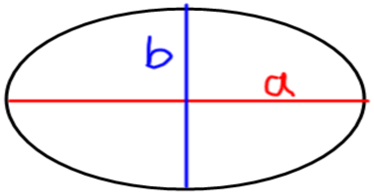
CHAPTER 4

(Simple line spectra and elements of atomic theory)

CONTINUED

Arnold Sommerfeld extended the Bohr model to include elliptical orbits



Bohr's concept of quantization of angular momentum led to the **principal quantum number** *n*, which determines the energy of the allowed states of hydrogen.

Sommerfeld's theory retained *n*, but also introduced a new quantum number ℓ called the **orbital quantum number**, where the value of ℓ ranges from 0 to *n* - 1 in integer steps.

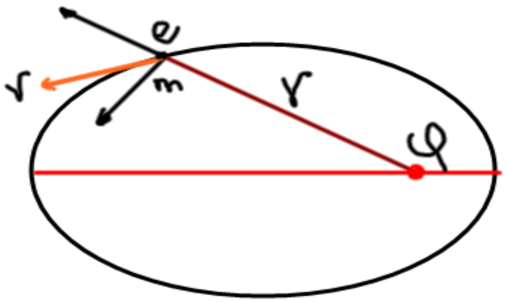
According to this model, an electron in any one of the allowed energy states of a hydrogen atom may move in any one of a number of orbits corresponding to different ℓ values.

Sommerfeld Quantization Rules

- For any physical system in which the coordinates are periodic function of time, there exists a quantum condition for each coordinate, these quantum conditions are:

$$\oint p_q dq = n_q h$$

where q is one of the coordinate, p_q is the momentum associated with that coordinate, n_q is the quantum number which take integral values. This means that the integration is taken over one period of the coordinate q.



- In polar coordinates the position of the electron is given by the azimuth angle ϕ and the electron nuclear distance r. applying the quantum conditions to these two degree of freedom,

$$\oint p_\varphi \, d\varphi = n_\varphi h \qquad 1$$

$$\oint p_r \, dr = n_r h \qquad 2$$

Where n_ϕ and n_r take integral values only and are called the **azimuthal and radial quantum number,** respectively

- ***If the particle is moving with a simple harmonic motion in one diminution the total energy would be:***

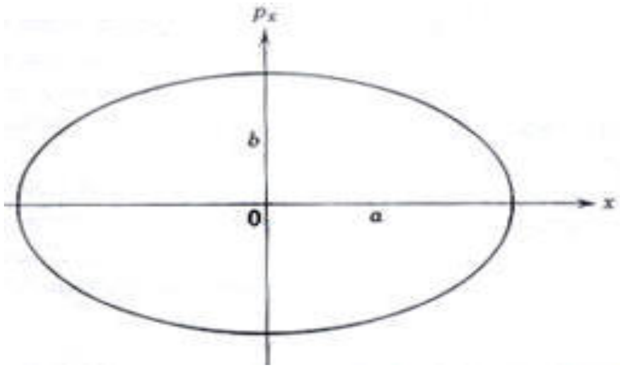
$$\boxed{E = K + V = \frac{1}{2}mv^2 + \frac{1}{2}kx^2} \qquad 3$$

since p=mv then $v^2=p^2/m^2$

From equation 3:

$$E = K + V = \frac{p_x^{\,2}}{2m} + \frac{kx^2}{2}$$

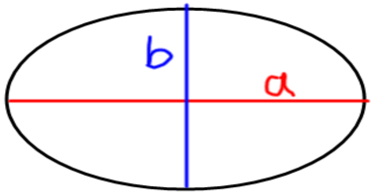
$$\frac{p_x^{\,2}}{2mE} + \frac{x^2}{2E/k} = 1 \longrightarrow \frac{P_x^{\,2}}{b^2} + \frac{x^2}{a^2} = 1$$



This equation of an ellipse $a = \sqrt{2E/k}$ ***and*** $b = \sqrt{2mE}$

Where a and b is the semi axes of the ellipse,

- *To find the integral* $\oint p_q \, dq$ *which represent the relation between the momentum* p_x *and the displacement of the on the x coordinates;* we can use the geometrical representation for the ellipse equation.



- This equation gives the amount of linear momentum for any displacement of the electron. By taking the x coordinate to represent the displacement and the vertical coordinate to represent the momentum.

