

MIT Intro to solid state chem

Ian Poon

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1 Introduction

Proposition 1

All matter is made of **atoms** and such atoms can combine in fixed ratios to form **molecules**

Definition 2 (the 4 quantum numbers)

The *principal quantum number* n tells us the **shell** that a particular orbital is in and the *angular momentum number* ℓ tell us the **sub-shell**. Finally the *magnetic quantum number* m tell us the particular **orbital** of our hydrogen atom state.

The last one will be mentioned shortly below

The total number of orbitals for a given n is

$$1 + 3 + 5 + \dots + (2n - 1) = n^2$$

It tells us that if we have a *one-electron* system with some nucleus of Z protons then there are n^2 **degenerate**(same energy) orbitals at energy

$$E = -\frac{RZ^2}{n^2}$$

where R is the Rydberg constant

Fact 3 (Aufbau principle)

Electrons occupy the lowest energy states available and there can be at most two electrons per orbital(one of **spin up** and **spin down**. Furthermore **Hund's rule** must be obeyed which states that we always put only one electron in each available orbital if there are multiple at the same energy

The 4th quantum number is the **spin magnetic quantum number** m_s which is dictates the spin state of the electron($\frac{1}{2}$ or $-\frac{1}{2}$)

Proposition 4

No orbital can have more than 2 electrons and if it has two electrons then they must have opposite spins

Definition 5

The **core electrons** are the electrons closest to the nucleus and the **valence electrons** are those farthest from the nucleus.

2 periodic trends(atoms)

Remark 6. We often use shorthand known as the **noble gas configuration** for example



To understand the order that we fill our orbitals in we downward left diagonal lines across the table and fill the orbitals from top to bottom. For example we will fill in the order 1s,2s,2p,3s,3p,4s...

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

Fact 7 (Exception to the Aufbau principle)

The electron configurations for *K*, *Ca*, *Sc*, *Ti*, *V*, *Cr* respectively are $[Ar]4s$, $[Ar]4s^2$, $[Ar]4s^23d$ and $[Ar]4s^24d^2$, $[Ar]4s^23d^2$, $[Ar]4s^13d^5$ respectively. Basically the 4s orbital turns out to have lower energy than the 3d orbital unlike the rule we mentioned above. The reason has got to do with atoms like have half-full or full orbitals.

Definition 8

An electronic configuration is **diamagnetic** if all electrons are paired up and is **paramagnetic** if there are unpaired electrons

Consider the following periodic trends

1. **ionization energy** (the energy required to remove an electron from its orbital in an atom). Ionization energy is given by

$$\frac{R(Z_{\text{eff}})^2}{n^2}$$

- As we move across the periodic table the effective nuclear charge increases because we are adding more protons and the corresponding electrons only partially shield the nucleus.
- As we move down the periodic table the value of n goes up and that makes more of an impact than the increase in effective nuclear charge. (i.e. shielding overcompensates for increase in effective nuclear charge)

So in general the ionization increases to the right and decreases downward except elements such as those with half filled shells like those discussed above

2. **electron affinity** is the amount of energy required to remove an electron from an anion of that element or equivalently the amount of energy by which the system becomes more stable when we add an electron. The trends are basically the same as the above.
3. **electronegativity** (how much a system wants another electron). The trend is basically the same as the above again
4. **atomic radius** We generally say that the atomic radius increases down the periodic table and decreases to the right because again the electrons are more tightly bound (so think about it should be the direct opposite of ionization energy trend)

In summary ionization energy, electron affinity, electronegativity

increases right across row and decreases down the column

this is opposite of atomic radius which

decreases right across row and increases down the column

3 periodic trends(ions)

The reactivity and periodic trends of *anions* and *cations* compared to their neutral atoms are governed by several key periodic properties, including *electronegativity*, *atomic size*, and *ionization energy*. Understanding how these properties change when atoms gain or lose electrons provides insight into the reactivity of ions.

3.1 Reactivity of Anions and Cations vs. Neutral Atoms

Cations (Positively Charged Ions)

- *Formation*: A cation forms when an atom *loses one or more electrons*, typically from its valence shell. This usually occurs for metals, which have relatively low ionization energies.
- *Reactivity*:
 - Cations are typically *electron-deficient*, which makes them *electrophilic* (electron-seeking). Their reactivity often involves accepting electrons or forming bonds with nucleophiles (electron-rich species).
 - Cations are more reactive than their neutral atoms in many cases, especially in polar reactions where they attract negatively charged species (like anions) or nucleophiles.
 - For example, the Na^+ ion is more reactive in polar solvents like water than neutral sodium (Na), which is relatively stable as a solid metal.

