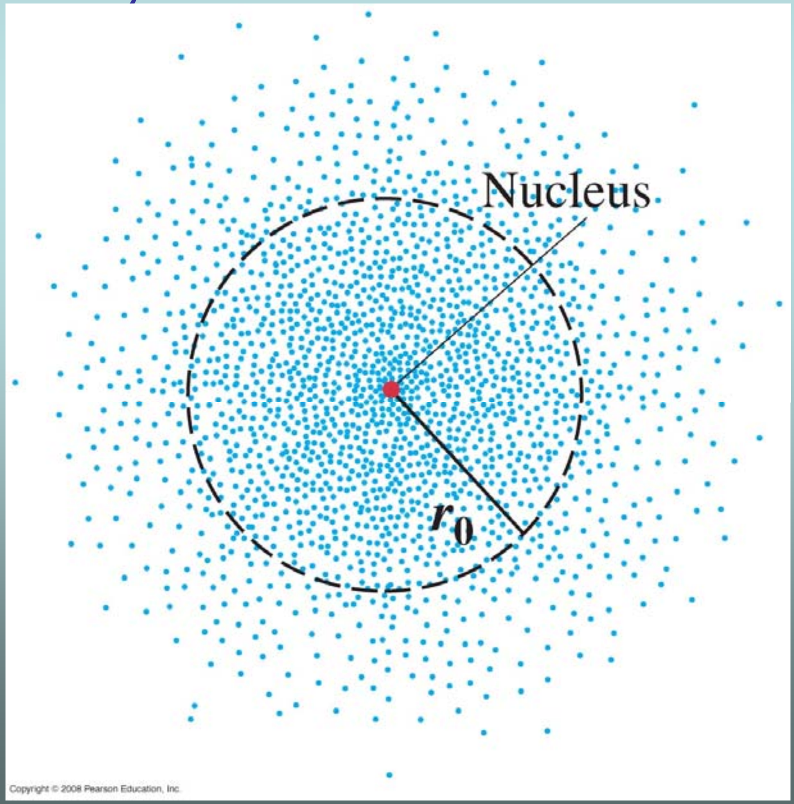
Quantum Mechanics and the hydrogen atom

Since we cannot say exactly where an electron is, the Bohr picture of the atom, with electrons in neat orbits, cannot be correct.

Quantum theory describes electron probability distributions:

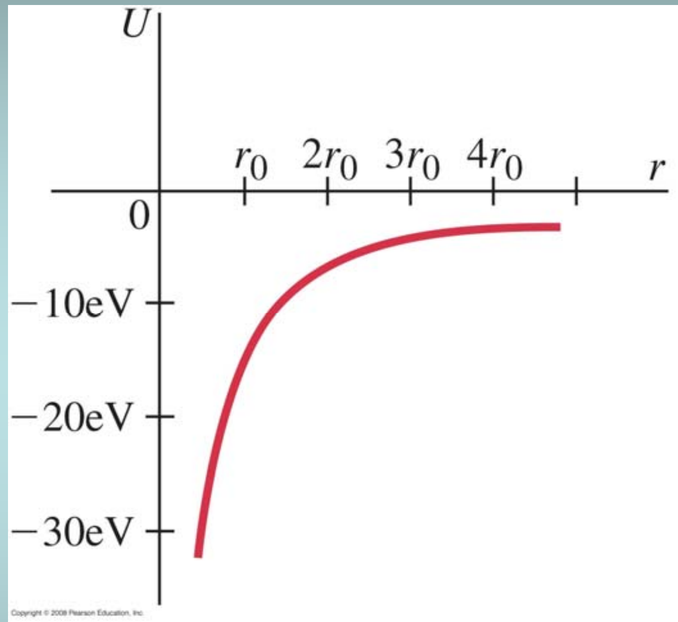
$$\psi(r) = \frac{1}{\sqrt{\pi r_0^3}} e^{-\frac{r}{r_0}}$$



Hydrogen Atom:
Schrödinger Equation and Quantum Numbers

Potential energy for the hydrogen atom:

$$U = -\frac{1}{4\pi\epsilon_0}\frac{e^2}{r}$$



The time-independent Schrödinger equation in three dimensions is then:

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)-\frac{1}{4\pi\epsilon_0}\frac{e^2}{r}\psi = E\psi,$$

Where does the quantisation in QM come from ?