- *This coordinate is called the phase-space and the figure is phase diagram for the moving particle in one demotion*
- The integration $\oint p_q dq$ give the area of the ellipse:

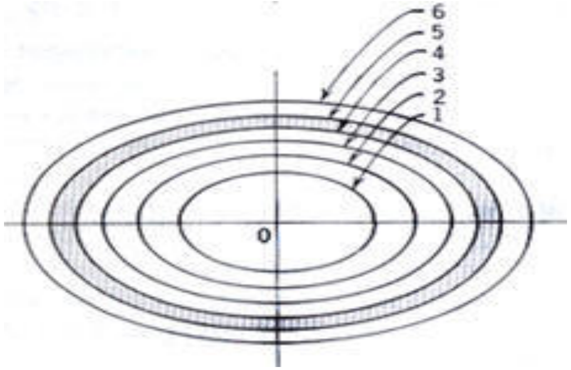
$$\oint p_q dq = \pi ab$$

Substitute for a and b:

$$\oint p_x dx = \pi ab \Rightarrow \oint p_x dx = \frac{2\pi E}{\sqrt{k/m}}$$

$$\because \nu = \frac{1}{2\pi}\sqrt{k/m} \longrightarrow \oint p_x dx = \frac{2\pi E}{2\pi\nu} \Rightarrow \oint p_x dx = \frac{E}{\nu} = n_x h = nh$$

The momentum of any particle moving in one dimensional simple harmonic motion :E=nhν which is the same of Bohr quantization



Example:

Use the Sommerfeld’s quantization principle to drive the Bohr quantization rule.

Solution:

In Bohr Theory the electron moves in circular orbits about the proton then the orbital angular momentum $\frac{nh}{2\pi} = L$

The electron nuclear distance r is constant and the orbital angular momentum $L = mvr = constant$

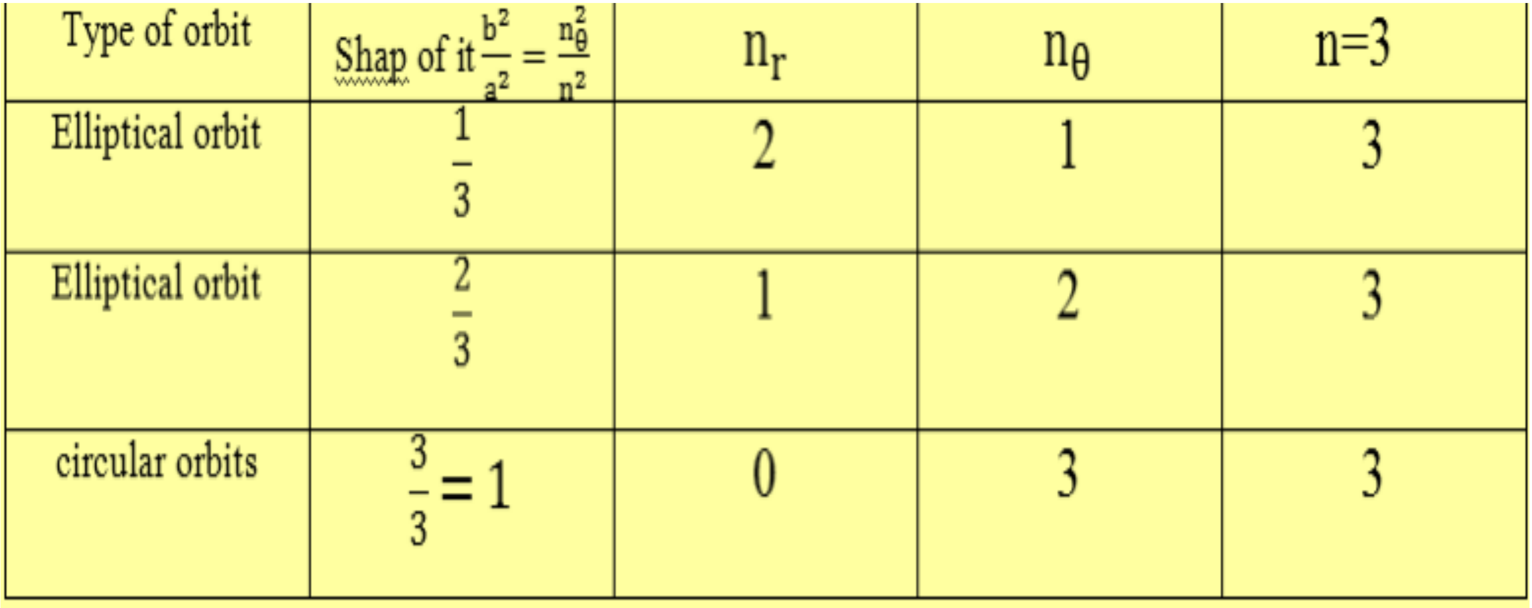
Sommerfeld’s quantization $\oint p_q dq = n_q h$, $\oint L d\theta = nh$

$$\oint L d\theta = L \oint_0^{2\pi} \theta = 2\pi$$

$$2\pi L = nh$$

This is Bohr $$L = \frac{nh}{2\pi} = n\hbar$$

- As long as the electron orbit is circle then n_r and n_ϕ has the same value. If n=3
- We can get all probabilities the electron can get. Here are three probabilities where $3=n_\phi+n_r$



