

## The Hydrogen Atom

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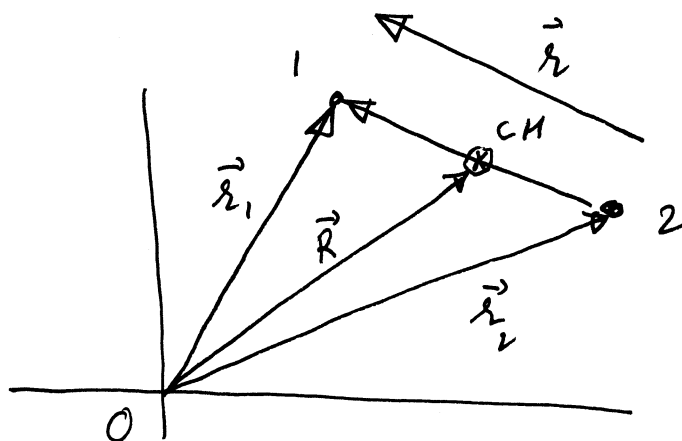
The potential energy  $V(r) = -Ze^2/4\pi\epsilon_0 r$ , which represents the attractive Coulomb interaction between an atomic nucleus of charge  $+Ze$  and an electron of charge  $-e$ , provides another equation that can be solved analytically.

The calculated energy levels are in agreement with the observed energy levels of the hydrogen atom ( $Z=1$ ), the singly charged helium ion ( $Z=2$ ) etc.

### Two-body system, reduced mass

The hydrogen atom is a two-body problem, consisting of a proton (the nucleus) and an electron. The proton is very heavy compared to the electron.

Let us consider a general two-body system where the particles are labelled 1 and 2.



Suppose that the force between the two particles is central, i.e., the line of action of the force that one particle exerts on the other is the same as the line joining the two particles. In such a situation the potential energy depends only upon the distance between the two particles, i.e.,

$$V = V(|\vec{r}_1 - \vec{r}_2|) \quad \dots \quad (1)$$

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The classical Hamiltonian of the system is

$$H = T + V = \frac{1}{2} m_1 \dot{\vec{r}}_1^2 + \frac{1}{2} m_2 \dot{\vec{r}}_2^2 + V(|\vec{r}_1 - \vec{r}_2|)$$

$$x \quad H = \frac{\vec{p}_1^2}{2m_1} + \frac{\vec{p}_2^2}{2m_2} + V(|\vec{r}_1 - \vec{r}_2|) \quad \dots (2)$$

In quantum mechanics, all physical observables are represented by Hermitian operators. In the coordinate representation, the momentum operator is

$$\hat{\vec{p}} \rightarrow -i\hbar \vec{\nabla}$$

and the position operator is a multiplicative operator

$$\hat{\vec{R}} \rightarrow \vec{r}$$

where  $\vec{r}$  is the eigenvalue of  $\hat{\vec{R}}$ .

The Hamiltonian operator of the two-body system is then

$$\hat{H} = -\frac{\hbar^2}{2m_1} \vec{\nabla}_1^2 - \frac{\hbar^2}{2m_2} \vec{\nabla}_2^2 + V(|\vec{r}_1 - \vec{r}_2|) \quad (3)$$

where

$$\vec{\nabla}_1^2 = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}$$

$$\vec{\nabla}_2^2 = \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2}$$

where  $(x_1, y_1, z_1)$  are the Cartesian coordinates of particle 1 and  $(x_2, y_2, z_2)$  are the Cartesian coordinates of particle 2.

Since  $V$  depends only on  $|\vec{r}_1 - \vec{r}_2|$  i.e.,  $V$  depends on  $(x_1 - x_2)$ ,  $(y_1 - y_2)$  and  $(z_1 - z_2)$ , it is convenient to make the following

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change of variables :

$$\vec{R} = \frac{m_1 \vec{r}_1 + m_2 \vec{r}_2}{m_1 + m_2}$$

$$\vec{r} = \vec{r}_1 - \vec{r}_2$$

where  $\vec{R}$  is the radius vector of the center of mass (CM) of the system and  $\vec{r}$  is the relative vector.

In terms of the new variables  $\vec{R}$  and  $\vec{r}$ , the classical Hamiltonian can be written as

$$H = \frac{1}{2} M \dot{\vec{R}}^2 + \frac{1}{2} \mu \dot{\vec{r}}^2 + V(|\vec{r}|)$$

$$= \frac{\vec{P}_R^2}{2M} + \frac{\vec{P}_r^2}{2\mu} + V(r) \quad \dots, (4)$$

where  $\vec{P}_R = M \dot{\vec{R}}$  and  $\vec{P}_r = \mu \dot{\vec{r}}$  and

$$M = m_1 + m_2$$

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

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We see that the classical Hamiltonian splits in two parts, one part containing only  $\vec{R}$  and the other containing  $\vec{r}$  only. The part depending on  $\vec{R}$ , i.e.,  ~~$\frac{1}{2} M \dot{\vec{R}}^2$~~   $\frac{1}{2} M \dot{\vec{R}}^2$ , is the kinetic energy of the CM as if all the mass is concentrated there. The other part,  $\frac{1}{2} \mu \dot{\vec{r}}^2 + V(r)$ , is the total energy (kinetic plus potential) of relative motion, i.e., the total energy in the CM frame.

The Hamiltonian operator  $\hat{H}$  as given in Eq. (3) can also be separated, in two parts — one part depending on  $\vec{R}$  and the other on  $\vec{r}$ .

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$$\hat{H} = -\frac{\hbar^2}{2M} \vec{\nabla}_R^2 - \frac{\hbar^2}{2\mu} \vec{\nabla}_r^2 + V(r) \quad \dots (5)$$

where

$$\vec{\nabla}_R^2 = \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2}$$

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

where  $(X, Y, Z)$  are the coordinates of the CM radius vector  $\vec{R}$  and  $(x, y, z)$  are the coordinates of the relative vector  $\vec{r}$ .

The Schrödinger equation for the system is

$$\left[ -\frac{\hbar^2}{2M} \vec{\nabla}_R^2 - \frac{\hbar^2}{2\mu} \vec{\nabla}_r^2 + V(r) \right] \Psi(\vec{r}, \vec{R}) = E \Psi(\vec{r}, \vec{R}) \quad \dots (6)$$

This equation can be solved by the technique of separation of variables.

First, we write

$$\Psi(\vec{r}, \vec{R}) = \Phi(\vec{R}) \psi(\vec{r}) \quad \dots \quad (7)$$

Substitute (7) in (6) and divide by  $\Psi(\vec{r}, \vec{R})$ . We get

$$\frac{1}{\Phi(\vec{R})} \left[ -\frac{\hbar^2}{2M} \vec{\nabla}_R^2 \Phi(\vec{R}) \right] + \frac{1}{\psi(\vec{r})} \left[ -\frac{\hbar^2}{2\mu} \vec{\nabla}_r^2 + V(r) \right] \psi(\vec{r}) = E \quad \dots \quad (8)$$

Since the first term on the left hand side depends only on  $\vec{R}$  and the second term depends only on  $\vec{r}$ , this equation is true if each term is equal to a constant. We write

$$\frac{1}{\Phi(\vec{R})} \left[ -\frac{\hbar^2}{2M} \vec{\nabla}_R^2 \Phi(\vec{R}) \right] = E_{CM} \text{ (constant)}$$

$$\frac{1}{\psi(\vec{r})} \left[ -\frac{\hbar^2}{2\mu} \vec{\nabla}_r^2 + V(r) \right] \psi(\vec{r}) = E' \text{ (constant)}.$$

Therefore

$$E_{CM} + E' = E.$$



We can interpret  $E_{CM}$  is the energy due to center-of-mass motion as observed in the lab frame and  $E'$  is the energy due to motion about the CM, i.e.,  $E'$  is the energy in the CM frame. ~~due to internal motion~~. Total energy  $E$  in the lab frame is the energy of the CM assuming the entire mass of the system is concentrated there, plus energy due motion about the center of mass, i.e.,  $E = E_{CM} + E'$ .

