

# Quantum Mechanics, some concepts and approximations

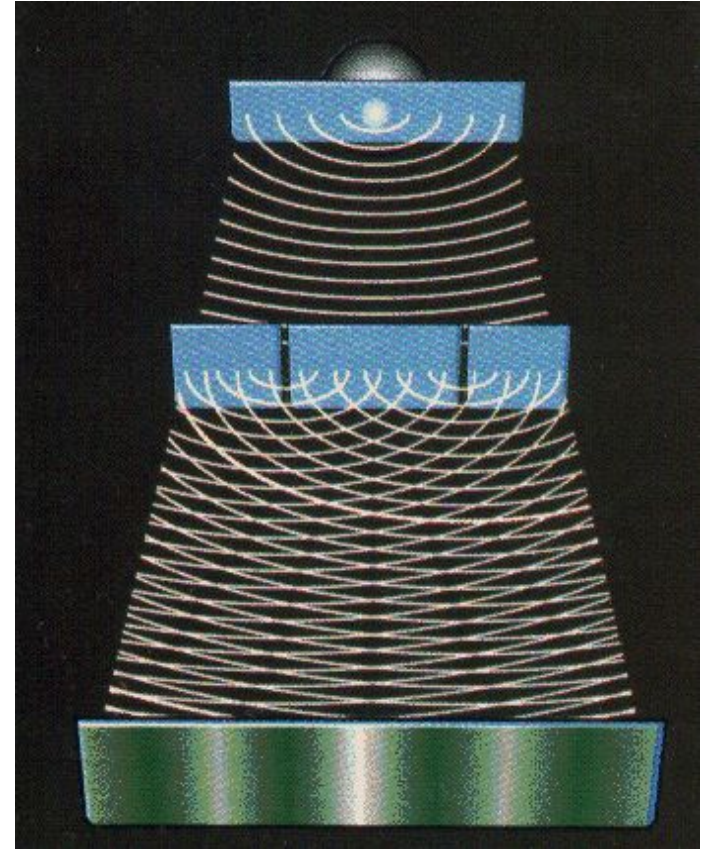
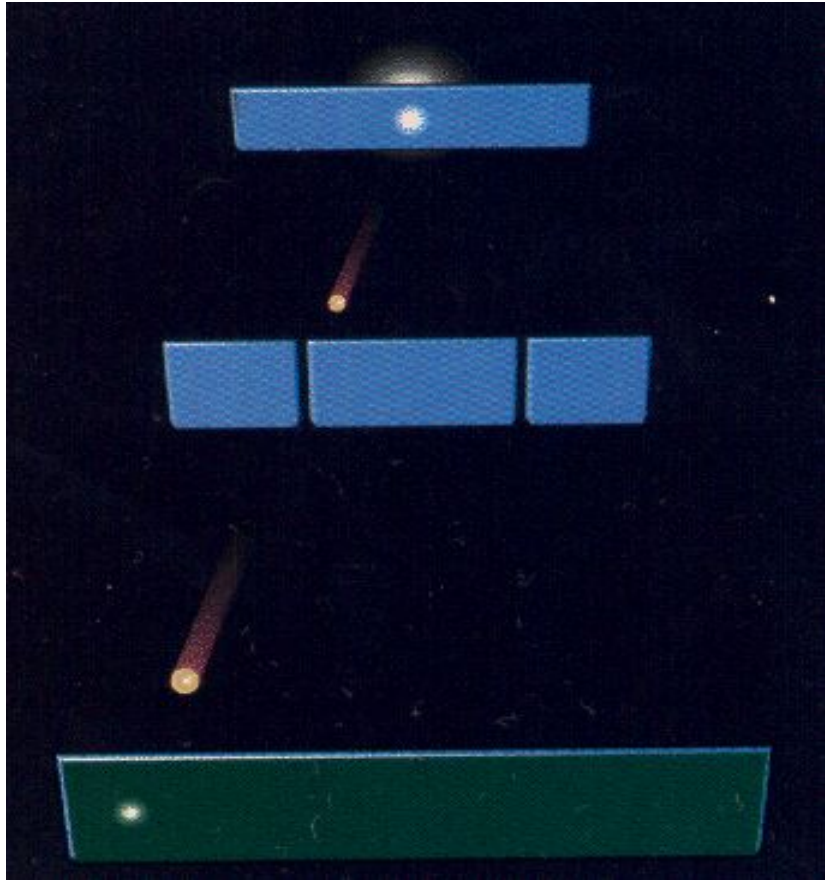
# Introduction to Quantum Mechanics

- Quantum mechanics is the theoretical framework within which it has been found possible to describe, correlate, and predict the behavior of a vast range of physical systems, from particles through nuclei, atoms and radiation to molecules and condensed matter.