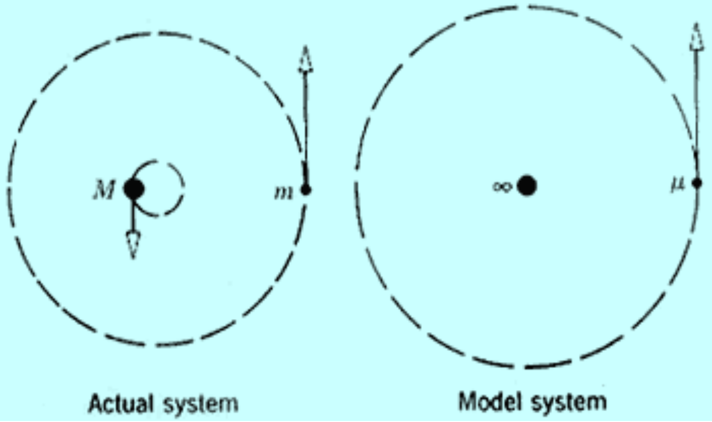
Type of orbit	Shap of it $\frac{b^2}{a^2}=\frac{n_\theta^2}{n^2}$	n_r	n_θ	n=3
Elliptical orbit	$\frac{1}{3}$	2	1	3
Elliptical orbit	$\frac{2}{3}$	1	2	3
circular orbits	$\frac{3}{3}=1$	0	3	3

- Home work get the possible orbits when n=5 and 7

Reduced Mass:

- There was a difference between the nucleus mass estimated by Bohr and the experimental values. This difference because Bohr considered that the much massed nucleus was in statuary state. To reduce the difference we have to consider that the mass of the nucleus is limited and both move around a centre of mass. Now we consider the electron move relative to the constant mass nucleus with a Reduced Mass μ

$$\mu = \frac{mM}{m+M}$$

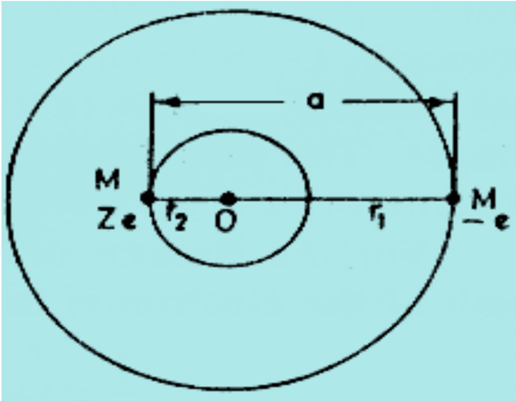


- where M is the mass of the nucleus and m is the mass of the electron

- ***To prove that relationship,*** consider that the electron and the nucleus move around the centre of mass O as shown in fuggier. Where r_1 is the reduce of the nucleus orbit and r_2 is the reduce of the electron among the centre of mass.
- Using the centre of mass theory that $mr_1 = Mr_2$. If a is the distance between the electron and the nucleus then:

$$r_1 = a - r_2 = a - \frac{mr_1}{M} \Rightarrow r_1 = \frac{aM}{(m+M)} \qquad \textbf{1}$$

$$r_2 = \frac{aM}{(m+M)} \qquad \textbf{2}$$



Both masses move in a circular orbit then the forces acting are in balance (the attraction force and centripetal force.

For the Nucleus the forces are:

$$\frac{Ze^2}{4\pi\varepsilon_o a^2} = \frac{Mv^2}{r_2}$$

For the electron are :

$$\frac{Ze^2}{4\pi\varepsilon_o a^2} = \frac{mv^2}{r_1}$$

- ***From the energy calculation for both:***

Total K.E. = $1/2\, mv_1^2 + 1/2\, MV_2^2$

where $v_1 = \omega r_1$ and $V_2 = \omega r_2$

Therefore, the total K.E. = $1/2\, m\omega^2 r_1^2 + 1/2\, M\omega^2 r_2^2$

Substitute for r_1 and r_2 from equation 1,2

$$K.E = \frac{1}{2}\left[\frac{mM}{m+M}\right]\omega^2 a^2$$

Therefore, $\boxed{\mu = \frac{mM}{m+M}}$ is the reduced mass for the electron

The second assumption of Bohr $\boxed{\mu v r = n\hbar}$

Also, we get $\frac{1}{\lambda} = R_M Z^2\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$ where $R_M = \frac{M}{m+M} R_\infty = \frac{\mu}{m} R_\infty$

Example

Consider a positronium atom consisting of a positron and electron revolving about their common centre of mass half way between them, If such a system were a normal atom (a) How would its emission spectrum compare to that of the hydrogen atom? (b) What would be the radius of the ground state orbit of positronium?

