<u>CHEM 1001 MIDTERM 2 REVIEW</u>

5.1-Orbital Energies

- When atoms absorb a photon, the electron transfers to a higher orbital
- Stability of an orbital determined by measuring **Ionization energy**, energy needed to remove e^-. Ex: He^+ four times as large IE as H= four times as stable at ground state
- Orbital energies of each element is unique, due to **electron-electron** interactions.
- When an electron-electron repulsion reduces some of the attraction between nucleus-electron it is called **Screening** (Partial Cancellation)
- (-1 bound e^- and +2 nucleus in He^+) The electron experiences a net attraction from an **effective nuclear charge** greater than +1 but less than +2. (1s orbital spread out).
- The ability to screen **decreases** as the orbital size **increases** (**n** quantum number), electrons are packed loosely in large orbitals.
- The **n** of a electron screens orbitals that have a larger **n**
- **s** orbitals are **more stable** than **p** orbitals, due to stronger attraction in nucleus.
- The higher the ***l*** quantum #, the higher # of e^- are screened by e^- in smaller/stabler orbitals
- Screening is effective when the e^- density of an orbital lies **between nucleus** and the e^- of another.

5.2-Structure of Periodic Table

- **Pauli Exclusion Principle:** Each electron in an atom has unique set of quantum #s
- **Aufbau Principle:** Electrons are placed into orbitals starting with lowest energy to highest energy e^-
- Each electron occupies most stable orbital available, the higher the **n** the less stable the orbital, for equal **n** the higher ***l*** is less stable.
- Chemical behavior determined by valence e^-, core e^- are inaccessible. Valence e^- are those of highest **n** plus those in partially filled d/f orbitals.

5.3-Electron Configurations

- Describes how an atoms e^- are distributed.
- **Hund's Rule:** The most stable e^- configuration of equal E orbitals has the maximum number of same spin electrons.
- Anomalous e^- configurations: occurs due to **stability** in **filled** or **half-filled** degenerate orbitals, removes e^--e^- repulsion, ex; s^1d^5 instead of s^2d^4
- **Isoelectronic:** Atoms/ions with the same number of e^-
- Transition metal cations are **always** more stable in d orbitals than s orbitals. (fill d first)

- Any atoms/ion with an unpaired e^- has a **non-zero** net spin and is attracted to a strong magnet.
- **Diamagnetic:** Atom/ion with all e^- paired, no attraction with magnet, **zero** net spin
- **Paramagnetic:** Atom/ion with unpaired e^- spins don't cancel out, has attraction, spins are additive, paramagnetism proportional to # of unpaired spins.
- Most substances are diamagnetic.
- **Excited State:** Occurs when an atom absorbs E, or with a new e^- configuration, they're **unstable**, spontaneously return to ground state releasing E.

5.4-Periodicity of Atomic Properties

- As **n** increases, orbitals get bigger and less stable, as the **atomic number** (Z) increases orbital gets smaller and more stable.
- As you go **down** the table, both **n** and Z increase, but with the additional e^- the screening largely cancels the effect of p^+, thereby reducing the effect of Z, <u>only **n** matters</u>
- **Atomic Radii: Decreases** left to right due to attractive forces with e^- and nucleus, little radius changes across d/f blocks due to screening. **Increases** top to bottom; more energy levels, bigger **n**
- **Ionization Energy:** Minimum amount of energy needed to remove an electron, **Increases** left to right(increased attraction), **Decreases** top to bottom, valence e^- further from nucleus.
- Ionization becomes more difficult as cationic charges increase, as number of e^- decrease each one feels greater attraction to nucleus. Removing core e^- = large energy needed
- **Electron Affinity:** Energy change when an e^- is added to an atom, **releases** energy, e^- goes into most stable orbital available.
- EA **more negative** left to right across row due to increasing nuclear charge, binds e^- tightly in nucleus. EA remain constant for elements in the same column.
- When the e^- that is added must occupy a new orbital, the anion is **unstable** (more positive), also occurs in elements with half filled orbitals, cause e^- need to overcome repulsive force, so energy is positive
- Screening and e^--e^- repulsion cause irregularities in IE.
- Cation is always **smaller** than neutral atom due to less e^--e^- repulsion, Anion is always **larger** due to more e^--e^- repulsion

