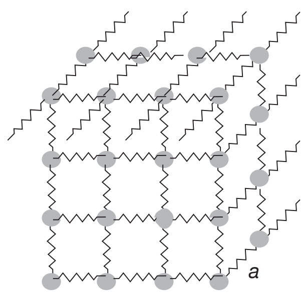
21_01_27

#3: Role of electronic structure in bonding among atoms

Bridging Length Scales - A constant reminder

•By and large, the elastic modulus, E (units GPa, also J m^{-3}) is related to the "spring constant" that is the stiffness of the bonds between neighboring atoms.



Therefore, the basic question is what the nature of the force-displacement curve is when atomic bonds are stretched.

•Atoms are a very small nucleus surrounded by a very large cloud of electrons. This cloud may have a spherical shape or it may have lobes - typically four.

•The nature of the bonding is determined by how the electron clouds interact with nearest neighbors (to a first approximation)

•Above depends on "electron affinity" that is the desire of atoms to draw in electrons, or share electrons with their neighbors. This property is called the electronegativity (EN) - higher EN means that atoms have greater affinity to share or grab electrons from their neighbors

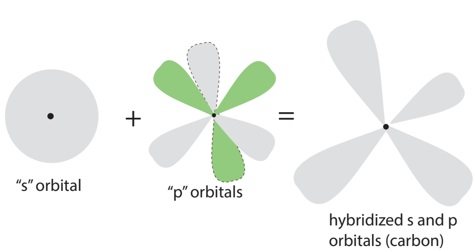
Topics for this Lecture

(i) Simple description of the electronic cloud of single atoms and its relationship to the periodic table. The electron orbitals.

(ii) Relationship among atoms (like copper or carbon) or atom-pairs (as in NaCL) from the point of view of sharing the electrons and thus create bonds. Metallic, ionic and covalent bonding

(iii) The possible nature of the Force, Displacement relationship when the bonds are stretched.

The Periodic Table



•The shape of the electron clouds. The electrons form clouds around the nucleus in orbitals, called s, p, d etc.

•The "s" orbital is full when it has two electrons, and the p orbital when it has 6 electrons, and the "d" shell when it has 10 electrons. Therefore 2, 8 and 18 electrons mark significant threshold in electron-electron interactions. The electrons may have spin up or spin down which can double these numbers.

•The s and p orbitals can hybridize to create 4 lobe shaped orbitals aligned symmetrically with respect to the nucleus. Since the total number of orbitals for s and p are 8, each lobe can contain 2 electrons.

Explore the chemical elements through this periodic table

Group	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period 1	1 H 1.008 Hydrogen																		2 He 4.0026 Helium
2	3 Li 6.94 Lithium	4 Be 9.0122 Beryllium												5 B 10.81 Boron	6 C 12.011 Carbon	7 N 14.007 Nitrogen	8 O 15.999 Oxygen	9 F 18.998 Fluorine	10 Ne 20.180 Neon
3	11 Na 22.990 Sodium	12 Mg 24.305 Magnesium												13 Al 26.982 Aluminium	14 Si 28.085 Silicon	15 P 30.974 Phosphorus	16 S 32.06 Sulfur	17 Cl 35.45 Chlorine	18 Ar 39.948 Argon
4	19 K 39.098 Potassium	20 Ca 40.078 Calcium		21 Sc 44.956 Scandium	22 Ti 47.867 Titanium	23 V 50.942 Vanadium	24 Cr 51.996 Chromium	25 Mn 54.938 Manganese	26 Fe 55.845 Iron	27 Co 58.933 Cobalt	28 Ni 58.693 Nickel	29 Cu 63.546 Copper	30 Zn 65.38 Zinc	31 Ga 69.723 Gallium	32 Ge 72.630 Germanium	33 As 74.922 Arsenic	34 Se 78.971 Selenium	35 Br 79.904 Bromine	36 Kr 83.798 Krypton
5	37 Rb 85.468 Rubidium	38 Sr 87.62 Strontium		39 Y 88.906 Yttrium	40 Zr 91.224 Zirconium	41 Nb 92.906 Niobium	42 Mo 95.95 Molybdenum	43 Tc 96.906 Technetium	44 Ru 101.07 Ruthenium	45 Rh 102.91 Rhodium	46 Pd 106.42 Palladium	47 Ag 107.87 Silver	48 Cd 112.41 Cadmium	49 In 114.82 Indium	50 Sn 118.71 Tin	51 Sb 121.76 Antimony	52 Te 127.60 Tellurium	53 I 126.90 Iodine	54 Xe 131.29 Xenon
6	55 Cs 132.91 Caesium	56 Ba 137.33 Barium	*	71 Lu 174.97 Lutetium	72 Hf 178.49 Hafnium	73 Ta 180.95 Tantalum	74 W 183.84 Tungsten	75 Re 186.21 Rhenium	76 Os 190.23 Osmium	77 Ir 192.22 Iridium	78 Pt 195.08 Platinum	79 Au 196.97 Gold	80 Hg 200.59 Mercury	81 Tl 204.38 Thallium	82 Pb 207.2 Lead	83 Bi 208.98 Bismuth	84 Po 208.98 Polonium	85 At 209.99 Astatine	86 Rn 222.02 Radon
7	87 Fr 223.02 Francium	88 Ra 226.03 Radium	**	103 Lr 262.11 Lawrencium	104 Rf 267.12 Rutherfordium	105 Db 270.13 Dubnium	106 Sg 269.13 Seaborgium	107 Bh 270.13 Bohrium	108 Hs 269.13 Hassium	109 Mt 278.16 Meitnerium	110 Ds 281.17 Darmstadtium	111 Rg 281.17 Roentgenium	112 Cn 285.18 Copernicium	113 Nh 286.18 Nihonium	114 Fl 289.19 Flerovium	115 Mc 289.20 Moscovium	116 Lv 293.20 Livermorium	117 Ts 293.21 Tennessine	118 Og 294.21 Oganesson

