

# How Quantum Mechanics Was Born?

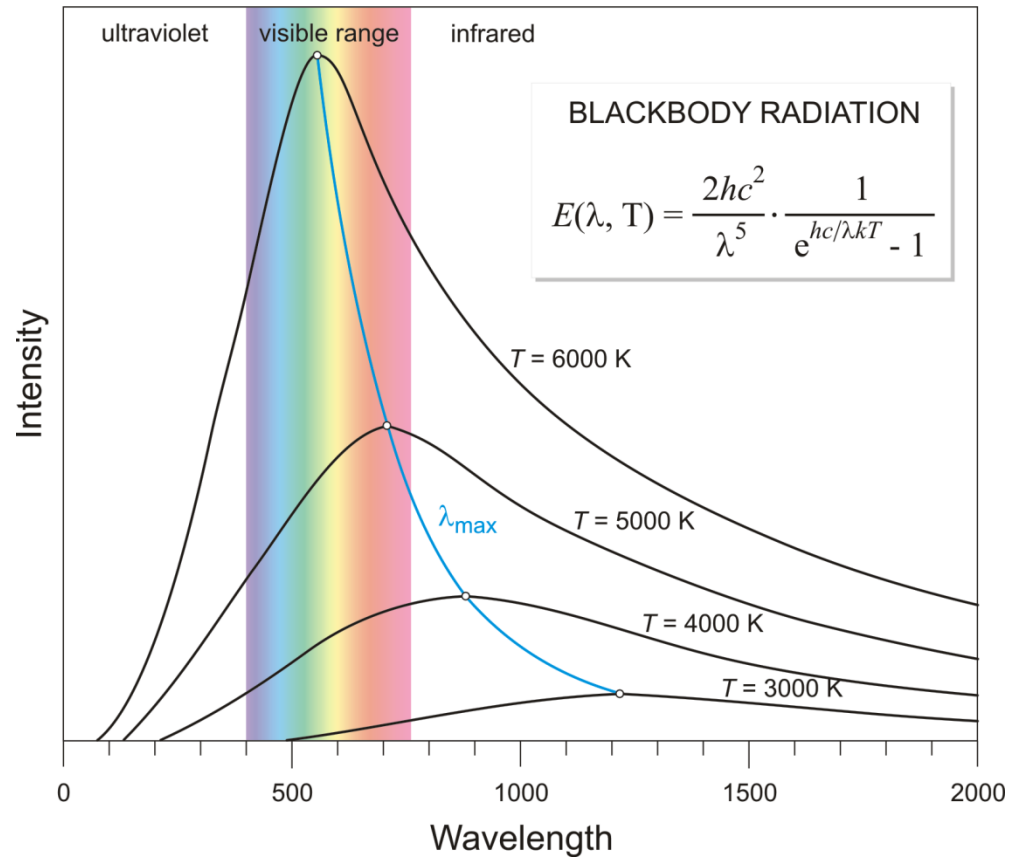
Cina Foroutan-Nejad

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University, Brno, Czech Republic

# The Story Begins

## Max Planck and Black Body Radiation

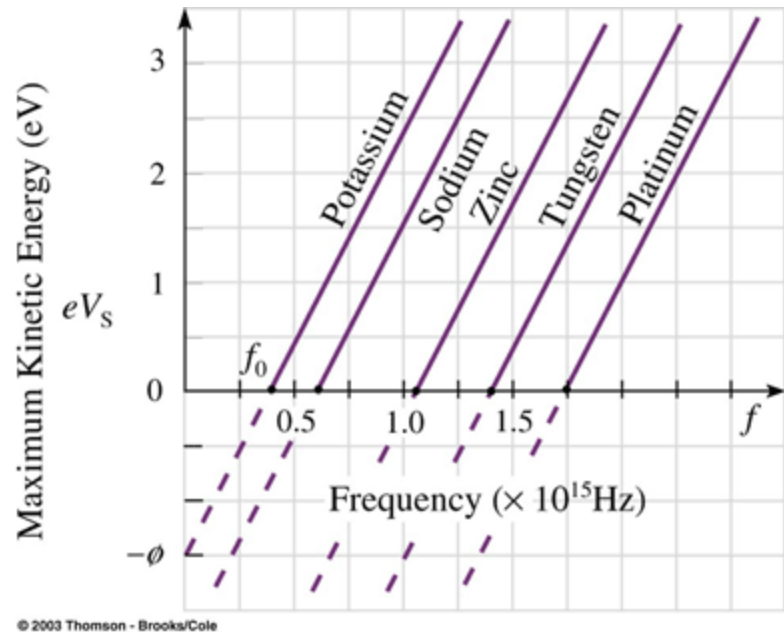
Energy is emitted & absorbed in discrete units called QUANTA



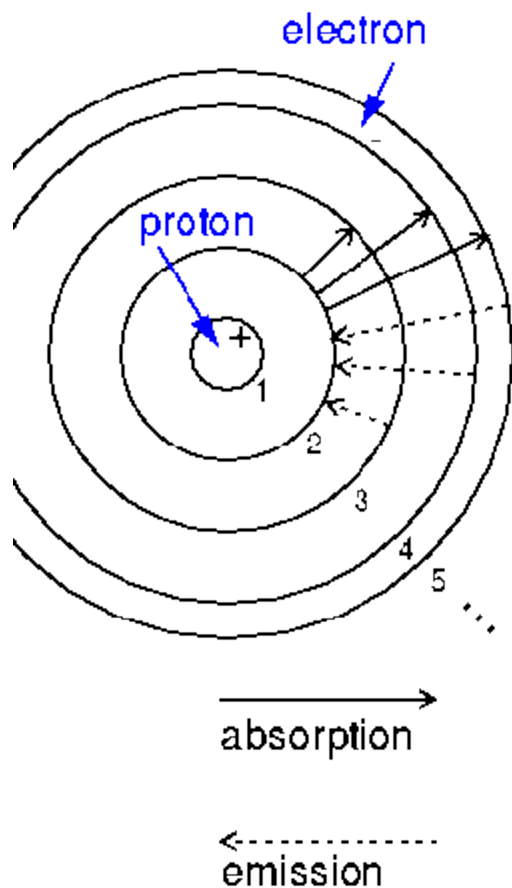
# The Story Begins

## Einstein and Photo Electric Effect

Light travels in isolated energy packages called Photons.



# Bohr-Sommerfeld Model of Atom



## Bohr Model of Hydrogen Atom

Ground State: Electron is in lowest energy level.

