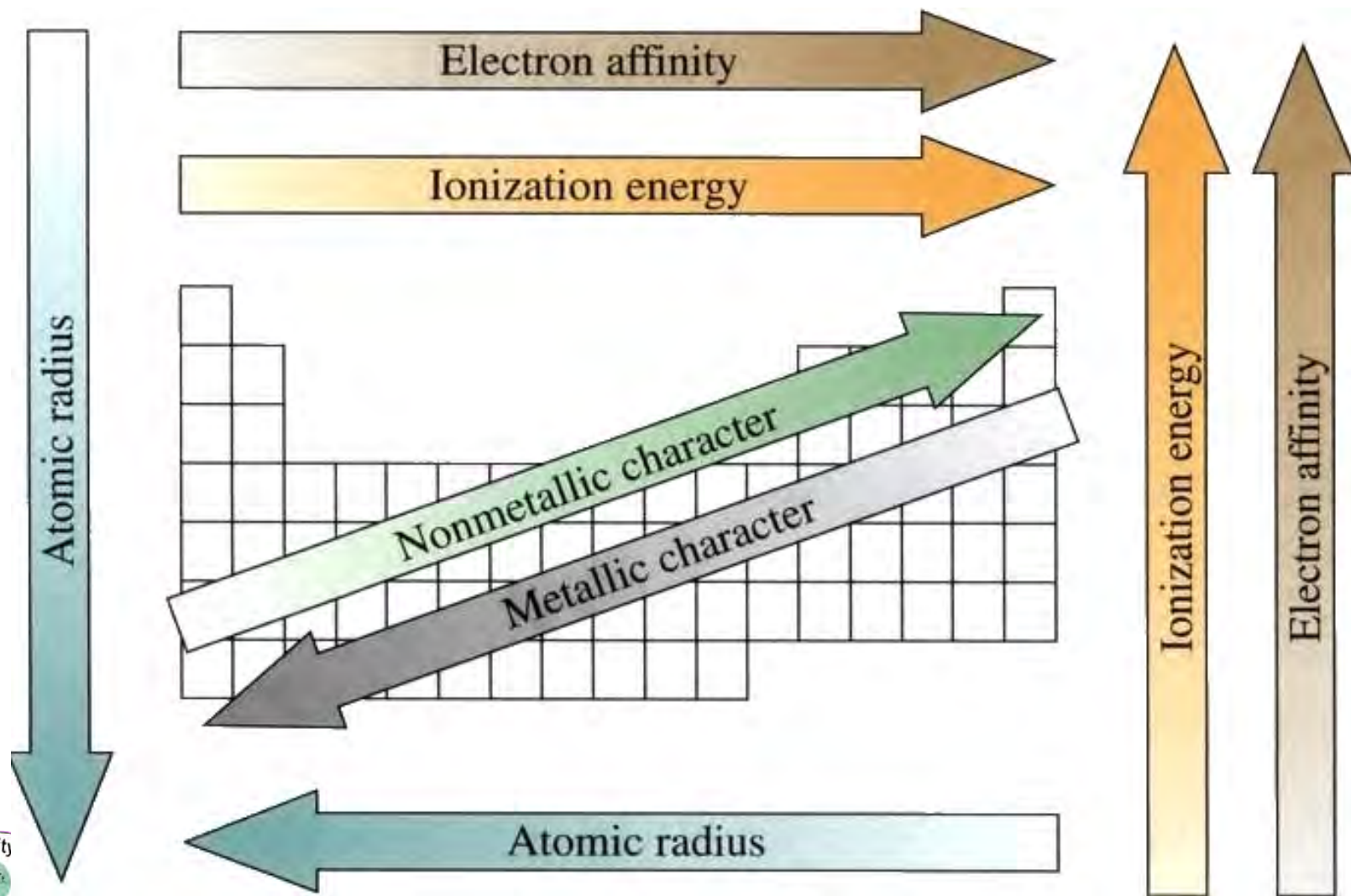
There are two links between an atom's **electronic structure** and its position in the **periodic table**:

- ✓ The number of occupied shells is the same as the period number(row in the **table**)
- ✓ The number of electrons in the outer shell is the same as the group number (column in the **table**)

The **position** of each **element** in the **table** gives information
about

its structure, properties, and behaviour in chemical reactions.