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)-\frac{1}{4\pi\epsilon_0}\frac{e^2}{r}\psi = E\psi,$$

The atomic problem is spherical so rewrite the equation in (r,θ,φ)

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

Rewrite all derivatives in (r,θ,φ), gives Schrödinger equation;

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

This is a partial differential equation, with 3 coordinates (derivatives);
Use again the method of separation of variables:

$$\Psi(r,\theta,\phi)=R(r)Y(\theta,\phi)$$

Bring r-dependence to left and angular dependence to right (divide by Ψ):

$$\frac{1}{R}\left[\frac{d}{dr}r^2\frac{dR}{dr}+\frac{2mr^2}{\hbar^2}(E-V(r))R\right]=-\frac{O_{\theta\phi}^{QM}Y(\theta,\phi)}{Y(\theta,\phi)}=\lambda$$

Separation of variables

Where does the quantisation in QM come from ?

Radial equation

$$\frac{1}{R}\left[\frac{d}{dr}r^2\frac{dR}{dr}+\frac{2mr^2}{\hbar^2}\left(E-V(r)\right)R\right]=\lambda$$

Angular equation

$$-\frac{O^{QM}_{\theta\phi}Y(\theta,\phi)}{Y(\theta,\phi)}=\frac{-\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)Y(\theta,\phi)}{Y(\theta,\phi)}=\lambda$$

$$\downarrow$$

$$-\frac{\partial^2 Y}{\partial\phi^2}=\sin\theta\frac{\partial}{\partial\theta}\sin\theta\frac{\partial Y}{\partial\theta}+\lambda\sin^2\theta Y$$

Once more separation of variables: $Y(\theta,\phi)=\Theta(\theta)\Phi(\phi)$

Derive:

$$-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=\frac{1}{\Theta}\left(\sin\theta\frac{\partial}{\partial\theta}\sin\theta\frac{\partial\Theta}{\partial\theta}+\lambda\sin^2\theta\Theta\right)=m^2$$

(again arbitrary constant)

Simplest of the three: the azimuthal angle;

$$\frac{\partial^2\Phi(\phi)}{\partial\phi^2}+m^2\Phi(\phi)=0$$

Where does the quantisation in QM come from ?

A differential equation with a boundary condition

$$\frac{\partial^2 \Phi(\phi)}{\partial \phi^2} + m^2 \Phi(\phi) = 0 \quad \text{and} \quad \Phi(\phi + 2\pi) = \Phi(\phi)$$

Solutions:

$$\Phi(\phi) = e^{im\phi}$$

Boundary condition; $\Phi(\phi + 2\pi) = e^{im(\phi+2\pi)} = \Phi(\phi) = e^{im\phi}$

$$e^{2\pi i m} = 1$$

→ ***m*** **is a positive or negative integer**

this is a quantisation condition

General: differential equation plus a boundary condition gives a quantisation

Where does the quantisation in QM come from ?

First coordinate $\Phi(\phi) = e^{im\phi}$ with integer m (positive and negative)

Second coordinate

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial\Theta}{\partial\theta} + \left(\lambda - \frac{m^2}{\sin^2\theta}\right)\Theta = 0$$

Results in $\lambda_\ell = \ell(\ell+1)$ with $\ell = 0,1,2,\ldots$

and $m = -\ell, -\ell+1, \ldots, \ell-1, \ell$

angular part

angular momentum

Third coordinate

$$\frac{1}{R}\left[\frac{d}{dr}r^2\frac{dR}{dr} + \frac{2mr^2}{\hbar^2}(E - V(r))R\right] = \ell(\ell+1)$$