Solution:

Calculate the reduced mass:

$$\mu = \frac{mM}{m+M} = \frac{m^2}{2m} = \frac{m}{2}$$

Calculate Rydberg constant

$$R_M = \frac{m}{m+m} R_\infty = \frac{R_\infty}{2}$$

The Bohr energy levels

$$E_{positronium} = -\frac{R_M hcZ^2}{n^2} = -\frac{R_\infty hcZ^2}{2n^2}$$

And the wavelength

$$\frac{1}{\lambda} = \frac{\nu}{c} = \frac{R_\infty}{2} Z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

- The positronium frequency is half the Hydrogen frequency and the positronium wavelength will be double as long of Hydrogen
- The positronium orbital radius

$$r_{positronium} = \frac{4\pi\varepsilon_o n^2\hbar^2}{\mu Z e^2} = 2\frac{4\pi\varepsilon_o n^2\hbar^2}{m Z e^2} = 2r_{hydrogen}$$

Also, double as long of Hydrogen

Example

Deuterium atom is a hydrogen atom whose nucleus contains a proton and a neutron. How does the doubled nuclear mass affect the atomic spectrum?

Solution:

Deuterium atom is a hydrogen atom with neutron in the nucleus, the Rydberg constant for hydreogen

$$R_H = \frac{\mu}{m} R_\infty = \frac{R_\infty}{\left(1+\frac{m}{M}\right)} = \frac{109737\ cm^{-1}}{\left(1+\frac{1}{1836}\right)} = 109678\ cm^{-1}$$

For Deuterium atom the Rydberg constant

$$R_D = \frac{\mu}{m} R_\infty = \frac{R_\infty}{\left(1+\frac{m}{M}\right)} = \frac{109737\ cm^{-1}}{\left(1+\frac{1}{2\times 1836}\right)} = 109707\ cm^{-1}$$

This result indicates that the Deuterium spectrum will be shifted to the longer wavelength

- According to Sommerfeld model, an electron in any one of the allowed energy states of a hydrogen atom may move in any one of a number of orbits corresponding to different ℓ values
- For each value of *n*, there are *n* possible orbits corresponding to different ℓ values(ℓ=0,n-1)
- the first energy level (ground state) we have
- *n* = 1 and ℓ= 0 there is only one possible orbit for this state
- The second energy level, with *n* = 2, has two possible orbits, corresponding to n=2, ℓ = 0 and ℓ = 1.
- The third energy level, with *n* = 3, has three possible orbits, corresponding to ℓ = 0, ℓ = 1, and ℓ= 2.

- For historical reasons: **all states with the same principal quantum number *n* are said to form a shell**.
- Shells are identified by the letters

  K, L, M, N, O, P this correspond to

n = 1, 2, 3, 4 , 5, 6 describe the states for n

the states with given values of *n* and ℓ are said to form a sub-shell.

The letters *s*, *p*, *d*, *f*, *g*, h, ..are used to describe the states for which ℓ = 0, 1, 2, 3, 4, . . .

- States that violate the restriction $0 \leq \ell \leq n - 1$, for a given value of n, can’t exist.
- *For example; the state 2d, would have $n = 2$ and $\ell = 2$, but can’t exist because the highest allowed value of ℓ is $n - 1$, or 1 in this case.*

For $n = 2$, 2s and 2p are allowed sub-shells, but 2d, 2f, . . . are not. For $n = 3$, the allowed states are 3s, 3p, and 3d.

- Another modification of the Bohr Theory arose when it was discovered that the spectral lines of a gas are split into several closely spaced lines when the gas is placed in a strong magnetic field.

- This is called the *Zeeman effect*, after its discoverer.
- The Zeeman effect explains the polarization of the light, as well as the splitting of the lines into three components.
- This indicates that the energy of an electron is slightly modified when the atom is immersed in a magnetic field.

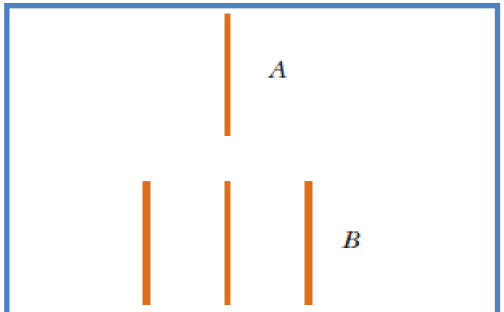


Figure 28.9 A single line (A) can split into three separate lines (B) in a magnetic field.