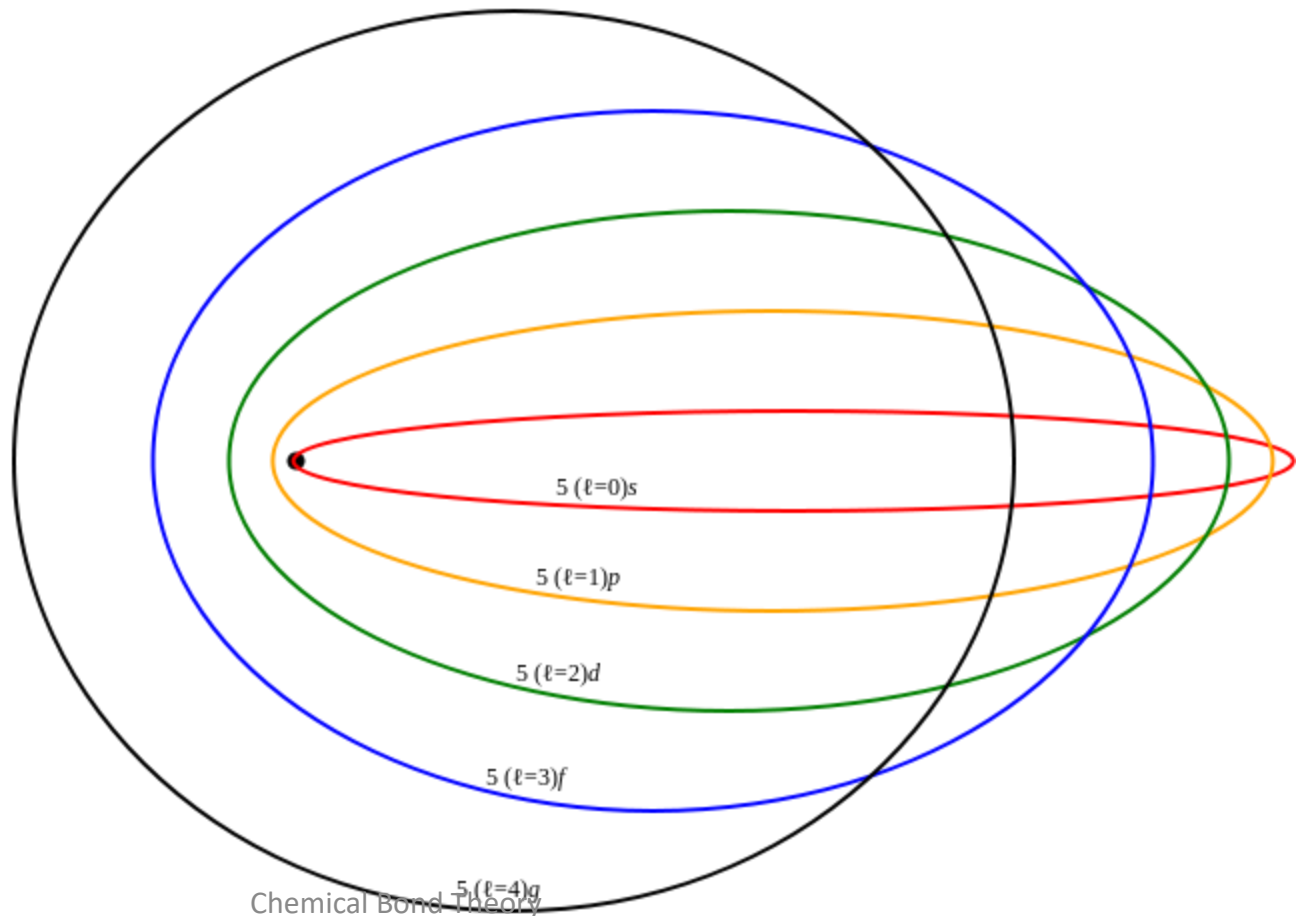
Absorption Spectrum: Electron absorbs light photons and jumps up to an excited state of higher energy .

Emission Spectrum: Electron emits light photon as it jumps down to a state of lower energy .

