The Hydrogen Atom

Thornton and Rex, Ch. 7

APPLICATION OF S's EQT TO THE HYDROGEN ATOM

USE $V(r) = -\frac{1}{4\pi\varepsilon_0} \frac{e^2}{r}$

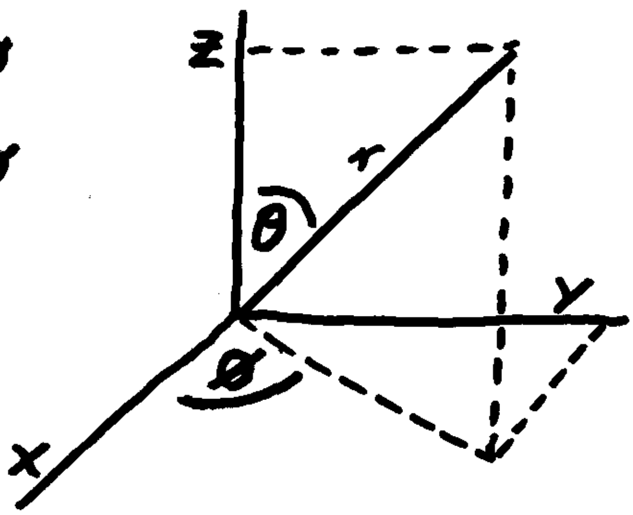
SINCE V DEPENDS ON THE RADIUS, WE RE-WRITE THE 3-DIMENSIONAL SCHRÖDINGER EQUATION IN TERMS OF SPHERICAL POLAR COORDINATES.

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2m}{\hbar^2}(E-V)\psi = 0$$

$x = r\sin\theta\cos\phi$

$y = r\sin\theta\sin\phi$

$z = r\cos\theta$



$r = \sqrt{x^2+y^2+z^2}$

$\theta = \cos^{-1}\left(\frac{z}{r}\right)$

THE POLAR ANGLE

$\phi = \tan^{-1}\left(\frac{y}{x}\right)$

THE AZIMUTHAL ANGLE

$\psi(r, \theta, \phi)$ IS SEPARABLE

$$\therefore \psi = R(r)\, f(\theta)\, g(\phi)$$

SUBSTITUTING THIS WAVEFUNCTION INTO S's EQT AND APPLYING APPROPRIATE BOUNDARY CONDITIONS TO R, f AND g WILL LEAD TO 3 SEPARATE EQUATIONS AND 3 QUANTUM NUMBERS.

THIS IS DONE IN SECTION 7.2.

WE HAVE:-

$$\frac{d^2 g}{d\phi^2} = -m_l^2 g$$

AZIMUTHAL EQUATION

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) + \frac{2m}{\hbar^2}\left(E - V - \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right) R = 0$$

RADIAL EQT.

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta \frac{df}{d\theta}\right) + \left(l(l+1) - \frac{m_l^2}{\sin^2\theta}\right) f = 0$$

ANGULAR EQUATION

m_l AND l ARE QUANTUM NUMBERS

THE RADIAL EQUATION

THE RADIAL EQUATION IS THE ASSOCIATED LAGUERRE EQUATION.

WE WILL SIMPLIFY BY LOOKING AT THE GROUND STATE — REQUIRE $m_l = 0$, $l = 0$.

$$\Rightarrow \quad \frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) + \frac{2m}{\hbar^2}(E - V)R = 0$$

SUBSTITUTING $V = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$ AND GUESSING

THAT $R = Ae^{-r/a_0}$ WE CAN FIND

$$a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{me^2}$$

(THE BOHR RADIUS

AND $E = -\frac{\hbar^2}{2ma_0^2}$

$(E = -E_0 = -13.6\text{ eV}$

HIGHER ORDER SOLUTIONS (INVOLVING ASSOCIATED LAGUERRE FUNCTIONS) CAN BE FOUND. THEY INTRODUCE A QUANTUM NUMBER n AND GIVE ENERGIES

THE PRINCIPAL Q #.

$$E = -\frac{E_0}{n^2}$$

(JUST LIKE THE BOHR PREDICTION

ANGULAR AND AZIMUTHAL EQUATIONS

THE AZIMUTHAL EQUATION IS JUST A SHO EQUATION, WITH A HARMONIC SOLUTION ($g \sim e^{i m_l \phi}$). m_l IS RESTRICTED TO BE $= 0$ OR AN INTEGER (+ OR −).