The equations satisfied by  $\Phi(\vec{R})$  and  $\psi(\vec{r})$  are then

$$-\frac{\hbar^2}{2M} \vec{\nabla}_R^2 \Phi(\vec{R}) = E_{CM} \Phi(\vec{R}) \quad \dots (9)$$

and

$$-\frac{\hbar^2}{2\mu} \vec{\nabla}_r^2 \psi(\vec{r}) + V(r) \psi(\vec{r}) = E' \psi(\vec{r}) \quad \dots (10)$$

(10)

The wave function  $\Phi(\vec{R})$  is that of a free particle of mass  $M$  moving with energy  $E_{CM}$ .  $\Phi(\vec{R})$  has the ~~immediate~~ form

$$\Phi(\vec{R}) = e^{i \vec{P} \cdot \vec{R} / \hbar}$$

where

$$P = \sqrt{2M E_{CM}}.$$

In the CM frame,  $\vec{R} = 0$  and  $\Phi(\vec{R}) = \text{constant}$ .

Equation (10) gives us the wave function  $\psi(\vec{r})$  and the energies  $E'$  due to the internal motion of the system. Note that  $\vec{r} = \vec{r}_1 - \vec{r}_2$  is the relative vector of the two particles and  $\psi(\vec{r})$  is the wave function of relative motion. Eq. (10) tells us that the wave function of relative motion is exactly that of a fictitious particle of mass  $\mu = m_1 m_2 / (m_1 + m_2)$  moving

in a central potential with a fixed center,  $\vec{r}$  being the radius vector of the fictitious particle from the force center.

We will solve Eq (10) to find the <sup>energy</sup> eigenvalues and eigenfunctions for a hydrogen atom. We will omit the prime on  $E$  from now on.

## Recapitulation.

For a single particle of mass  $\mu$  in a central potential, the time-independent Schrödinger equation is

$$\left[ -\frac{\hbar^2}{2\mu} \nabla^2 + V(r) \right] \psi(\vec{r}) = E \psi \quad \dots \dots (1)$$

We know

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right]$$

and

$$\hat{L}^2 = -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right]$$

Therefore

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) - \frac{\hat{L}^2}{\hbar^2 r^2} \quad \dots \dots (2)$$

Note that, we can write

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) = \frac{1}{r} \frac{\partial^2}{\partial r^2} r.$$

This relation will be useful when we want to write <sup>the differential</sup> equation for  $u_l(r) = r R_l(r)$  from the radial equation satisfied by  $R_l(r)$ . The full wave function is

$$\begin{aligned} \Psi_{Elm}(r, \theta, \phi) &= R_{El}(r) Y_{lm}(\theta, \phi) \\ &= \frac{u_{El}(r)}{r} Y_{lm}(\theta, \phi) \quad \dots \quad (3) \end{aligned}$$

We also note that

$$\hat{L}^2 Y_{lm}(\theta, \phi) = l(l+1)\hbar^2 Y_{lm}(\theta, \phi) \quad \dots \quad (4)$$

Now, using Eqs. (2), (3) and (4) in Eq. (1) we have

$$\begin{aligned}
 & -\frac{\hbar^2}{2\mu} \left[ Y_{lm}(\theta, \phi) \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR_l}{dr} \right) - \frac{l(l+1)\hbar^2}{2\mu r^2} Y_{lm} R_l \right] \\
 & + V(r) Y_{lm} R_l = E Y_{lm} R_l,
 \end{aligned} \tag{14}$$

Here, we have written  $R_{El}(r) \equiv R_l(r)$  omitting the subscript  $E$ . We cancel  $Y_{lm}$  and rearrange terms in the above equation to get

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR_l}{dr} \right) + \frac{2\mu}{\hbar^2} \left[ E - V(r) - \frac{l(l+1)\hbar^2}{2\mu r^2} \right] R_l(r) = 0 \quad \dots (5)$$

Noting that

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) = \frac{1}{r} \frac{d^2}{dr^2} r,$$

Eq. (5) can also be written as

$$\frac{1}{r} \frac{d^2}{dr^2} (r R_l) + \frac{2\mu}{\hbar^2} \left[ E - V(r) - \frac{l(l+1)\hbar^2}{2\mu r^2} \right] R_l = 0 \quad \dots (6)$$

Now, let

$$R_\ell(r) = \frac{u_\ell(r)}{r},$$

i.e.,  $u_\ell(r) = r R_\ell(r)$ . Then Eq (6) is

$$\frac{1}{r} \frac{d^2 u_\ell(r)}{dr^2} + \frac{2\mu}{\hbar^2} \left[ E - V(r) - \frac{\ell(\ell+1)\hbar^2}{2\mu r^2} \right] R_\ell(r) = 0$$

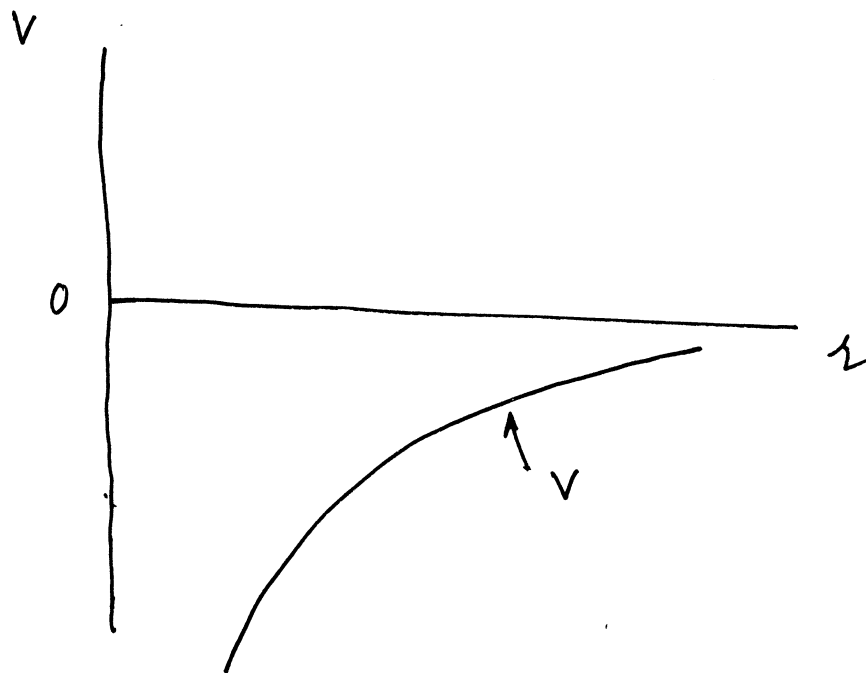
$$\text{or} \quad \frac{d^2 u_\ell}{dr^2} + \frac{2\mu}{\hbar^2} \left[ E - V(r) - \frac{\ell(\ell+1)\hbar^2}{2\mu r^2} \right] u_\ell(r) = 0. \quad \dots (7)$$

## Hydrogen atom

Noting that the proton charge is  $+e$  and the electron charge is  $-e$ , the potential energy for the attractive Coulomb force between the proton and the ~~nearest~~ electron is

$$V(r) = - \frac{e^2}{4\pi\epsilon_0 r} \quad \dots \dots \dots (8)$$

where  $r$  is the distance between the proton and the electron.





We are looking for bound state solutions of the Schrödinger equation. For bound states in the above Coulomb potential  $E < 0$ , so we write  $E = -|E|$ . The radial equation for  $u_\ell(r)$  is then (see Eq. (7))

$$\frac{d^2 u_\ell}{dr^2} + \frac{2\mu}{\hbar^2} \left[ -|E| + \frac{e^2}{4\pi\epsilon_0 r} - \frac{\ell(\ell+1)\hbar^2}{2\mu r^2} \right] u_\ell = 0 \quad \dots (8)$$

Let us define a positive parameter  $\kappa$  (kappa) as

$$\kappa = \sqrt{\frac{2\mu(-E)}{\hbar^2}} = \sqrt{\frac{2\mu|E|}{\hbar^2}} \quad \dots (9)$$

The parameter  $\kappa$  has the dimensions of inverse length, i.e., the units of  $\kappa$  in the SI system is  $\text{m}^{-1}$ .