Anions (Negatively Charged Ions)

- *Formation*: An anion forms when an atom *gains one or more electrons*. This occurs more readily for nonmetals, which have high electronegativities and strong tendencies to accept electrons.
- *Reactivity*:
 - Anions are *electron-rich*, making them *nucleophilic* (donating electrons to electrophiles). They tend to react with positively charged or electron-deficient species.
 - Anions are generally more reactive than their neutral atoms, especially in reactions that involve donating electrons or forming bonds with electrophiles.
 - For instance, Cl^- is more reactive as a nucleophile than neutral chlorine (Cl_2), which exists as a diatomic molecule.

3.2 Periodic Trends in Anions and Cations vs. Neutral Atoms

Electronegativity

- *Definition*: Electronegativity is the tendency of an atom to attract shared electrons in a bond.
- *Trend in the Periodic Table*:
 - Electronegativity *increases across a period* (left to right) as atoms become smaller and the nuclear charge increases.
 - Electronegativity *decreases down a group* (top to bottom) as the atomic size increases and the effective nuclear charge experienced by the valence electrons decreases.
- **Impact on Ions**:
 - *Cations*: When an atom becomes a cation (loses electrons), it typically becomes *more electronegative* compared to its neutral form because the remaining electrons are held more tightly by the nucleus. The higher positive charge pulls the electron cloud closer, increasing the atom's tendency to attract electrons in future bonds.

- Example: Na^+ is more electronegative than neutral sodium (Na) because of its smaller size and stronger nuclear attraction to the remaining electrons.
- *Anions*: When an atom becomes an anion (gains electrons), its *effective electronegativity decreases* slightly. This is because the additional electron(s) increase repulsion within the electron cloud, spreading the charge over a larger space and weakening the attraction of the nucleus for additional electrons.
- Example: Cl^- is less electronegative than neutral chlorine (Cl) due to the electron-electron repulsion after gaining an electron.

Atomic Size (Atomic Radius)

- *Definition*: Atomic size is the distance from the nucleus to the outermost electron shell (valence shell).
- *Trend in the Periodic Table*:
 - Atomic size *decreases across a period* as nuclear charge increases, pulling the electron cloud closer to the nucleus.
 - Atomic size *increases down a group* as new electron shells are added, increasing the distance between the nucleus and the outermost electrons.
- **Impact on Ions**:
 - *Cations*: Cations are always *smaller* than their neutral atoms because the loss of electrons reduces electron-electron repulsion and allows the remaining electrons to be pulled closer to the nucleus. Additionally, the loss of a valence shell (in many cases) significantly decreases the size.
 - Example: Na^+ is much smaller than neutral sodium (Na) because it loses its outermost electron and the remaining electron cloud is pulled inward by the nucleus.
 - *Anions*: Anions are always *larger* than their neutral atoms because gaining electrons increases electron-electron repulsion in the outer shell, causing the electron cloud to expand.
 - Example: Cl^- is larger than neutral chlorine (Cl) because the extra electron increases repulsion, spreading out the electron cloud.

Ionization Energy

- *Definition*: Ionization energy is the amount of energy required to remove an electron from a neutral atom in its gaseous state.
- *Trend in the Periodic Table*:
 - Ionization energy *increases across a period* as nuclear charge increases and the electrons are held more tightly to the nucleus.
 - Ionization energy *decreases down a group* as the outermost electrons are farther from the nucleus and easier to remove.
- **Impact on Ions**:
 - *Cations*: The ionization energy for forming a cation (removing an electron) is generally *high*, but after a cation is formed, subsequent ionization energies are even higher due to the stronger pull of the nucleus on the remaining electrons. Cations, once formed, typically have *higher ionization energies* than their neutral counterparts because of the increased effective nuclear charge.

- Example: Na^+ has a much higher ionization energy than neutral sodium (Na), making it difficult to remove further electrons from Na^+ .
- *Anions*: Since anions are formed by gaining electrons, they do not have ionization energies directly related to their formation. However, if you were to remove an electron from an anion, it would generally have *lower ionization energy* than the corresponding neutral atom because the added electron weakens the effective nuclear charge experienced by the outermost electrons.
- Example: Removing an electron from Cl^- to revert to neutral chlorine is easier (lower ionization energy) than removing an electron from neutral Cl .