THE ANGULAR EQUATION IS THE ASSOCIATED LEGENDRE EQUATION.

BECAUSE IT CONTAINS THE AZIMUTHAL QUANTUM NUMBER, m_l, IT IS CUSTOMARY TO LINK THE SOLUTIONS TO THE 2 EQUATIONS. THE SOLUTIONS ARE CALLED

SPHERICAL HARMONICS $Y(\theta, \phi)$

THE QUANTUM NUMBERS ARE ALSO LINKED SO THAT

$$l = 0, 1, 2, 3, \ldots\ldots$$

AND

$$m_l = -l, -l+1, -l+2, \cdots 0 \cdots l-1, l$$

(l ALSO DEPENDS ON n, THE PRINCIPAL QUANTUM NUMBER

$$l < n$$

TABLE 7.1

Normalized Spherical Harmonics $Y(\theta, \phi)$

ℓ	m_ℓ	$Y_{\ell m_\ell}$
0	0	$\frac{1}{2\sqrt{\pi}}$
1	0	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$
1	±1	$\mp\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta\, e^{\pm i\phi}$
2	0	$\frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1)$
2	±1	$\mp\frac{1}{2}\sqrt{\frac{15}{2\pi}}\sin\theta\cos\theta\, e^{\pm i\phi}$
2	±2	$\frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta\, e^{\pm 2i\phi}$
3	0	$\frac{1}{4}\sqrt{\frac{7}{\pi}}(5\cos^3\theta - 3\cos\theta)$
3	±1	$\mp\frac{1}{8}\sqrt{\frac{21}{\pi}}\sin\theta(5\cos^2\theta - 1)e^{\pm i\phi}$
3	±2	$\frac{1}{4}\sqrt{\frac{105}{2\pi}}\sin^2\theta\cos\theta\, e^{\pm 2i\phi}$
3	±3	$\mp\frac{1}{8}\sqrt{\frac{35}{\pi}}\sin^3\theta\, e^{\pm 3i\phi}$

ATOMIC QUANTUM NUMBERS

n PRINCIPAL QUANTUM NUMBER

l ORBITAL ANGULAR MOMENTUM QUANTUM NUMBER

m_l MAGNETIC QUANTUM NUMBER

$$n = 1, 2, 3, \ldots$$

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

$$m_l = -l, -l+1, \ldots 0, \ldots l-1, l$$

IN SUMMARY

$$n > 0$$

$$l < n$$

$$|m_l| \leq l$$

ANGULAR MOMENTUM

THE ANGULAR MOMENTUM OF AN ELECTRON IN THE ATOM, $L = mvr = \sqrt{\ell(\ell+1)}\,\hbar$.

NOTE THAT THIS DISAGREES WITH BOHR'S ORIGINAL GUESS ($L = n\hbar$).

FOR A GIVEN n, THE ENERGY WILL BE

$$E_n = -\frac{E_0}{n^2} \quad \text{FOR ALL VALUES OF } \ell.$$

THE DIFFERENT ℓ STATES ARE DEGENERATE.

HISTORICAL NOTATION:

$$\begin{array}{ccccccc} \ell = & 0 & 1 & 2 & 3 & 4 & 5 \\ & \updownarrow & \updownarrow & \updownarrow & \updownarrow & \updownarrow & \updownarrow \\ & s & p & d & f & g & h \end{array}$$

WE USUALLY USE THE n # AND THE ℓ LETTER.

FOR EXAMPLE: $n = 3$, $\ell = 1$ IS CALLED THE 3p STATE.