*Lanthanoids	*	57 La 138.91 Lanthanum	58 Ce 140.12 Cerium	59 Pr 140.91 Praseodymium	60 Nd 144.24 Neodymium	61 Pm 144.91 Promethium	62 Sm 150.36 Samarium	63 Eu 151.96 Europium	64 Gd 157.25 Gadolinium	65 Tb 158.93 Terbium	66 Dy 162.50 Dysprosium	67 Ho 164.93 Holmium	68 Er 167.26 Erbium	69 Tm 168.93 Thulium	70 Yb 173.05 Ytterbium
**Actinoids	**	89 Ac 227.03 Actinium	90 Th 232.04 Thorium	91 Pa 231.04 Protactinium	92 U 238.03 Uranium	93 Np 237.05 Neptunium	94 Pu 244.06 Plutonium	95 Am 243.06 Americium	96 Cm 247.07 Curium	97 Bk 247.07 Berkelium	98 Cf 251.08 Californium	99 Es 252.08 Einsteinium	100 Fm 257.10 Fermium	101 Md 258.10 Mendelevium	102 No 259.10 Nobelium

The standard form of the periodic table shown here includes periods (shown horizontally) and groups (shown vertically). The properties of elements in groups are similar in some respects to each other.

Please note that,

i. The first row has two elements since 2 electrons fill the s orbital

ii. The second and third rows have eight elements corresponding to filling of s and p orbitals; they are called main group elements

iii. Further down the d orbitals, and even further down, f orbitals start to fill up

The origin of bonds amongst atoms

The sharing of electrons amongst neighboring atoms determines the strength of the bond they form with each other. For example consider the sodium atom and the chlorine atoms. The sodium atom an one electron in its outer most shell while chlorine and 7 (as given by their position in the periodic table). Therefore both atoms can complete their orbitals by the sodium donating and the chlorine accepting one electron. This exchange forms the bond.

The Na+/Cl- is called an ionic bond. But there can be other kinds of electron sharing, but always driven by the desire of atoms to have complete shell around them.

For example in metals, consider Na as an example, each atom can give up one electron to have a complete shell. This donation of electron forms a continuum which is the source of metallic bonding.

Another possibility is that electrons can be shared in time, with an electron spending half its time with one atom and the other half with the neighboring atom. This is common in sp hybridized atoms. Each lobe on its own has one electron but by sharing it, and its neighbor can have two electrons (but half the time). The four lobes then add up to eight electrons which is a full shell. However, note that the lobes must overlap to have this form of bonding, which is called covalent bonding. It is self evident that covalent bonding will have directional character.

Remember that the ionic, metallic and covalent bonding as described above are ideal cases or models. In reality the bonds can be a mixture of any two of them. For example it can be partly ionic and partly covalent. This flexibility can be made quantitative by consideration of electronegativity.

