

Chapter Four: Single electron atom (H-atom)

4.1 Line spectra of Hydrogen atoms

It is found that hydrogen always gives a set of line spectra in the same position, sodium another set, iron still another and so on the line structure of the spectrum extends into both the ultraviolet and infrared regions. It is impossible to explain such a line spectrum phenomenon without using quantum theory. For many years, unsuccessful attempts were made to correlate the observed frequencies with those of a fundamental and its overtones (denoting other lines here). Finally, in 1885, Balmer found a simple formula which gave the frequencies of a group of lines emitted by atomic hydrogen. Since the spectrum of this element is relatively simple, and fairly typical of a number of others, we shall consider it in more detail.

Under the proper conditions of excitation, atomic hydrogen may be made to emit the sequence of lines illustrated in Fig. 4.1. This sequence is called *series*.

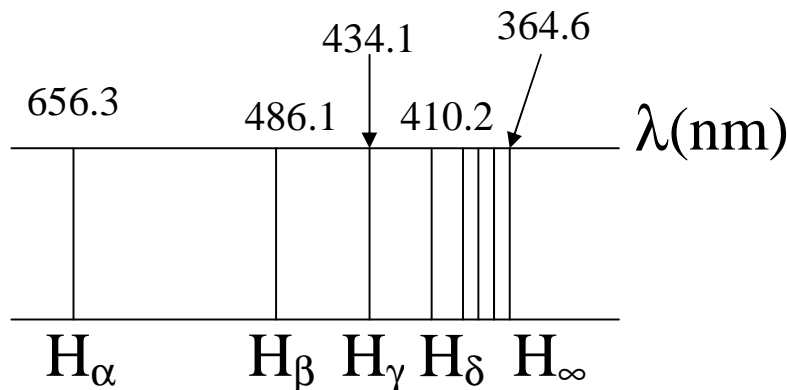


Fig. 4.1 The Balmer series of atomic hydrogen.

There is evidently a certain order in this spectrum, the lines becoming crowded more and more closely together as the limit of the series is approached. The line of longest wavelength or lowest

frequency, in the red, is known as H_{α} , the next, in the blue-green, as H_{β} , the third as H_{γ} , and so on.

Balmer found that the wavelength of these lines were given accurately by the simple formula

$$\frac{1}{\lambda} = R_{\infty} \left(\frac{1}{2^2} - \frac{1}{n^2} \right), \quad n = 3, 4, 5, \Lambda$$

where λ is the wavelength, R_{∞} is a constant called the *Rydberg constant*, and n may have the integral values 3, 4, 5, etc., if λ is in meters,

$$R_{\infty} = 1.097 \times 10^7 \text{ m}^{-1}$$

Substituting R and $n = 3$ into the above formula, one obtains the wavelength of the H_{α} -line:

$$\lambda = 656.3 \text{ nm}$$

For $n = 4$, one obtains the wavelength of the H_{β} -line, etc. for $n = \infty$, one obtains the limit of the series, at $\lambda = 364.6 \text{ nm}$ –shortest wavelength in the series.

Other series spectra for hydrogen have since been discovered. These are known, after their discoveries, as Lyman, Paschen, Brackett and Pfund series. The formulas for these are

$$\text{Lyman series:} \quad \frac{1}{\lambda} = R_{\infty} \left(\frac{1}{1^2} - \frac{1}{n^2} \right), \quad n = 2, 3, 4, \Lambda$$

$$\text{Paschen series:} \quad \frac{1}{\lambda} = R_{\infty} \left(\frac{1}{3^2} - \frac{1}{n^2} \right), \quad n = 4, 5, 6, \Lambda$$

$$\text{Brackett series:} \quad \frac{1}{\lambda} = R_{\infty} \left(\frac{1}{4^2} - \frac{1}{n^2} \right), \quad n = 5, 6, 7, \Lambda$$

$$\text{Pfund series:} \quad \frac{1}{\lambda} = R_{\infty} \left(\frac{1}{5^2} - \frac{1}{n^2} \right), \quad n = 6, 7, 8, \Lambda$$

The Lyman series is in the ultraviolet, and the Paschen, Brackett, and Pfund series are in the infrared. All these formulas can be generalized into one formula which is called the general Balmer series.

$$\frac{1}{\lambda} = R_{\infty} \left(\frac{1}{k^2} - \frac{1}{n^2} \right), \quad n = k + 1, k + 2, k + 3, \dots$$

All the spectra of atomic hydrogen can be described by this simple formula. As no one can explain this formula, it was ever called *Balmer formula puzzle*.