Differential equation

Results in quantisation of energy

$$E_n = -\frac{Z^2}{n^2}R_\infty = -\frac{Z^2}{n^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\frac{m_e}{2\hbar^2}$$

with integer n (n>0)

radial part

Angular wave functions

Operators:

$$L^2 = \frac{\hbar}{i}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

$$L_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$$

Angular momentum

$$\vec{L} = (L_x, L_y, L_z)$$

There is a class of functions that are simultaneous eigenfunctions

$$L^2 Y_{lm}(\theta,\phi) = \ell(\ell+1)\hbar^2 Y_{lm}(\theta,\phi) \qquad L_z Y_{lm}(\theta,\phi) = m\hbar Y_{lm}(\theta,\phi)$$

with $\ell = 0,1,2,\ldots$ **and** $m = -\ell, -\ell+1, \ldots, \ell-1, \ell$

Spherical harmonics (**Bolfuncties**) $Y_{lm}(\theta,\phi)$

$$Y_{00} = \sqrt{\frac{1}{4\pi}} \qquad Y_{11} = -\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\phi}$$

$$Y_{10} = -\sqrt{\frac{3}{4\pi}}\cos\theta$$

$$Y_{1,-1} = \sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\phi}$$

Vector space of solutions

$$\int_\Omega |Y_{lm}(\theta,\phi)|^2 d\Omega = 1$$

$$\int_\Omega Y^*_{lm} Y_{l'm'} d\Omega = \delta_{ll'}\delta_{mm'}$$

Parity

$$P_{op} Y_{lm}(\theta,\phi) = Y(\pi-\theta, \phi+\pi) = (-)^\ell Y_{lm}(\theta,\phi)$$

The radial part: finding the ground state

$$\frac{1}{R}\left[\frac{d}{dr}r^2\frac{dR}{dr}+\frac{2mr^2}{\hbar^2}(E-V(r))R\right]=\lambda$$

Find a solution for $\ell=0, m=0$

$$-\frac{\hbar^2}{2m}\left(R''+\frac{2}{r}R'\right)-\frac{Ze^2}{4\pi\varepsilon_0 r}R=ER$$

Physical intuition; no density for $r\to\infty$

trial: $R(r)=Ae^{-r/a}$

$$R'=-\frac{A}{a}e^{-r/a}=-\frac{R}{a}$$

$$R''=\frac{A}{a^2}e^{-r/a}=\frac{R}{a^2}$$

→ $$-\frac{\hbar^2}{2m}\left(\frac{1}{a^2}-\frac{2}{ar}\right)-\frac{Ze^2}{4\pi\varepsilon_0 r}=E$$

must hold for all values of r

Prefactor for $1/r$: $$\frac{\hbar^2}{ma}-\frac{Ze^2}{4\pi\varepsilon_0}=0$$

→ Solution for the length scale paramater

$$a_0=\frac{4\pi\varepsilon_0\hbar^2}{Ze^2 m}$$ Bohr radius

Solutions for the energy

$$E=-\frac{\hbar^2}{2ma}=-Z^2\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\frac{m_e}{2\hbar^2}$$

Ground state in the Bohr model $(n=1)$

Hydrogen Atom:
Schrödinger Equation and Quantum Numbers

There are four different quantum numbers needed to specify the state of an electron in an atom.

1. The principal quantum number n gives the total energy.
2. The orbital quantum number ℓ gives the angular momentum; ℓ can take on integer values from 0 to n - 1.

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

3. The magnetic quantum number, m , gives the ℓ direction of the electron's angular momentum, and can take on integer values from $-\ell$ to $+\ell$.