All known **elements** are **arranged** in a table according to their **periodic properties**



Sen

PERIODIC TABLE OF ELEMENTS

Today it is known that these **properties are due** to the **number of electrons** in the atom and how they are **statistically distributed** in orbitals according to **Hunds rule** and **Pauli exclusion Principles**.

Each atom and therefore **each element** has its **own and unique number of electrons**.

This is why and how we can **distinguish** between them!



This is also what makes **Matter so diverse!**

.....Molecular Orbitals



Molecular Orbitals (MO) form from allowed interactions between atomic orbitals, which are allowed if the symmetries of the atomic orbitals are compatible with each other.

Efficiency of atomic orbital interactions is determined from the overlap - **constructive interaction between two atomic orbitals**. This is most likely if the atomic orbitals are **close in energy**.

The number of molecular orbitals formed must be equal to the number of atomic orbitals in the atoms being combined to form the molecule.

2 theories to address MO formation :

Valence Bond Model & Molecular Orbital Theory



Molecular Orbitals: Valence Bond Model vs. Molecular Orbital Theory

Valence-bond Model

Arguments based on atomic orbitals focus on the bonds formed between valence electrons on an atom, they are often said to involve a **valence bond theory based on Lewis structures of valence electrons**.

The valence-bond model can't adequately explain many features of molecules and chemical bonding; to account for them it is understood that molecules are mixtures, or hybrids, of the two Lewis structures that can be written for these molecules.

Molecular Orbital Model

Molecular orbital theory is **more powerful** than valence-bond theory because the orbitals reflect the geometry of the molecule to which they are applied. But this power carries a significant cost in terms of the ease with which the model can be visualized.

- When atomic orbitals interact, the resulting molecular orbital can be of 3 types:

bonding, antibonding or **nonbonding**.

- The type of interaction between atomic orbitals can be further categorized by the molecular-orbital symmetry labels:

σ (sigma), π (pi), δ (delta), ϕ (phi), γ (gamma)

the Greek letters corresponding to the atomic orbitals s, p, d, f and g respectively.

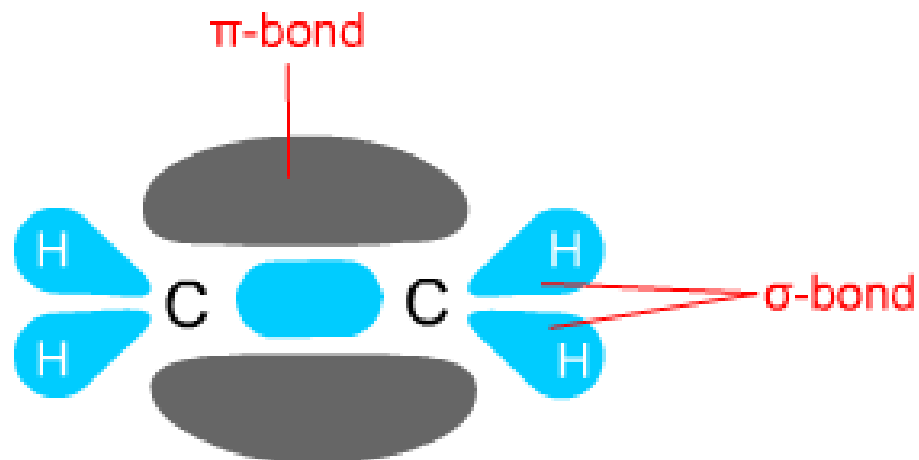
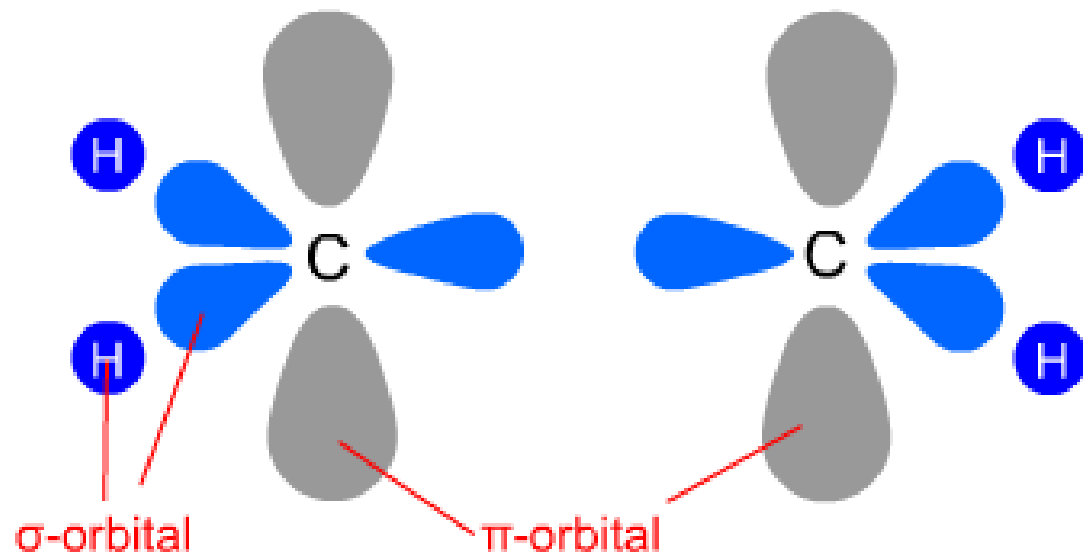
σ symmetry results from the interaction of either two atomic s-orbitals or two atomic p_z -orbitals (top-top interaction)

