CHAPTER 17:
Many-Electron Atoms and Chemical Bonding

• Many-Electron Atoms and the Periodic Table
• Experimental Measures of Orbital Energies
• Sizes of Atoms and Ions
• Properties of the Chemical Bond
• Ionic and Covalent Bonds
• Oxidation States and Chemical Bonding
Many-electron atoms

• We can solve $H\Psi=\varepsilon\Psi$ exactly for H atom to get energies and orbitals
• For more than one electron, can no longer solve exactly ("many-body" problem)
• **Approximation:** assume each electron moves around in the electrostatic field of the nuclei and the *average* charge distribution of the other electrons. *Mean field* or *self-consistent-field* or *Hartree-Fock* theory. For $>1$ atom, this is also *molecular orbital* theory
• In Hartree-Fock theory, each pair of electrons (one $\alpha$, one $\beta$) move in their own orbital $\phi_i(x_i, y_i, z_i)$
Electronic structure of atoms

• Just as H atom orbitals have quantum numbers \((n, l, m_l, m_s)\), the approximate orbitals for other atoms do also

• Problem: which orbitals do the electrons prefer to occupy?

• Answer: lower energy ones filled first. Aufbau ("filling up") principle
Aufbau principle

• Fill lowest-energy orbitals first
• H atom energy levels are not valid for larger atoms; however, general idea (energy increases with n) is roughly true
• For non-H atoms, energy also depends on L (e.g., s orbitals usually lower than p)
• Usual order
  1s<2s<2p<3s<3p<4s<3d<4p<5s<4d<5p<6s<4f<5d<6p<7s<5f<6d<7p
• Recalling that there’s 1 s orbital, 3 p orbitals; 5 d orbitals, 7 f orbitals, we see how the periodic table matches this order!
Aufbau and Periodic Table

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Experimental “orbital energies”

Energy required to remove an electron from various orbitals for the first 97 elements based on photoelectron spectroscopy

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Hund’s rules

- (Simplified version): When adding electrons to orbitals with equal energy, a single electron enters each orbital before a second electron enters any orbital.

- Allows us to predict diamagnetic or paramagnetic. Diamagnetic atoms/molecules have all electrons paired and are repelled by a magnetic field. Paramagnetic atoms/molecules have 1 or more unpaired electrons and are attracted to magnetic fields.

- Is C atom diamagnetic or paramagnetic? How about Ne atom?
Aufbau/Hund for atoms

Ne: 1s\(^2\) 2s\(^2\) 2p\(^x\) 2p\(^y\) 2p\(^z\)
F: 1s\(^2\) 2s\(^2\) 2p\(^x\) 2p\(^y\) 2p\(^z\)
O: 1s\(^2\) 2s\(^2\) 2p\(^x\) 2p\(^y\) 2p\(^z\)
N: 1s\(^2\) 2s\(^2\) 2p\(^x\) 2p\(^y\) 2p\(^z\)
C: 1s\(^2\) 2s\(^2\) 2p\(^x\) 2p\(^y\) 2p\(^z\)
B: 1s\(^1\) 2s\(^2\)
Be: 1s\(^2\) 2s\(^2\)
Li: 1s\(^2\) 2s\(^1\)
He: 1s\(^2\)
H: 1s\(^1\)
Exceptions to Aufbau principle

- Sometimes filling or half-filling a subshell is preferred over regular rules (subshell: all orbitals for a given $n$ and $l$, e.g., $2p$)
- Cu: should be $[\text{Ar}] \ 4s^2 \ 3d^9$ by Aufbau, but instead it’s $[\text{Ar}] \ 4s^1 \ 3d^{10}$
- Ag: $[\text{Kr}] \ 5s^1 \ 4d^{10}$
- Cr: $[\text{Ar}] \ 4s^1 \ 3d^5$
- Mo: $[\text{Kr}] \ 5s^1 \ 4d^5$
- Au: $[\text{Xe}] \ 6s^1 \ 5d^{10}$
Valence electrons and Periodicity

• Only the electrons added in the lowest available row of the periodic table for a given atom are “valence” electrons. Electrons from higher rows are “core.”

• Mg is $1s^2 \ 2s^2 \ 2p^6 \ 3s^2$ … the 3rd row is lowest, so only $3s^2$ is valence

• What are the valence electrons for Zr?
Valence electrons and Periodicity

• Notice: any 2 elements in the same column of the periodic table have the same type and number of valence electrons (just different values for n)

• This explains why elements in the same column react the same way! Quantum mechanics explains periodicity!