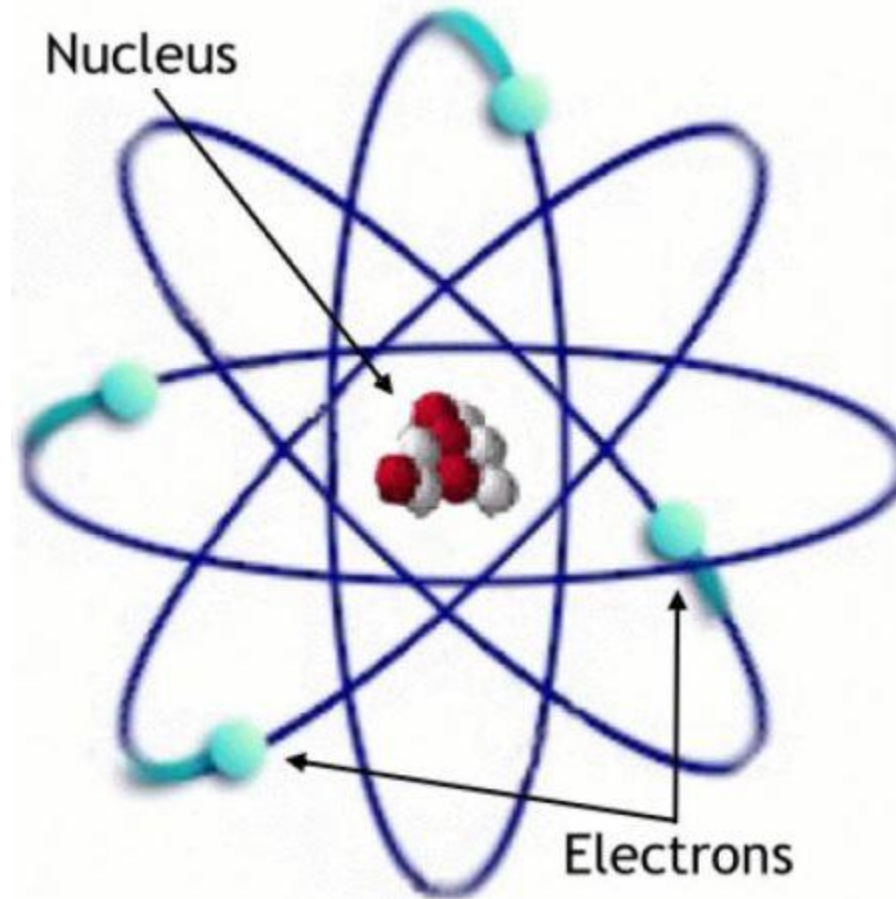
# Bohr-Sommerfeld Model of Atom

- Orbitals were first introduced by Sommerfeld

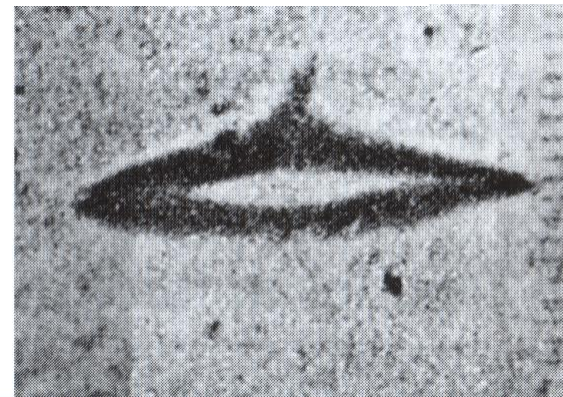
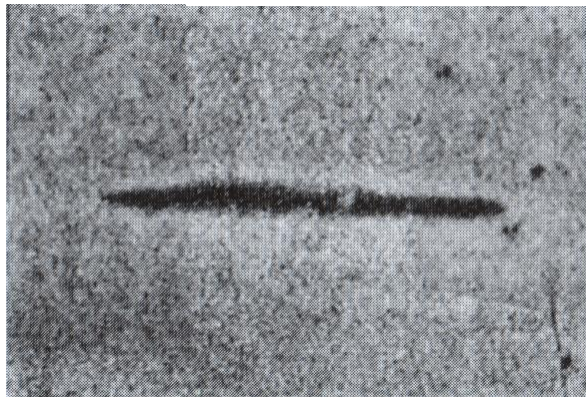
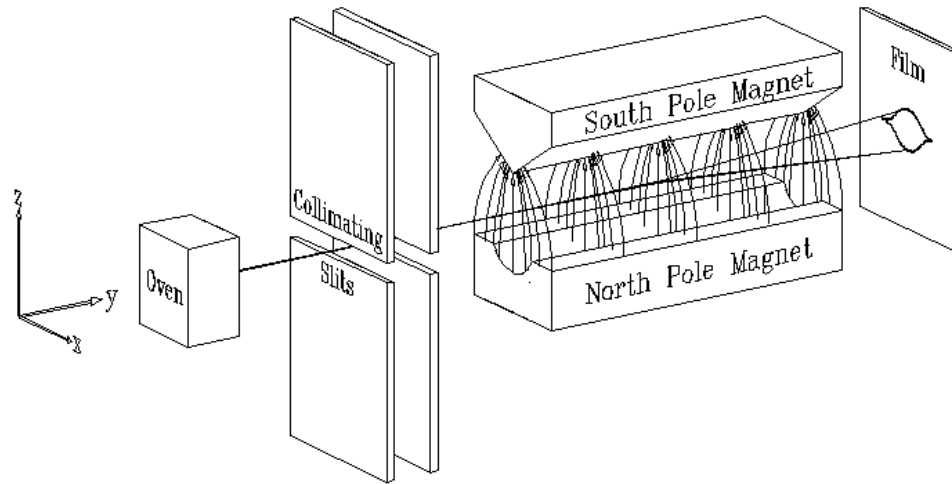
$$\frac{a}{b} = \frac{l + 1}{n}$$



# Quantum Magnetic Number

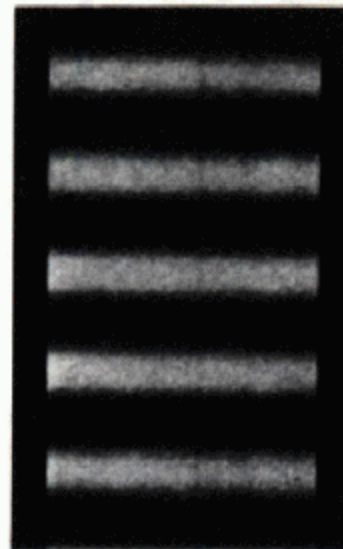
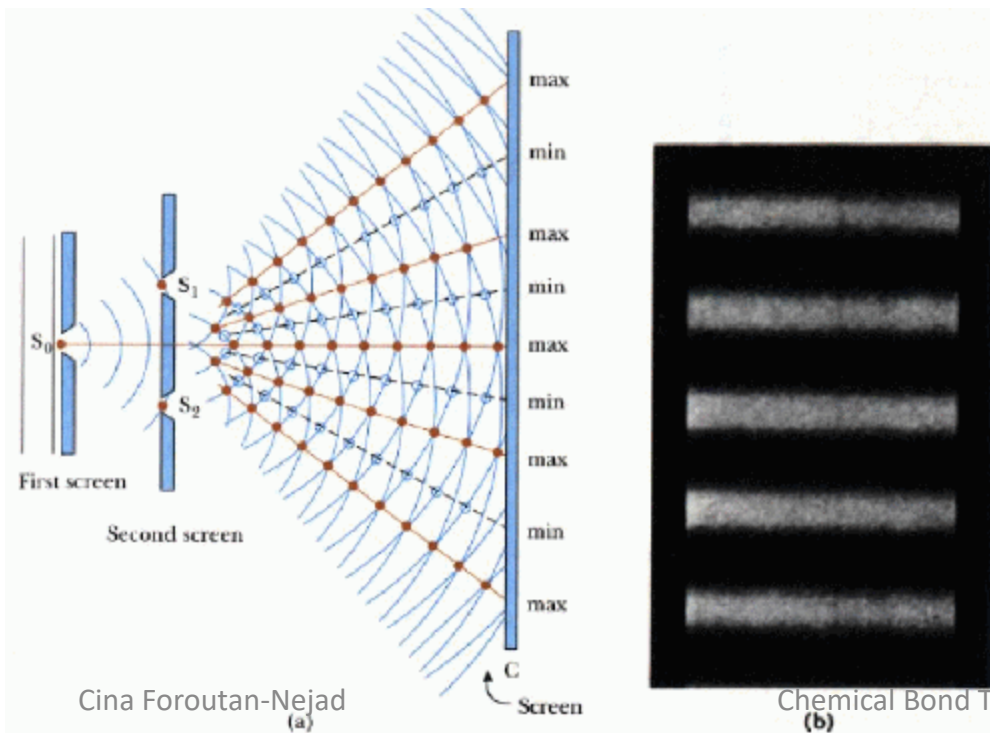