In order to explain this observation, a new quantum number, m_ℓ, called the **orbital magnetic quantum number**, was introduced. The theory is in accord with experimental results when m_ℓ is restricted to values ranging from $-\ell$ to $+\ell$ in integer steps. For a given value of ℓ, there are $2\ell+1$ possible values of m_ℓ.

- high resolution spectrometers revealed that spectral lines of gases are in fact two very closely spaced lines even in the absence of an external magnetic field. This splitting was referred to as **fine structure.**
- The results of Goudsmit and Uhlenbeck work introduced yet another quantum number, m_s, called the **spin magnetic quantum number**.
- For each electron there are two spin states. A sub-shell corresponding to a given factor of ℓ can contain no more than $2(2\ell+1)$ electrons.
- This number comes from the fact that electrons in a sub-shell must have unique pairs of the quantum numbers (m_ℓ, m_s).

- There are $2\ell + 1$ different magnetic quantum numbers m_ℓ, and two different spin quantum numbers m_s, making $2(2\ell+1)$ unique pairs (m_ℓ, m_s).

For example:

the *p* sub-shell ($\ell = 1$) is filled when it contains

$2(2 \times 1 + 1) = 6$ electrons.

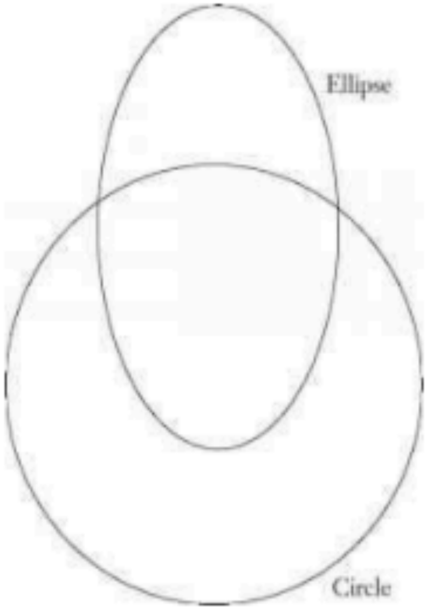
- This fact can be extended to include all four quantum numbers, as will be important to us later when we discuss the *Pauli Exclusion Principle*.

SUMMARY

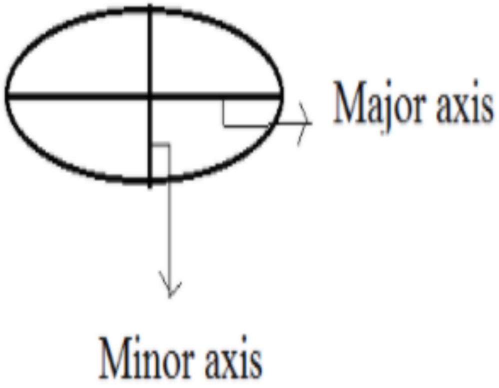
Sommerfeld atomic model –

This model explains the fine spectrum of Hydrogen atom.The important postulates of Sommerfeld atomic model are-

1) The orbits may be both circular or elliptical.



2) When path is elliptical , then there are two axis – major axis & minor axis. When length of major & minor axis become equal then orbit is circular.



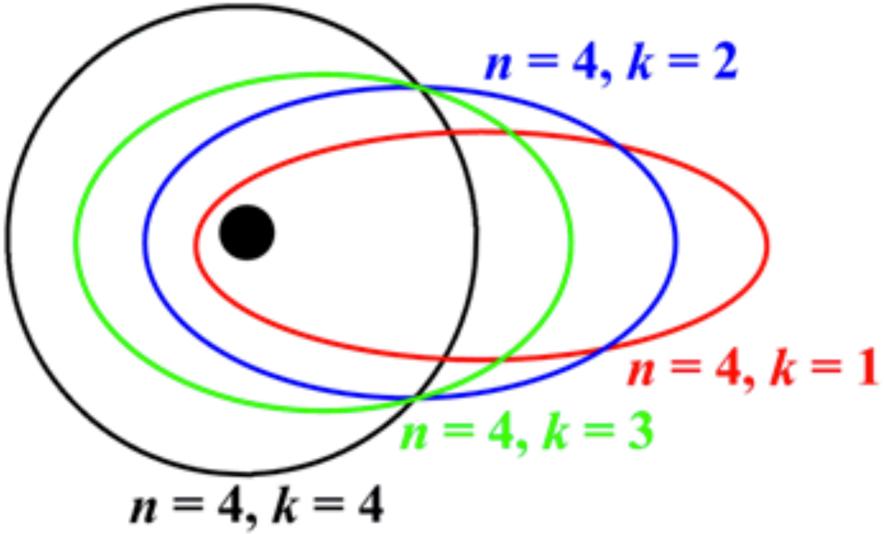
3) The angular momentum of electron moving in an elliptical orbit is $kh/2\pi$.

k is an integer except zero.

