2019

Discovering Chemical Structure with Linus Pauling

Jin H. Kim
Parkland College

Discovering Chemical Structure

With Linus Pauling
Jin Kim CHE-101-006, Dr. Mullen, Parkland College

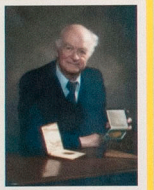
Contents

Linus Pauling - Biography

- Only person to have two unshared Nobel Prizes
- Born: February 28, 1901 Portland, Oregon, U.S.
- B.Sc. in chemical engineering in 1922
- Full-time teacher of quantitative analysis in the State College (1919-1920)
- Teaching Fellow in Chemistry and graduate student in Caltech (California Institute of Technology) 1922 - 1925
- Ph.D. (*summa cum laude*) in chemistry, with minors in physics and mathematics 1925
- Research Associate at Caltech, 1925
- National Research Fellow in Chemistry, 1925-1926
- Fellow of the John Simon Guggenheim Memorial Foundation, 1926-1927
- Assistant Professor of Chemistry, 1927-1929
- Associate Professor, 1929-1931
- Professor at Caltech, 1931-1963
- Professor at UC san diego, 1967-1969
- Professor at Stanford, 1969-1975
- Died August 19, 1994 (aged 93) Big Sur, California, U.S.

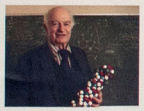
Awards

ACS Award in Pure Chemistry (1931)
Irving Langmuir Award(1931)
Davy Medal (1947)
Nobel Prize in Chemistry(1954)
Nobel Peace Prize (1962)
Roebling Medal (1967)
Lenin Peace Prize (1968 - 69)
National Medal of Science(1974)
Lomonosov Gold Medal(1977)
NAS Award in Chemical Sciences (1979)
Priestley Medal (1984)
Vannevar Bush Award (1989)



http://scarc.library.oregonstate.edu/coll/pauling/awards/index.html

Pauling with two Nobel prizes



https://www.kpbs.org/news/2011/dec/15/linus-pauling/

Linus Pauling

References

1. L. Pauling, The Shared-Electron Chemical Bond, *Proc. Natl. Acad. Sci. U.S.*, 14 (1928)359-362.

2. L. Pauling, The Nature of the Chemical Bond. Application of Results Obtained from the Quantum Mechanics and from a Theory of Paramagnetic Susceptibility to the Structure of Molecules, *J. Am. Chem. Soc.*, *53* (1931) 1367-1400.

3. L. Pauling, The Nature of the Chemical Bond. IV. The Energy of Single Bonds and the Relative Electronegativity of Atoms, *J. Am. Chem. Soc*, *54* (1932) 3570-3582.

4. L. Pauling, Interatomic Distances in Covalent Molecules and Resonance between Two or More Lewis Electronic Structures, Proc. *Natl. Acad. Sci. U.S.*, 18 (1932) 293-297.

5. L. Pauling, L. O. Brockway, and J. Y. Beach, The Dependence of Interatomic Distance on Single Bond-Double Bond Resonance, *J. Am. Chem. Soc.*, *57* (1935) 2705-2709.

6. L. Pauling, The Principles Determining the Structure of Complex Ionic Crystals, *J Am. Chem. Soc.*, 51 (1929) 1010-1026.

7. L. Pauling, The Nature of the Interatomic Forces in Metals, *Phys. Rev.*, *54* (1938) 899-904.

8. L. Pauling, A Resonating-Valence-Bond Theory of Metals and Intermetallic Compounds, *Proc. Roy. Soc. London*, A 196 (1949) 343-362.

9. L. Pauling, Atomic Radii and Interatomic Distances in Metals, *J. Am. Chem. Soc.*, 69 (1947) 542-553.

10. L. Pauling and R. B. Corey, Two Hydrogen-Bonded Spiral Configurations of the Polypeptide Chain, *J. Am. Chem. Soc.*, *72* (1950) 5349; L. Pauling, R. B. Corey, and H. R. Branson, The Structure of Proteins, Two Hydrogen-Bonded Helical Configurations of the Polypeptide Chain, *Proc. Natl. Acad. Sci. U.S.*, *37* (1951) 205-511; L. Pauling and R. B. Corey, Stable Configurations of Polypeptide Chains, *Proc. Roy. Soc. London*, B 141 (1953) 21-33

11. L. Pauling, Modern structural chemistry, Nobel lecture, December, 11, 1953

Early history of structural chemistry

Edward Frankland (1852) Introducing concept of valence

Alexander Butlerov (1861) First to use term "structural chemistry"

Alfred Werner (1904) Proposing octahedral configuration of transition metal complex

Introduction of Quantum Mechanics

Fritz London and Walter Heitler (1927) Applied the new quantum mechanics to deal with exchange forces within hydrogen molecule.

Friedrich A. Kekulé (1858) Idea of tetravalence of carbon Ability of carbon to link to each other

Van 't Hoff (1874) Formulating the theory of the tetrahedral carbon atom

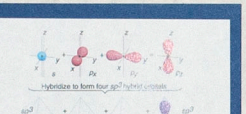
Gilbert N. Lewis (1916) discovery of the covalent bond and tendency to obtain complete 8 electrons. Lewis dot structures

Erwin Schrödinger (1925) Developed Schrödinger equation to calculate wave function .

