September 2, 2004 - Lecture 1: Atomic Structure I.

Particle Historical Background:
1. Goldstein (1886): detection of rays in gas tubes cathode rays/canal rays ⇒ various charge/mass ratio
2. Thomson (1897): analysis of cathode rays ⇒ negatively charged and behave like particles ⇒ mass of the electron
3. Milliken (1903): oil drop experiment ⇒ cathode rays ionize oil drop suspended in electrostatic field (U) ⇒ varying U, rate of the dropping changes ⇒ charge of the electron
4. Moseley (1910): X-ray emission from metals bombarded with high energy electrons ⇒ extra atomic weight in the nucleus (half of the total mass) ⇒ neutrons

Atomic Models:
1. Thomson (1900): static model – atom is a ball build from + and - fragments
2. Rutherford (1911): α particles deflected at large angles as passing through metal foils ⇒ most of the foil is empty space ⇒ a small nucleus is at the center of the atom – the electron does not collapse to the nucleus
3. Bohr (1913): accepted Rutherford’s nucleus model ⇒ electron is on a quantized circular orbit ⇒ electromagnetic radiation emitted or absorbed only if orbit changes, no radiation due to acceleration of a charged particle ⇒ classical mechanics laws

Considering orbiting electron around a proton (H atom) the Coulomb force, \((Ze)e/r^2\), equal with centrifugal force, \(mv^2/r\), of a particle on a quantized orbit, \((mvr) = n(h/2\pi)\)

\[
\nu = Ze^2 \frac{2\delta}{nh}; \text{ the electron is traveling close to the speed of light } (2.187 \cdot 10^8 \text{ cm s}^{-1})
\]

\[
r = \frac{n^2h^2}{4\delta^2mZe^2} = \frac{a_0n^2}{Z}; \text{ where } a_0 \text{ is the Bohr radius } (52.9 \text{ pm})
\]

Total Energy = Kinetic + Potential \(E = \frac{1}{2}mv^2 - Ze^2/r\)

\[
E = -\frac{2\delta^2mZe^4}{n^3h^2} = Z^2 \frac{E_{n=1}}{n^2}; \text{ where } E_{n=1} \text{ is the ground state energy } (-13.6 \text{ eV}) (\text{eV} \leftrightarrow \text{kcal/mol, kJ/mol})
\]

The success of Bohr model is that it explains spectral features of hydrogen-like atoms/ions:
- Ground and excited states; ionization and separation energy - by thermal/X-ray emission
- Rydberg’s empirical formula \((\Delta E = T_1 - T_2 = \frac{R}{n_1^2} - \frac{R}{n_2^2} = \frac{\lambda}{\lambda} = \frac{1}{\lambda})\) for the term values of the hydrogen \((R = 109.677.6 \text{ cm}^{-1} / 8065 \text{ eV cm} = 13.6 \text{ eV})\) (1 in Å = 12398/E in eV)
- Moseley’s empirical formula \((\nu = M (Z - \sigma)^2 (n_1^2 - n_2^2))\) for X-ray emission frequencies ⇒ shielding \((\sigma)\) by the core electrons \(M = -2\delta^2m e^4/h^3\)
- Try to describe He atom with the Bohr model. How do you treat the second electron particle?

Wave Historical Background:
1. Planck (1900): black body problem ⇒ light entering into a hollow sphere through a small hole ⇒ cannot escape, absorbed by tiny oscillators ⇒ experimental emitted radiation curve has a maximum ⇒ the oscillators can vibrate only at discrete frequencies ⇒ light comes in packets/quantized ⇒ \(E = h \cdot \nu\)
2. Einstein (1905): photoelectric effect ⇒ light below certain \(\lambda\) (blue vs. red), regardless of the intensity can eject electron from metals ⇒ photon has kinetic energy \(E = m \cdot c^2\)
3. DeBroglie (1910): studying electron diffraction suggests that all moving particles have an associated wave
⇒ connects wavelength of a photon and its momentum \( \lambda = \frac{h}{m \cdot v} \). ⇒ reciprocal relationship between
wavelength and momentum or energy and periodicity.