We rewrite Eq. (8) as

$$\frac{d^2 u_l}{dr^2} + \left[ -K^2 + \frac{2\mu}{\hbar^2} \cdot \frac{e^2}{4\pi\epsilon_0 r} - \frac{l(l+1)}{r^2} \right] u_l = 0$$

Dividing by  $K^2$  and shifting the term within the square brackets to the right, we have

$$\frac{1}{K^2} \frac{d^2 u_l}{dr^2} = \left[ 1 - \frac{\mu e^2}{2\pi\epsilon_0 \hbar^2 K^2 r} + \frac{l(l+1)}{K^2 r^2} \right] u_l \quad \text{--- (9)}$$

We now make a change of variable

$$\rho = Kr \quad \text{--- (10)}$$

where  $\rho$  is dimensionless. We also define

$$\rho_0 = \frac{\mu e^2}{2\pi\epsilon_0 \hbar^2 K} \quad \text{--- (11)}$$

Hence, Eq. (9) becomes

$$\frac{d^2 u_l}{dp^2} = \left[ 1 - \frac{p_0}{p} + \frac{l(l+1)}{p^2} \right] u_l \quad \dots (12)$$

where  $u_l$  in this equation is considered a function of  $p$ .

### Solutions

Next we examine the asymptotic forms of the solution. As  $p \rightarrow \infty$ , the constant term in the brackets on the right hand side of (12) dominates, so (approximately)

$$\frac{d^2 u_l}{dp^2} = u_l.$$

The general solution is

$$u_l(p) = A e^{-p} + B e^p.$$

But  $e^p$  blows up as  $p \rightarrow \infty$ , so  $B = 0$ . Evidently

$$u(p) \sim A e^{-p}$$

for large  $p$ .

Next, we examine the behaviour of the solution as  $\rho \rightarrow 0$ . If  $l$  is not zero, the centrifugal term dominates as  $\rho \rightarrow 0$ . Then we have approximately

$$\frac{d^2 u}{d\rho^2} = \frac{l(l+1)}{\rho^2} u.$$

The general solution is

$$u(\rho) = C\rho^{l+1} + D\rho^{-l}$$

But  $\rho^{-l}$  blows up as  $\rho \rightarrow 0$ , so  $D=0$ . Thus

$$u_l(\rho) \sim C\rho^{l+1} \quad (l > 0) \quad \dots \dots \dots (13)$$

for small  $\rho$ . The above analysis breaks down for  $l=0$ .

For  $l=0$ , we have

$$\frac{d^2 u_0}{d\rho^2} = \left(1 - \frac{\rho_0}{\rho}\right) u_0$$

To find the behaviour of  $u_0$  as  $\rho \rightarrow 0$ , we write  $u_0$  as a power series. Suppose that the lowest power of  $\rho$  in the series is  $\rho^s$ . So, we write

$$u_0 \approx \rho^s (a_0 + a_1 \rho + \dots) \quad \text{with } a_0 \neq 0$$

(2)

Substituting this in the differential equation, we get

$$s(s-1)a_0\rho^{s-2} + (s+1)sa_1\rho^{s-1} + \dots$$

$$= (a_0\rho^s + a_1\rho^{s+1} + \dots) - \rho_0(a_0\rho^{s-1} + a_1\rho^s + \dots).$$

The coefficients of the same power of  $\rho$  on both sides of this equation must be equal. We notice that the lowest power of  $\rho$  on the left side is  $\rho^{s-2}$  while the lowest power on the right hand side is  $\rho^{s-1}$ . Therefore, the coefficient of  $\rho^{s-2}$  on the left side is zero. Since  $a_0 \neq 0$ , we must have

$$s(s-1) = 0$$

$\therefore s = 0$  or  $s = 1$ . If  $s = 1$ , then

$$u_0(\rho) \underset{\rho \rightarrow 0}{\sim} \rho \rightarrow 0$$

On the other hand if  $s = 0$

$$u_0(\rho) \underset{\rho \rightarrow 0}{\sim} c \quad (c = \text{constant}).$$

With  $s=0$ , the full wave function near the origin would be

$$\psi \underset{r \rightarrow 0}{\sim} \frac{C}{r} Y_{00} = \frac{C}{r} \frac{1}{\sqrt{4\pi}} = \frac{\text{const}}{r}.$$

So the wave function would diverge at the origin.

This in itself is not a disqualification for  $\psi$  is still square integrable. The problem is that  $\psi$  does not satisfy the Schrödinger equation at the origin. This is because

$$\nabla^2 \frac{1}{r} = -4\pi \delta(\vec{r}).$$

Thus  $V(r)$  must contain a delta function at the origin. But  $V(r) = -\text{const}/r$  does not contain a delta function.

Hence for  $l=0$ , we must have  $u \sim \rho^s = \rho$  ( $s=1$ ).

Thus for all  $l$

$$u_l(r) \sim \rho^{l+1} \text{ as } \rho \rightarrow 0, \text{ (for all } l). \quad \dots (14)$$

The next step is to peel off the asymptotic behaviour from  $u_\ell(\rho)$ , <sup>by</sup> introducing a new function  $v_\ell(\rho)$ ;

$$u_\ell(\rho) = \rho^{\ell+1} e^{-\rho} v_\ell(\rho) \quad - - - - - (15)$$

We can ~~so~~ now substitute Eq. (15) in Eq. (12) to get a differential equation for  $v_\ell(\rho)$ . First, we have to calculate  $d^2 u_\ell / d\rho^2$  in terms of the derivatives of  $v_\ell(\rho)$  using Eq. (15).

$$\begin{aligned} \frac{du_\ell}{d\rho} &= (\ell+1)\rho^\ell e^{-\rho} v_\ell(\rho) - \rho^{\ell+1} e^{-\rho} v_\ell(\rho) + \rho^{\ell+1} e^{-\rho} \frac{dv_\ell}{d\rho} \\ &= \rho^\ell e^{-\rho} \left[ (\ell+1-\rho) v_\ell + \rho \frac{dv_\ell}{d\rho} \right] \end{aligned}$$

$$\begin{aligned} \therefore \frac{d^2 u_\ell}{d\rho^2} &= \left[ \ell \rho^{\ell-1} e^{-\rho} - \rho^\ell e^{-\rho} \right] \left[ (\ell+1-\rho) v_\ell + \rho \frac{dv_\ell}{d\rho} \right] \\ &\quad + \rho^\ell e^{-\rho} \left[ (\ell+1-\rho) \frac{dv_\ell}{d\rho} - v_\ell(\rho) + \rho \frac{d^2 v_\ell}{d\rho^2} + \frac{dv_\ell}{d\rho} \right] \\ &= \rho^\ell e^{-\rho} \left( \frac{\ell}{\rho} - 1 \right) \left[ (\ell+1-\rho) v_\ell + \rho \frac{dv_\ell}{d\rho} \right] \\ &\quad + \rho^\ell e^{-\rho} \left[ (\ell+1-\rho) \frac{dv_\ell}{d\rho} - v_\ell(\rho) + \rho \frac{d^2 v_\ell}{d\rho^2} + \frac{dv_\ell}{d\rho} \right] \end{aligned}$$

$$\begin{aligned}
 \frac{d^2 u_l}{d\rho^2} &= \rho^l e^{-\rho} \left\{ \left[ \frac{(l-\rho)}{\rho} (l-\rho+1) v_l \right. \right. \\
 &\quad \left. \left. + \left[ \frac{l-\rho}{\rho} \cdot \rho + (l+1-\rho) + 1 \right] \frac{dv_l}{d\rho} + \rho \frac{d^2 v_l}{d\rho^2} \right\} \\
 &= \rho^l e^{-\rho} \left\{ \left[ \frac{l(l+1)}{\rho} + \rho - 2l - 2 \right] v_l(\rho) \right. \\
 &\quad \left. + 2(l+1-\rho) \frac{dv_l}{d\rho} + \rho \frac{d^2 v_l}{d\rho^2} \right\} \dots (16)
 \end{aligned}$$

Substitute (16) in (12). We get

$$\rho \frac{d^2 v_l}{d\rho^2} + 2(l+1-\rho) \frac{dv_l}{d\rho} + [l(l+1) - 2(l+1)\rho] v_l = 0. \dots (17)$$