# Stern Gerlach Experiment 1921

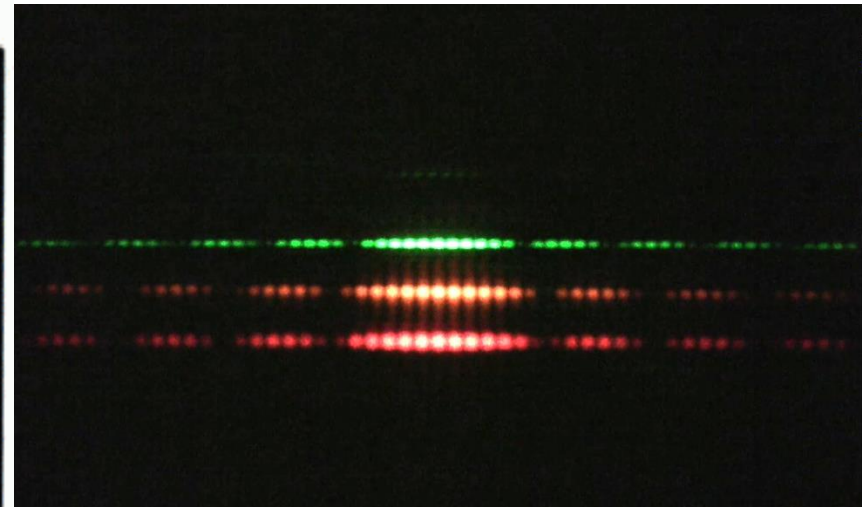


# The Nature of Light

- Einstein description of light is more consistent with a corpuscular light
- Light has wave behavior as well



Chemical Bond Theory  
(b)





# Wave-Matter Duality; A Sign From a Different World

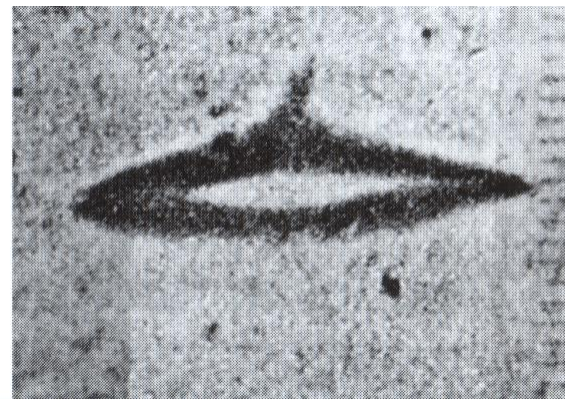
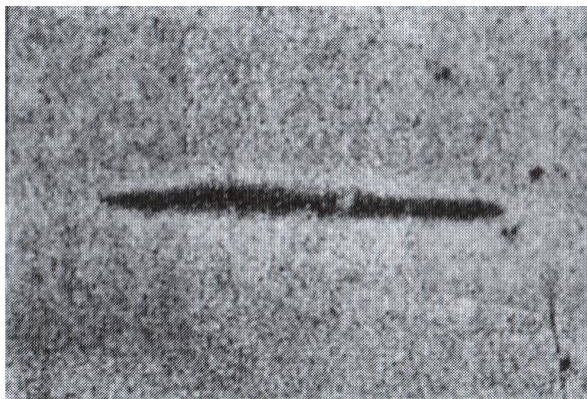
In 1924 de Broglie made a bold suggestion about the nature of matter concerning the nature of light

$$h\nu = mc^2$$
$$\nu = \frac{c}{\lambda}$$
$$\lambda = \frac{h}{mc} \quad \rightarrow \quad \lambda = \frac{h}{mv}$$

This was confirmed in 1927 by Davisson and Thompson in different experiments

# Another Sign From a Different World

- In 1925 Uhlenbeck and Goudsmit realized that electrons have an intrinsic magnetic momentum.
- This has been identified 4 years earlier!
- This intrinsic momentum called *SPIN*.



# Heisenberg Uncertainty Principle

In 1927 Heisenberg proposed that it is impossible to define both position and momentum of a small particle

$$\Delta x \Delta p \geq \frac{h}{2\pi}$$

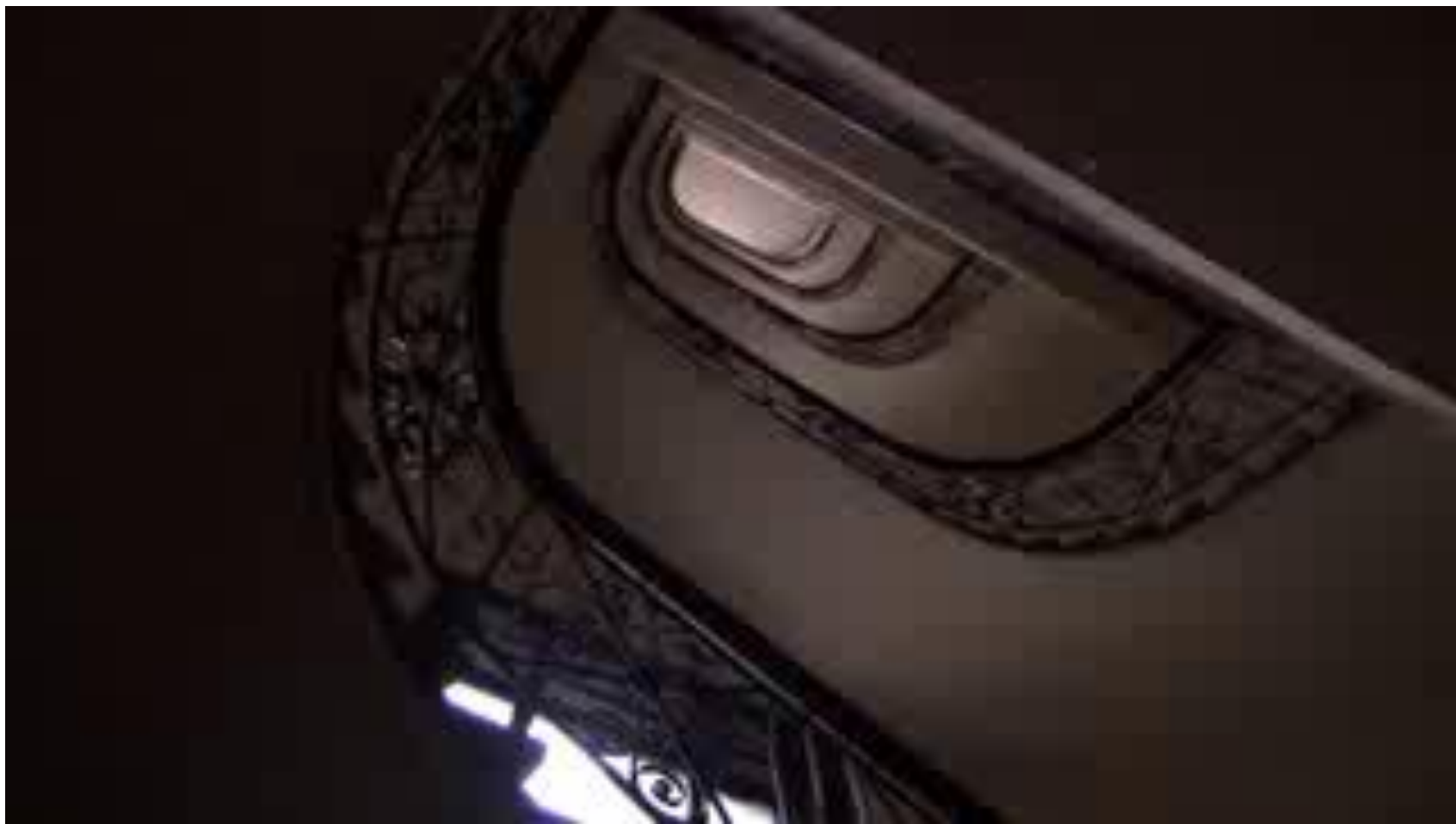
We cannot define position of a small particle like an electron since decreasing the wave length of light increases the momentum of the particle

$$p = \frac{h}{\lambda}$$

# Think Deeply

- Some physicists and philosophers believe that Heisenberg uncertainty is an inherent property of matter.
- All aspects of the uncertainty principle has not yet understood...