$$L_z = m_\ell \hbar$$

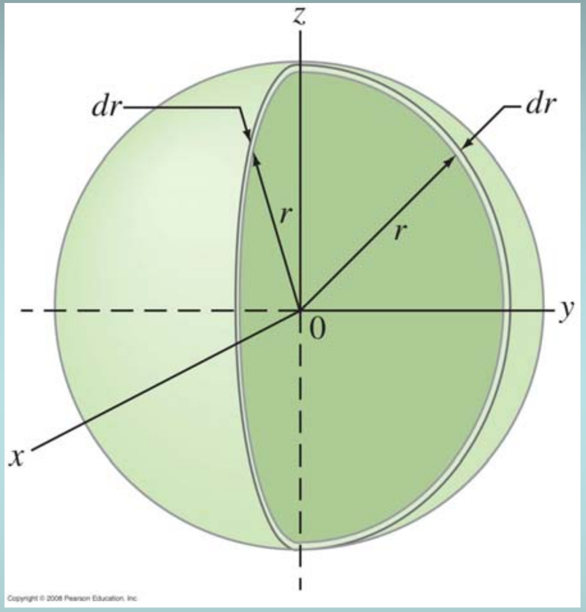
Hydrogen Atom Wave Functions

The wave function of the ground state of hydrogen has the form:

$$\psi_{100} = \frac{1}{\sqrt{\pi r_0^3}} e^{-\frac{r}{r_0}}$$

The probability of finding the electron in a volume dV around a given point is then $|\psi|^2 \, dV$.

Radial Probability Distributions



Spherical shell of thickness **d*r***, inner radius **r** and outer radius **r+dr**.

Its volume is **$dV=4\pi r^2 dr$**

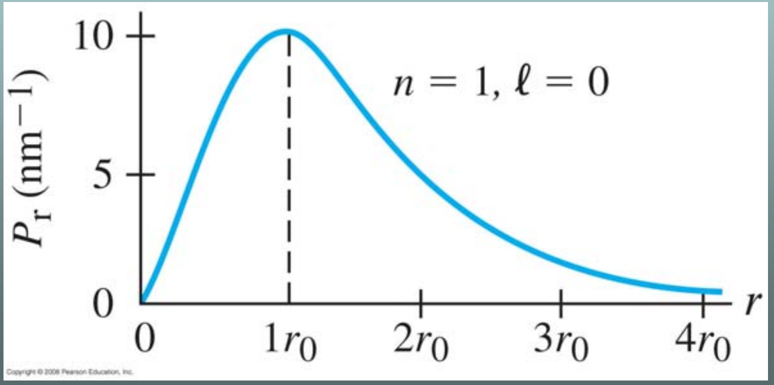
Density: **$|\psi|^2 dV = |\psi|^2 4\pi r^2 dr$**

The radial probablity distribution is then:

