CHEM334 Lecture 7: Qualitative valence bond theory, oxidation states, formal charges, resonance structure

MT Chapters 3

Atoms = mononuclear polyelectronc systems

- foundation of atomic orbitals – know where quantum numbers, Hund’s rules, Pauli exclusion principle, atomic orbitals come from, what do they mean
- concept of effective nuclear charge (shielding, Slater’s rules)
- problems with the Schrödinger solution – lack of magnetic description
- Zeeman effect: H atom in a magnetic field (B) ⇒ the number of atomic emission lines (Lyman/Balmer/Paschen/Brackett) increases (splitting) due to magnetic interaction of angular momentum and magnetic field
- Stern and Gerlach (1922): beam of Ag atoms in B split into two beams ⇒ valence electron has no angular momentum (l=0)
- Uhlenbeck and Goudsmit (1924): definition of spin angular momentum, S, as electron rotation ⇒ parallel and antiparallel alignment with the magnetic field ⇒ spin quantum number m_s = ± ½.
- Pauli (1925): exclusion principle requires unique n, l, m_l, m_s quantum numbers for each electron (in wave mechanics: Slater determinants ⇒ antisymmetry of ψ; changes sign upon pairwise permutation: $\psi_{nm} = ls(1)(s)(2)[l(2) − ls2s](2)(2)$)
- Hund: defines rules based on pure electrostatic considerations (valid for atomic orbitals only)
  - 1st: it takes energy to bring electrons closer together ⇒ antiparallel spins are closer to each other, (max. S) ⇒ exchange stabilization in wave mechanics
  - 2nd: the electrons stay as far apart as possible ⇒ highest stable is the largest angular momentum (max. m_l) with everything else the same ⇒ electron repulsion due to correlation in wave mechanics
  - 3rd: orbital (L) and spin moments (S) are not independent; define total angular momentum, J; antiparallel for less than half occupied orbitals (2l +1) and vice versa ⇒ spin–orbit coupling
- Orbital penetration: lifts the degeneracy of orbitals with same n due to outer orbital’s probability at distances more typical for inner orbitals with lower principal numbers in the order of s > p > d
- Building up atoms: “aufbau” process: start with the lowest available empty orbital in the order of (n+1) with smaller n first (3p vs. 4s) and fill each orbital up before start pairing up electrons

Molecules = polynuclear polyelectronc systems

- Lewis (electron dot) structures: atoms in molecules adapt a noble gas electron configuration - octet rule s^2 (H2, s^p^6 (F, O, N), hypervalency - extended octet rule s^p^d (Cl, S, P) - representation of lone pairs, single and double bonds
  - examples: H_2O, H_2O_2, OF_2 - see the computer outputs, what are the differences?
- oxidation number: more electronegative atom has more negative charge ⇒ go to the ionic limit and count the valence electrons relative to the atomic configuration
- partial charges: consider electronegativity differences ⇒ stay with a covalent bonding and allow for bond polarization.
- formal charges: split the bonds 50/50% and count the electrons ⇒ indicative of dative bonds
- dative/coordinative covalence: donation of a complete electron pair ⇒ creation of formal charges (split the electrons equally and calculate the difference relative to the atomic electron configuration
  - examples: CO - see the computer output, (PPh_3)^+, (PPh_3-P-CH_3)^+ + strong base, AlCl_3, ICl_3
- resonance: a series/combination of Lewis structures describe the electron distribution in a molecule ⇒ fractional bond orders
a quick reminder of the rules of how to draw resonance structures:
- move electrons only and as little as possible (smallest energy difference)
- check the electron count including number of unpaired ones
- minimize the formal charge separation
- maximize the number of multiple bonds
- more electronegative atom has the negative charge and vice versa

example: valence bond picture of N₂O and SCN

Pauling-Slater (1931): chemical bonds are formed by sharing electron pairs
- shape of the orbitals determines the shape of the molecule through orbital directionality (ang.mom.)
- bonding results from orbital overlap (size, shape, phase are important)
- hybridization: promotion of electrons and combination of AOs on the same atomic centers to give equivalent valence bonds (valid for single bonds only!)

\[
\phi_{\text{hybrid}} = c_1 \phi_1 + c_2 \phi_2 + c_3 \phi_3 + c_4 \phi_4 + c_5 \phi_5 + c_6 \phi_6 + c_7 \phi_7 + \ldots
\]

- most common hybridizations

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<thead>
<tr>
<th>Hybridization</th>
<th>sp</th>
<th>sp²</th>
<th>sp³</th>
<th>sp³d (sp²-pd)</th>
<th>sp³d² (sp-pd-pd)</th>
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<td>s + px</td>
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BeCl₂, HNa₂CO₃; SO₂, [SiO₄]²⁻; CH₄, H₂O, NH₃, PCl₃, TeCl₄, BrF₅, [PCl₅]; SF₆, BrF₅

(more detailed list on webCT)

- molecular shapes:
  - p²: trigonal pyramidal
  - sp³: tetrahedral
  - sp³: trigonal planar
  - sp³d: square planar
  - sp³d²: octahedral

- electrons excluded from hybridization and stay on atomic orbitals form multiple bonds (π, δ) – nodal planes of electron density

Sidgwick-Powell (1940) VSEPR theory: valence shell electron-pair repulsion = exact description of molecular shapes using Pauli exclusion principle and Coulomb repulsion – NOT STERIC REPULSION!

size of the electron pair: lone pair > π bonding > σ bonding > bonding pair to an electronegative atom

- difference between the electron pairs:
  - tetrahedron: 4 equivalent bonds, bond angle 109.5° (cos⁻¹(-1/3))
  - 3 bonds + 1 lone pair, bond angle 107.2°
  - 2 bonds + 2 lone pairs, bond angle 104.5°

- steric vs. electronic electronic effects: H₂O vs. OF₂; NH₃ vs. NF₃ = bond angles decrease
- bond angle decreases as going right (more lone pairs) and down (larger lone pairs) in a period or a group, respectively
- effect of multiple bonds: PH₃ vs. PF₃ = bond angles increase (change in hybridization + increased repulsion) + multiple bonds are bigger and therefore need more space (deprotonate [PH₃]⁺)
- lone pairs are larger than bonds = occupy positions (SF₄, ClF₅) with more available space (equatorial in trigonal bipyramid, axial in octahedral)
- more electronegative ligand goes to the axial site (SF₅Cl)
- electron pair with dominantly `s` character is stereochemically inactive = consider the series of NH₃, PH₃, AsH₃, SbH₃ (as principal quantum number increases s and p hybridization becomes less effective) sp³ goes to p² with s lone pairs (note that p electrons on peripheral atoms can form dπ bonds)

examples: Which of the following in each pair has the larger bond angle and why?
  - (a) CH₄ and NH₃
  - (b) OF₂ and OCl₂
  - (c) NH₃ or NF₃
  - (d) PH₃ or NH₃