Value of k = 1,2,3,4.....

n/k = length of major axis / length of minor axis

With increase in value of k , ellipticity of the orbit decreases. When n= k,then orbit is circular.



4) Sommerfeld suggested that orbits are made up of sub energy levels . These are s,p,d,f. These sub shells possess slightly different energies.

Bohr gave a quantum number 'n', which determines the energy of electron.

Sommerfeld introduced a new quantum number called Orbital or Azimuthal Quantum number (l) which determines the orbital angular momentum of electron.

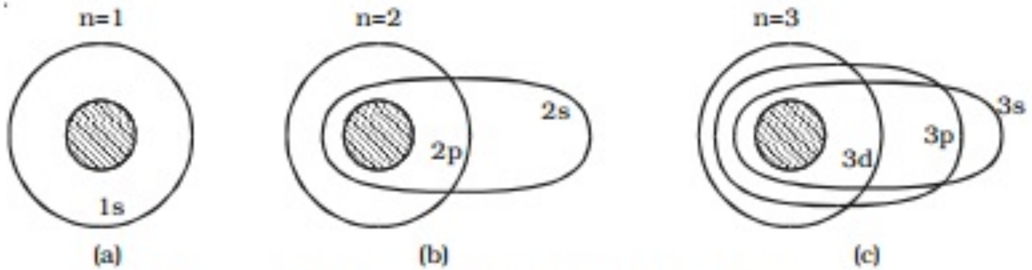
Values of l =0 to (n-1)

For, n=1 ; l=0 ; 1s su

n=2 ; l=0,1 ; 2s , 2p sub shell

n=3 ; l=0,1 ,2 ; 3s , 3p , 3d sub shell

n=4 ; l=0, 1, 2 , 3 ; 4s , 4p , 4d , 4f sub shell



(a) (b) (c)

Fig Various sub-shells for the electrons

5) When an electron jumps from one orbit to another orbit, the difference of energy (ΔE) depends upon sub energy levels.

6) It explains the splitting of individual spectral lines of hydrogen & thus fine spectrum . It could not predict the exact number of lines which are actually present in the fine spectrum.

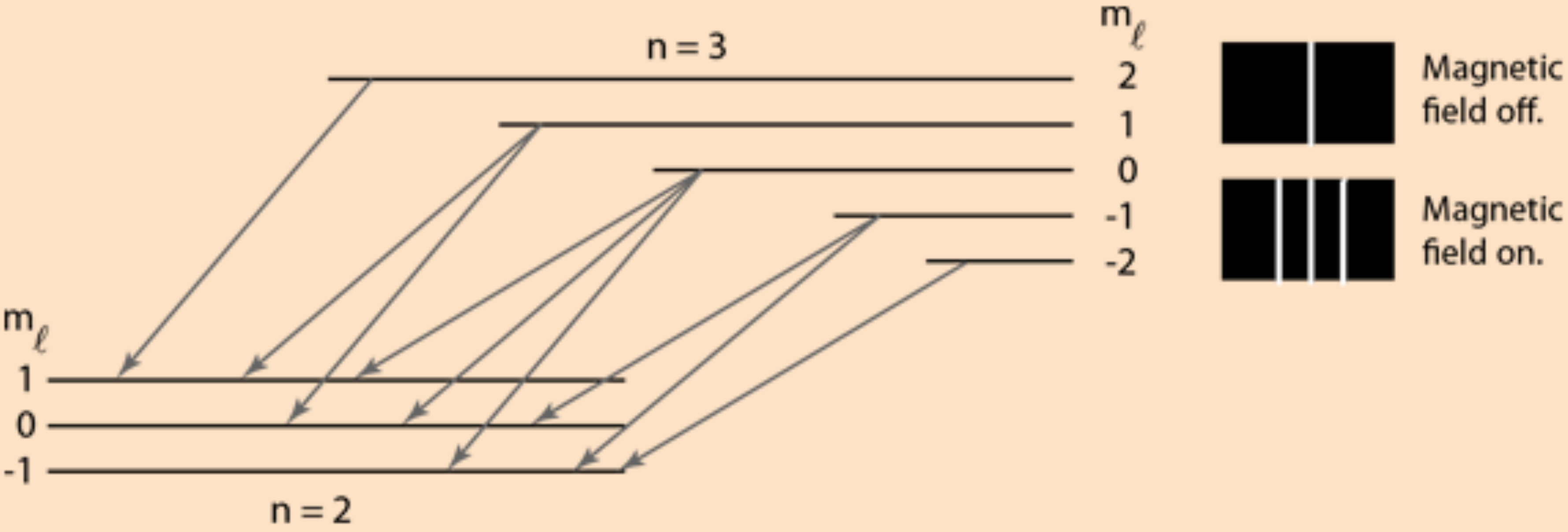
Defects of Sommerfeld atomic model-

1) This model does not explain the behavior of system having more than one electron.

