

CHEM 245 ATOMIC STRUCTURE

Understanding the Electronic Structures → Quantum Theory and Wave Mechanics

Older Theories (1900-1925) = Classical Quantum Theory

- Electron is treated as a particle (electronic configurations).
- At low T, radiation emitted is of low E (i.e. in IR). As T increases, radiation becomes red, bright red, then white.
- Planck: Energy can be absorbed or emitted only in quanta of magnitude ΔE , where
 $\Delta E = h\nu$ ν = frequency and $h = 6.626 \times 10^{-34}$ J s
Hence $\Delta E = hc/\lambda$ $c = 2.998 \times 10^8$ m s⁻¹

Recent Models

- Electron is treated as a wave (stereochemistry).

Important application of “Classical Quantum Theory” → Interpretation of the Atomic Spectrum of H, based on the “Rutherford-Bohr” model.

Balmer Series, Lyman Series etc.

Discrete lines corresponding to electronic transitions.

Wavelength of spectral lines obey the equation:

$$\bar{\nu} = \frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad R = \text{Rydberg constant} = 1.097 \times 10^5 \text{ cm}^{-1}$$

Lyman Series: $n_1 = 1$

$$\bar{\nu} = \frac{1}{\lambda} = R \left(\frac{1}{1^2} - \frac{1}{n_2^2} \right)$$

Balmer Series: $n_1 = 2$

$$\bar{\nu} = \frac{1}{\lambda} = R \left(\frac{1}{2^2} - \frac{1}{n_2^2} \right)$$

(IR region)

Paschen Series: $n_1 = 3$

Brackett Series: $n_1 = 4$

Pfund Series: $n_1 = 5$

BOHR ATOM (1913)

Electrons move around the nucleus in “circular orbits” with an angular momentum, mvr , given by

$$mvr = n \left(\frac{h}{2\pi} \right) \quad m = \text{mass of } e^- \quad v = \text{velocity of } e^- \quad r = \text{radius of orbit}$$

h = Planck's constant n = principle quantum number

Energy is absorbed or emitted only when an e^- moves from one state to another.

$$\Delta E = E_{n_2} - E_{n_1} = h\nu$$

When Bohr model is applied to H atom, the radius of each allowed “circular” orbit is given by:

$$r = \frac{\epsilon_0 h^2 n^2}{\pi Z m e^2} \quad \epsilon_0 = \text{permittivity of vacuum} \quad m = \text{mass of } e^- \quad e = \text{charge of an } e^-$$

$$n = 1, 2, 3, 4, \dots, \infty \quad Z = \text{elementary charge of } e^-$$

When $n = 1$, $r = 5.292 \times 10^{-11} \text{ m} = \text{Bohr radius of an H atom} = 0.53 \text{ \AA}$

From this equation, only certain orbits whose radii are given by this equation are allowed to the electron.

Simplify this equation by combining all physical constants into one, called the Bohr radius, a_0 :

$$\text{Define; } a_0 = \frac{\epsilon_0 h^2}{\pi m e^2}$$

$$r = \frac{n^2}{Z} a_0$$

$$a_0 = 5.2917706(44) \times 10^{-11} \text{ m} = 0.053 \text{ nm}$$

The total energy, E , of an electron is the sum of its kinetic energy (K.E.) and potential energy (P.E.):

$$E = K.E. + P.E. = \frac{1}{2} m v^2 - \frac{Z e^2}{4 \pi \epsilon_0 r} \quad (\text{the P.E. is negative because nucleus and electron attract each other})$$

$$\text{Since } m v^2 = \frac{Z e^2}{4 \pi \epsilon_0 r}$$

We can substitute this equation into the equation defining energy and obtain the following, surprisingly simple result:

$$E = \frac{1}{2} \times \frac{Z e^2}{4 \pi \epsilon_0 r} - \frac{Z e^2}{4 \pi \epsilon_0 r} = -\frac{1}{2} \times \frac{Z e^2}{4 \pi \epsilon_0 r}$$

So, in a stable orbit, the P.E. is negative and 2 times as large as the K.E.

Substituting for $r = \frac{n^2}{Z} a_0$ into this equation gives that only certain energies are allowed for the atom:

$$E = -\frac{Z^2}{2 n^2} \times \frac{e^2}{4 \pi \epsilon_0 a_0} \quad n = 1, 2, 3, \dots$$

In atomic units (a.u.):

$$E(\text{a.u.}) = -\frac{Z^2}{2n^2} \quad n = 1, 2, 3, \dots$$

Once E(a.u.) is obtained, we can later convert them into any SI or non-SI units:

$$1 \text{ hartree} = 1 \text{ a.u.} = \frac{e^2}{4\pi\epsilon_0 a_0} = 4.3598 \times 10^{-18} \text{ J}$$

INTRODUCTION TO WAVE MECHANICS (1924)

Louis de Broglie → If light were composed of particles and showed wave-like properties, the same should be true for electrons and other particles.