# The Mystery of Uncertainty



# Quantum Atom

- In 1925 Erwin Schrödinger postulated his famous equation based on the proposal of de Broglie

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \left[ \frac{-\hbar^2}{2m} \nabla^2 + V(\mathbf{r}, t) \right] \Psi(\mathbf{r}, t)$$

$$E\Psi(\mathbf{r}) = \left[ \frac{-\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \Psi(\mathbf{r})$$

# Molecular Hamiltonian

- The Hamiltonian operator of a molecule, neglecting relativistic effects and spin-orbit can be written as the following

$$\hat{H} = -\frac{\hbar^2}{2} \sum_{\alpha} \frac{1}{m_{\alpha}} \nabla_{\alpha}^2 - \frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_{\alpha} \sum_{\beta > \alpha} \frac{Z_{\alpha} Z_{\beta} e^2}{r_{\alpha\beta}} - \sum_{\alpha} \sum_i \frac{Z_{\alpha} e^2}{r_{i\alpha}} + \sum_i \sum_{j > i} \frac{e^2}{r_{ij}}$$

# Born-Oppenheimer Approximation

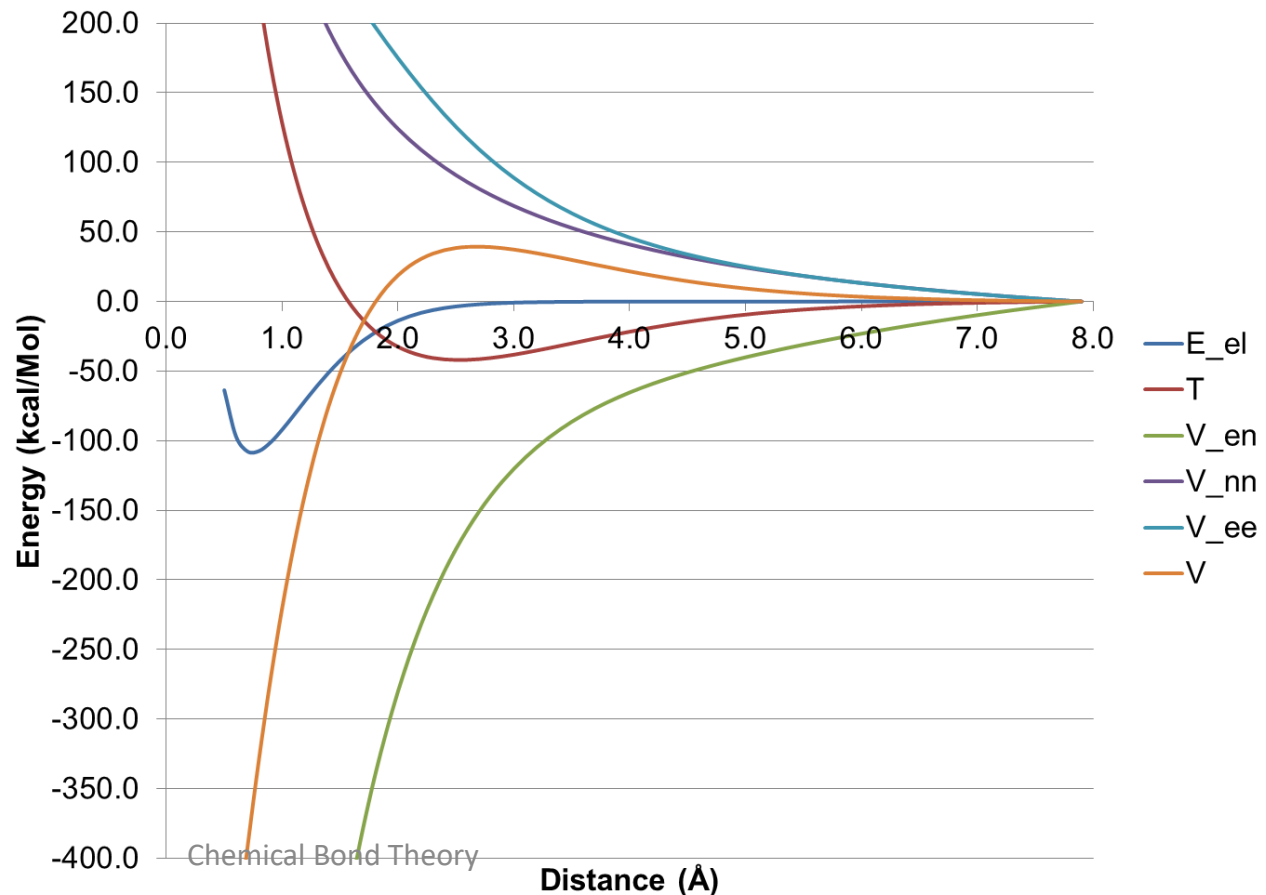
- Concerning the fact that nuclei are way heavier than electrons one can imagine that nuclei almost remain still while electrons circle around the molecule. Therefore, nuclear kinetic energy can be separated from the *Electronic Hamiltonian*

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 +$$
$$- \sum_{\alpha} \sum_i \frac{Z_{\alpha} e^2}{r_{i\alpha}} + \sum_i \sum_{j>i} \frac{e^2}{r_{ij}} + \sum_{\alpha} \sum_{\beta>\alpha} \frac{Z_{\alpha} Z_{\beta} e^2}{r_{\alpha\beta}}$$