π symmetry results from the interaction of either two atomic p_x orbitals or p_y orbitals (side interaction)

etc

σ (sigma), **π** (pi), **δ** (delta), **ϕ** (phi), **γ** (gamma) bonds
are **covalent bonds**



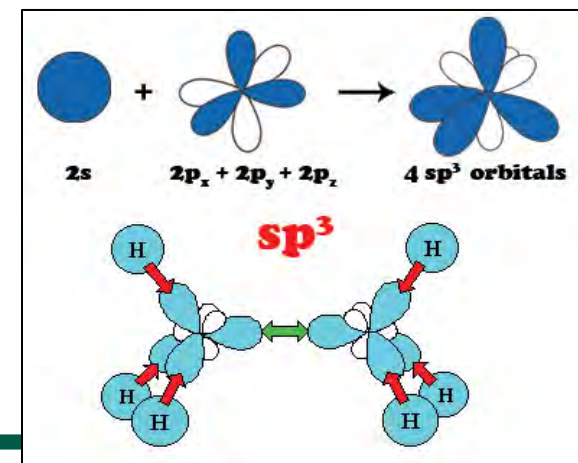
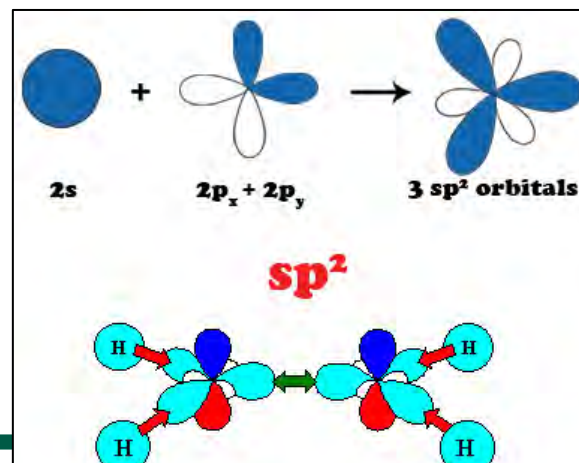
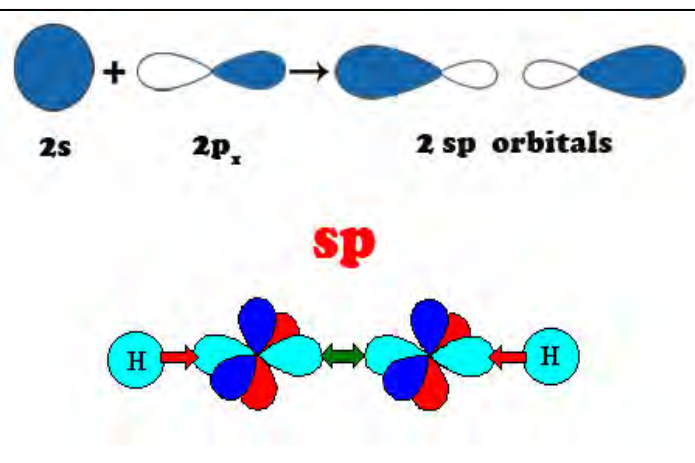