5.5-Energetics of Ionic Compounds

- Not all elements form ionic compounds
- They form when the stabilization gained through ionic attraction **exceeds** the energy required to create ions from neutral atoms
- Reaction Path for ionic compounds;

- **Sublimation (Metal) :** Turning solid into gas, requires energy
- **Ionization of (Metal):** Removing an e^- from metal, requires energy
- **Bond Dissociation (Diatomic Nonmetal):** Molecule must be broken into individual atoms, requires energy, *"BE"*, ex; **($1/2Cl_2 \rightarrow Cl$ $\Delta E = 1/2 \cdot 240 = 120$ kJ/mol)**
- **Electron Attachment (NM):** Depending on sign of EA of the element, energy is either absorbed or released when adding e^- ex; ***Cl* EA negative, energy released**
- **Condensation:** Ions condense into 3-D array of ions, energy released due cation-anion attraction, **calculated as electrical energy**, only **part** of total energy released
- **Lattice Energy(*LE*):** Energy needed to decompose ionic compound into its ions, sum of all ion interactions in solid ionic compound, electrical energy equation
- Doubly charged ions cost more energy to make compounds, ex; Na^{2+} and Cl^{2+}
- *LE* **increases** with ionic charge, **decreases** as ionic size increases, **increases** with number of ions in chemical formula

5-6: Ions and Chemical Periodicity

- **S-block:** Most form ionic compounds, reactive, alkaline/alkaline earth metals
- **P-block:** Properties varies heavily, most have covalent bonds.

6.1-Overview of Bonding

- ANY group of particles arrange themselves to **maximize** electrical attraction, and have the **most** stable arrangement of charges
- Total electrical energy of molecule happen in 3 types of interactions;
- Electrons and nuclei **attract** each other, **releases** energy, **more stable**(lower energy)
- Electrons **repel** each other, **raises** energy, **less stable**
- Nuclei **repel** each other, **reduces stability**
- 3 interactions are balanced to give molecule greatest stability, achieved when e^- concentrated between nuclei
- **Covalent Bond:** Mutual attraction of bonding electrons to two nuclei, attractive energy of e^- and nuclei surpasses repulsive energy
- For H_2 to be stable, attractive energie must **exceed** repulsive
- Molecules are **dynamic**, e^- move, spread over entire molecule
- Amount of increased stability dependant on distance between nuclei
- At **large** distances interaction energy is almost **zero**, at **close** distances attraction with e^- of one side and nuclei of another **increases** and stability **increases**
- At **really close** distance nucleus-nucleus repulsion **surpasses** electron-nucleus attraction

- **Bond length:** Separation distance where molecule is **most** stable
- **Bond Energy:** Amount of stability at that separation
- Equal electron sharing product of symmetrical distribution of electron density between atoms(diatomic molecules)
- Unequal attractive forces lead to unsymmetrical distribution of electrons, gives partial negative/positive charges, equal in magnitude, results in a **polar bond**
- **Electronegativity:** Increases from lower left to upper right, <0.5 = polar. >0.5 <1.7 = polar covalent. >1.7 = ionic
- Sometimes atoms share e^- unequally but don't fully transfer e^-

6.2-Lewis Structures

- Least electronegative atom in middle.
- To optimize e^- distribution about inner atom, move e^- from outer atoms to make double/triple bonds until octet is complete
- Atoms with valence *d* orbitals allow them to have more than 8 e^- in octet, atoms with more than 4 valence e^- may be most stable with more than octet
- **Formal Charge(FC):** Difference between valence e^- in free atom and valence e^- assigned in lewis structure, determines if there's a deficiency of electrons
- If **positive** FC, shift e^- to make multiple bonds
- Atoms are assigned all of its lone pairs and 1 half of its bonding e^-
- For a **neutral** molecule sum of all formal charges must be **zero**
- Sum of FC must **equal** total charge on species
- **Row 2:** Limited to having octets
- **Resonance Structure:** More than 1 way to construct lewis structure, often having to do with placement of double bond, they're not always equivalent