4.1 Bohr model for H-atom

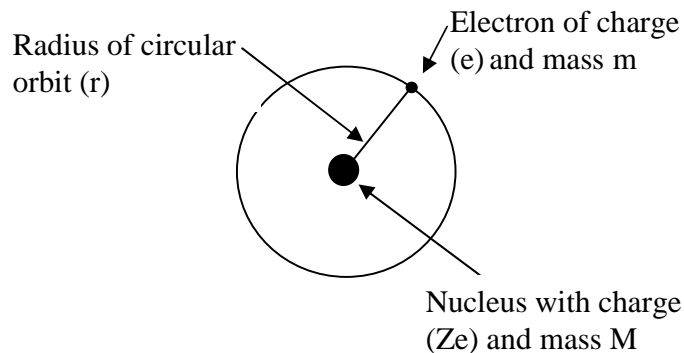
Let's suppose an atom consists of nucleus with charge (Ze) and mass M and electron of charge (e) and mass m moving in circular orbit around the nucleus.

The electron moving around the nucleus under the influence of the Coulomb force keeps the electron in its orbit therefore;

$$\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r^2} = m \frac{v^2}{r} \quad \dots(4.1)$$

and by using the second postulate of Bohr

$$mvr = n \frac{h}{2\pi} \quad n = 1, 2, 3, \dots \quad (4.2)$$



Dr. Fouad Attia Majeed Fig. 4.1: Electron moving around the nucleus under the effect of Coulomb force

And by substituting the value of v from eq. (4.2) into eq. (4.1) we get;

$$Ze^2 = 4\pi\epsilon_0 m v^2 r = 4\pi\epsilon_0 m r \left(\frac{n\eta}{mr} \right)^2 = 4\pi\epsilon_0 \frac{n^2 \eta^2}{mr} \quad \dots(4.3)$$

$$\therefore r_n = 4\pi\epsilon_0 \frac{n^2 \eta^2}{mZe^2} \quad \dots(4.4) \quad \text{where } r_n \text{ is } n^{\text{th}} \text{ Bohr radius}$$

$$v_n = \frac{n\eta}{mr} = \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{n\eta} \quad \dots(4.5) \quad v_n \text{ is the velocity of the electron in the } n^{\text{th}} \text{ orbit.}$$

For hydrogen atom $Z=1$ and we take $n=1$ (ground state) and substitute into eq. (4.4) we will find first Bohr radius (a_0)

$$a_0 = \frac{\eta^2}{(e^2/4\pi\epsilon_0) m} = 5.3 \times 10^{-11} \text{ m} = 0.53 \text{ \AA}$$

$$v = \frac{e^2}{4\pi\epsilon_0 \eta} = 2.2 \times 10^6 \text{ m/s}$$

Therefore eq. 4.4 can be written in terms of first Bohr radius as

$$r = a_0 n^2 \quad n = 1, 2, 3 \dots$$

to calculate the total energy for the H-atom we use r_n and v_n from equations (4.4) and (4.5) respectively.

$$E_n = K.E + P.E = \frac{1}{2} m v_n^2 + \frac{-e^2}{4\pi\epsilon_0 r_n} = -\frac{mZ^2 e^4}{(4\pi\epsilon_0)^2 2\eta^2 n^2} \quad \dots (4.6)$$

To calculate the electron energy in the ground state we put $n=1$ and $Z=1$ in eq. (4.6) we get;

$$E = -\frac{(9 \times 10^9)(9.11 \times 10^{-31})(1.6 \times 10^{-19})^4}{2(1.05 \times 10^{-34})} = -2.17 \times 10^{-18} \text{ J} = -13.6 \text{ eV}$$

(-13.6 eV) is called the binding energy of the electron in the first orbit in H-atom.