$P_r = 4\pi r^2 |\psi|^2$

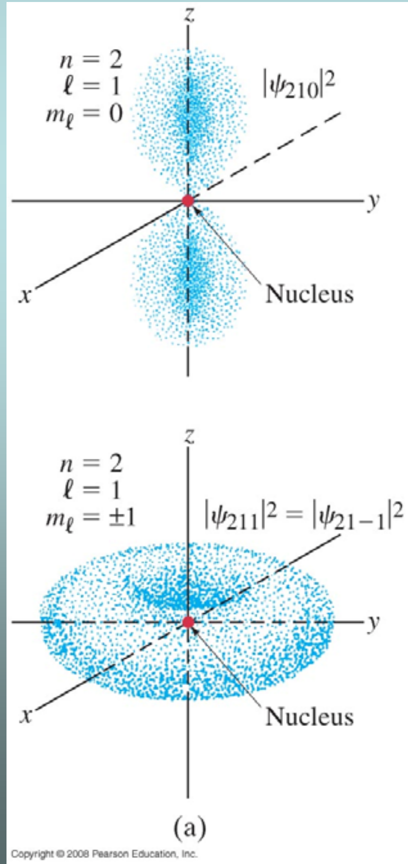
Ground state

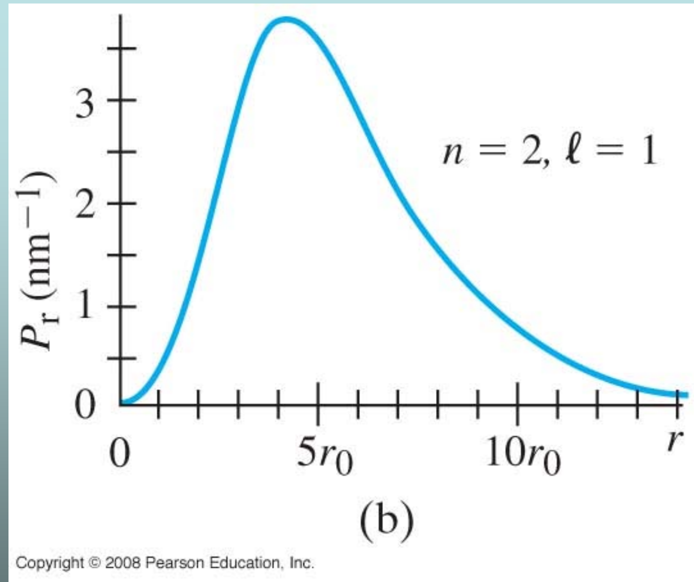
$$P_r = 4\frac{r^2}{r_0^3}e^{-\frac{2r}{r_0}}$$



Hydrogen Atom Wave Functions

This figure shows the three probability distributions for $n = 2$ and $\ell = 1$ (the distributions for $m_\ell = +1$ and $m_\ell = -1$ are the same), as well as the radial distribution for all $n = 2$ states.





Hydrogen “Orbitals” (electron clouds)

$$\left|\Psi\left(\vec{r},t\right)\right|^2$$

Represents the probability to find a particle
At a location *r* at a time *t*

The probability density
The probability distribution

Max Born

The Nobel Prize in Physics 1954
"for his fundamental research in quantum mechanics, especially for his statistical interpretation of the wavefunction"

Atomic Hydrogen Radial part

Analysis of radial equation yields:

$$E_{nlm} = -\frac{Z^2}{n^2} R_\infty$$

with $$R_\infty = \frac{m_e e^4}{8\varepsilon_0 h^3 c}$$

Wave functions:

$$\Psi_{nlm}(\vec{r},t) = R_{nl}(r) Y_{lm}(\theta,\phi) e^{-iE_n t/\hbar}$$

$n=1$	$\ell=0$	$R_{10} = \frac{2}{\sqrt{a^3}} e^{-\rho}$
$n=2$	$\ell=0$	$R_{20} = \frac{1}{\sqrt{2a^3}} \left(1 - \frac{\rho}{2}\right) e^{-\rho/2}$
	$\ell=1$	$R_{21} = \frac{1}{2\sqrt{6a^3}} \rho e^{-\rho/2}$
$n=3$	$\ell=0$	$R_{30} = \frac{2}{3\sqrt{3a^3}} \left(1 - \frac{2}{3}\rho + \frac{2}{27}\rho^2\right) e^{-\rho/3}$
	$\ell=1$	$R_{31} = \frac{8}{27\sqrt{6a^3}} \rho \left(1 - \frac{\rho}{6}\right) e^{-\rho/3}$
	$\ell=2$	$R_{32} = \frac{4}{81\sqrt{30a^3}} \rho^2 e^{-\rho/3}$

For numerical use:

$$R = \frac{u_{n\ell}(r)}{r}$$

$$u_{n\ell}(\rho) = \sqrt{\frac{2Z}{na_0}} \sqrt{\frac{(n-\ell-1)!}{2n(n+1)!}} e^{-Z\rho/n} \left(\frac{2Z\rho}{n}\right)^{\ell+1} L_{n-\ell-1}^{2\ell+1}\left(\frac{2Z\rho}{n}\right)$$

$$\rho / r = 2Z / na \qquad a = 4\pi\varepsilon_0 \hbar^2 / \mu e^2$$

Quantum analog of electromagnetic radiation

Classical electric dipole radiation → Transition dipole moment

Classical oscillator → Quantum jump

$$I_{rad} \propto \left| e\ddot{\vec{r}} \right|^2 \longrightarrow I_{rad} \propto \left| \int \psi_1^* e\vec{r}\psi_2 d\tau \right|^2$$