3.3 Summary of Reactivity and Periodic Trends

Property	Cations	Anions	Neutral Atoms
Reactivity	Highly reactive (electrophilic)	Highly reactive (nucleophilic)	Varies by element
Electronegativity	Higher than neutral atom	Lower than neutral atom	Follows periodic trend
Atomic Size	Smaller than neutral atom	Larger than neutral atom	Follows periodic trend
Ionization Energy	Higher than neutral atom	Lower than neutral atom	Increases across period, decreases down group

4 molecular orbital theory

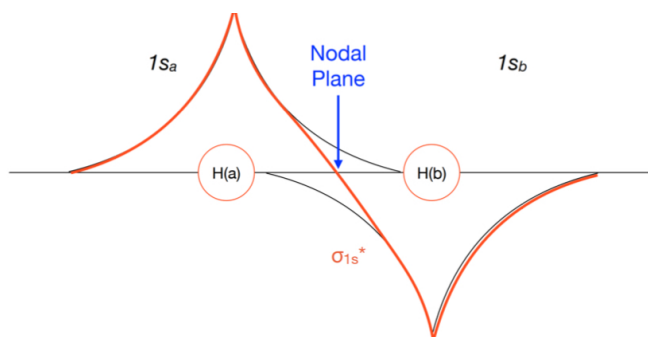


Figure 1: Antibonding orbital

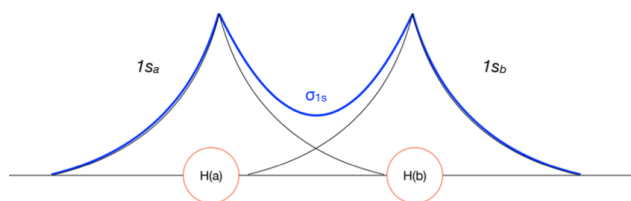
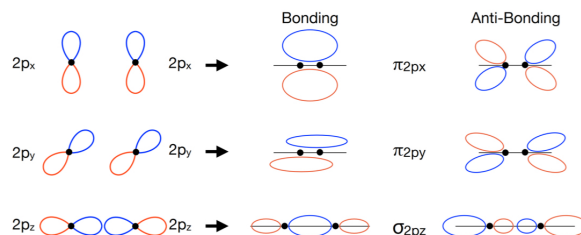


Figure 2: Bonding orbital

Remark 9. Note that the middle is a plane view. the π orbitals are overlapping side on



Definition 10

The **bond order** calculates the number of bonds formed between two atoms and it is given by

$$BO = \frac{1}{2}(\text{number of electrons in bonding molecular orbitals} - \text{number in anti-bonding molecular orbitals})$$

Example 11

Consider the following **molecular orbital diagram**

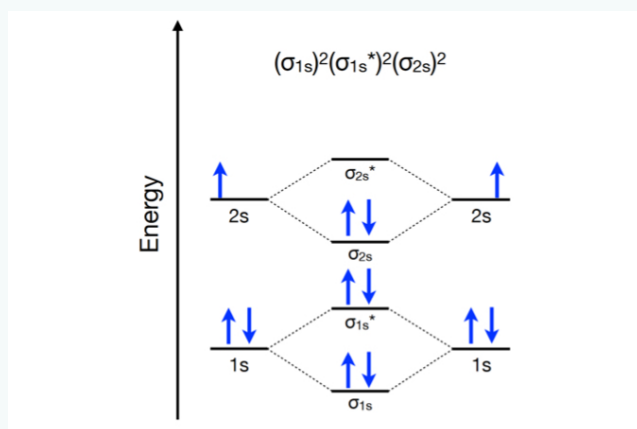


Figure 3: Dilithium

Note that we only needed to look at valence electrons because core electrons always have the same number of bonding and anti bonding orbitals and electrons in those orbitals

Note that it matters whether the orbitals are aligned in the direction of the bond axis or not

Definition 12

HOMO (highest occupied molecular orbital) is the one highest energy with electrons and **LUMO** (lowest unoccupied molecular orbital) is the one lowest energy without electrons