The other energy levels can be calculated from the relation

$$E_n = -\frac{13.6 \text{ eV}}{n^2} \quad n = 1, 2, 3, \dots$$

It is easy to see that all the energy in atoms should be discrete not continuous. When the electron transits from n^{th} orbit to k^{th} orbit, the frequency and wavelength can be calculated as

$$\nu = \frac{E_n - E_k}{h} = \frac{me^4}{8\epsilon_0^2 h^3} \left(\frac{1}{k^2} - \frac{1}{n^2} \right) \quad n > k$$

$$\frac{1}{\lambda} = \frac{\nu}{c} = \frac{me^4}{8\epsilon_0^2 h^3 c} \left(\frac{1}{k^2} - \frac{1}{n^2} \right) = R_\infty \left(\frac{1}{k^2} - \frac{1}{n^2} \right) \quad \dots(4.7)$$

Where $R_\infty = \frac{me^4}{8\epsilon_0^2 h^3 c}$ is *Rydberg constant*. It is found that the value of R is matched with experimental data very well. Till then, the 30-years puzzle of line spectra of atoms was solved by Bohr since equation (4.7) is exactly the general Balmer formula.

When Bohr's theory met problems in explaining a little bit more complex atoms (He) or molecules (H₂), Bohr realized that his theory is full of contradictions as he used both quantum and classical theories. The problem was solved completely after De Broglie proposed that electron also had the wave-particle duality. Since then, the proper theory

describing the motion of the micro-particles, quantum mechanics, have been gradually established by many scientists.

4.2 Solution of Schrödinger equation for H-atom

4.2.1 The Schrödinger equation

This is a quantum-mechanical equivalent of Newton's laws: in fact it is just the (non-relativistic) conservation of energy applied to wavefunctions.

The full, 3D, time-dependent Schrödinger equation (TDSE) is given by:

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

The first 2 terms (in []) are the Hamiltonian. The first term represents the kinetic energy; the second (V) is the potential energy. On the right-hand side of the equation is the total energy of the system. However, these are all operators, and they have to act on the wavefunction to give the energies.

Note that, in cartesian coordinates,

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

The time-independent Schrödinger equation (TISE) is given by:

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

4.2.2 Potential for hydrogen atom

A nucleus has charge (Ze). Coulomb attraction gives the potential of the electric field generated by this charge:

$$\frac{Ze}{4\pi\epsilon_0 r}$$

For a system with one electron (e.g. H, He⁺, Li⁺⁺ etc), the electron in this electric field has *potential energy*

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

So for hydrogenic systems, the Schrödinger equation becomes:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \right] \psi(r) = E\psi(r) \quad \dots(4.8)$$

For hydrogen, Z = 1.

- This is an example of an eigenequation.
- Eigenvalues are allowed values of E.
- Eigenfunctions are corresponding functions $\psi(r)$.
- Spherically symmetric system, so we'll use spherical polar coordinate:

$$\psi(\vec{r}) = \psi(x, y, z) \rightarrow \psi(r, \theta, \phi)$$

4.2.3 Separation of variables

Now, assume that we can separate the variables, i.e. that ψ is a multiple of completely separate factors R, Θ and Φ containing terms in r, θ and ϕ respectively:

$$\psi(\vec{r}) = R(r) \Theta(\theta) \Phi(\phi) \quad \dots(4.9)$$

And since ∇^2 in spherical coordinates is given by:

$$\nabla^2 \psi = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin(\theta)} \frac{\partial}{\partial \theta} \left(\sin(\theta) \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2(\theta)} \frac{\partial^2 \psi}{\partial \phi^2} \quad \dots(4.10)$$

Put equations (4.9) and (4.10) into eqⁿ (4.8), and separate the variables.