# Classical *VS* QM

- All matter (particles) has wave-like properties
  - so-called particle-wave *duality*
- Particle-waves are described in a probabilistic manner
  - electron doesn't whiz around the nucleus, it has a probability distribution describing where it might be found
  - allows for seemingly impossible “quantum tunneling”
- Some properties come in dual packages: can't know both simultaneously to arbitrary precision
  - called the Heisenberg Uncertainty Principle
  - not simply a matter of measurement precision
  - position/momentum and energy/time are example pairs

# The Double slit Experiment



# Solving Sch. Equation for hydrogen atom

$$\mathcal{H} |E_i\rangle = E_i |E_i\rangle$$

$$-\frac{\hbar^2}{2m} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \psi + V(r)\psi = E\psi.$$

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

$$Y_{l,m}(\theta, \phi) = (-1)^m \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} P_{l,m}(\cos \theta) e^{im\phi} \quad m \geq 0.$$

$$R_{n,l}(r) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-r/na_0} \left(\frac{2r}{na_0}\right)^l L_{n-l-1}^{2l+1} \left(\frac{2r}{na_0}\right)$$

## Quantum Numbers

- There are different quantum numbers needed to specify the state of an electron in an atom  $n$ ,  $l$ ,  $m_l$  and  $S$ .
1. The principal quantum number  $n$  gives the total energy.
  2. The orbital quantum number gives the angular momentum; it can take on integer values from 0 to  $n - 1$
  3. The magnetic quantum number,  $m_l$ , gives the direction of the electron's angular momentum, and can take on integer values from  $-l$  to  $+l$ .

Schrödinger Equation can only be solved exactly for simple systems like

– Rigid Rotor, Harmonic Oscillator, Particle in a Box, Hydrogen Atom

- For more complex systems (i.e. many electron atoms/molecules) we need to make some simplifying assumptions/approximations and solve it numerically.
- However, it is still possible to get very accurate results.

In general, the “cost” of the calculation increases with the accuracy of the calculation and the size of the system.

All what we previously discussed represents the case where the potentials are symmetric. Now what will happen in case that there is different interactions between electrons and positive charges (Nucleus)

Several approximations have been done.

1- perturbation theorem

2- Variational method

3- (Wentzel, Kramers, and Brillouin) WKB approximation.



# Hartree-Fock method

$$\hat{H} \Psi(R_1, R_2, \dots, R_N, r_1, r_2, \dots, r_n) = E \Psi(R_1, R_2, \dots, R_N, r_1, r_2, \dots, r_n)$$

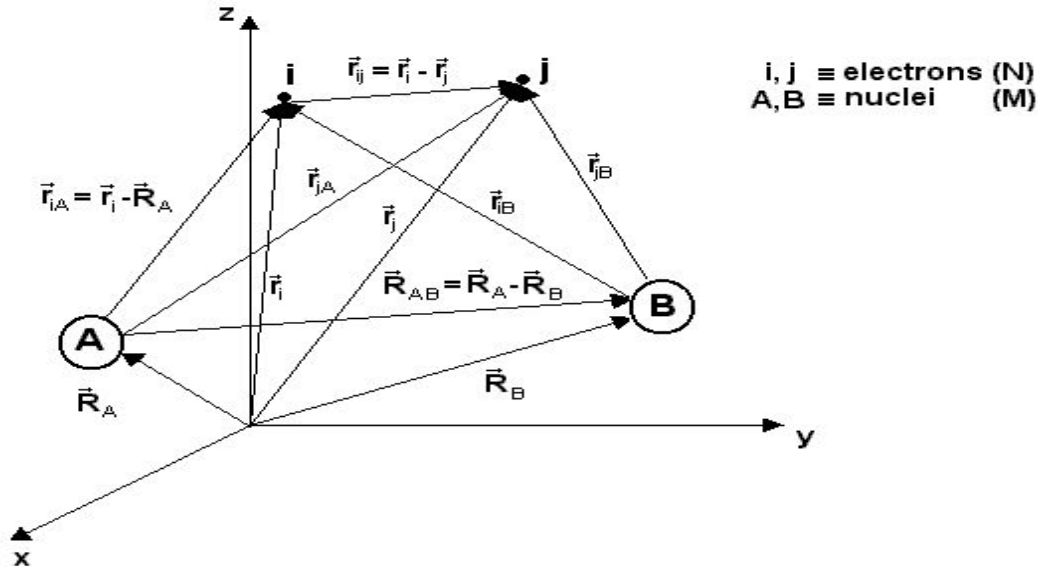
- The non-relativistic Hamiltonian for a system consisting n electrons and N nuclei is given by

$$\hat{H} = -\frac{1}{2} \sum_I \nabla_I^2 - \frac{1}{2} \sum_i \nabla_i^2 - \sum_i \sum_I \frac{Z_I}{r_{Ii}} + \sum_{I>J} \frac{Z_I Z_J}{r_{IJ}} + \sum_{i<j} \frac{1}{r_{ij}}$$

- **Born-Oppenheimer Approximation**

Qualitatively, the Born-Oppenheimer approximation says that the nuclei are so slow moving that we can assume them to be fixed when describing the behavior of electrons. Mathematically, the Born-Oppenheimer approximation allows to treat the electrons and protons independently

$$H = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{|\mathbf{r}_{ij}|} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{|\mathbf{R}_{AB}|}$$



## Born-Oppenheimer approximation

- usually a good approximation
- bad approximation for:
  - excited states
  - degenerate state

# Linear Combination of Atomic Orbitals (LCAO) approximation

- Orbitals span the entire molecule and the molecular orbitals (MO's) is the regions in a molecule where an electron is likely to be found. The solution of Hartree-Fock equation, is known as the molecular orbitals (MO's). In principle, the electronic structure of molecules can be worked out in the same way as for atoms and this can be done by solving the Schrödinger equation. This gives molecular orbitals rather than atomic orbitals. It is difficult to solve the Schrödinger equation for molecular species only if an approximation is introduced known as Linear combination of Atomic Orbitals (LCAO). The wavefunction can be expressed as

$$\psi_i = \sum_{j=1}^N C_{ij} \phi_j$$

# Density Functional Theory

- Will be discussed separately but in brief
- >>>>>

- *The end*
- *Thanks for attendance*