Series solution of Eq. (17)

We assume that the solution of (17) can be written in the form

$$v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j, \dots (18)$$

Our problem is to determine the coefficients  $(c_0, c_1, \dots, c_n, \dots)$ . Differentiating term by term



$$\frac{dv}{d\rho} = \sum_{j=0}^{\infty} j c_j \rho^{j-1}$$

Let

$$j-1 \rightarrow j$$

in the above sum. Then

$$\frac{dv}{d\rho} = \sum_{j=-1}^{\infty} (j+1) c_{j+1} \rho^j = \sum_{j=0}^{\infty} (j+1) c_{j+1} \rho^j \quad \dots (19)$$

Differentiating again

$$\frac{d^2 v}{d\rho^2} = \sum_{j=0}^{\infty} j(j+1) c_{j+1} \rho^{j-1} \quad \dots (20)$$

Substituting Eqs. (18), (19) and (20) into Eq. (17),

we have

$$\begin{aligned} & \sum_{j=0}^{\infty} j(j+1) c_{j+1} \rho^j + 2(\ell+1) \sum_{j=0}^{\infty} (j+1) c_{j+1} \rho^j \\ & - 2 \sum_{j=0}^{\infty} j c_j \rho^j + (\rho_0 - 2\ell - 2) \sum_{j=0}^{\infty} c_j \rho^j = 0 \end{aligned}$$

Equating coefficients of like powers yields

$$j(j+1)c_{j+1} + 2(l+1)(j+1)c_{j+1} - 2jc_j + (p_0 - 2l - 2)c_j = 0$$

$$^* \quad c_{j+1} = \left[ \frac{2(j+l+1) - p_0}{(j+1)(j+2l+2)} \right] c_j \quad \dots \dots (21)$$

This recursive formula determines the coefficients and hence the function  $v(\rho)$ . We start with  $c_0$ , then equation (21) gives us  $c_1$ . Putting  $c_1$  back in Eq. (21) we get  $c_2$  and so on. The constant  $c_0$  becomes an overall constant which is found from normalization.

For large  $j$  (this corresponds to large  $\rho$  where the higher powers dominate), the recursion formula (Eq. (21)) can be written as

$$c_{j+1} \approx \frac{2j}{j(j+1)} = \frac{2}{j+1} c_j$$

If this were exact, then

$$\begin{aligned} c_j &= \frac{c_j}{c_{j-1}} \cdot \frac{c_{j-1}}{c_{j-2}} \cdot \dots \cdot \frac{c_1}{c_0} c_0 \\ &= \frac{2}{j} \cdot \frac{2}{j-1} \cdot \dots \cdot \frac{2}{1} c_0 \\ &= \frac{2^j}{j!} c_0, \end{aligned}$$

so

$$v_l(p) \approx c_0 \sum_{j=0}^{\infty} \frac{2^j}{j!} p^j = c_0 e^{2p}$$

and hence

$$u_l(p) = p^{l+1} e^{-p} v_l(p) = p^{l+1} e^{-p} c_0 e^{2p}$$

$$u_l(p) = c_0 p^{l+1} e^p \dots \dots \dots (22)$$

which blows up at large  $p$ . The only way to

salvage the situation is to impose an extra

condition ~~condition~~ so that the series for

$v_l(p)$  terminates, i.e.,  $v_l(p)$  becomes a polynomial.

Suppose that the highest power of  $p$  in the polynomial is  $j_{\max}$ . Then we must have  $c_{j_{\max}} \neq 0$ , but

$$c_{j_{\max}+1} = 0 \quad . \quad . \quad . \quad . \quad . \quad (23)$$

This will ensure that ~~all~~ all coefficients higher than  $c_{j_{\max}+1}$  are also zero. Imposing the restriction

(23) on the recursion relation (Eq. (21)) we have

$$2(j_{\max} + l + 1) - p_0 = 0.$$

Defining

$$n = j_{\max} + l + 1 \quad . \quad . \quad . \quad . \quad . \quad (23)$$

(the so-called principle quantum number), we have

$$p_0 = 2n \quad . \quad . \quad . \quad . \quad . \quad (24)$$

Note that, since  $j_{\max}$  and  $l$  are either positive integers or zero,  $n$  can only assume values which are positive integers i.e.,  $n = 1, 2, 3, \dots$ .

(29)

But  $\rho_0$  determines  $E$  in accordance to Eqs. (9) and

(11) :

$$E = - \frac{\hbar^2 k^2}{2\mu} = - \frac{\hbar^2}{2\mu} \cdot \left( \frac{\mu e^2}{2\pi\epsilon_0 \hbar^2 \rho_0} \right)^2$$

$$= - \frac{\hbar^2}{2\mu} \frac{\mu^2}{\hbar^4} \left( \frac{e^2}{2\pi\epsilon_0} \right)^2 \frac{1}{4n^2}$$

i.e

$$\begin{aligned} E_n &= - \left[ \frac{\mu}{2\hbar^2} \cdot \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2} \\ &= \frac{E_1}{n^2} ; \quad n = 1, 2, \dots \end{aligned}$$

..... (25)

This is the famous Bohr formula.

## Numerical calculation. of the energy levels

$$\hbar = 1.054\,572 \times 10^{-34} \text{ J s}$$

$$c = 2.997\,925 \text{ m s}^{-1}$$

$$\hbar c = 197.326\,979 \text{ MeV fm} \quad (1 \text{ fm} = 10^{-15} \text{ m})$$

Mass of proton

$$m_p = 1.672\,62 \times 10^{-27} \text{ kg}$$

$$= 938.272 \text{ MeV}/c^2$$

Mass of electron

$$m_e = 9.109\,384 \times 10^{-31} \text{ kg}$$

$$= 0.510\,999 \text{ MeV}/c^2$$

$\therefore$  electron-proton reduced mass

$$\mu = \frac{m_e m_p}{m_e + m_p} = 0.510\,721 \text{ MeV}/c^2$$

$$e = 1.602177 \times 10^{-19} \text{ C}$$

$$\epsilon_0 = 8.8541878 \times 10^{-12} \text{ F m}^{-1}$$

$$\therefore \frac{1}{4\pi\epsilon_0} = 8.987551 \times 10^9 \text{ N m}^2 \text{ C}^{-2}$$

Fine structure constant

$$\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} = \frac{1}{137.035999}$$

Now

$$\frac{\mu}{2\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \quad \left| E_n = - \left[ \frac{\mu}{2\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2} \right.$$

$$= \frac{\mu c^2}{2} \left( \frac{e^2}{4\pi\epsilon_0 \hbar c} \right)^2$$

$$= \frac{0.510721 \text{ MeV}}{2} \times \frac{1}{(137.036)^2}$$

$$~~= 0.00186345 \text{ MeV}~~$$

$$= 13.598 \times 10^{-6} \text{ MeV}$$

$$= 13.6 \text{ eV}$$

$$\therefore \boxed{E_n = - \frac{13.6}{n^2} \text{ eV}} \quad n = 1, 2, \dots \quad (26)$$

### Bohr radius

Previously we defined  $p_0$  as (Eq. (11))

$$p_0 = \frac{\mu e^2}{2\pi\epsilon_0 \hbar^2 K}$$

and the energy quantitation condition is (Eq. (24))

$$p_0 = 2n, \quad n = 1, 2, \dots$$

Therefore

$$2n = \frac{\mu e^2}{2\pi\epsilon_0 \hbar^2 K}$$

$$\text{or } K = \frac{\mu e^2}{4\pi\epsilon_0 \hbar^2 n} = \frac{1}{na} \dots (27)$$



(33)

where we have defined

$$a = \frac{4\pi\epsilon_0 \hbar^2}{\mu e^2} = 0.529 \times 10^{-10} \text{ m} \quad (28)$$

The quantity  $a$  is called the Bohr radius.