• E.g., Mg is [Ne] 3s\(^2\) and Ca is [Ar] 4s\(^2\) … both have 2 valence s electrons, and they react similarly!

• The core electrons are lower in energy and usually do not affect chemistry
Periodic Trends in Ionization Energies

- **Ionization energy**: the minimum amount of energy needed to detach an electron from an atom/molecule.
- Going across a row to the right, IE increases because the nuclear charge is increasing and holds electrons tighter.
- Does this mean IE always increases for larger atoms? No, because core electrons are held close to nucleus and effectively screen (cancel out) part of the nuclear charge. The IE “resets” to low value at each row.
- Elements on left have low IE, elements on right have high IE. QM explains origin of electropositivity and electronegativity!
First ionization energies
**Electron affinity**

- **Electron affinity** is the energy change when an atom gains an electron:
  \[ X \text{ (g)} + e^- \rightarrow X^- \text{ (g)} \quad - \Delta E = EA \]

- A positive $\Delta E$ (unfavorable reaction) gives a negative $EA$, and a negative $\Delta E$ (favorable reaction) gives a positive $EA$.

- Based on arguments for IE, expect EA to increase across a row (except for noble gases; they have filled shells and won’t want electrons).

- Basically true but EA has more variation with filled subshells --- the atom is happy and doesn’t really want electrons. Alkaline earth elements and Zn/Cd/Hg don’t care for electrons (low or negative EA). Mn/Tc/Re low EA because half-filled d subshell also fairly stable.
Electron affinities
Sizes of Atoms & Ions

• Can determine sizes by theory or experiment (see how close atoms/ions get to each other in crystals, etc)
• Cations usually slightly smaller, anions slightly larger than their parent atoms
• Higher effective nuclear charge as go across a row because nuclear charge Z increases, but the added electrons all into the same shell and are not very effective at screening each other. Atoms get smaller because electrons held closer in
• As go down a column, size gets bigger (electrons take more room); effective nuclear charge felt by valence electrons is constant going down a row because of screening
Periodic trends in atomic radius
Bond length, bond enthalpy, bond order

• We already mentioned that the more bonds between two atoms, the stronger that bond (higher bond enthalpy) and the shorter that bond

• See book for more details
Ionic and Covalent Bonds

- Can tell the difference between these two types of bonding using concept of electronegativity
- Mulliken’s definition: electronegativity is proportional to \((\text{IE} + \text{EA}) / 2\)
- Halogens: high IE and EA, so high electronegativity
- Alkali metals: low IE and EA, so low electronegativity
- Electronegativity increases across a row, decreases going down a column [as go down, bigger size of atom means easier to take off electrons]
Electronegativity and bonding

• If two elements have very different electronegativities, they will form an ionic bond in which the electropositive element donates electrons to the electronegative element, e.g., Na⁺Cl⁻. Atoms held together by electrostatic attraction.

• If two elements have similar electronegativities, they can form a covalent bond in which the 2 atoms share electrons equally; e.g., H–H. Atoms held together because each wants a piece of the other atom’s electrons.
Percent Ionic Character

• Ionic and perfect covalent bonds are idealized extremes. Many bonds will be in between

• H --- F only partial charge transfer
  +0.41  -0.41
  call this “41%” ionic

• (Although “partial atomic charges” do not really exist…they are a crutch to help us understand what’s going on but can’t be rigorously defined)
Ionic and Covalent Bonding

Potential energy (kJ mol$^{-1}$)

$R_e = 2.13 \text{ Å}$

$\Delta E_0 = 489 \text{ kJ mol}^{-1}$

$\Delta E^\circ = -241 \text{ kJ mol}^{-1}$

Free ions: $\text{K}^+(g) + \text{F}^-(g)$

Free atoms: $\text{K}(g) + \text{F}(g)$

Free molecules: $\text{KF}(g)$

Ionic solid: $\text{KF}(s)$
Oxidation states and bonding

- Group I metals usually have oxidation state of +1 in compounds; Group II is usually +2. Now we see this is because they have 1 or 2 outermost electrons which are not held very tightly.

- Likewise, halogens usually have an oxidation state of -1 in compounds --- they want to grab one electron to complete their shell

- C, Si, Ge usually +4 (want 4 electrons) but could also be +2 if give up 2e⁻ from p subshell only (and not from s subshell). Both SnCl₂ and SnCl₄ exist.

- Transition metals have a wide variety of oxidation states. Mn can be +7, for example, but can also be +2, +3, +4