A particle with momentum mv possesses a wavelength, λ .

$$\lambda = \frac{h}{mv} \quad m = \text{mass of the particle} \quad v = \text{velocity of the particle} \quad h = \text{Planck's constant}$$

Heisenberg's Uncertainty Principle:

If an electron has wave-like properties, it is impossible to know both the momentum and the position of the electron simultaneously.

Now, instead of trying to define the exact position and momentum of an e⁻, we use the probability of finding the electron in a given volume of space.

The probability of finding an electron at a given point in space is determined from ψ^2 where ψ = wave function = mechanical function which describes the behaviour of an e⁻ wave.

Some Principles of Quantum Mechanics:

- Matter has wave-like properties!
- An electron is described by a wavefunction, ψ . (ψ = mathematical function of coordinates x , y , z and of time t)

Born interpretation:

$\psi^2 \propto$ Probability of finding the electron (i.e. particle) in an infinitesimal region of space

- If ψ^2 is large → high probability of finding the electron
- If $\psi^2 = 0$ → No probability of finding the electron
-

Hence ψ^2 = Probability density of the particle

Schrödinger (1927)

(Schrödinger equation is solved for H-like systems)

- An equation for all moving particles, including electrons
- In Schrödinger's theory, there are no discrete orbitals around the nucleus
- He describes the wave associated with the electron

Wave mechanics: Theory of behaviour of atomic particles according to wave equation.

ψ has a precise value at each point in space:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2} (E - V)\psi = 0 \quad m = \text{mass} \quad E = \text{Total energy} \quad V = \text{Potential energy}$$

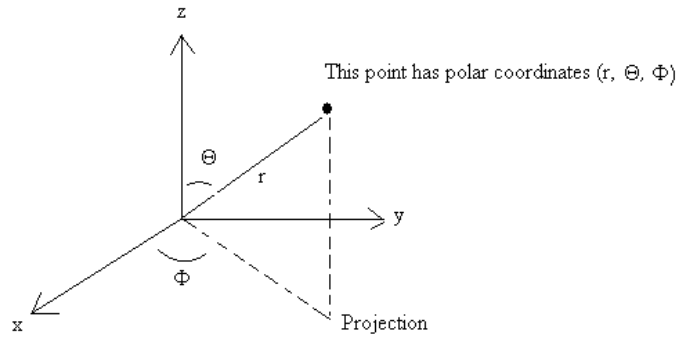
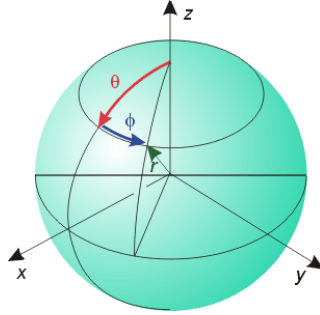
Electrons move in 3-D space and an appropriate form Schrödinger equation is given by:

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi + \frac{8\pi^2 m}{h^2} (E - V)\psi = 0$$

We are not interested in solving this equation but it is advantageous to work with it in spherical polar coordinates.

$$\begin{array}{ccc} \psi(x, y, z) & \rightarrow & \psi(r, \theta, \phi) \\ \text{Cartesian coordinates} & & \text{Polar coordinates} \end{array}$$

The relationship between spherical polar coordinates and Cartesian coordinates:



$$x = r \sin\theta \cos\phi \quad y = r \sin\theta \sin\phi \quad z = r \cos\theta$$

The coordinates x , y and z are expressed in terms of the distance r and the angles θ and ϕ .

When we look at the results obtained from Schrödinger wave equation, we talk in terms of the radial and angular parts of the wave function.

$$\begin{array}{ccccccc} \psi(x, y, z) & = & \psi(r) \psi(\theta, \phi) & = & R(r) A(\theta, \phi) \\ \text{Cartesian} & & \text{radial} & \text{angular} & \text{radial} & \text{angular} \\ & & & & \text{func.} & \text{func.} & \text{(determines the shape} \\ & & & & & & \text{and direction of the orbitals)} \end{array}$$

Results obtained when the wave equation is solved:

- The wave function ψ is a solution of the Schrödinger equation and describes the behaviour of an e^- in a region of space, called “atomic orbital”.
- We can determine energy values that are associated with particular wave functions.