But we can have other types resulting from **hybridization** of standard atomic orbitals to form new orbitals – which can be used to describe bonding in molecules:

sp

sp²

sp³



Molecular geometries can be specified in terms of **bond lengths**, **bond angles** and **torsional angles**.

The **bond length** is defined to be the average distance between the nuclei of two atoms bonded together in any given molecule.

A **bond angle** is the angle formed between three atoms across at least two bonds.

There are rules to (roughly) determine or estimate a certain molecular geometry.

★ Molecular geometry is determined rigorously by spectroscopy methods.



Electronic Geometries



linear

trigonal
planar

tetrahedral

trigonal
bipyramidal

octahedral

Electron Domains

2

3

4

5

6

Lone Pairs

0



linear

trigonal
planar

tetrahedral

trigonal
bipyramidal

octahedral

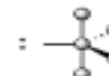
1



linear



bent

trigonal
pyramidal

seesaw

square
pyramidal

2



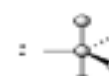
linear



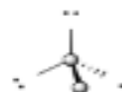
bent



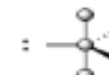
bent



T-shaped

square
planar

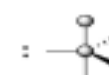
linear



linear



T-shaped



linear



linear



linear

Molecular Geometry

linear

trigonal planar

tetrahedral

trigonal bipyramidal

Hybridization

sp

sp²sp³sp³d

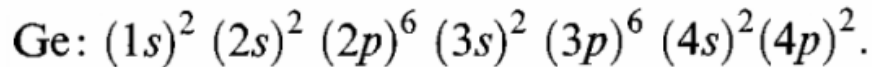
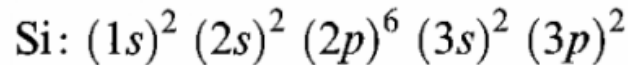
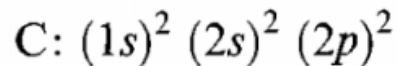
MOLECULAR
GEOMETRIES



1. General Properties of Semiconductors

1.5. Chemical bonding

Diamond structure semiconductors

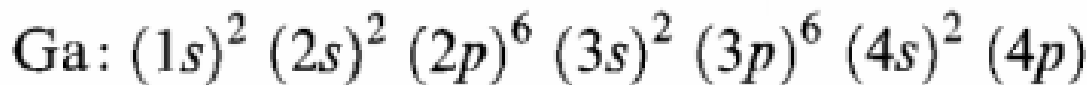


C (diamond): 7.30 eV per atom (712 kJ/mol);

Si: 4.64 eV per atom (448 kJ/mol);

Ge: 3.87 eV per atom (374 kJ/mol).

Zincblende structure semiconductors



sp³ hybrid orbitals

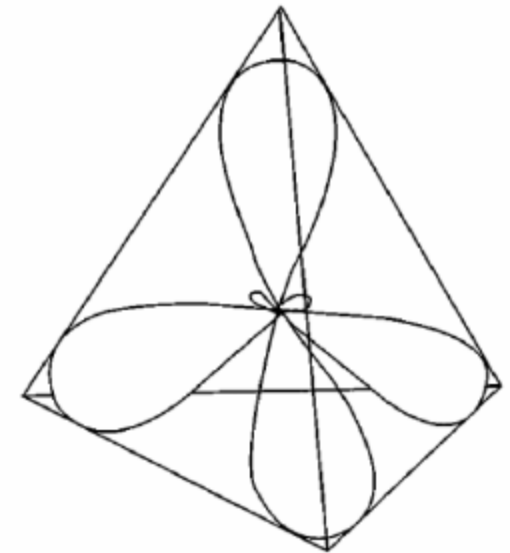


Image source: Balkanski

hybrid orbitals or tetrahedral orbitals

Band formation in Semiconductors !