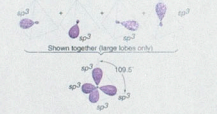
Linus Pauling (1931–)
- Resonance and Orbital hybridization
- Electronegativity
- Structure of ionic and metal compound

Nature of chemical bond

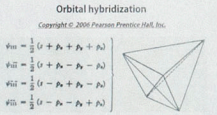
Orbital hybridization



Hybridize to form four sp^3 hybrid orbitals

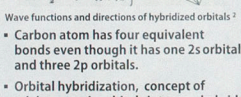


Shown together (large lobes only)



Orbital hybridization

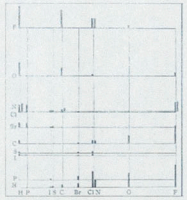
Copyright © 2006 Pearson Prentice Hall, Inc.



Wave functions and directions of hybridized orbitals [2]

- Carbon atom has four equivalent bonds even though it has one 2s orbital and three 2p orbitals.
- Orbital hybridization, concept of mixing atomic orbitals into new hybrid orbitals, was introduced to explain tetrahedral carbon atom[2].

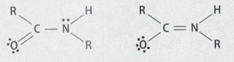
Electronegativity



Electronegativity map

- Further detailed information about the chemical bond resulted from a consideration of the energy of single bonds in relation to the relative electronegativity of the bonded atoms
- The postulate of the additivity of the energies of normal covalent bonds is then formulated, and it is found that deviations from additivity, Δ, are positive for all bonds (with one doubtful exception), and increase as the ionic character of the bond increases.

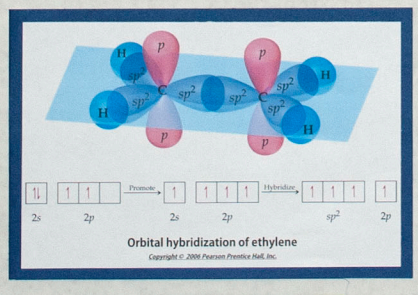
Resonance



Two structures of amide group

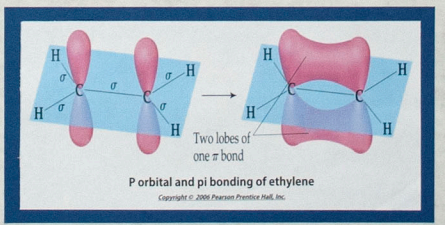
- Amide group, an important structural feature of proteins, can be described as resonating between two structures, one with the double bond between the carbon atom and the oxygen atom and the other with single bond[4].
- The estimate of 40% double-bond character for the C-N bond is supported by the experimental value of the bond length, 1.32 A, interpreted with the aid of the empirical relation between double-bond character and interatomic distance[5].
- Several molecule, especially aromatic compound cannot be fixed to single valence bond structure.
- 1931, E. Huckel and Slater has explained structure of benzene using the concept of resonance.

Example of covalent bonding



Orbital hybridization of ethylene

Copyright © 2006 Pearson Prentice Hall, Inc.



P orbital and pi bonding of ethylene

Copyright © 2006 Pearson Prentice Hall, Inc.

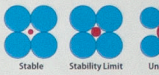
Structure of Ionic compound

Pauling's rules

1. First rule: the radius ratio rule
2. Second rule: the electrostatic valence rule
3. Third rule: sharing of polyhedron corners, edges and faces
4. Fourth rule: crystals containing different cations
5. Fifth rule: the rule of parsimony

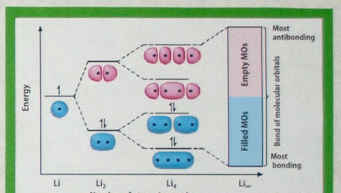
First rule: the radius ratio rule

C.N.	Polyhedron	Radius ratio
3	triangular	0.155
4	Tetrahedron	0.225
6	Octahedron	0.414
7	capped octahedron	0.592
8	square antiprism	0.645
8	Cube	0.732
9	triaugmented triangular prism	0.732
12	cuboctahedron	1.00



- Pauling discovered that a simple theory of complex crystals with largely ionic structures.
- Theory of complex crystals could be developed based on assumption that each cation or metal atom divides its charge or valence equally among the anions that are coordinated about it[6].

Structure of metallic compound



Metallic orbital of lithium

Brown, Theodore E. Chemistry. Pearson, 2017

- Unlike other compounds, Larger number of bonding electrons are used in the transition metals. For instance, iron can be illustrated as having six valance electrons, which occupy hybrid sp2d3 orbitals.
- Pauling reported the idea of the structure of metals and intermetallic compounds by using the concept of valance bonds that resonate among alternative positions[8].
- Metallic orbital has been found of value through the discussion of the properties of metal atoms and intermetallic compounds.
- The resonating-bond theory of metal (metallic orbital) is strongly supported by the consideration of interatomic distances in metals and intermetallic compunds[9].

Structure of organic compound

- The interatomic distances and bond angles in the polypeptide chains of proteins are precisely known to within about 0.02 Å and 2° respectively.
- Extensive numerical calculation was necessarily required to make hydrogen-bonded structure of polypeptide due to requirements including planar amide group and reducing steric repulsion.
- Pauling has proposed two stereochemically equivalent hydrogen-bonded helical structures for a polypeptide chain with 3.7 and 5.1 residues per turn[10].
- This has shown the value of the use of structural arguments that go beyond those of the classical structure theory of organic chemistry[11].

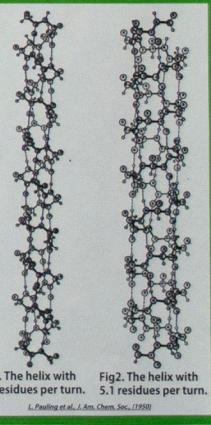


Fig1. The helix with 3.7 residues per turn.

Fig2. The helix with 5.1 residues per turn.

L. Pauling et al., J. Am. Chem. Soc., (1950)