- **The radial equation:**

$$-\frac{\eta^2}{2mr^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial R}{\partial r} \right] + \left[-\frac{Ze^2}{4\pi\epsilon_0 r} + \frac{\lambda}{r^2} \right] R = ER \quad \dots(4.11)$$

- **And two angular equations:**

$$\sin \theta \frac{\partial}{\partial \theta} \left[\sin \theta \frac{\partial \Theta}{\partial \theta} \right] + \frac{2m}{\eta^2} \lambda \sin^2 \theta \cdot \Theta = \Lambda \Theta \quad \dots(4.12)$$

$$\frac{\partial^2 \Phi}{\partial \phi^2} = -\Lambda \Phi \quad \dots(4.13)$$

At this stage, λ and Λ are just arbitrary constants.

- **Note that three 1D equations are much better (easier to solve) than one 3D equation!**

What should we expect of our solutions?

- ◆ **3 quantum numbers, as we have boundary conditions in 3D**
- ◆ **The potential will only appear in the radial equation, as it is spherically symmetric**
- ◆ **The radial equation will tell us about the energy: this must depend on how far away the electron is from the nucleus.**
- ◆ **θ and ϕ equations will tell us about angular momentum.**

- **The ϕ equation**

Equation (4.6) is:

$$\frac{\partial^2 \Phi}{\partial \phi^2} = -\Lambda \Phi$$

This is the usual equation for simple harmonic motion! It has the general solution.

$$\Phi(\phi) = A e^{i\sqrt{\Lambda}\phi}$$

We must normalize this: $|\Phi(\phi)|^2$ represents the probability of finding the electron at angle ϕ , and integrated over all angles it must therefore give 1:

$$\int_0^{2\pi} |\Phi(\phi)|^2 = 1$$

Which yields

$$A = \frac{1}{\sqrt{2\pi}}$$

Furthermore, Φ must be single-valued; we require $\Phi(\phi + 2\pi) = \Phi(\phi)$. Hence, the only allowed values of Λ are given by

$$\sqrt{\Lambda} = 0, \pm 1, \pm 2, \dots$$

By convention, we define $\sqrt{\Lambda} = m_\lambda$

– this is called the magnetic quantum number. The final solutions for Φ , labelled by $m_\lambda = -\lambda, \dots, +\lambda$, are therefore:

$$\Phi_{m_\lambda}(\phi) = \frac{1}{\sqrt{2\pi}} e^{im_\lambda\phi}$$

• The θ equation

Substituting $\Lambda = m_\lambda^2$, equation (4.12) becomes

$$\sin \theta \frac{\partial}{\partial \theta} \left[\sin \theta \frac{\partial \Theta}{\partial \theta} \right] + \frac{2m}{\eta^2} \lambda \sin^2 \theta \cdot \Theta = m_\lambda^2 \Theta$$

We have to solve this for $m_\lambda = 0, \pm 1, \pm 2, \dots, \Lambda$ It turns out that this is only possible if $\lambda = \frac{\eta^2}{2m} \lambda(\lambda+1)$.

where $\lambda = 0, 1, 2, \dots, (n-1)$ and $\lambda \geq |m_\lambda|$.

l is called the *orbital angular momentum* quantum number. Solutions are labelled $\Theta_{\lambda, m_\lambda}(\theta)$;

• The radial equation

Re-write eqⁿ (4.11) using $\lambda = \frac{\eta^2}{2m} \lambda(\lambda+1)$:

$$-\frac{\eta^2}{2mr^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial R}{\partial r} \right] - \frac{Ze^2}{4\pi\epsilon_0 r} R + \frac{\eta^2}{2mr^2} \lambda(\lambda+1) R = ER$$

These terms are, in order, the radial kinetic energy, the potential energy, and the rotational kinetic energy; on the RHS is the total energy.

There are solutions to this equation if, and only if,

$$E = E_n = -\frac{R_y Z^2}{n^2}, \quad n = 1, 2, 3, \dots$$

Where $R_y = R_\infty hc = 2.18 \times 10^{-18} J = 13.6 \text{ eV}$ is called Rydberg energy.

n is called the *principal quantum number*.

The solutions $R_{n\lambda}(r)$ are labelled by n, λ and are called “radial wavefunctions”.