4. Heisenberg (1924): particle is a wave and does not have a well defined simultaneous position and
momentum ⇒ position and momentum cannot be determined at the same time with higher accuracy than the
Planck constant (h) ⇒ reciprocal relationship between position and momentum \( \Delta p_x \cdot \Delta x \geq \frac{h}{4\pi} \).
“digestable” example: listening to the radio ⇒ want to know the exact frequency at an exact moment ⇒ this
is impossible: need to sample over time to have an accurate measurement of frequency

5. Schrödinger (1925): wave mechanical definition of the electrons: \( \mathcal{H} \Psi = E \Psi \). \( \mathcal{H} = -\frac{h^2}{8\pi^2 m} \nabla^2 + V \)
The Hamilton operator perform an operation (total energy expression = kinetic (Laplacian) + potential) on the function (e.g.:
electron orbital) that follows it. If the result is constant times the function itself then the function is called eigenfunction
(molecular orbitals as set of atomic orbitals) and the constant is eigenvalue (orbital energy).

Wavefunction \( \Psi(x,y,z) \) as an electron orbit, three-dimensional standing wave
– general form of \( \sin x \cdot \cos y \cdot e^{-z} \)
– must be normalized = probability of finding and electron \( \int \Psi \Psi^* \, dr = 1 \)

Wave Mechanical Model:
For an electron wave, define a wavefunction (\( \Psi \)) and use Maxwell’s equation of motion for waves
\[
E \Psi = -\frac{\hbar^2}{8\pi^2 m} \left( \frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \right) + V \Psi
\]
"Digestable" solution: Particle in a box ⇒ \( V = 0 \) inside, \( V = \infty \) outside the box, \( y = z = 0 \), max(\( x \)) = \( L \)
\[
E \Psi = -\frac{\hbar^2}{8\pi^2 m} \frac{\partial^2 \Psi}{\partial x^2} \Rightarrow \text{second derivative of a function is the function itself}
\]
\[
\Psi = A \sin kx , \text{ for a box with one particle (after normalization } \Psi = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \)
\]
\[
E = \frac{n^2 \hbar^2}{8mL} \quad \text{and for a 3D box } E = \frac{(n_1^2 + n_2^2 + n_3^2) \hbar^2}{8mL} \quad \text{- note the integer constants (n,)}
\]
practical application: electron/electron holes in polymeric materials

One-electron atoms:
- \( V = -\frac{Ze^2}{r} \) - set the origin of the Cartesian space at the center of the nucleus \( \Psi(x, y, z) \) can be converted
to \( \Psi(r, \theta, \phi) \) in polar coordinates = \( R(r) \cdot \Theta(\theta)\Phi(\phi) \) ⇒ separates into radial and angular functions
- To satisfy boundary conditions – certain constants needs to be introduced ⇒ quantum numbers
\[
n = 1, 2, 3, \ldots \quad \text{ approximate energy and size of the wavefunction}
1 = 0, 1, 2, \ldots \quad \text{ absolute value of the angular momentum}
m_l = -l, \ldots, 0, \ldots l \quad \text{ real angular momentum (vectors with sign)}
\]
\[
\Psi_{n,l,m} \text{ defines a solution commonly called orbital}
\]
- Radial Function \( R_{nl}(r) \)
o The orbital size increases as \( n \) increases, average distance over time is close to \( n^2 \cdot a_0 \)
o s-type orbitals have infinite density at the nucleus (Mössbauer spectroscopy) - exponential decay
to zero at large distances
o Radial nodes (n-l-1) define the zero probability of finding electrons at a certain distance
- Angular Functions \( \Theta_{lm}(\theta)\Phi_m(\phi) \)
o Define the shape and sign of the atomic orbitals with quantum numbers
o Angular nodes (l) define the zero probability of finding electrons in a certain plane

Linear combination of the orbitals as mathematical objects