MAGNETIC QUANTUM NUMBER

l DETERMINES THE TOTAL ANGULAR MOMENTUM, L

$$L = \sqrt{l(l+1)}\,\hbar$$

m_l GIVES THE z COMPONENT OF L

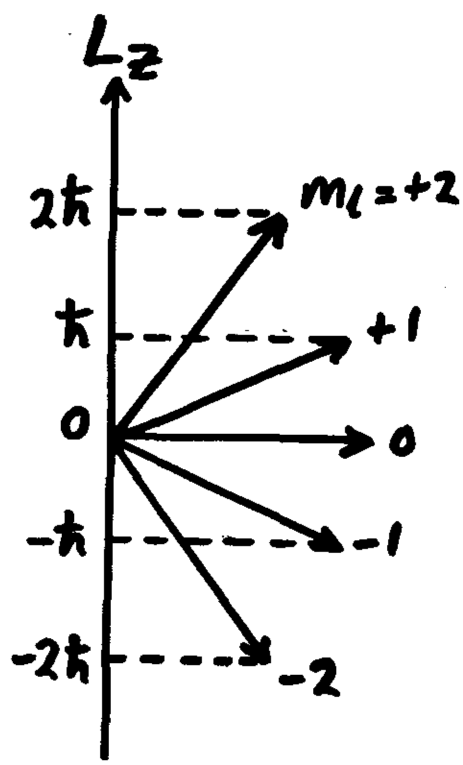
$$L_z = m_l \hbar$$

THE COMBINATION SHOWS SPACE QUANTIZATION AND (BECAUSE m_l IS ALWAYS $< \sqrt{l(l+1)}$) THE ANGULAR MOMENTUM CAN NEVER LINE UP ALONG THE z AXIS.

z IS USUALLY DEFINED BY AN EXTERNAL MAGNETIC FIELD AND THAT IS WHY m_l IS CALLED THE MAGNETIC QUANTUM NUMBER.

AN EXAMPLE FOR $l = 2$

$\Rightarrow L = \sqrt{6}\,\hbar$

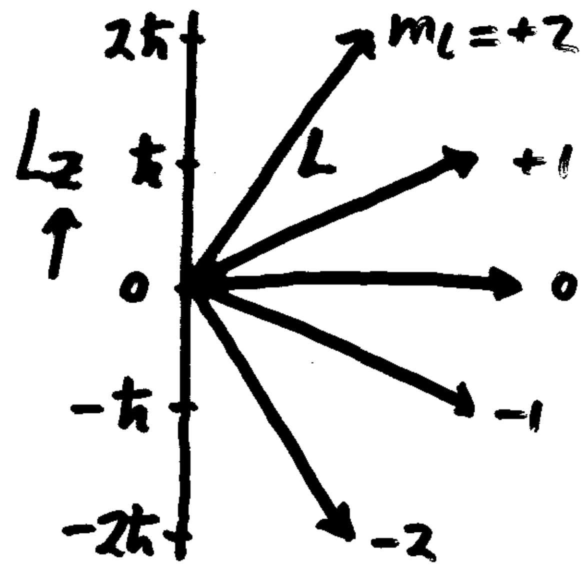


7.14 FOR A 3d STATE DRAW ALL THE POSSIBLE ORIENTATIONS OF THE ANGULAR MOMENTUM VECTOR $\vec{L}$. WHAT IS $L_x^2 + L_y^2$ FOR THE $m_l = -1$ COMPONENT?

$$3d \Rightarrow l = 2$$

$$\therefore L = \sqrt{l(l+1)}\,\hbar = \sqrt{6}\,\hbar$$

POSSIBLE VALUES OF $m_l = -2 \quad -1 \quad 0 \quad +1 \quad +2$
WITH $L_z = m_l \hbar$



FOR $m_l = -1 \Rightarrow L_z = -\hbar$

$$L^2 = L_x^2 + L_y^2 + L_z^2$$

$$\therefore 6\hbar^2 = L_x^2 + L_y^2 + \hbar^2$$

$$\therefore L_x^2 + L_y^2 = \boxed{5\hbar^2}$$

What is the degeneracy of any n state?