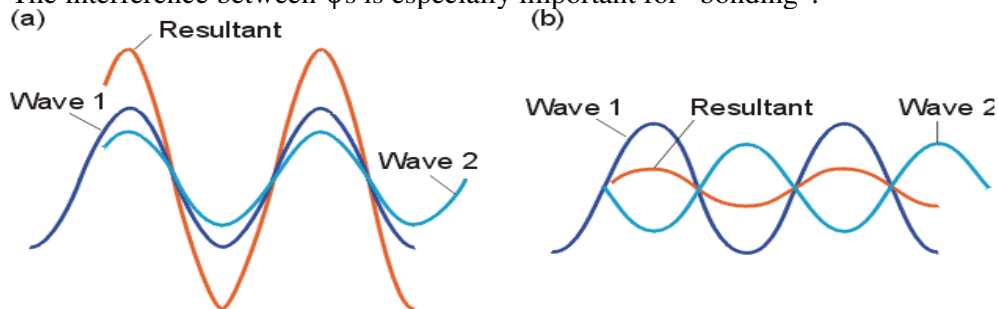
ψ has + and – amplitudes, although the sign has no significance. We should look at its magnitude, not its sign.

The sign becomes important when two ψ s spread into the same region of space. They might interfere:

a) If they have the same sign in a region, the waves interfere **CONSTRUCTIVELY!** (e.g. when 2 atoms are close enough to form a bond, there might be enhanced probability of finding the particles in that region)

b) If the wave functions have opposite signs, then they interfere **DESTRUCTIVELY!** This means very, very low probability of finding the particle in that region.

The interference between ψ s is especially important for “bonding”.



Interpretation of the wave function, ψ :

1. The electron is considered as a “discrete” particle; the square of the wave function, ψ^2 , tells the relative probability of its being at any given point!
2. The electron is considered as a “smeared out” distribution of negative charge, the density of which changes from place to place according to ψ^2 .

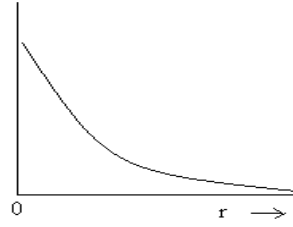
Electron distribution as a function of r , from the nucleus in the most stable orbital of the hydrogen atom for:

a) the Bohr atom:



The e^- is found entirely at one sharply Defined distance (a_0) from the nucleus

b) the wave-mechanical atom:



The e^- is spread over a range of distances

ATOMIC ORBITALS IN WAVE MECHANICS

Entire set of wave functions for the e^- in the H atom = Orbitals

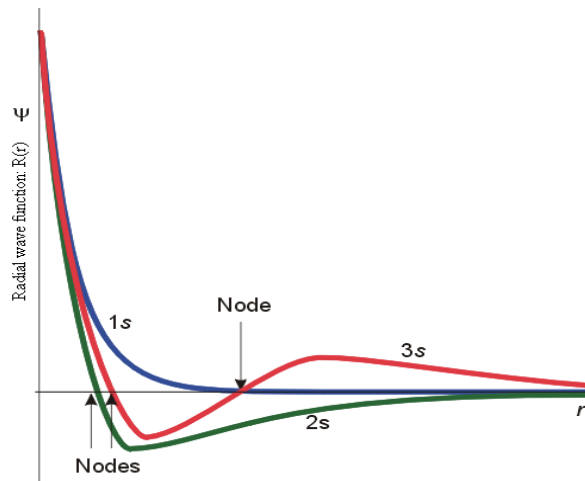
(they are wave-mechanical analogues of Bohr's orbit)

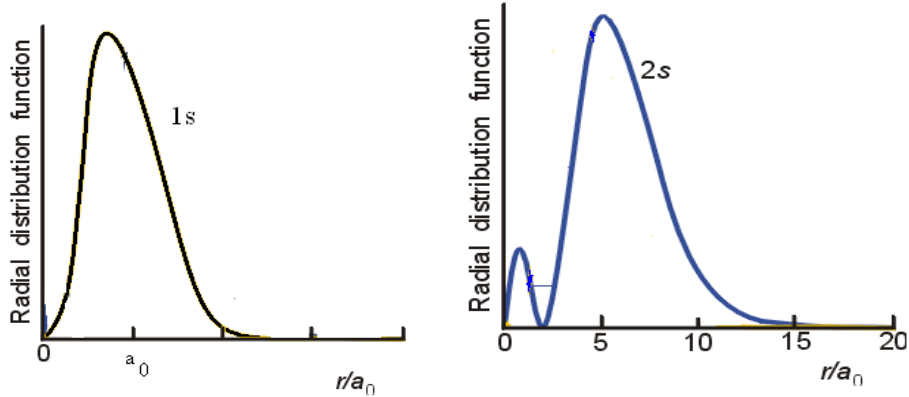
In wave mechanics, n is again a quantum number:

$$\begin{aligned} n &= 1, 2, 3, \dots, \infty \\ l &= 0, 1, 2, 3, \dots, (n-1) = s, p, d, f, \dots \\ m_l &= -l, \dots, 0, \dots, +l \end{aligned}$$

s orbital:

- spherically symmetrical
- 1s is positive everywhere
- Beginning with 2s, there are + and – alternating regions





When $\psi = 0$ (i.e. $\psi^2 = 0$) there are radial nodes.