2) This model does not explain the Zeeman & Stark effect.

Zeeman Effect in Hydrogen

When an external magnetic field is applied, sharp spectral lines like the n=3→ 2 transition of hydrogen split into multiple closely spaced lines. First observed by Pieter Zeeman, this splitting is attributed to the interaction between the magnetic field and the magnetic dipole moment associated with the orbital angular momentum. In the absence of the magnetic field, the hydrogen energies depend only upon the principal quantum number n, and the emissions occur at a single wavelength.



Note that the transitions shown follow the selection rule which does not allow a change of more than one unit in the quantum number m_l.

Zeeman Interaction

An external magnetic field will exert a torque on a magnetic dipole and the magnetic potential energy which results in

$$U(\theta) = -\mu \cdot B$$

The magnetic dipole moment associated with the orbital angular momentum is given by

$$\mu_{orbital} = \frac{-e}{2m_e} L$$

For a magnetic field in the z-direction this gives

$$U = \frac{e}{2m} L_z B = m_\ell \frac{e\hbar}{2m} B$$

Considering the quantization of angular momentum, this gives equally spaced energy levels displaced from the zero field level by

$$\Delta E = m_\ell \frac{e\hbar}{2m} B = m_\ell \, \mu_B \, B \qquad \mu_B = Bohr \;\; magneton$$

$$\mu_B = \frac{e\hbar}{2m_e} = 9.2740154 \, x \, 10^{-24} J \, / \, T = 5.788382 \, x \, 10^{-5} \, eV \, / \, T$$

This displacement of the energy levels gives the uniformly spaced multiplet splitting of the spectral lines which is called the Zeeman effect.

The magnetic field also interacts with the electron spin magnetic moment, so it contributes to the Zeeman effect in many cases. The electron spin had not been discovered at the time of Zeeman's original experiments, so the cases where it contributed were considered to be anomalous. The term "anomalous Zeeman effect" has persisted for the cases where spin contributes. In general, both orbital and spin moments are involved, and the Zeeman interaction takes the form

$$\Delta E = \frac{e}{2m}(\vec{L} + 2\vec{S})\cdot\vec{B} \quad = \quad g_L \mu_B m_j B$$