• Total solution

$$\psi_{n\lambda m_\lambda}(\mathbf{r}) = R_{n\lambda}(r) \Theta_{\lambda, m_\lambda}(\theta) \Phi_{m_\lambda}(\phi)$$

It is conventional to combine the Θ, Φ parts into one *spherical harmonics*:

$$\psi_{n\lambda m_\lambda}(\mathbf{r}) = R_{n\lambda}(r) Y_\lambda^{m_\lambda}(\theta, \phi)$$

For $n = 1; \lambda = 0; m_\lambda = 0$

$$\psi_{100}(r, \theta, \phi) = R_{10}(r) Y_0^0(\theta, \phi) = \frac{1}{\sqrt{\pi a_o^3}} e^{-r/a_o}, \text{ where } a_o \text{ is Bohr radius.}$$

For $n = 2; \lambda = 0, 1; m_\lambda = -1, 0, 1$

$$\psi_{200}(r, \theta, \phi) = R_{20}(r) Y_0^0(\theta, \phi) = \frac{1}{\sqrt{8\pi a_o^3}} \left(1 - \frac{r}{2a_o}\right) e^{-r/2a_o}$$

$$\psi_{210}(r, \theta, \phi) = R_{21}(r) Y_1^0(\theta, \phi) = \frac{1}{4\sqrt{2\pi a_o^3}} \frac{r}{a_o} e^{-r/2a_o} \cos \theta$$

$$\psi_{21\pm 1}(r, \theta, \phi) = R_{21}(r) Y_1^{\pm 1}(\theta, \phi) = \mu \frac{1}{8\sqrt{\pi a_o^3}} \frac{r}{a_o} e^{-r/2a_o} \sin \theta e^{\pm i\phi}$$

4.3 Selection rules

Only transitions between certain specific states are allowed; the so-called *selection rules* for allowed transitions,

$$\Delta\lambda = \lambda - \lambda' = \pm 1$$

$$\Delta m_\lambda = m_\lambda - m'_\lambda = 0, \pm 1$$

4.3 Classification of atomic orbitals

The angular momentum quantum number ℓ is conventionally designated by the following code:

$$\begin{array}{cccccc} \lambda=0 & 1 & 2 & 3 & 4 & \\ & s & p & d & f & g \end{array}$$

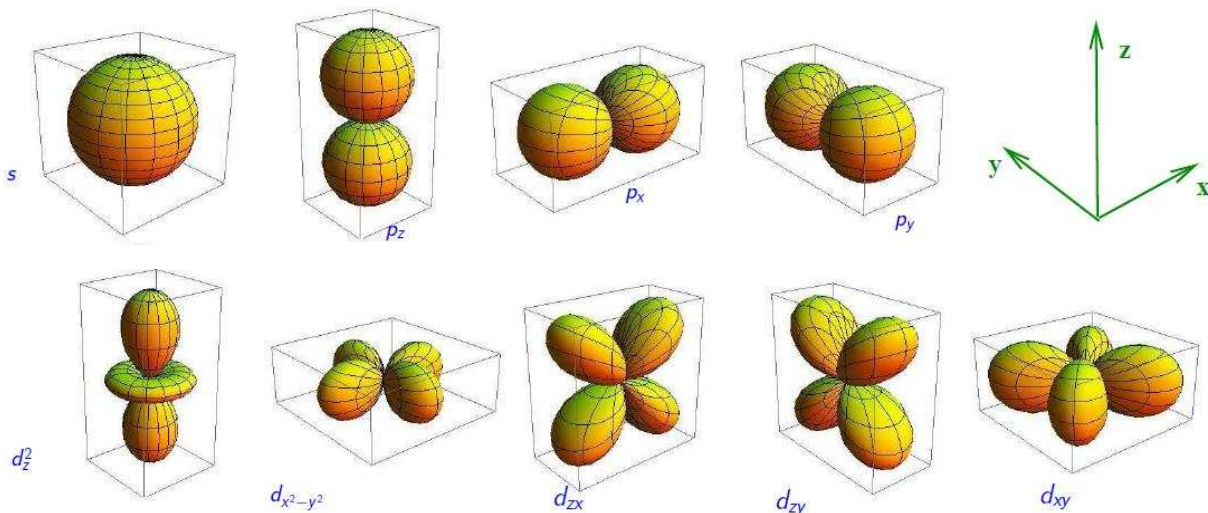
which comes from an old classification of atomic spectral lines: *sharp, principal, diffuse, fundamental*.

i) **s-orbitals** have $\lambda=0$ and therefore only $m_\lambda=0$ (see Fig. 4.1)..

ii) **p-orbitals** have $\lambda=1$, and, thus there are three of them ($m_\lambda = -1, 0, 1$).

