Chemical Bonding & Reactivity (CY61010 & CY60032)
Spring Semester 2016-2017

Course of Study

1. **Forces in Molecules**
   Chemical bond via virial theorem; Hellmann-Feynman electrostatic theorem; Electrostatic interpretation of chemical bond.

2. **Bonding in Diatomics**
   Valence bond and Molecular orbital treatment of H_2; Comparison of VB and MO theory; LCAO-MO theory of homo- and hetero-nuclear diatomics.

3. **Bonding in Polyatomics**
   Construction of MO of H_n and AH_n systems using LCAO and SALC; Molecular structure and reactivity from Walsh Diagrams for AH_2 (C_{2v}, $D_{\infty h}$), AH_3 (C_{3v}, D_{3h}), AH_4 (C_{4v}, D_{4h}, T_d), Ethane (A_2H_6) (staggered, eclipsed), and Ethylene (A_2H_4).

4. **π-Molecular Orbital Theory**
   $\sigma - \pi$ separation; Hückel MO theory of π-electrons; Frost circle; Aromaticity; Extension of HMO to band theory.

5. **Frontier Molecular Orbitals**
   Effect of substituents on the frontier MOs and reactivity of carbocations, carbanions, and conjugated polyenes.

6. **Perturbation Theory of Reactivity**
   Salem Klopman equation and applications; HSAB principle.

7. **Reactivity From Thermodynamics**
   Hammond's Postulate; Marcus Theory; Marcus inverted region.

8. **Potential Energy Surfaces**
   Critical points on PES; Minimum energy path; Hessian index; Adiabatic and non-adiabatic states; von Neumann-Wigner's non-crossing rule; Conical intersection of PES.

9. **Pericyclic Reactions**
   Frontier molecular orbital approach (Fukui) and/*vs.* Conservation of orbital symmetry approach (Hoffmann) to explain thermal and photochemical cycloaddition and electrocyclic reactions.

10. **Reactivity Descriptors**
    Electronic chemical potential (μ), electronegativity (χ_M), hardness (η), principle of maximum hardness, Fukui functions ($f^{\pm}(r)$) and applications, Molecular Electrostatic Potentials.

References:

- **Books**
- Quantum Chemistry, I. N. Levine; Molecular Quantum Mechanics, P. W. Atkins and R. Friedman; Quantum Chemistry D. A. Mc Quarrie.
- Orbital Interactions in Chemistry, T. A. Albright, J. K. Burdett, M. H. Whangbo; Molecular Orbitals and Organic Chemical Reactions, I. Fleming.
- Chemical Reactivity Theory, Ed. P. K. Chattaraj (chapters 2, 12, 18).
- **Research articles**
- A never-ending rivalry between MO and VB. Acc. Chem. Res., 36, 2003, 750.
- SCF LCAO MO for diatomics. Rev. Mod. Phys., 32, 1960, 245.
- Simple Hückel Molecular Orbital Calculator at http://www.chem.ucalgary.ca/SHMO/.
- Nobel Lecture of R. A. Marcus, Dec 1992.
- Conservation of orbital symmetry, Hoffmann, Angew. Chem. Internat. Edit. 8 (1969) 781.
- Application of reactivity descriptor to enzyme catalysis, Baeten et. al., J. Theor. Biol. 195, 1998, 27.