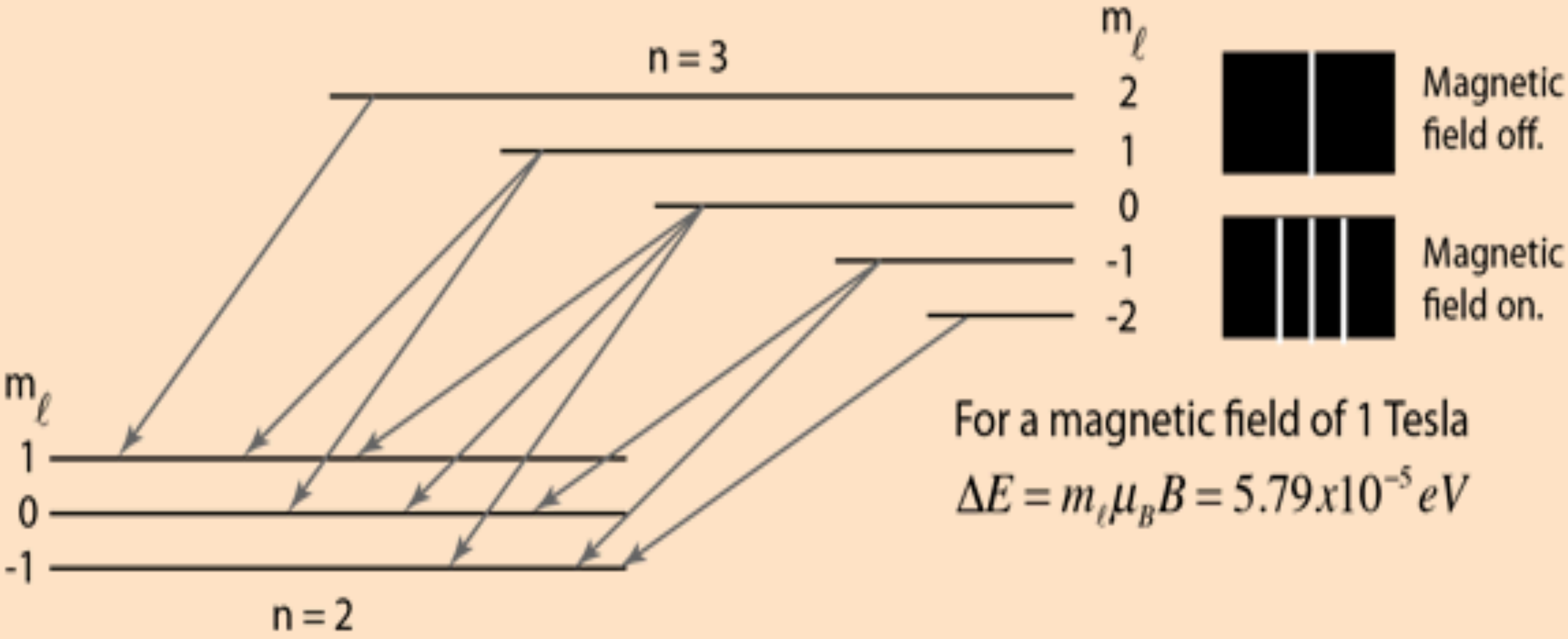
Magnetic interaction energy

The factor of two multiplying the electron spin angular momentum comes from the fact that it is twice as effective in producing magnetic moment. This factor is called the spin g-factor or gyromagnetic ratio. The evaluation of the scalar product between the angular momenta and the magnetic field here is complicated by the fact that the S and L vectors are both precessing around the magnetic field and are not in general in the same direction. The persistent early spectroscopists worked out a way to calculate the effect of the directions. The resulting geometric factor g_L in the final expression above is called the Lande g factor. It allowed them to express the resultant splittings of the spectral lines in terms of the z-component of the total angular momentum, m_j.

The above treatment of the Zeeman effect describes the phenomenon when the magnetic fields are small enough that the orbital and spin angular momenta can be considered to be coupled. For extremely strong magnetic fields this coupling is broken and another approach must be taken. The strong field effect is called the Paschen-Back effect.

Hydrogen Zeeman Example

The Zeeman effect for the hydrogen atom offered experimental support for the quantization of angular momentum which arose from the solution of the Schrodinger equation.



For a magnetic field of 1 Tesla

$$\Delta E = m_\ell \mu_B B = 5.79x10^{-5}\,eV$$

"Anomalous" Zeeman Effect

While the Zeeman effect in some atoms (e.g., hydrogen) showed the expected equally-spaced triplet, in other atoms the magnetic field split the lines into four, six, or even more lines and some triplets showed wider spacings than expected. These deviations were labeled the "anomalous Zeeman effect" and were very puzzling to early researchers. The explanation of these different patterns of splitting gave additional insight into the effects of electron spin. With the inclusion of electron spin in the total angular momentum, the other types of multiplets formed part of a consistent picture. So what has been historically called the "anomalous" Zeeman effect is really the normal Zeeman effect when electron spin is included.

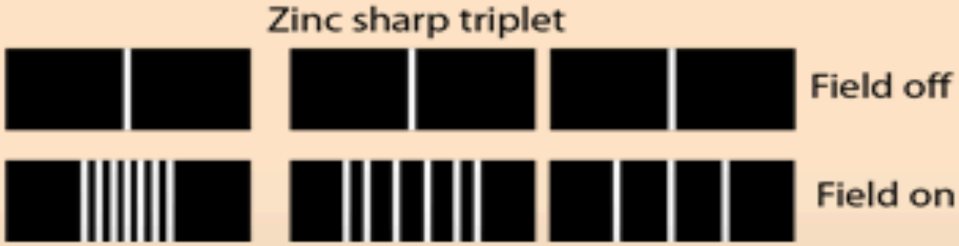
"Normal" Zeeman effect

This type of splitting is observed with hydrogen and the zinc singlet.

This type of splitting is observed for spin 0 states since the spin does not contribute to the angular momentum.

"Anomalous" Zeeman effect

When electron spin is included, there is a greater variety of splitting patterns.



The Electron Spin g-factor

When the Zeeman effect was observed for hydrogen, the observed splitting was consistent with an electron orbit magnetic moment given by

$$\mu_{\text{orbital}} = -\frac{e}{2m}\vec{L} \quad \text{giving energy shifts of the form} \quad \frac{e\hbar}{2m} m_l B = \mu_B m_l B$$

where the splittings followed the z-component of angular momentum and the selection rules explained why you got a triplet of closely-spaced lines for the 3 -> 2 transition of hydrogen. But when the effects of electron spin were discovered by Goudsmit and Uhlenbeck, they found that the observed spectral features were matched by assigning to the electron spin a magnetic moment

$$\mu_{spin} = -g\frac{e}{2m}\vec{S}$$

where g is approximately 2.

More precise experiments showed that the value was slightly greater than 2, and this fact took on added importance when that departure from 2 was predicted by quantum electrodynamics. In the experimental measurement of the Lamb shift, the value of g has been determined to be

$$g = 2.002319304386$$