5 hybridization

the act of combining orbitals in different ways

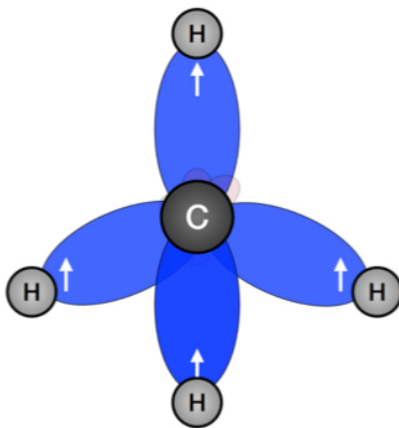


Figure 4: Methane

Carbon $1s^2 2s^2 2p^2$ has 4 valence electrons so it promotes one its electrons into the $2p_z$ orbitals to form 4 $2sp^3$ orbitals (named as such because this 4 orbitals are made from one s and three p orbitals) where we have formed 4 $\sigma(C2sp^3, H1s)$ bonds

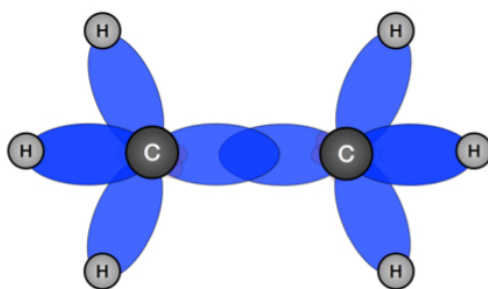


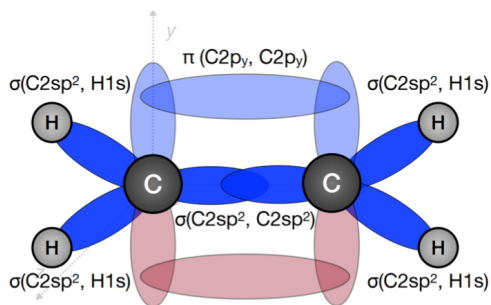
Figure 5: Ethane

Formed by a single $\sigma(C2sp^3, C2sp^3)$ as well as size $\sigma(C2sp^3, H1s)$ bond. See that now the electronic configuration becomes



Figure 6: Hybridization: get spin pairing during bonding

Note that we cant twist the hydorgen atoms bonded to the carbon atoms spearthey without the snapping the pi bond.



6 VSEPR and lewis

Consider

Formula	SN	Structure	Hybridization	Angle	Example
AX ₂	2	Linear	sp	180°	CO ₂
AX ₃	3	Trigonal planar	sp ²	120°	BH ₃
AX ₄	4	Tetrahedral	sp ³	109.5°	CH ₄
AX ₅	5	Trigonal bipyramidal	sp ³ d	90° and 120°	PF ₅
AX ₆	6	Octahedral	sp ³ d ²	90°	SF ₆

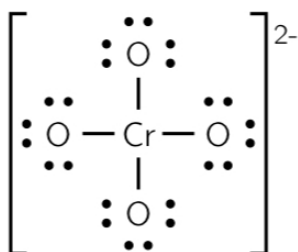
Formula	SN	Structure	Hybridization	Angle	Example
AX ₃ E ₂	5	T-shaped	< 90°		ClF ₃
AX ₂ E ₃	5	Linear	180°		I ₃ ⁻
AX ₅ E	6	Square pyramidal	< 90°		BrF ₅
AX ₄ E ₂	6	Square planar	90°		XeF ₄

Formula	SN	Structure	Hybridization	Angle	Example
AX ₂ E	3	Bent	< 120°	SO ₂	
AX ₃ E	4	Trigonal pyramid	< 109.5°	NH ₃	
AX ₂ E ₂	4	Bent	< 109.5°	H ₂ O	
AX ₄ E	5	See-saw	< 90°, < 120°	SF ₄	

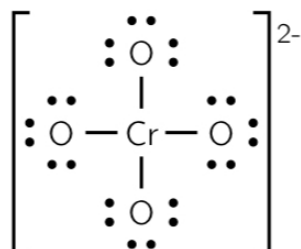
Consider expanded octet

Example 13

The anion CrO_4^{2-} does not have normal octet(maximum 8 valence) since it has extra orbitals to accommodate Cr : $[\text{Ar}]4s^13d^5$ It is said to have an **expanded octet**



See that in total it has 32 valence electrons. But this gives us a +2 formal charge on chromium and -1 formal charge on the oxygen. But it could be made more stable with the following rearrangement



where now we have two -1 formal charges on two oxygens and 0s everywhere else for a total of -2 formal charge which is the lowest and hence most stable you can get.