Electronegativity

Electronegativity is a quantity that was developed by Pauling based upon his experience of bonding among atoms. It gives a number for electron affinity that is The periodic table gives a qualitative understanding of the preference of atoms to donate or to accept electrons. Thus, atoms have a varying degree of affinity to draw electrons to themselves. This nature of atoms was given a quantitative value, called electronegativity, by Pauling and is given in the following table:

Electronegativity of Elements

						H										
						2.1										
Li	Be	B											C	N	O	F
1.0	1.5	2.0											2.5	3.0	3.5	4.0
Na	Mg	Al											Si	P	S	Cl
0.9	1.2	1.5											1.8	2.1	2.5	3.0
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
0.8	1.0	1.3	1.5	1.6	1.6	1.5	1.8	1.9	1.9	1.9	1.6	1.6	1.8	2.0	2.4	2.8
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
0.8	1.0	1.2	1.4	1.6	1.8	1.9	2.2	2.2	2.2	1.9	1.7	1.7	1.8	1.9	2.1	2.5
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
0.7	0.9	1.0-1.2	1.3	1.5	17	1.9	2.2	2.2	2.2	2.4	1.9	1.8	1.9	1.9	2.0	2.2
Fr	Ra	Ac	Th	Pa	U	Np-No										
0.7	0.9	1.1	1.3	1.4	1.4	1.4-1.3										

The values of electronegativity are consistent with the examples of chemical bonding in metals, carbon and NaCl for example. The metals yield electrons and oxygen accepts them. Thus oxygen has a higher electronegativity than metals—a value of 3.5 relative to those of the metals, which lies between 1 and 2. We now ask the significance of the difference between the electronegativity values between two different metals and oxygen. For instance, the difference between the electronegativities of Ca and O is 3.5-1.0 = 2.5 while the difference between Zr and O is 3.5-1.4 = 2.1. We will return to this question after reconsidering the discussion of ionic and covalent bonding.

In a purely ionic bond, the electron transfers completely from one atom to another. For example, if the Ca-O bond were to be purely ionic, then two electrons from Ca will move over entirely to the oxygen atom, giving a whole charge of +2 to the Ca atom and –2 to the oxygen atom. However, electrons are not stationary entities, which are either all in one place or the other. Rather, they are constantly orbiting the nucleus of the atom. When an ionic bond forms, the electrons can choose to spend a greater amount of time with one atom than the other. Thus, the transfer of electron is a probability rather than a certainty. This fact leads to the concept of the degree of ionicity of a bond. The electronegativity series gives a value to the ionic character via the following equation:

$$I_C = 1 - \exp\left[1 - \frac{(\chi_A - \chi_B)^2}{4}\right]$$

where I_C is the amount of ionic character of the bond A-B, and where χ_A and χ_B are the electronegativity of atoms A and B. Note that I_C ranges from zero, when $\chi_A = \chi_B$ (therefore bonds between like atoms are entirely non–ionic), to one when the difference becomes very large. Note that ($|_A$- $|_B$) is always calculated in such a way that it is always a positive quantity, that is, x_A always has the higher value of electronegativity. Equation 2.3 is highly non–linear, that is, small changes in the electronegativity can have a large effect on ionicity. Therefore, it is useful to have a numerical table of the predictions, which are given in the table on the next page.

We are now able to say that the bond between Zr and O is about 67% ionic while that between Ca and O is nearly 80% ionic. In general, bonds are more than 50% ionic if the difference in the electronegativity between the atoms is greater than 1.7.

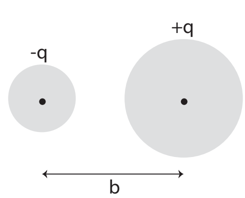
The relationship between the difference in the electronegativity between two atoms A and B, and the ionic character of the bond between then.

$x_A - x_B$	Amount of ionic Character (%)	$x_A - x_B$	Amount of ionic Character (%)
0.2	1	1.8	55
.4	4	2.0	63
.6	9	2.2	70
.8	15	2.4	76
1.0	22	2.6	82
1.2	30	2.8	86
1.4	39	3.0	89
1.6	47	3.2	92

(iii) Polar nature of bonds (the dipole moment)

Molecules and crystals are often described qualitatively as being polar or non-polar. Being polar means that a single molecule has a net dipole moment. In a crystal it means that a large aggregate of atoms have a net dipole moment.

Therefore a molecule by itself may have a dipole moment but when in a crystal of a certain structure the dipole moments of individual bonds cancel leaving a net value of zero dipole moment.



The dipole moment is given the units of D (Debyes or μ).

A charge of 1 electron separated by 100 pm (=1Angstrom) has a dipole moment of 4.803 Debye (μ)