If $n = 2 \Rightarrow \ell = 0$ OR 1

$$\underbrace{m_\ell = 0 \qquad\qquad m_\ell = -1, 0, +1}_{\text{4 possible states}}$$

If $n = 3 \Rightarrow \ell = 0$ OR 1 OR 2

$$\underbrace{m_\ell = 0 \qquad\qquad m_\ell = -1, 0, +1 \qquad\qquad m_\ell = -2, -1, 0, +1, +2}_{\text{9 possible states}}$$

7.16 PROVE THAT THE DEGENERACY OF AN n STATE IS n^2.

FOR EACH n STATE THERE ARE n POSSIBLE VALUES OF l

$0 \quad 1 \quad 2 \quad \ldots\ldots (n-1)$

FOR EACH l STATE THERE ARE $(2l+1)$ POSSIBLE VALUES OF m_l

$-l \quad -l+1 \quad \ldots\ldots \quad -1 \quad 0 \quad +1 \quad +l-1 \quad +l$

$\therefore$ DEGENERACY $= \sum_{n=1}^{n}(2l+1)$

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

$$= \sum_{n=1}^{n}(2n-1)$$

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

$$= n^2 \checkmark$$

MAGNETIC EFFECTS

AN ELECTRON ORBITING AROUND A NUCLEUS IS A CURRENT LOOP i.e. HAS A MAGNETIC MOMENT, μ.

$$\vec{\mu} = IA = \frac{-e}{2\pi \frac{r}{v}} \cdot \pi r^2 = -\frac{erv}{2} = \frac{-e}{2m} \vec{L}$$

$$\mu_z = \frac{-e}{2m} L_z = \frac{-e}{2m} m_l \hbar = -m_l \mu_B$$

WHERE $\mu_B = \frac{e\hbar}{2m}$ IS THE BOHR MAGNETON,

A UNIT OF MAGNETIC MOMENT $= 9.27E\text{-}24 \ \frac{J}{T}$

IN AN EXTERNAL MAGNETIC FIELD, B, THE MAGNETIC DIPOLE WILL FEEL A TORQUE

$$\vec{\tau} = \vec{\mu} \wedge \vec{B}$$

AND WILL HAVE A POTENTIAL ENERGY OF

$$V_B = -\vec{\mu} \cdot \vec{B}$$

IF $\vec{B}$ IS IN THE z DIRECTION THEN

$$V_B = -\mu_z B = m_l B \mu_B$$

THE POTENTIAL ENERGY IS THUS QUANTIZED ACCORDING TO m_l AND DEGENERATE ENERGY LEVELS ARE SEPARATED INTO $2l+1$ DIFFERENT LEVELS.