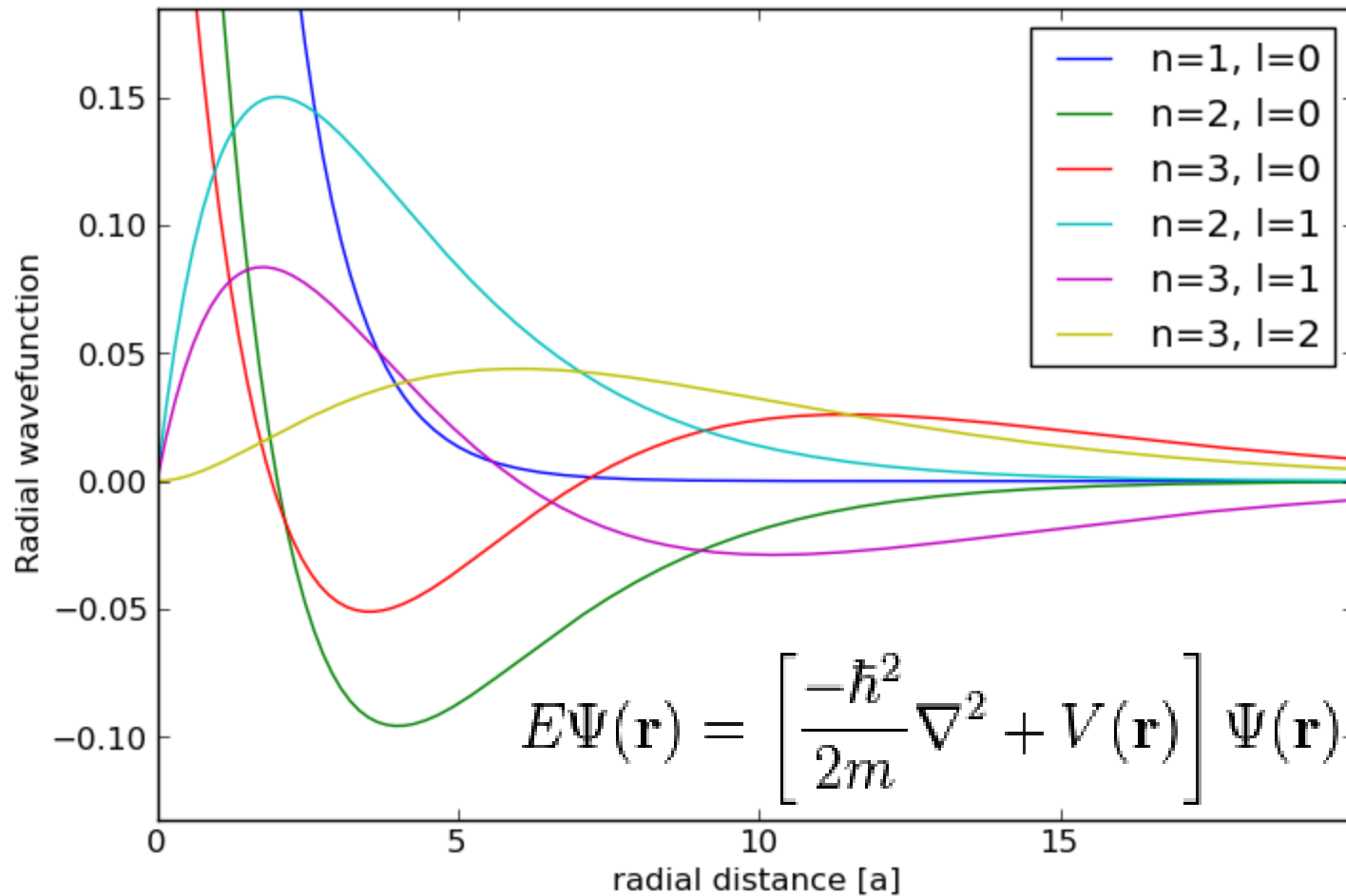
# Covalency

Unlike ionic bonds, which are formed by attraction between ions, formation of covalent bonds does not have an electrostatic driving force.<sup>[1]</sup>



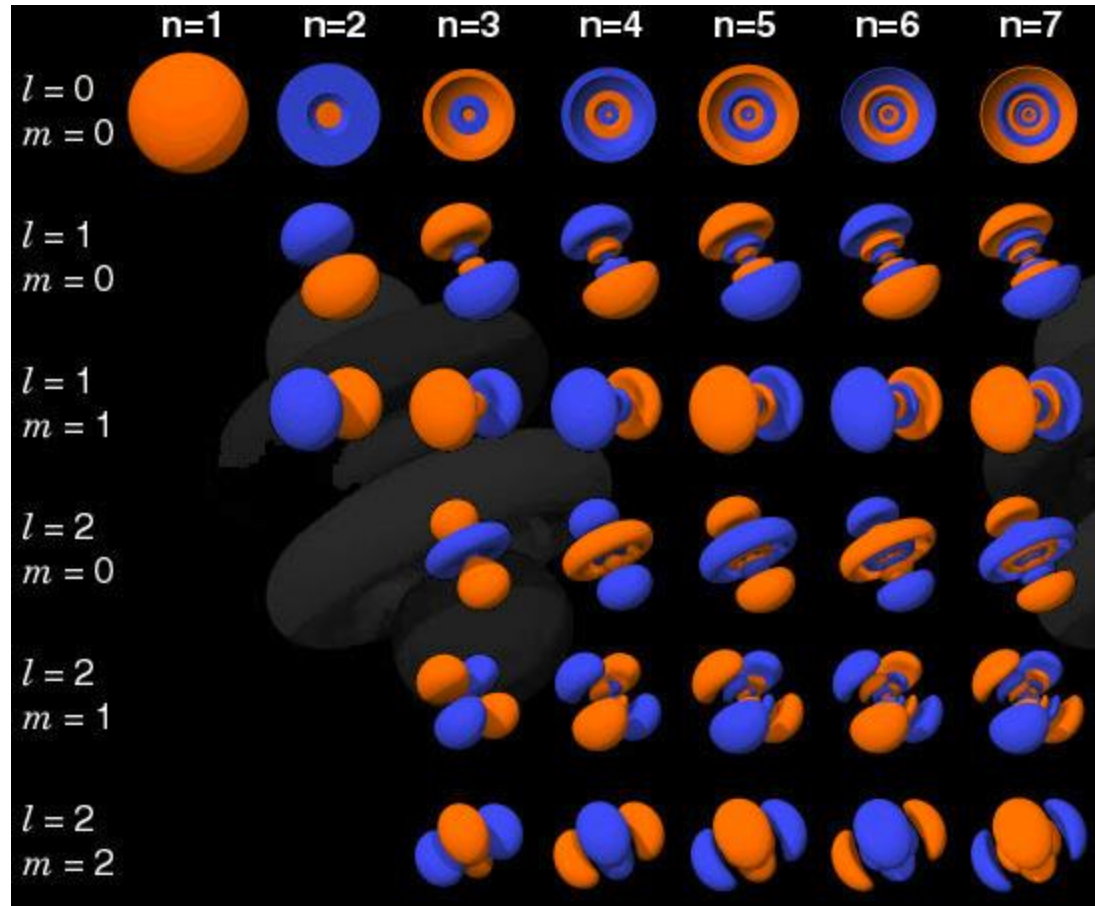
[1] J. C. Slater, J. Chem. Phys., 1933, 1, 687.