6.3-Molecular Shapes: Tetrahedral Shapes

- **Tetrahedron:** 109.5° bond angles, pyramid, 4 identical faces and corners
- Stable molecule = **Maximizing** electron-nuclear **attractions**, **Minimizing** nuclear-nuclear and electron-electron **repulsions**
- **VSEPR:** Principle of minimizing electron-electron repulsion, done by keeping chemical bonds as far as possible
- assumes e^--e^- repulsion determines arrangement of valence e^- around inner atom by positioning pairs as far apart as possible
- **Structural Isomers:** 2 or more compounds with same formula but different placement of atoms
- **Electron Group:** Set of e^- in a specific region around atom, 1x bond =$2e^-$, 2x bond=$4e^-$, a pair of nonbonding e^- or a single e^-

- **Ligand:** An atom/group of atoms bonded to an inner atom
- **Steric Number (SN):** Sum of ligands + # of lone pairs, ie. total # of groups with atom,
- **E$^-$ Group Geometry:** 3-dimensional arrangement of valence shell e$^-$ groups, identified by steric number
- **Molecular Shape:** Describes how **ligands** are arranged in space
- Silicon displays tetrahedral shapes in all of its stable compounds, oxide of Si= **silica**, continuous network of Si-O bonds, Si=tetrahedron, O=bent, **silicate** minerals

6.4-Other Molecular Shapes

- **Linear Geometry:** Two ligands and **no** lone pairs, 180° SN=2
- Double/Triple Bond = 1 **single** ligand
- **Trigonal Plane:** Three ligands and **no** lone pairs, 120° SN =3 common in C-compounds with double bonds
- 1 lone pair + 2 ligands = **Bent**
- 2 lone pair + 2 lone pair = **Bent**
- 1 lone pair + 3 ligands = **Trigonal Pyramidal**, SN=4
- **Trigonal Bipyramidal:** SN=5, 2 pyramids that share triangular base, positions are **not** equivalent, the 3 positions at the corner have 120°, **equatorial**, other two at 90°, **axial**
- Lone pairs **always** occupy equatorial position
- 1 lone pair + 4 ligands = **Seesaw Shape**
- 2 lone pairs + 3 ligands = **T-shaped**
- 3 lone pairs +2 ligands = **Linear**
- **Octahedral:** Six ligands and **no** lone pairs, 8 triangular faces, 90°
- 1 lone pair + 5 ligands = **Square Pyramidal**
- 2 lone pairs + 4 ligands = **Square Planar**

6.5-Properties of Covalent Bonds

- Lone pairs **alter** bond angles by small amounts due to their **greater** e$^-$-e$^-$ **repulsion** compared to bonding pairs
- For SN=5 lone pair repulsion **reduces** axial position angles, and **increases** equatorial position angles
- **Dipole Moment:** Asymmetrical distribution of e$^-$ density tend to give negative and positive end, caused by electronegativity differences
- Measured using **electrical field**, positive ends points to negative, vice versa, extent of alignment depends on magnitude of dipole moment, debyes, proportional to ΔX
- If lone pair replaces bond, dipole moment. Replacing bonds with a bond to a different atom makes dipole moment, polar group makes dipole moment

- **Bond Length:** Become **longer** as radii **increases,** vary with *n*-value, becomes **shorter** as nuclear charge **increases** since atomic size decreases**,** becomes **shorter** as bond polarity **increases** partial charges pull atoms closer together, multiple bonds **shorter** than single bonds since addition e^- increases net attraction pulls atoms closer
- **Bond Energy: Increases** as more e^- shared between atoms "glue", **increases** as ΔX increases gains stability, **decreases** as bonds become longer e^- density spread out decreases attraction

7.1-Localized Bonds

- E^- are either localized in bonds between 2 atoms or on a single atoms in pairs,
- Two types of orbitals from localized bonds
- **Bonding Orbital:** High e^- density between two atoms
- Orbital located on a **single** atom
- **Orbital Overlap:** Due to wave-like properties, when two orbitals are superimposed a new orbital that's composite of the originals
- Typically the highest energy occupied orbitals bond with other atoms
- Lone pairs must occupy the remaining orbitals that the bonds don't
- Atomic orbitals **can't** point towards corners of tetrahedrons

7.2-Hybridization of Atomic Orbitals

- **Hybridization:** Combining atomic orbitals of an atom to form a special set of directional orbitals, with a lope of high e^- density in a specific direction
- Named from atomic **valence orbitals** its constructed from
- Number of hybrid orbitals = Number of valence atomic orbitals from start
- The SN of an **inner atom** is used to infer hybrid orbitals in use, ex; if SN=4 then sp^3 hybridization
- Hybrid orbitals form localized bonds by **overlapping** with atomic/hybrid orbitals
- No hybrid orbitals for outer atoms due to absence of bond angles
- Elements beyond the **second row** have more than 4 ligands, more than an octet, *d* hybridization introduced, ex; sp^3d and sp^3d^2