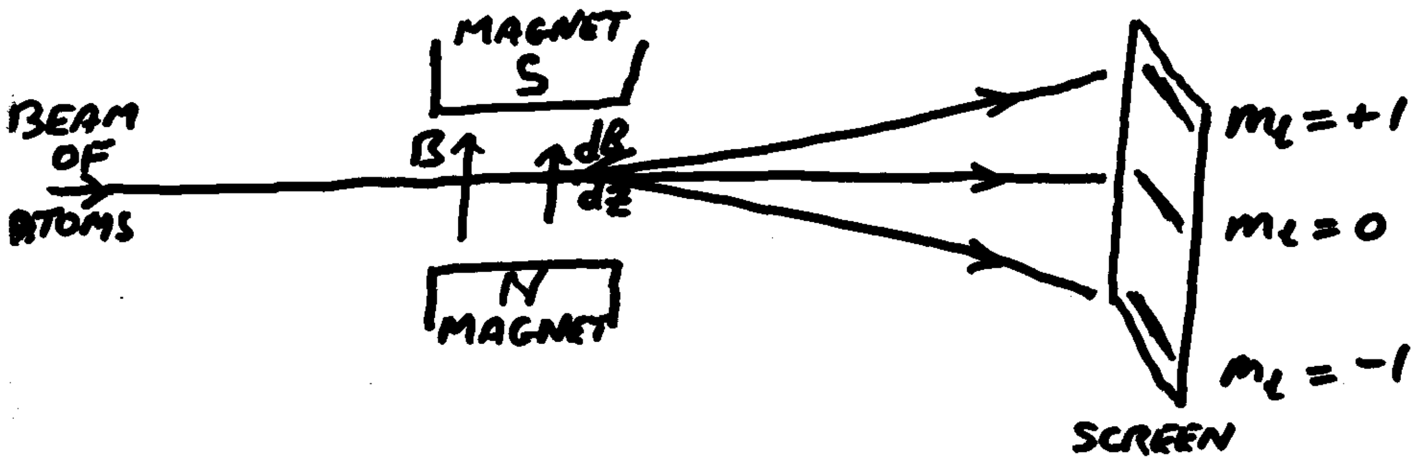
THE STERN-GERLACH EXPERIMENT

UNDER THE APPLICATION OF A MAGNETIC FIELD THE ENERGY LEVELS SPLIT. HOW CAN WE OBSERVE THIS?

IF THE MAGNETIC FIELD IS INHOMOGENEOUS THERE WILL BE A NET FORCE ON EACH ATOM.

$$F_z = -\frac{dV_B}{dz} = m_l \mu_B \frac{dB}{dz}$$

i.e. IN THE $+z$ DIRECTION FOR $+m_l$
NO FORCE FOR $m_l = 0$
IN THE $-z$ DIRECTION FOR $-m_l$



7.25 A HYDROGEN ATOM IN A 5f STATE IS IN A MAGNETIC FIELD OF 3T. WHAT IS THE ENERGY IN THE ABSENCE OF THE MAG. FIELD? HOW MANY STATES ARE THERE, AND WHAT ARE THEIR ENERGIES IN THE MAG. FIELD?

$n = 5 \quad l = 3 \quad m_l = 0, \pm 1, \pm 2, \pm 3$

$$E_5 = \frac{-13.6}{25} = -0.544 \text{ eV}$$

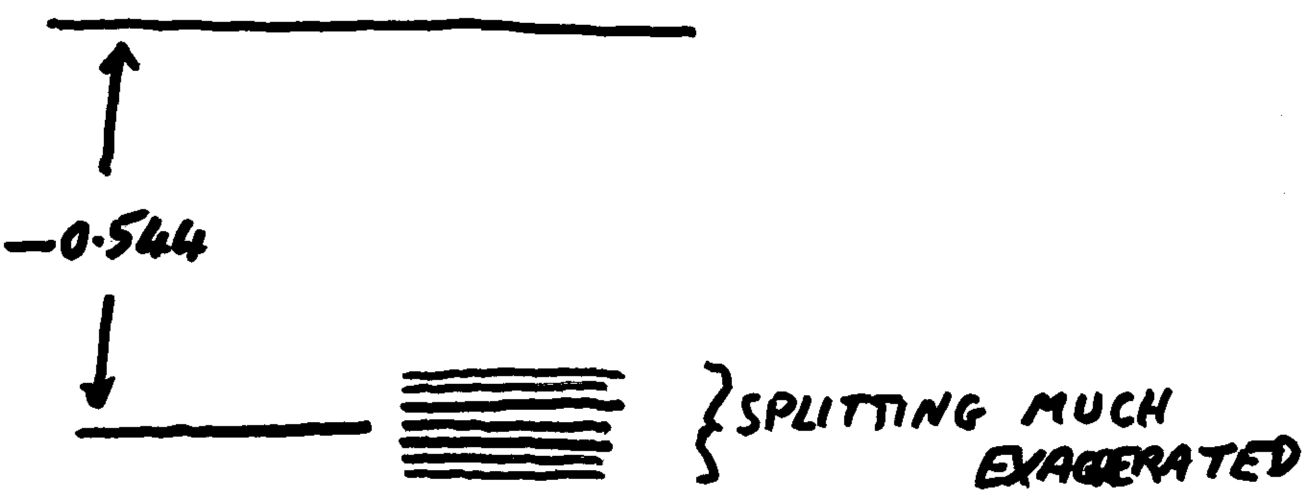
$$V_B = m_l B \mu_B = m_l \cdot 3 \cdot 5.79E{-5} \text{ eV/T}$$