### Calculation of Bohr radius

$$a = \frac{4\pi\epsilon_0 \hbar^2}{\mu e^2} = \frac{4\pi\epsilon_0 \hbar^2 c^2}{\mu c^2 e^2} = \frac{\hbar c}{(\mu c^2) (e^2 / 4\pi\epsilon_0 \hbar c)}$$

$$= \frac{\hbar c}{(\mu c^2) \alpha} = \frac{197.3269788 \text{ MeV fm}}{(0.510721 \text{ MeV}) \left( \frac{1}{137.036} \right)}$$

$$= 5.29 \times 10^4 \text{ fm}$$

$$= 5.29 \times 10^4 \times 10^{-15} \text{ m}$$

$$= 5.29 \times 10^{-11} \text{ m}$$

$$= 0.529 \text{ \AA} \quad (1 \text{ \AA} = 10^{-10} \text{ m})$$

$$= 0.0529 \text{ nm} \quad (1 \text{ nm} = 10^{-9} \text{ m}).$$

### Wave function.

Previously we defined  $\rho$  as (Eq. (10))

$$\rho = \kappa r.$$

In view of Eq. (27),

$$\rho = \frac{r}{na} \quad \dots \quad (29)$$

The spatial wave functions for hydrogen are labeled by three quantum numbers  $n, l$  and  $m$ :

$$\Psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi) \quad \dots \quad (30)$$

where

$$R_{nl}(r) = \frac{1}{r} \rho^{l+1} e^{-\rho} v_{nl}(\rho) \quad \dots \quad (31)$$

where  $v_{nl}(\rho)$  is a polynomial of degree

$$j_{\max} = n - l - 1$$

in  $\rho$ . The coefficients<sup>of  $v_{nl}$</sup>  are determined (up to an overall normalization factor) by the recursion formula (Eq. (21) with  $\rho_0 = 2n$ ):

$$C_{j+1} = \frac{2(j+l+1-n)}{(j+1)(j+2l+2)} C_j \dots \dots (32)$$

### Ground state

For the ground state  $n=1$  and

$$E_1 = -13.6 \text{ eV}.$$

The wavefunction ~~in~~ <sup>for</sup> a general state  $(n, l, m)$  is

$$\begin{aligned} \psi_{nlm}(r, \theta, \varphi) &= R_{nl}(r) Y_{lm}(\theta, \varphi) \\ &= \frac{1}{r} U_{nl}(r) Y_{lm}(\theta, \varphi) \\ &= \frac{1}{r} \rho^{l+1} e^{-\rho} v_{nl}(\rho) Y_{lm}(\theta, \varphi) \quad (33) \end{aligned}$$

where  $\rho = kr = \frac{r}{na}$  and  $v_{nl}(\rho)$  is a polynomial in

$\rho$  with degree  $n-l-1$ , i.e., the highest power  $j_{\max}$  of  $\rho$

in  $v_{nl}(\rho)$  is

$$j_{\max} = n - l - 1 \quad (j_{\max} \geq 0; j_{\max} \text{ is not negative})$$

$$\text{or} \quad n = j_{\max} + l + 1 \quad (34)$$

If  $n=1$  (ground state) then we have  $l=0$  and  $j_{\max} = 0$ .

So  $V_{nl}(r)$  is in fact a constant when  $n=1$  and  $l=0$ .  
i.e.,

$$V_{10}(r) = C_0 \text{ (const).}$$

Therefore the radial wave function for the ground state is

$$\begin{aligned} R_{10}(r) &= \frac{1}{2} r e^{-r/a} C_0 \\ &= \frac{1}{2} \left( \frac{r}{a} \right) e^{-r/a} C_0 \\ &= \frac{C_0}{a} e^{-r/a} \\ &= C e^{-r/a} \quad \dots \dots \dots (35) \end{aligned}$$

where  $C$  is a constant. The value of  $C$  is to be found from normalization. The normalization condition for the full wave function  $\psi_{nlm}$  is

$$\int \psi_{n\ell m}^*(r, \theta, \phi) \psi_{n\ell m}(r, \theta, \phi) d^3r = 1$$

$$\text{or } \int_0^\infty R_{n\ell}^2(r) r^2 dr \underbrace{\int Y_{\ell m}^*(\theta, \phi) Y_{\ell m}(\theta, \phi) d\Omega}_{=1} = 1$$

$$\text{or } \int_0^\infty R_{n\ell}^2(r) r^2 dr = 1 \quad \text{--- (36)}$$

In terms of  $u_{n\ell}(r) = r R_{n\ell}(r)$ , we have

$$\int_0^\infty u_{n\ell}^2(r) dr = 1 \quad \text{--- (37)}$$

For the ground state ( $n=1, \ell=0$ ), the radial wave function is given in Eq. (35). Normalizing the radial function we have

$$|C|^2 \int_0^\infty e^{-2r/a} r^2 dr = 1$$

We have the standard integral

$$\int_0^{\infty} x^n e^{-ax} dx = \frac{n!}{a^{n+1}}, \quad a > 0, \quad n = 0, 1, 2, \dots$$

Therefore

$$|C|^2 \frac{2!}{(2/a)^3} = 1$$

$$\propto |C|^2 a^3 / 4 = 1$$

$$\propto |C|^2 = \frac{4}{a^3}$$

Taking  $C$  to be real and positive

$$C = \frac{2}{\sqrt{a^3}}$$

Therefore, the normalized radial wave function for the ground state of hydrogen atom is ( $n=1, l=0$ )

$$R_{10}(r) = \frac{2}{\sqrt{a^3}} e^{-r/a}$$

The normalized full wave function for the ground state is then ( $n \ell m = 100$ )

$$\Psi_{100} = \frac{2}{\sqrt{a^3}} e^{-r/a} Y_{00} \quad \left| \quad Y_{00} = \text{const} = \frac{1}{\sqrt{4\pi}} \right.$$

$$\propto \Psi_{100} = \frac{2}{\sqrt{a^3}} e^{-r/a} \frac{1}{\sqrt{4\pi}}$$

$$\propto \boxed{\Psi_{100} = \frac{2}{\sqrt{4\pi a^3}} e^{-r/a}} \quad \dots \dots \dots (38)$$

Note that the ground state wave function does not depend on  $\theta$  and  $\varphi$ .

Wave function for the first excited state ( $n=2$ )

---

The energy of the first excited state is

$$E_2 = - \frac{13.6}{2^2} = - \frac{13.6}{4} = - 3.4 \text{ eV}$$

Now

$$n = j_{\max} + l + 1$$

where  $j_{\max}$  is the maximum power of  $\rho$  in  $\psi_{nl}$  (Eq. (31)).

With  $n=2$ , we can have either ( $l=0, j_{\max}=1$ ) or

( $l=1$  and  $j_{\max}=0$ ). Thus the states can be labelled

as  $2s$  or  $2p$ . The  $2s$  states are nondegenerate

while the  $2p$  states are three fold degenerate corresponding

to  $m = -1, 0, 1$ .

$n$	$l$	$j_{\max}$	state	degeneracy
2	0	1	$2s$	1 ( $m=0$ )
	1	0	$2p$	3 ( $m = -1, 0, 1$ )

---



(41)

There are thus four states corresponding to the energy level  $E_2 = -3.4 \text{ eV}$ . The states are

$$\psi_{200}, \psi_{21-1}, \psi_{210}, \psi_{21,1}$$

where a general state  $(nlm)$  is written  $\psi_{nlm}$ .

Radial wavefunction.

$$R_{20}(r) = \frac{1}{2} \cdot \left(\frac{r}{2a}\right) e^{-r/2a} v_{20}(\rho) \quad \left| \quad R_{nl}(r) = \frac{1}{2} \rho^{l+1} e^{-\rho} v_{nl}(\rho) \right.$$

$$\rho = kr = r/na$$

NW

$$C_{j+1} = \frac{2(j+l+1-n)}{(j+1)(j+2l+2)} C_j$$

Here  $C_1 = \frac{2(0+0+1-2)}{(0+1)(0+0+2)} C_0 = -C_0$

$$C_2 = C_3 = \dots = 0$$

$$\therefore v_{20}(\rho) = C_0(1-\rho)$$

Hence

$$R_{20}(r) = \frac{1}{2a} e^{-r/2a} C_0(1-r/2a)$$

$$R_{20} = C(1-r/2a) e^{-r/2a} \quad \dots \dots (39)$$

where  $C$  has to be found from normalization condition

Radial wave functions for the states

$$\psi_{210}, \psi_{211} \text{ and } \psi_{21-1}.$$

All these states have the same radial function  $R_{21}(r)$ ,

$$R_{21}(r) =$$

$$R_{21}(r) = \frac{1}{2} (r)^2 e^{-r/2a} v_{21}(r) \quad | \quad r = r/2a$$

Here  $v_{21}(r) = \text{constant}$  (since  $j_{\max} = 0$ ). From the

recursion relation we see that if  $n=2$ ,  $l=1$ , then  $c_1 = c_2 = \dots = 0$ .