- The $m_\lambda=0$ state is also called p_z because it is oriented along z (see Fig. 4.1).
- The $m_\lambda = \pm 1$ p-orbitals are in principle complex. However, one can take two suitable linear combination of them and obtain real orbitals. Remember that linear combinations of degenerate eigenfunctions are also eigenfunction with the same energy. Therefore one is free to take such linear combinations (see Fig. 4.1).
- Specifically, instead of the two complex orbitals with $m_\lambda = \pm 1$ orbitals, one can more conveniently take the two real orbitals p_x and p_y which have the same shape as p_z but are oriented along the x and y axes, respectively (see Fig. 4.1).

iii) **d-orbitals** have $\lambda=2$, and, thus, there are five of them. As for p orbitals, one can make them real with the use of linear combinations. In this real representation, d orbitals are termed $d_{z^2}, d_{x^2-y^2}, d_{xy}, d_{yz}, d_{zx}$ (see Fig. 4.1).



Example: The normalized wave function for the ground state of a hydrogen atom has the form

$$\psi_{100} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

Calculate the maximum probability of finding the electron in it's orbit.

Solution

The *radial probability density* is defined by

$$P_{n\lambda}(r)dr = \int_0^{2\pi} \int_0^\pi \psi_{n\lambda m_\lambda}^* \psi_{n\lambda m_\lambda} r^2 \sin \theta dr d\theta d\phi$$

$$P_{n\lambda}(r)dr = r^2 |R_{n\lambda}(r)|^2 dr \int_0^{2\pi} \int_0^\pi Y_\lambda^{*m_\lambda} Y_\lambda^{m_\lambda} \sin \theta d\theta d\phi$$

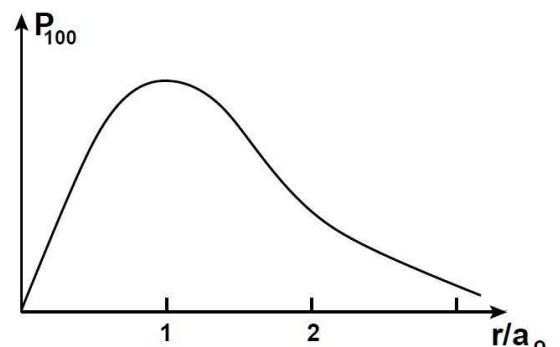
$$P_{10}(r)dr = \int_0^{2\pi} \int_0^\pi \left(\frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \right)^* \cdot \left(\frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \right) r^2 \sin \theta dr d\theta d\phi$$

$$P_{10}(r)dr = \frac{r^2}{\pi a_0^3} e^{-2r/a_0} dr \int_0^{2\pi} \int_0^\pi \sin \theta d\theta d\phi$$

$$P_{10}(r)dr = \frac{4r^2}{a_0^3} e^{-2r/a_0} dr$$

Now to find the maximum probability of P(r) we set

$$\frac{dP(r)}{dr} = 0$$



$$\frac{4}{a_0^3} \left[r^2 (-2/a_0) e^{-2r/a_0} + 2r e^{-2r/a_0} \right] = 0$$

$$e^{-2r/a_0} \left[-\frac{8r^2}{a_0^4} + \frac{8r}{a_0^3} \right] = 0 \Rightarrow r = a_0$$



Homework:

The normalized wave function for the 2s state of a hydrogen atom has the form

$$\psi = \frac{1}{\sqrt{8\pi a_0^3}} \left(1 - \frac{r}{2a_0} \right) e^{-r/2a_0}$$

Calculate the maximum probability of finding the electron in its orbit.