7.3-Multiple Bonds

- **Sigma Bond(σ):** An overlap that gives high e^- density distributed symmetrically along internuclear axis, '**head on collisions**'
- *P* orbital has zero e^- density-a node- in a plane passing through nucleus
- **Pi Bond(π):** High e^- density concentrated above/below x-axis, side by side collisions
- Outer O atoms have some pi character in their bonding, inner O don't have pi bonding
- In general pi bonding requires presence of **second-row** element

- **Triple Bond:** Made up of 1 sigma and two pi bonds

7.4-MO Theory: Diatomic Molecules

- Delocalized e^- occupy molecular orbitals(MO) they span the entire molecule
- Due to wavelike properties orbital interactions involve addition/subtraction of amplitudes
- **Bonding MO:** When 2 atoms interact their orbitals generate two new ones, one of these interactions is **additive** which gives orbital with high e^- density between nuclei = **more attraction**
- Results from positive overlap of orbitals and stabilizes the bond
- **Antibonding MO:** Negative overlap of orbitals, destabilizes bond, **low** e^- density
- **Bond order:** Shows amount of bonding between two atoms, represents single/double/triple bonds, **cannot** be 0 or negative
- For Second-Row Diatomic Molecules
- The bonding/antibonding σ_s are filled **first** because they're more stable
- The two bonding/antibonding π orbitals are **degenerate** (same energy), so are *p* orbitals
- Antibonding orbitals formed by 2p are at the **top of diagram**, sigma higher than pi
- Paramagnetism arises from **unpaired** e^-
- As Bond Order **increases** bond energy **increases** and bond length **decreases**
- For atomic #>7 (Starts at O) σ_p lower in diagram than π caused by **orbital mixing**
- It's **easier** to remove antibonding electron than a antibonding electron
- **Delocalized π orbitals:** Forms when **more** than 2 *p* orbitals overlap
- If double bonds/lone pairs appear in different locations(**resonance**), it signals **delocalized π bonding**
- π electrons extend over **entire** molecule

- **Conjugated π systems:** Molecules with alternating single and double bonds
- **HOMO:** Highest Occupied MO(Filled)
- **LUMO:** Lowest Unoccupied MO(Empty)
- Unconjugated system = **large** energy gap. Conjugated system = **small** energy gap, less energetic photon, coloured visible light
- **Band Theory of Solids:** Accounts for properties of metals and metalloids, energy levels are continuous within the band
- Separation between energy levels is so **small** for solids with billions of atoms, e^- can posses any energy levels between HOMO and LUMO

8.1-Effects of Intermolecular Forces

- **Non-Polar Species:** $\Delta X = 0$
- **Polarizable Species:** $\Delta X > 0$, more polarizable if **larger**
- Boiling point **increases** with number of e^-
- **Ion-Dipole:** Charged ion with opposite charged dipole end
- **Dipole-Dipole:** Mutual attraction of 2 dipoles
- **H-bonds:** Positively polarized H, attracted to lone pair of NOF
- **Ion-Induced Dipole:** Ion creates dipole from polarizable species and is attracted to it
- **Dipole-Induced Dipole:** A dipole creates dipole from polarizable species, attraction
- **Dispersion (London):** Shifts in electron clouds, makes momentary dipoles which attract

- **Surface Tension:** Measures resistance of liquid to increase surface area, affect by IF
- **Capillary Action:** Upward movement of water against force of gravity
- **Viscosity:** A liquid's resistance to flow, affected by IF
- **Vapor Pressure:** Pressure at which the number of molecules escaping = number of molecules captured

- **Molecular Solids:** Held by dispersion/dipolar/h-bonds
- **Network Solids:** Contain array of covalent bonding
- **Metallic Solids:** Held by delocalized bonding
- **Ionic Solids:** Cations/Anions electrically attracted
- **Simple Cubic:** 1 particle/cell, C#=6, l=2r
- **Body Centred Cubic:** 2 particle/cell, C#=8, l=4/sqrt(3)*r
- **Face Centred Cubic:** 4 particle/cell, C#=12, l=sqrt(8)*r