Thus

$$R_{21}(r) = C r e^{-r/2a} \dots \dots \dots (40)$$

where  $C$  is determined by imposing the normalization condition.

Arbitrary  $n$ 

We have (Eq (23))

$$n = j_{\max} + l + 1$$

i.e.,  $j_{\max} = n - l - 1$

Therefore we have the following possibilities for a given  $n$ :

$$n \quad l=0 \quad j_{\max} = n-1$$

$$l=1 \quad j_{\max} = n-2$$

$$l=2 \quad j_{\max} = n-3$$

$$\vdots$$

$$l=n-1 \quad j_{\max} = 0$$

For a given  $l$ , the degeneracy is  $(2l+1)$  corresponding

to  $m = -l, -l+1, \dots, l-1, l$ . Thus the total

degeneracy for the energy level  $E_n$  is

$$d(n) = \sum_{l=0}^{n-1} (2l+1) = 2 \sum_{l=0}^{n-1} l + \sum_{l=0}^{n-1} 1$$

$$= 2 \cdot \frac{n(n-1)}{2} + n = n^2$$

In the figure below we show the energy levels and values of  $l$  for each  $n$ .

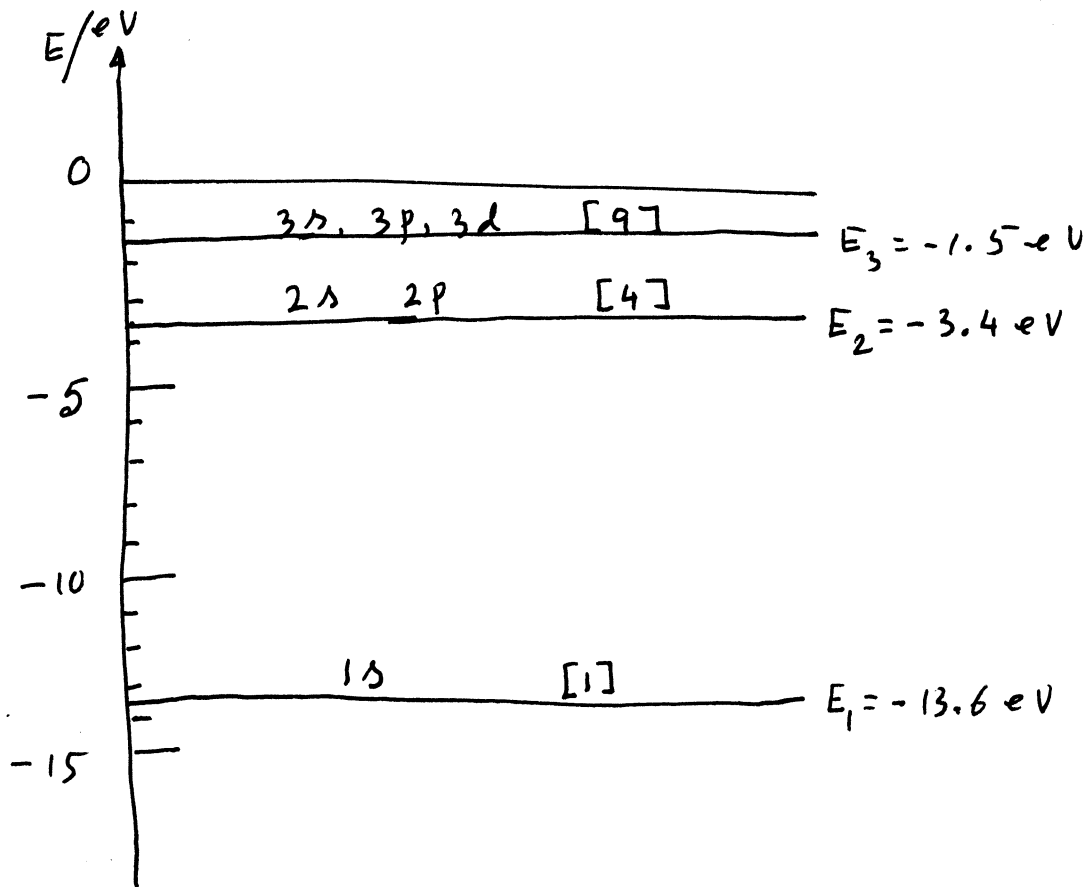


Fig: Energy levels of hydrogen atom. The number within square brackets  $[ ]$  is the degeneracy for the energy eigenvalue.

## Accidental degeneracy

For the hydrogen atom, the discrete energy levels depend only upon the ~~reduced~~ principal quantum number  $n$ ,

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

For any  $n$ , the orbital angular momentum quantum number  $l$  can be

$$l = 0, 1, 2, \dots, n-1,$$

and for each  $l$ ,  $m$  can vary between  $-l$  to  $l$  in steps of 1, i.e.,

$$m = -l, -l+1, \dots, l-1, l.$$

For a central potential, the energy levels (i.e., energy eigenvalues) depend on  $n$  and  $l$  in general.

However, for the Coulomb potential, which is inversely proportional to  $r$ , the energy levels do not depend on  $l$ . So there is degeneracy with respect to both  $l$  and  $m$ . This is called special degeneracy for Coulomb potential.



Bound state wave functions of hydrogen atom in terms of standard functions of mathematical physics:

---

Mathematical notes:

Laguerre functions  $L_N(x)$  satisfy the differential equation

$$x y''(x) + (1-x) y'(x) + N y = 0, \quad \dots \quad (41)$$

with  $y = L_N(x)$ . For integer  $N$ ,  $L_N(x)$  is a polynomial of degree  $N$ . The Laguerre polynomials  $L_N(x)$  can be calculated using the following formula

$$L_N(x) = e^x \left( \frac{d}{dx} \right)^N (e^{-x} x^N) \quad (\text{integer } N) \quad (42).$$

There are many normalization conditions in the literature. For example, if we include an overall multiplicative constant in (42),  $L_N(x)$  would still satisfy the same differential equation (Eq. (41)), because the differential equation is homogeneous. In many texts, there is a factor  $\frac{1}{N!}$  on the right hand side of (42). However, Eq. (42) is the usual definition

of Laguerre polynomial of integer order  $N$ .  
 This convention is followed by ~~Griffith~~ Griffiths,  
 Shankar, Hertzbecker <sup>and</sup> ~~say~~ many others.

### ~~Associated Laguerre~~

Using Eq. (42) we find

$$L_0(x) = 1$$

$$L_1(x) = -x + 1$$

$$L_2(x) = x^2 - 4x + 2$$

$$L_3(x) = -x^3 + 9x^2 - 18x + 6$$

Laguerre polynomial of order  $N$  ( $N = \text{positive integer}$   
 or zero),  $L_N(x)$ , is a polynomial of degree  $N$ .



## Associated Laguerre Polynomials

(49)

We define associated Laguerre polynomials

$L_N^R(x)$  ( $N$  and  $R$  positive integers or zero) as

$$L_N^R(x) = (-1)^R \frac{d^R}{dx^R} L_{N+R}(x) \quad \dots \quad (43)$$

where  $L_{N+R}(x)$  is defined in Eq. (42). With

this definition, it follows that

$$L_N^0(x) = L_N(x) \quad \dots \quad (44)$$

Also note that  $L_N^R(x)$  is a polynomial of degree  $N$  no matter what the value of  $R$  is.

In Eq. (43), writing  $R = p$  and  $N + R = N + p = q$ , we have

$$L_{q-p}^p(x) = (-1)^p \frac{d^p}{dx^p} L_q(x) \quad \dots \quad (45)$$

$(q \geq p)$

which is the definition of associated Laguerre

polynomials given in Griffiths<sup>†</sup>. Note that in Eq. (45)  $p \leq q$ . According to the equivalent definitions (43) or (45),  $L_0^p$  for any positive integer  $p$  is a constant, the value of the constant being dependent on  $p$ .