Radial part of the wave function, $R(r)$, determines the variation of the orbital with increasing distance from the nucleus.

1s orbital with $n = 1$, $l = 0$ and $m_l = 0$ decays exponentially and never passes through zero. The locations where radial wavefunction passes through zero are called **radial nodes!**

The radial parts of the wave function decay exponentially as r increases but the decay is slower for $n = 2$ than for $n = 1$.

Important points from the plots above:

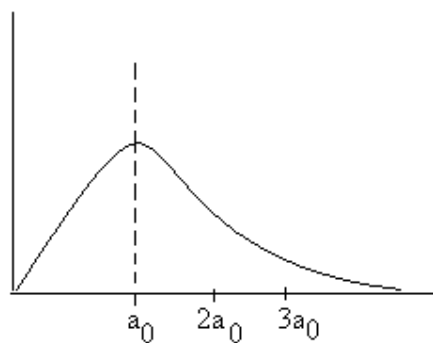
1. The “s” atomic orbitals have a finite value of $R(r)$ at the nucleus.
2. For all orbitals other than “s”, $R(r) = 0$ at the nucleus.
3. For the 1s orbital, $R(r)$ is always positive for the first orbital other types (e.g. 2p, 3d, 4f) and $R(r)$ is positive everywhere except at the origin.

Radial Distribution Function:

“An electron in an atom is the probability of finding the electron in a given volume of space.”

The function ψ^2 is proportional to the probability density of the electron at a point in space. By considering values of ψ^2 at points around the nucleus, we can define a surface boundary which encloses the volume of space in which the electron will spend 95% of its time.

The radial distribution function for the most stable orbital of the hydrogen atom:



Radial distribution function = $4\pi r^2 \psi^2 = 0$ when $r = 0$ and goes through a maximum.

The maximum point is at precisely the orbit radius in Bohr's theory, $a_0 = 0.529 \text{ \AA}$

Some examples:

1.6

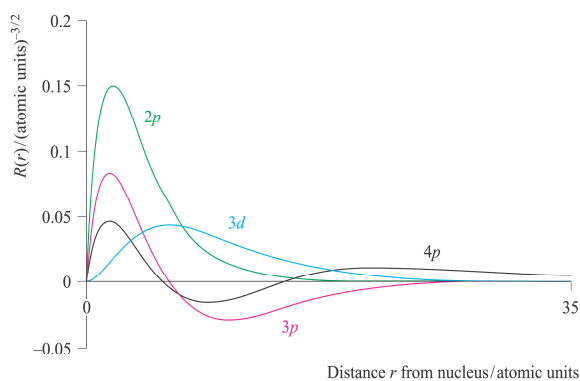


Fig. 1.6 Plots of radial parts of the wavefunction $R(r)$ against r for the $2p$, $3p$, $4p$ and $3d$ atomic orbitals; the nucleus is at $r = 0$.

1.7

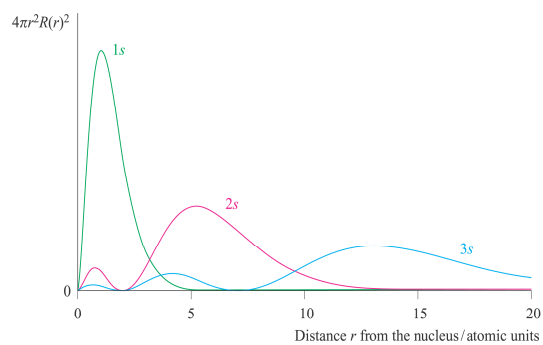


Fig. 1.7 Radial distribution functions, $4\pi r^2 R(r)^2$, for the 1s, 2s and 3s atomic orbitals of the hydrogen atom.

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1.8

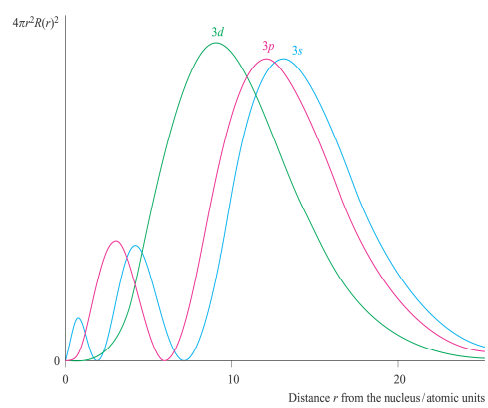


Fig. 1.8 Radial distribution functions, $4\pi r^2 R(r)^2$, for the 3s, 3p and 3d atomic orbitals of the hydrogen atom.

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