7 solubility, acids and bases

Definition 14

A **solution** is a homogeneous mixture (of solids, liquids and gases)

We call the base liquid the **solvent** and the other materials dissolved in it the **solute**

Fact 15

Solvation(dissolving a solute into a solvent) occurs spontaneously if the solvent-solute attraction is stronger than the solute-solute and solvent-solvent interactions

Fact 16

In general "like dissolves like" polar liquids like water are good solvents for ionic and polar compounds while nonpolar liquids like hexane are good solvents for nonpolar compounds

Definition 17

We say a solution is **saturated** when there is undissolved solute remaining because the solvent has dissolved all that it can

Definition 18

The **molar solubility** is the molar concentration (in moles per liter also denoted M) of a solute in a saturated solution

Definition 19

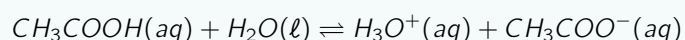
An **arrhenius acid** is a substance that increases the H^+ concentration in water and an **arrhenius base** is a substance that increases the H^- concentration.

Definition 20

A **bronsted-lowry acid** denotes a proton H^+ while a **bronsted-lowry base** accepts a proton H^+

Definition 21

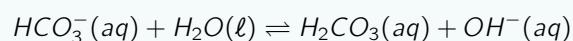
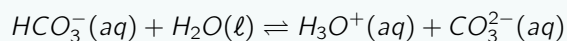
Acids and bases also have conjugate bases and acids respectively corresponding to removing or adding a H^+ ion respectively

Example 22

we can think CH_3COO^- as the **conjugate base** of the original acid CH_3COOH and H_3O^+ as the **conjugate acid** of H_2O

Example 23

This is an example of an **amphoteric** molecule which can either be an acid or base

**Definition 24**

A **lewis acid** is a species that accepts lone pair electrons and a **lewis base** is one that donates lone pair electrons

Definition 25

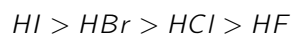
The **pH** and **pOH** of a water based solution are given by

$$pH = -\log[H_3O^+], \quad pOH = -\log[OH^-]$$

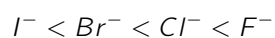
and

$$pH + pOH = 14.0$$

Recall from organic chemistry that we know for hydrogen halides in general down the group means stronger acid
Acidity rank



and that basicity rank

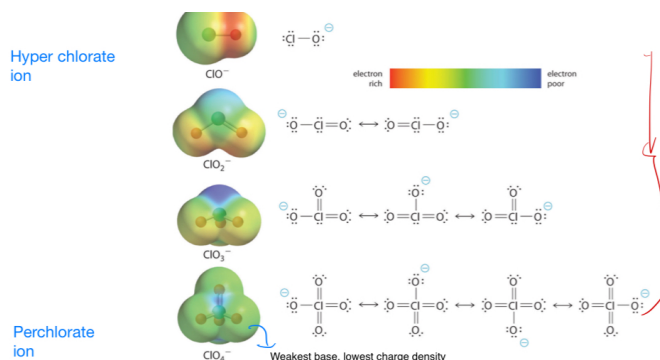


where the weaker the base the better it stabilizes a negative charge. However this is not true for hypohalous acids(HOX) with X representing a halogen. Acid rank



this is due to **inductive effects** where the electronegativity of X increases the distribution of electron density within the molecule shifts away from the $O-H$ bond making it weaker as easier to lose proton H^+

Another factor to consider is **electron delocalization in the conjugate base**



Clearly the weakest conjugate base (the most stable) as seen here has the most resonance structures which means its acid is more acidic (it wants to achieve this more stable end result more badly). This is also covered in organic chemistry

8 redox

Definition 26

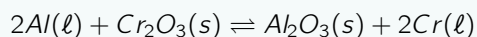
oxidation is the term for a compound "losing electrons" and **reduction** is the term for "gaining electrons"

oxidation numbers increase when an atom loses electrons and decrease when an atom gains electrons

Definition 27

The **oxidizing agent** in a reaction is the reactant that is reduced (gaining electrons) and the reducing agent is the reactant that is being oxidized (losing electrons)

Example 28



where Chromium(III) is the oxidizing agent (reduced from +3 to 0) and aluminum is the reducing agent (oxidized to a number of +3)

9 covalent bonding

in general the higher the bond order and the stronger the covalent bond. But size matters too

Remark 29. note the strength of bond is similar ranked in decreasing order for



and



the size of atom increases more than proportionately compared volume of orbital overlap resulting in decreasing bond strength(see saylor page 146 chapter 8.8)