Using either Eq. (43) or Eq. (45),  $L_N^k(x)$  is

$$L_N^k(x) = \frac{[(N+k)!]}{N! k!} \left[ 1 - \frac{N}{(k+1)} \frac{x}{1!} - \frac{N(1-N)}{(k+1)(k+2)} \frac{x^2}{2!} - \frac{N(1-N)(2-N)}{(k+1)(k+2)(k+3)} \frac{x^3}{3!} - \dots \right] \quad (46)$$

For  $N$  zero or a positive integer the above expression is a polynomial of degree  $N$ .

---

<sup>†</sup> Eqs. (43) and (45) are identical definitions of the associated Laguerre polynomials.

Using (46) or (43) or (45) we can easily work out the associated Laguerre polynomials  $L_N^k(x)$ . Some of these polynomials with low values of  $N$  and  $k$  are shown in the table below:

Table: Some associated Laguerre polynomials

---


$$L_0^0 = 1 \quad L_0^1 = 1 \quad L_0^2 = 2 \quad L_0^3 = 6$$

$$L_1^0 = -x+1, \quad L_1^1 = -2x+4, \quad L_1^2 = -6x+18, \quad L_1^3 = -24x+96$$


---

In the explicit expression for  $L_N^k(x)$  (Eq. (46)) we have an overall multiplicative constant  $[(N+k)!]^2 / (N! k!)$ . This multiplicative factor is a consequence of our definition of associated Laguerre polynomials according to Eqs. (42) and (43). Different definitions of Laguerre polynomials ~~Eq. (46)~~  $L_N(x)$  and associated Laguerre polynomials  $L_N^k$

exist in the literature. These definitions only differ in the overall multiplicative constants. For example, in Wolfram Mathematica, the overall multiplicative factor in Eq (46) is  $\frac{(N+k)!}{N!k!}$ . Therefore

$$(N+k)! \left. L_N^k(x) \right|_{\text{Wolfram}} = \left. L_N^k(x) \right|_{\text{Griffiths}} \quad (47)$$

Differential equation for associated Laguerre polynomials.

---

Associated Laguerre polynomials  $L_N^k(x)$

( $N = 0, 1, 2, \dots$  ;  $k = 0, 1, 2, \dots$ ) satisfy the differential equation

$$x \frac{d^2 y}{dx^2} + (k+1-x) \frac{dy}{dx} + N y = 0 \quad (48)$$

with  $y = L_N^k(x)$ . This differential equations has solutions in the form of infinite series

for arbitrary  $N$  and  $k$ . However, the solutions are polynomials of degree  $N$  if  $N$  is zero or positive integers. Further, if  $k$  is also a positive integer or zero, the polynomials would be the associated Laguerre polynomials.

Also, note that the differential equation satisfied by associated Laguerre polynomials (Eq. (48)) is homogeneous. So if a solution of this equation is multiplied by a constant, the new function still remains a solution. Thus many different definitions of  $L_N^k(x)$ , all satisfying the differential equation, Eq. (48), but differing in an overall multiplicative constant, are possible.

For arbitrary  $N$  and  $k$ , the series solution of Eq. (48) regular at the origin is of the form:

$$L_N^k(x) = a_0 \left[ 1 - \frac{N}{(k+1)} x - \frac{N(1-N)}{(k+1)(k+2)} \frac{x^2}{2!} - \frac{N(1-N)(2-N)}{(k+1)(k+2)(k+3)} \frac{x^3}{3!} - \dots \right] \quad (49)$$

where the constant  $a_0$  can be chosen arbitrarily. The recurrence relation is

$$a_{j+1} = \frac{(j-N)}{(j+1)(j+k+1)} a_j \quad \dots \quad (50)$$

Again we observe either ~~from the above analysis~~ that for  $N$  equal to a positive integer or zero,  $L_N^k(x)$  is a polynomial of degree  $N$ .

Our choice for  $a_0$  is

$$a_0 = \frac{[(N+k)!]^2}{N! k!}$$

which follows directly from the definition of  $L_N^k(x)$  we have adopted (see Eqs. (43) and (42)).

Note: If the recurrence relation for the Laguerre polynomials is

$$a_{j+1} = \frac{2(j-N)}{(j+1)(j+k+1)} a_j,$$

instead of (50), then the polynomial would be  $L_N^k(2x)$  rather than  $L_N^k(x)$ .

---

## Orthonormality of Laguerre and associated Laguerre polynomials

We ~~do~~ have defined Laguerre polynomials  $L_N(x)$  (integer  $N \neq \text{zero}$ ) according to Eq. (42) and associated Laguerre polynomials according to Eq. (43). With these definitions, we have the following integrals:

$$\int_0^{\infty} e^{-x} L_m(x) L_n(x) dx = 0 \quad m \neq n \quad (51)$$

$$\int_0^{\infty} e^{-x} [L_n(x)]^2 dx = (n!)^2 \quad - - - (52)$$

$$\text{i.e.} \quad \int_0^{\infty} e^{-x} L_m(x) L_n(x) dx = (n!)^2 \delta_{mn} \quad - - (53)$$



(57)

$$\int_0^{\infty} e^{-x} x^k L_n^k(x) L_m^k(x) dx = \frac{[(n+k)!]^3}{n!} \delta_{nm} \quad (54)$$

$$\int_0^{\infty} e^{-x} x^{k+1} [L_n^k(x)]^2 dx = \frac{[(n+k)!]^3}{n!} (2n+k+1) \quad (55)$$

Hydrogen atom wave function in terms of associated Laguerre polynomials.

---

To recapitulate, the full wave function is written as

$$\begin{aligned}
 \psi_{nlm}(r, \theta, \phi) &= R_{nl}(r) Y_{lm}(\theta, \phi) \\
 &= \frac{1}{r} u_{nl}(r) Y_{lm}(\theta, \phi) \\
 &= \frac{1}{r} \rho^{l+1} e^{-\rho} v_{nl}(\rho) Y_{lm}(\theta, \phi) \dots \quad (56)
 \end{aligned}$$

where  $v_{nl}(\rho)$  is polynomial in  $\rho$  of degree  $n-l-1$  and  $n$  is the principal quantum number ( $n = 1, 2, 3, \dots$ ).

Here  $\rho = Kr$ , with

$$K \equiv \sqrt{\frac{2\mu|E|}{\hbar^2}} = \frac{1}{na}$$

where  $a$  is the Bohr radius (Eq. (28))

$$a = \frac{4\pi\epsilon_0 \hbar^2}{\mu e^2}$$

The differential equation satisfied by  $v_{nl}(\rho)$  is given in Eq (17) with  $\rho_0 = 2n$  (Eq. (24)) :

$$\rho \frac{d^2 v_{nl}}{d\rho^2} + 2(l+1-\rho) \frac{dv_{nl}}{d\rho} + 2(n-l-1) v_{nl} = 0$$

Dividing by 2 we have

$$\frac{\rho}{2} \frac{d^2 v_{nl}}{d\rho^2} + \frac{(2l+2-2\rho)}{2} \frac{dv_{nl}}{d\rho} + (n-l-1) v_{nl} = 0$$

$$\times 2\rho \frac{d^2 v_{nl}}{d(2\rho)^2} + (2l+2-2\rho) \frac{dv_{nl}}{d(2\rho)} + (n-l-1) v_{nl} = 0$$

Compare this with the differential equation for associated Laguerre polynomials  $L_N^k(\rho)$ , Eq(48), ( $N$  and  $k$  are zero or positive integers) :

$$\rho \frac{d^2 L_N^k(\rho)}{d\rho^2} + (k+1-\rho) \frac{dL_N^k(\rho)}{d\rho} + N L_N^k(\rho) = 0$$