# In Depth; What is Wave Function?



# In Depth; What is Wave Function?

- Max Born suggested that square of wave function represents the probability of finding an electron in space
- Square of wave function provides the picture of hydrogen-like orbitals



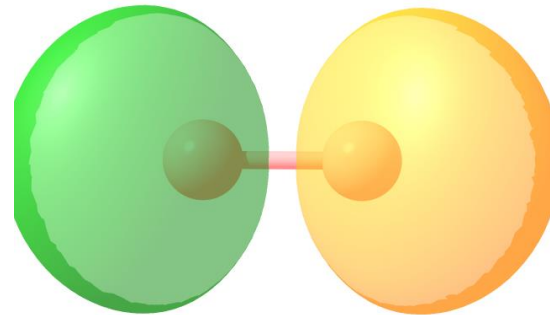
# In Depth; What is Wave Function?

- Schrödinger was worry about using the concept, introduced by Born
- What is an orbital?

Please tell me what you know  
about an orbital!

# In Depth; Spin and Pauli Force

- All tiny elements of our universe are interacting with each other by spin!
- Spin is a sub-atomic postman in the Universe!
- Pauli Exclusion Principle controls the energy of matter as traffic light controls car crashes!



**Now You Know the Concepts (Hopefully!)**

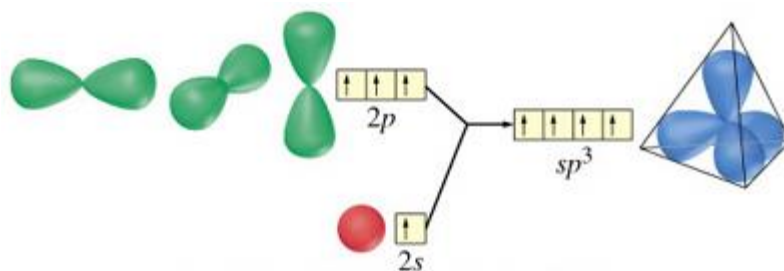
# How Molecules Form from Atoms

## VBT vs. MO

- VBT and MO originate from different philosophies but follow the same method
- Both build up molecules from Linear Combination of (Hydrogen-Like) Atomic Orbitals (LCAO)

# VB

- The most important concept in VB is “the principle of maximum overlap”, i.e. the greater the overlap of orbitals, the lower the energy of molecule(s)
- In order to achieve maximum overlap, Pauling invented the concept of hybridization



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# VB; Drawbacks

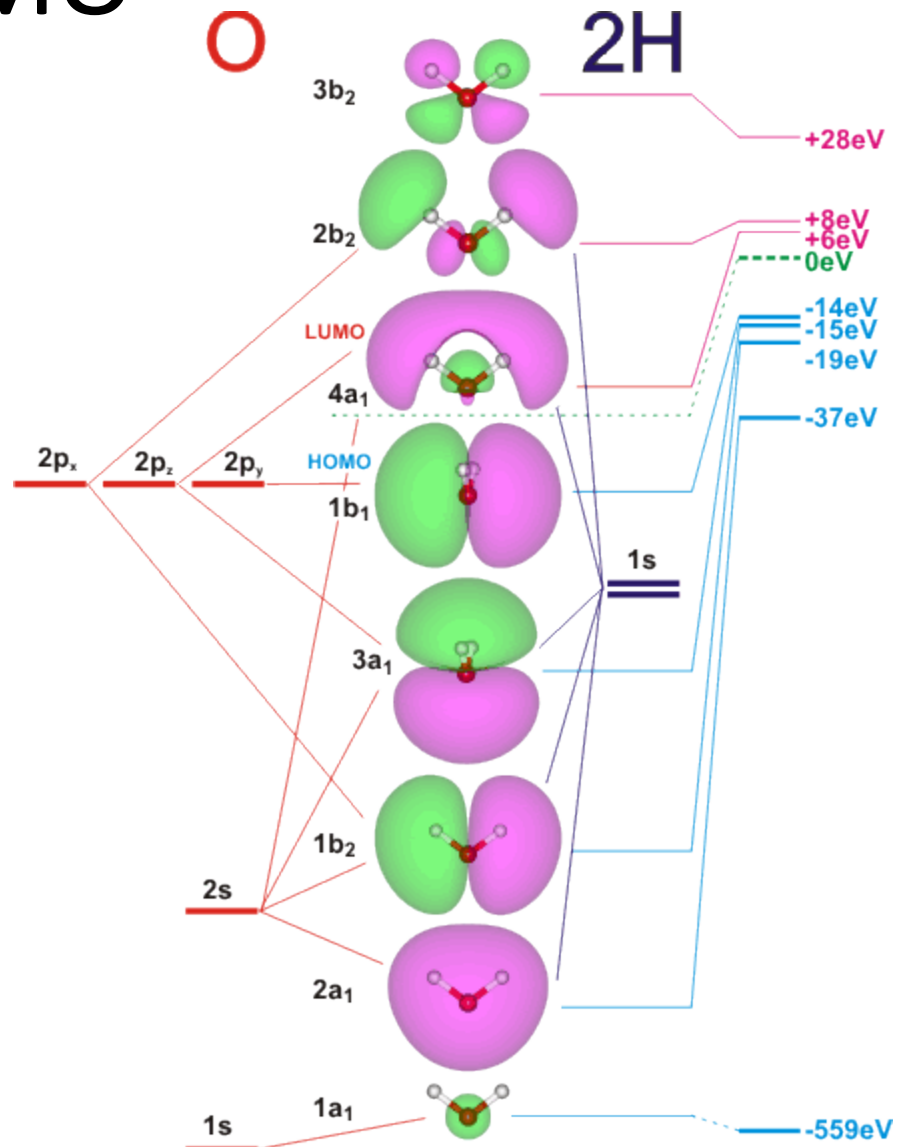
- Hybridization is not a physical concept; it is just a mathematical operation
- Neither hybridization nor maximum overlap principle can predict the equilibrium geometry of a molecule