$\Rightarrow \quad = 0$ FOR $m_l = 0$

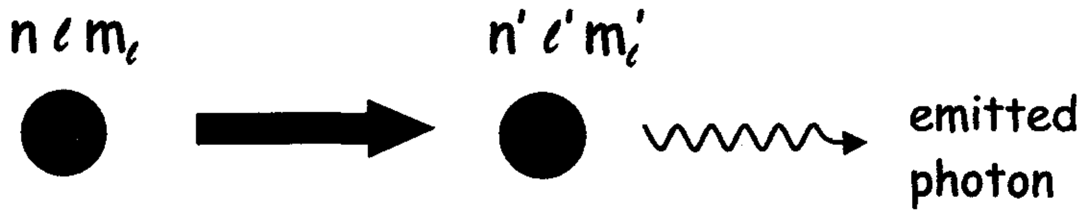
$= \pm 1.74E{-4}$ eV FOR $m_l = \pm 1$

$= \pm 3.47E{-4}$ eV FOR $m_l = \pm 2$

$= \pm 5.21E{-4}$ eV FOR $m_l = \pm 3$



Selection Rules



<u>Allowed transitions:</u>

- lifetimes $\tau \sim 10^{-9}$ sec

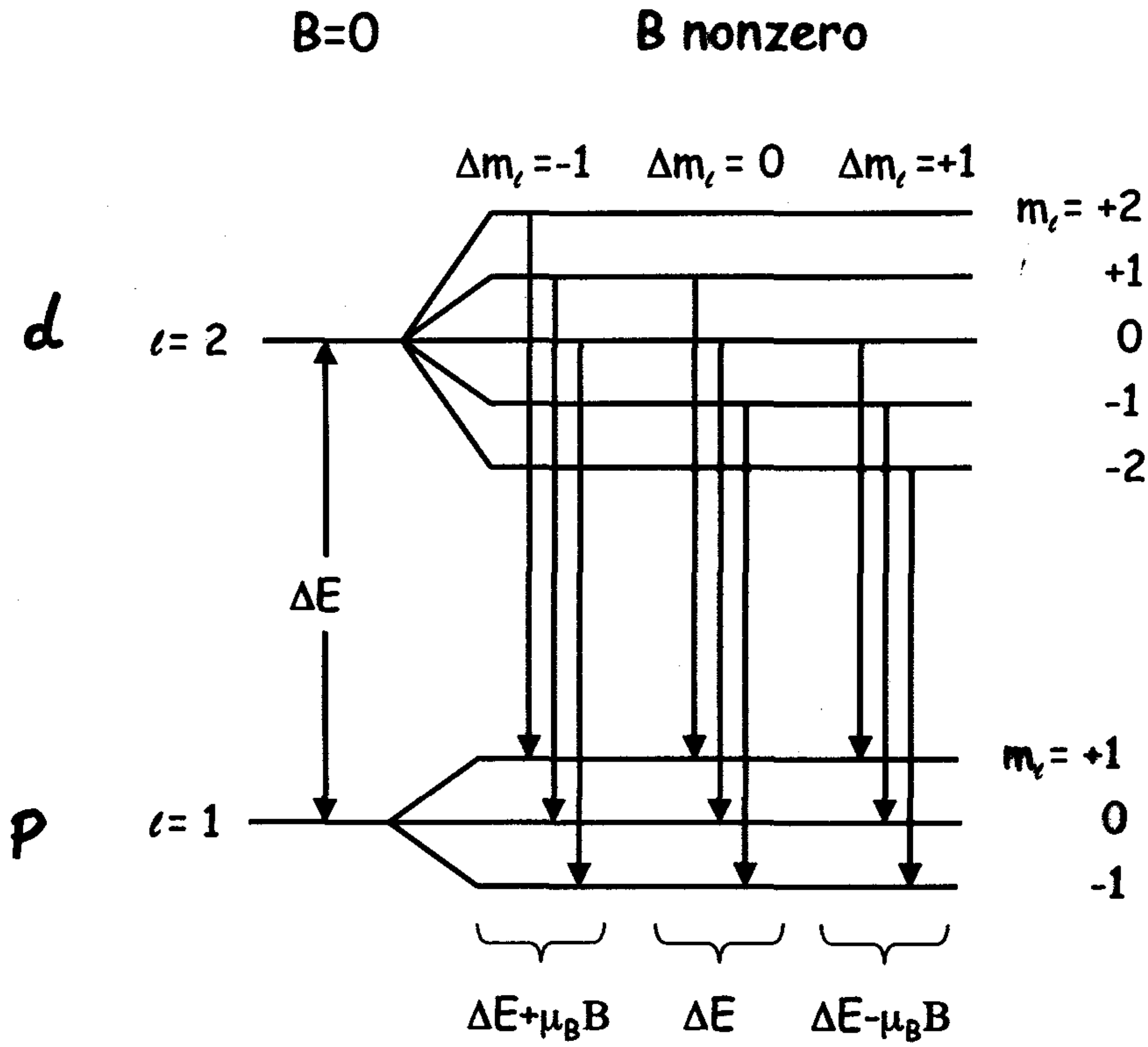
Δn = anything, $\Delta \ell = \pm 1$, $\Delta m_\ell = 0, \pm 1$