On comparison we find that

$$v_{nl} \propto L_{n-l-1}^{2l+1}(2\rho).$$

Hence the full wave function can be written as

$$\psi_{nlm}(r, \theta, \phi) = C \rho^l e^{-\rho} L_{n-l-1}^{2l+1}(2\rho) Y_{lm}(\theta, \phi)$$

$$= R_{nl}(r) Y_{lm}(\theta, \phi) \quad | \quad \rho = kr = r/na$$

The const has to be chosen that the wave function is normalized to unity, since  $Y_{lm}(\theta, \phi)$  are normalized, we must have

$$\int_0^\infty R_{nl}^2(r) r^2 dr = 1$$

$$\propto |C|^2 \int_0^\infty \rho^{2l} e^{-2\rho} \left[ L_{n-l-1}^{2l+1}(2\rho) \right]^2 r^2 dr = 1$$

Now

$$\rho = kr \quad (k = \frac{1}{na})$$

(61)

$$|C|^2 \int_0^\infty \rho^{2l} e^{-2\rho} \left[ L_{n-l-1}^{2l+1}(2\rho) \right]^2 \frac{(Kz)^2 d(Kz)}{K^3} = 1$$

$$\propto \frac{|C|^2}{K^3} \int_0^\infty \rho^{2l} e^{-2\rho} \left[ L_{n-l-1}^{2l+1}(2\rho) \right]^2 \rho^2 d\rho = 1$$

$$\propto \frac{|C|^2}{8K^3 2^{2l}} \int_0^\infty (2\rho)^{2l} e^{-2\rho} \left[ L_{n-l-1}^{2l+1}(2\rho) \right]^2 (2\rho)^2 d(2\rho) = 1$$

$$\propto, \frac{|C|^2}{\left(\frac{2}{na}\right)^3 2^{2l}} \int_0^\infty x^{2l+2} e^{-x} \left[ L_{n-l-1}^{2l+1}(x) \right]^2 dx = 1$$

Now make use of the standard integral (Eq. (55))

$$\int_0^\infty e^{-x} x^{k+1} \left[ L_N^k(x) \right]^2 dx = \frac{[(N+k)!]^3}{N!} (2N+k+1)$$

We get (here  $N = n-l-1$ ,  $k = 2l+1$ )

$$\frac{|C|^2}{\left(\frac{2}{na}\right)^3 2^{2l}} \cdot \frac{[(n-l-1+2l+1)!]^3}{(n-l-1)!} (2n-2l-2+2l+1+1) = 1$$

(62)

$$\frac{|c|^2}{\left(\frac{2}{na}\right)^3 2^{2l}} \cdot \frac{[(n+l)!]^3}{(n-l-1)!} 2^n = 1$$

$$|c|^2 = \left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2^n [(n+l)!]^3} 2^{2l}$$

$$\text{as } |c| = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2^n [(n+l)!]^3}} \cdot 2^l$$

Therefore

$$\psi_{nlm} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2^n [(n+l)!]^3}} (2\rho)^l e^{-\rho} L_{n-l-1}^{2l+1} \left(\frac{2\rho}{na}\right) Y_{lm}(\theta, \phi)$$

$$\rho = kr = \frac{r}{na}$$

∴

$$\psi_{nlm}(r, \theta, \phi) = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2^n [(n+l)!]^3}} e^{-r/na} \left(\frac{2r}{na}\right)^l \times L_{n-l-1}^{2l+1} \left(\frac{2r}{na}\right) Y_{lm}(\theta, \phi)$$

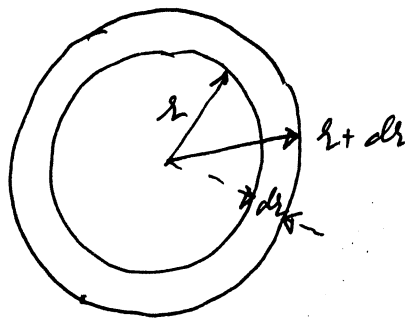
..... (57)

## Position probability density.

We interpret

$$|\Psi_{n\ell m}(\vec{r})|^2 d^3r$$

where  $d^3r = r^2 dr \sin\theta d\theta d\phi = r^2 dr d\Omega$ , as the probability that the electron would be found in a small volume  $d^3r$  at  $\vec{r} = (r, \theta, \phi)$ . Integrating over  $\theta$  &  $\phi$  we find the probability  $P(r)dr$  that the electron would be found in an annular region  $r$  to  $r+dr$ .



Thus

$$\begin{aligned}
 P(r)dr &= R_{n\ell}^2(r) r^2 dr \underbrace{\int_{\Omega} Y_{\ell m}^*(\theta, \phi) Y_{\ell m}(\theta, \phi) d\Omega}_{=1} \\
 &= R_{n\ell}^2(r) r^2 dr
 \end{aligned}$$

Therefore, probability density that the electron would be found at a radial distance  $r$  irrespective of  $\theta$  and  $\phi$  is

$$P(r) = r^2 R_{nl}^2(r).$$

Now consider the ground state  $n=1, l=0$ . The normalised radial wave function (i.e.  $\int_0^\infty R_{nl}^2 r^2 dr = 1$ )

for the ground state is (p 38)

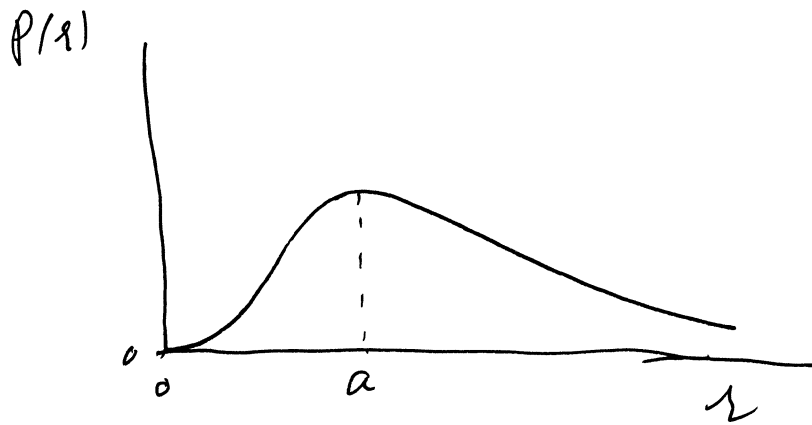
$$R_{10}(r) = \frac{2}{\sqrt{a^3}} e^{-r/a}.$$

Therefore, for the ground state

$$P(r) = r^2 R_{10}^2(r) = \frac{4}{a^3} r^2 e^{-2r/a}.$$

Note that  $P(r)$  is zero at  $r=0$  and  $P(r)$  tends to zero as  $r \rightarrow \infty$ . Since  $P(r)$  is positive for other  $r$ , there must be a maximum of  $P(r)$  at some finite  $r$ . The graph of  $P(r)$  against  $r$  should of the shape shown in the figure below:





At the maximum,

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

$$\therefore \frac{4}{a^3} \left[ 2r e^{-2r/a} - r^2 \cdot \frac{2}{a} e^{-2r/a} \right] = 0$$

$$\therefore \frac{4}{a^3} (2r) e^{-2r/a} \left( 1 - \frac{r}{a} \right) = 0$$

$$\text{i.e., } r = a$$

Thus  $P(r)$  attains its maximum at  $r = a$  as shown in the above figure.

Expectation value of  $r$  in the ground state of the Hydrogen atom.

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Before doing the calculations, we note that  $P(r)$  is not symmetric around  $r=a$ . (Diagram above). It has a long tail. So we expect  $\langle r \rangle$  to be somewhat larger than  $a$ . Now

$$\langle 100 | r | 100 \rangle = \langle r \rangle_{gs} \quad [gs = \text{ground state}]$$

$$= \int_{\text{All volume}} \psi_{100}^*(r, \theta, \phi) r \psi(r, \theta, \phi) r^2 dr d\Omega$$

$$= \int_0^\infty r^3 R_{10}^2(r) dr$$

$$= \frac{4}{a^3} \int_0^\infty r^3 e^{-2r/a} dr$$

$$= \frac{4}{a^3} \cdot \frac{3!}{\left(\frac{2}{a}\right)^4}$$

$$= \frac{4}{a^3} \cdot \frac{6 a^4}{16}$$

$$= 1.5a$$

$$\boxed{\langle r \rangle_{gs} = 1.5a}$$

$$\left| \int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}} \right. \\ a > 0$$

— x — END