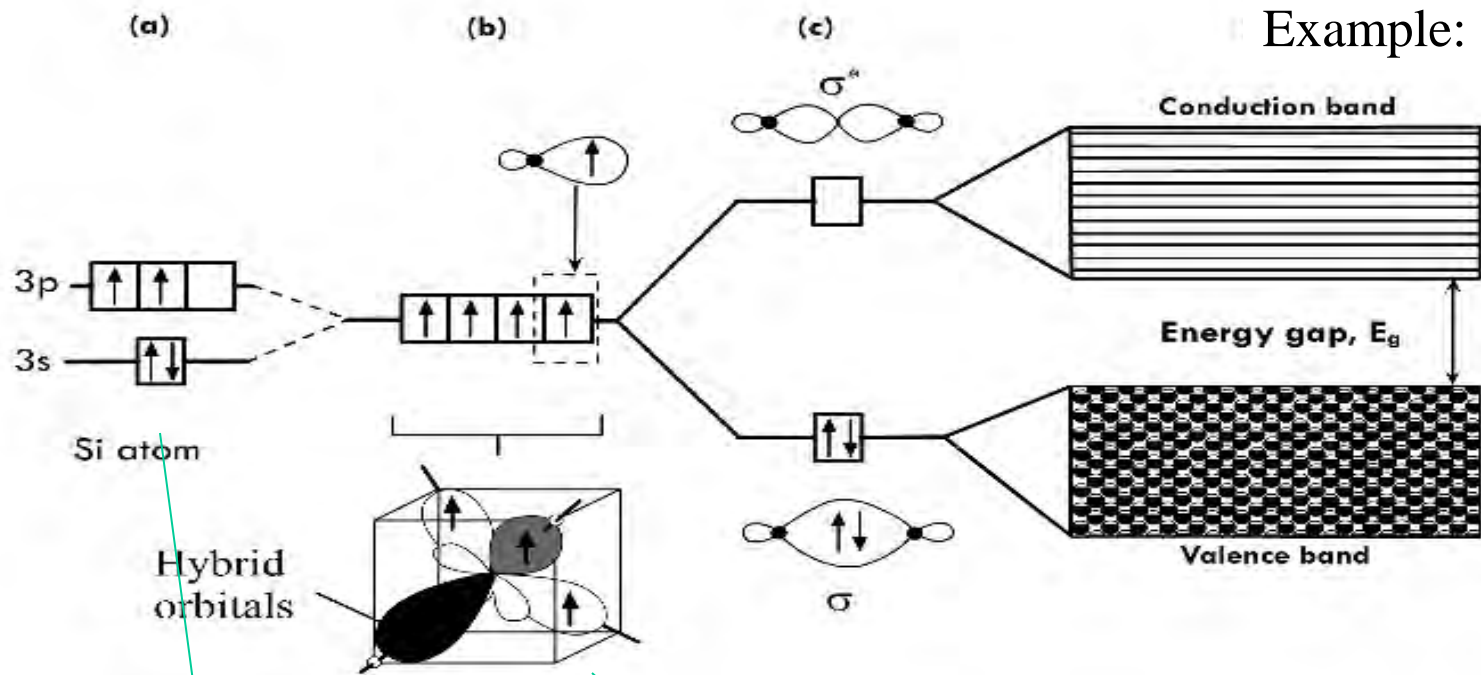


Figure 4: Formation of energy bands in Si. (a) Si atom with 4 electrons in outer shell form (b) 4 sp^3 hybrid orbitals. (c) The hybrid orbitals form σ and σ^* orbitals. (d) These orbitals overlap in a solid to form the valence and conduction band. Adapted from *Principles of Electronic Materials* - S.O.



Figure 2: Electronic configuration of Si atom. The 3s and 3p together forms the outer shell while the others form the inner shells. Adapted from *Principles of Electronic Materials* - S.O. Kasap.

Figure 3: (a) Isolated Si atoms showing the outer shell orbitals. (b) In a solid, these orbitals hybridize to form 4 sp^3 orbitals, just before bonding. Adapted from *Principles of Electronic Materials* - S.O. Kasap.

Next lecture

Electronic properties of semiconductors