<u>Forbidden transitions:</u>

- lifetimes much longer

Ex. $2s \rightarrow 1s$, $\tau \sim 1/7$ sec

Selection Rules and Normal Zeeman Effect



B field always splits spectral lines into 3 for normal Zeeman effect.

ELECTRON SPIN

ONE LAST COMPLICATION! STUDY OF ATOMIC SPECTRA IN MAGNETIC FIELDS SHOWED MORE SPLITTING THAN EXPECTED.

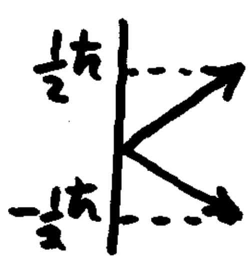
WOLFGANG PAULI PROPOSED THAT AN EXTRA QUANTUM NUMBER WAS NEEDED
$\Rightarrow$ 4 CORRESPONDING TO THE 4 DIMENSIONS

IN 1925, SAM GOUDSMIT AND GEORGE UHLENBECK, 2 DUTCH GRADUATE STUDENTS, PROPOSED THAT THE ELECTRON HAD A SPIN AND (SINCE IT IS CHARGED) AN INTRINSIC MAGNETIC MOMENT.

IN ANALOGY WITH ORBITAL ANGULAR MOMENTUM THEY PROPOSED A MAGNETIC SPIN QUANTUM NUMBER

$$m_s = \pm \frac{1}{2}$$

THE ELECTRON'S SPIN WILL EITHER BE ORIENTED "UP" OR "DOWN" IN A MAGNETIC FIELD



THE SPIN QUANTUM NUMBER IS $s = \frac{1}{2}$

$$|\vec{S}| = \sqrt{s(s+1)}\,\hbar = \sqrt{\tfrac{3}{4}}\,\hbar$$

$$\vec{\mu}_s = -\frac{e}{m}\vec{S} = -2^{*}\frac{\mu_B}{\hbar}\vec{S}$$

COMPARE WITH

$$\vec{\mu}_l = -\frac{e}{2m}\vec{L} = -1^{*}\frac{\mu_B}{\hbar}\vec{L}$$

"THE INTRINSIC SPIN OF THE ELECTRON IS TWICE AS EFFECTIVE IN MAKING A MAGNETIC MOMENT AS THE ORBITAL ANGULAR MOMENTUM." THIS IS AN EFFECT OF RELATIVITY; EXPLAINED BY THE DIRAC EQUATION.

* THESE NUMBERS ARE CALLED THE <u>GYROMAGNETIC RATIO</u>

$$g_s = 2 \qquad g_l = 1$$