**Only Energy Can Predict the Real Local  
Minimum**

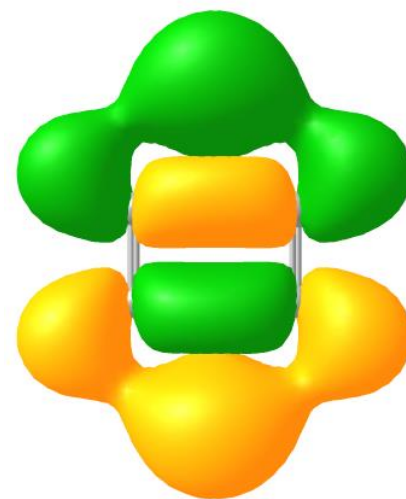
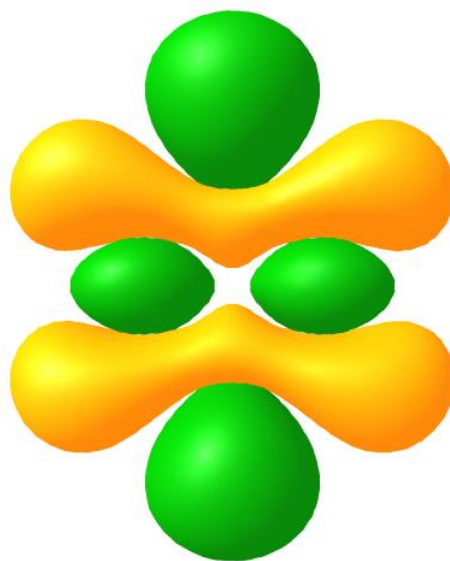
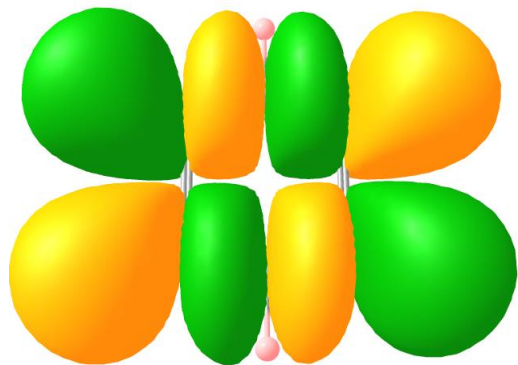
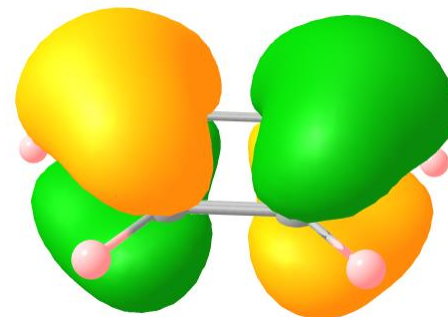
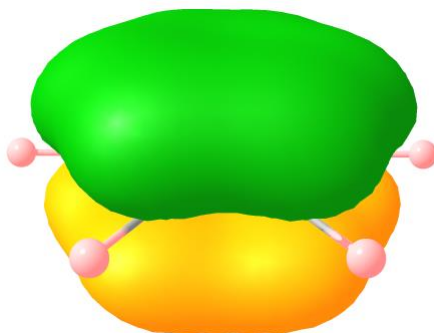
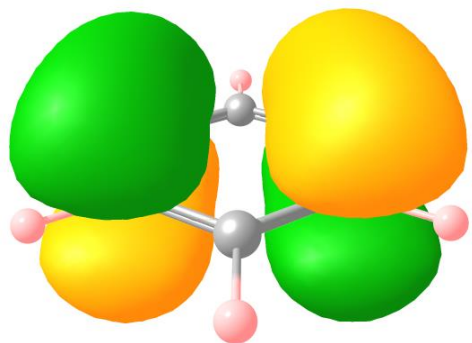


# MO

- MOs are made of overlap if all AOs which have proper energy and symmetry
- Unlike VB, MO orbitals cover whole molecule



# MO and Super Computer Era



# Molecular Geometry

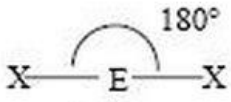
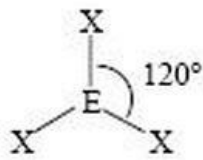
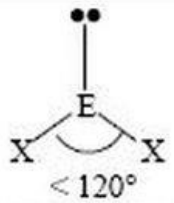
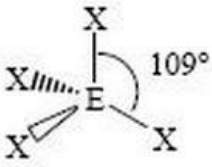
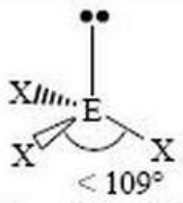
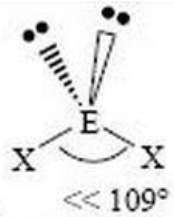
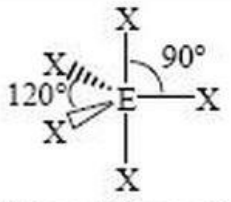
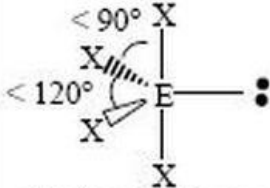
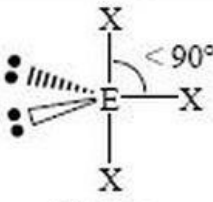
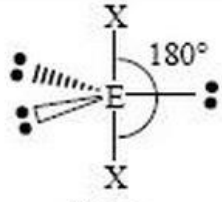
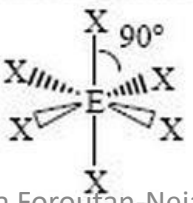
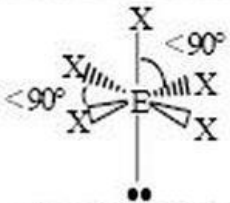
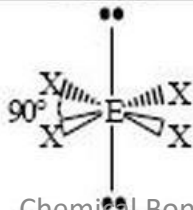
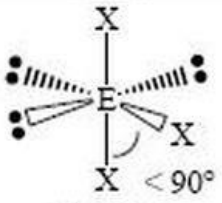
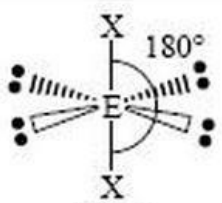
- 3D structure of molecules was introduced by le Bel and van't Hoff in 1874
- Werner in 1893 proposed octahedral structure for 6-coordinated TM complexes
- In 1911 Werner separated an optically active TM complex and proved his hypothesis
- In 1930s for the first time X-ray crystallography revealed the structure of molecules and bond lengths, bond angles and torsional angles were directly identified

# Molecular Geometry

- In 1940 Sidgwick and Powell proposed that the geometry of  $Ax_n$  molecules can be determined by the total number of electron pairs
- In 1957 Gillespie and Nyholm founded VSEPR theory
- It's all about electron domains

**What is the physics behind the VSEPR model?**

# Geometry From VSEPR

 <p>Linear</p>				
 <p>Trigonal Planar</p>	 <p>Bent or Angular</p>			
 <p>Tetrahedral</p>	 <p>Trigonal Pyramid</p>	 <p>Bent or Angular</p>		
 <p>Trigonal Bipyramid</p>	 <p>Sawhorse or Seesaw</p>	 <p>T-shape</p>	 <p>Linear</p>	
 <p>Octahedral</p>	 <p>Square Pyramid</p>	 <p>Square Planar</p>	 <p>T-shape</p>	 <p>Linear</p>