The atom does not radiate when it is in a stationary state !
The atom has no dipole moment

$$\mu_{ii} = \int \psi_1^* \vec{r}\,\psi_1 d\tau = 0$$

Intensity of spectral lines linked
to Einstein coefficient for absorption:

$$B_{if} = \frac{\left|\mu_{fi}\right|^2}{6\varepsilon_0\hbar^2}$$

Selection rules

Mathematical background: function of odd parity gives **0** when integrated over space

In one dimension: $\left\langle \Psi_f \middle| x \middle| \Psi_i \right\rangle = \int_{-\infty}^{\infty} \Psi_f^* x \Psi_i dx = \int_{-\infty}^{\infty} f(x) dx$ with $f(x) = \Psi_f^* x \Psi_i$

$$\int_{-\infty}^{\infty} f(x)dx = \int_{-\infty}^{0} f(x)dx + \int_{0}^{\infty} f(x)dx = \int_{\infty}^{0} f(-x)d(-x) + \int_{0}^{\infty} f(x)dx = \int_{0}^{\infty} f(-x)dx + \int_{0}^{\infty} f(x)dx$$

$= 2\int_{0}^{\infty} f(x)dx \neq 0$ if $f(-x) = f(x)$ $\longrightarrow$ Ψ_i and Ψ_f opposite parity

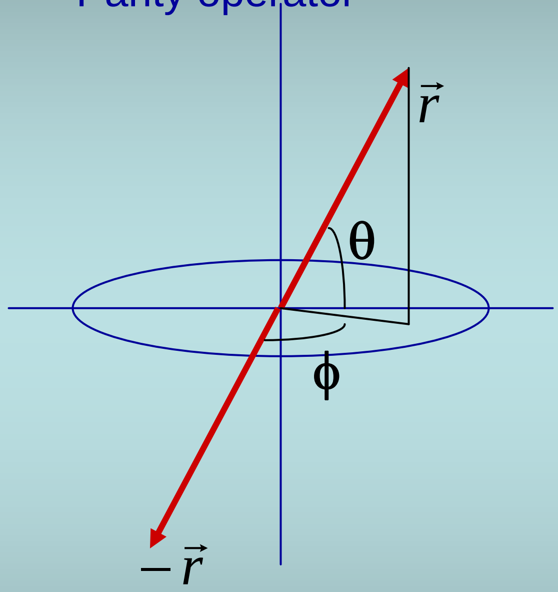
$= 0$ if $f(-x) = -f(x)$ $\longrightarrow$ Ψ_i and Ψ_f same parity

Electric dipole radiation connects states of opposite parity !

Selection rules

depend on <u>angular</u> behavior of the wave functions

Parity operator



$$P\vec{r} = -\vec{r}$$

$$(x, y, z) \rightarrow (-x, -y, -z)$$

$$(r, \theta, \phi) \rightarrow (r, \pi - \theta, \phi + \pi)$$

All quantum mechanical wave functions have a definite parity

$$\Psi(-\vec{r}) = \pm\Psi(\vec{r})$$

$$\langle \Psi_f | \vec{r} | \Psi_i \rangle \neq 0$$

If Ψ_f and Ψ_i have opposite parity

Rule about the $Y_{\ell m}$ functions

$$PY_{\ell m}(\theta, \phi) = (-)^{\ell} Y_{\ell m}(\theta, \phi)$$

Hydrogen Atom:
Schrödinger Equation and Quantum Numbers

"Allowed" transitions between energy levels occur between states whose value of ℓ differ by one:

$$\Delta\ell = \pm 1$$

Other, "forbidden," transitions also occur but with much lower probability.

"selection rules, related to symmetry"

Selection rules in Hydrogen atom

Intensity of spectral lines given by

$$\mu_{fi} = \int \Psi_f^* \vec{\mu} \Psi_i = \langle \Psi_f | -e\vec{r} | \Psi_i \rangle$$

1) Quantum number n
   no restrictions

2) Parity rule for ℓ

$$\Delta \ell = odd$$

3) Laporte rule for ℓ

Angular momentum rule:

$\vec{\ell}_f = \vec{\ell}_i + \vec{1}$ so $\Delta \ell \leq 1$

From 2. and 3. $\Delta \ell = \pm 1$