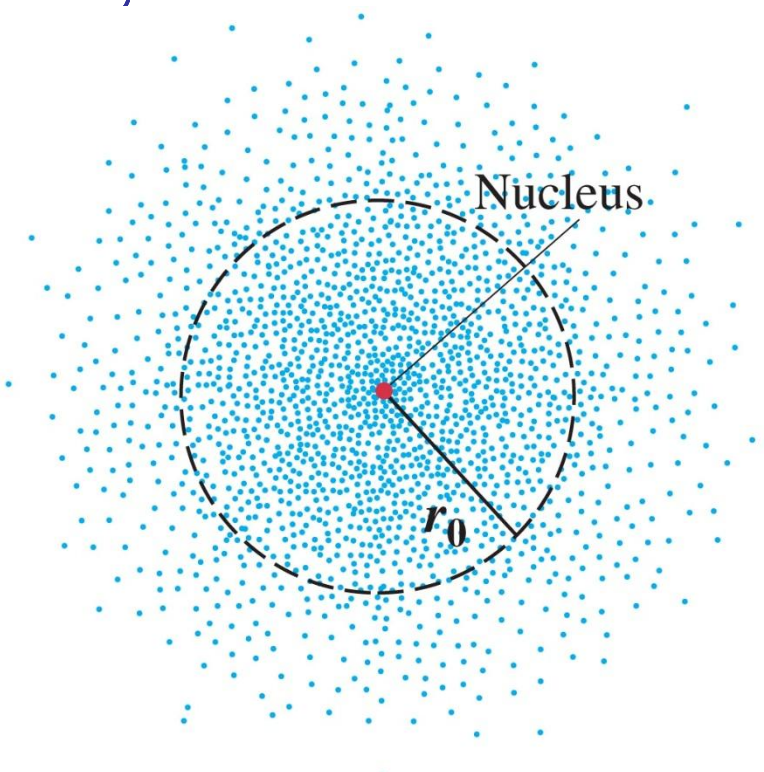
Quantum Mechanics of Atoms

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:

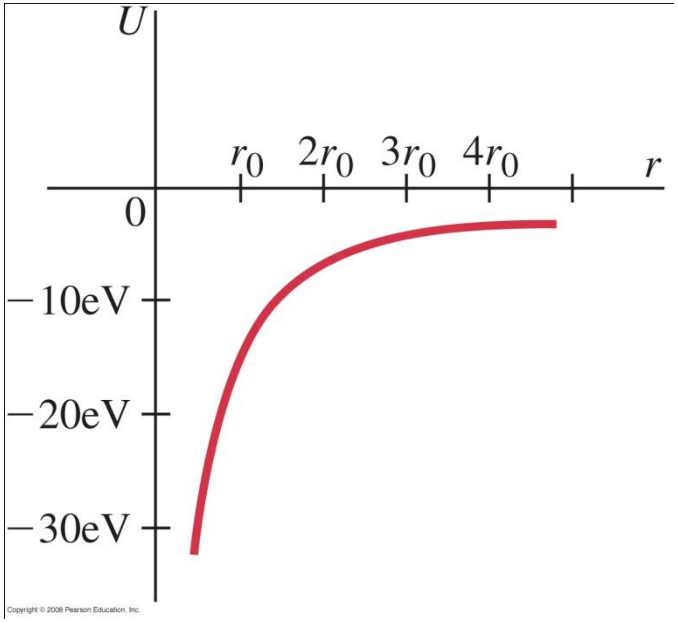
$$\psi(r) = \frac{1}{\sqrt{\pi r_0^3}} e^{-\frac{r}{r_0}}$$



Hydrogen Atom:
Schrödinger Equation and Quantum Numbers

Potential energy for the hydrogen atom:

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



Hydrogen Atom:
Schrödinger Equation and Quantum Numbers

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

$$E_n = -\frac{13.6\,\mathrm{eV}}{n^2} \qquad n = 1, 2, 3, \cdots$$

Note, this 13.6 ev is the Rydberg constant, that is also found via QM

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

Rydberg constant = 13.6 eV

Intermezzo

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):

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

Intermezzo

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;

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

Intermezzo

Where does the quantisation in QM come from ?

A differential equation with a boundary condition

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

Solutions:

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

Boundary condition;

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

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

$\longrightarrow$ ***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

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

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

Intermezzo

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

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

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

Parity

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

Intermezzo

The radial part: finding the ground state

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

must hold for all values of r !!

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

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

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

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

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

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

Solution for the length scale paramater

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

Solutions for the energy

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

$$\boxed{E=-\frac{\mu}{m_e}Z^2E_0}$$

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

Isotope effect

Hydrogen Atom:
Schrödinger Equation and Quantum Numbers

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

This partial differential equation can be separated into three equations;
General solution:

$$\Psi(r,\theta,\phi)=R(r)\Theta(\theta)\Phi(\varphi)$$

1) Radial equation:

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

Eigenfunctions: $R(r)$

Eigenvalues: n **and** $E_n=-\frac{Z^2}{n^2}R_\infty$

2) Equation for θ:

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

Eigenfunctions: $\Theta(\theta)$

Eigenvalues: ℓ

3) Equation for ϕ:

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

Eigenfunctions: $\Phi(\varphi)$

Eigenvalues: m

NB: connections between *n*, *l* and m derive from solutions of Schrödinger Equation

Hydrogen Atom: Schrödinger Equation and Quantum Numbers

There are **three** different quantum numbers needed to specify the state of an electron in an atom (**plus one**).

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_ℓ, gives the direction of the electron's angular momentum, and can take on integer values from $-\ell$ to $+\ell$.

$$L_z = m_\ell \hbar$$

NB: connections between *n*, *l* and m derive from solutions of Schrödinger Equation

Hydrogen Atom Wave Functions

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

$$\psi_{100} = \frac{1}{\sqrt{\pi r_0^3}} e^{-\frac{r}{r_0}} \qquad (r_0 = a_0)$$

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

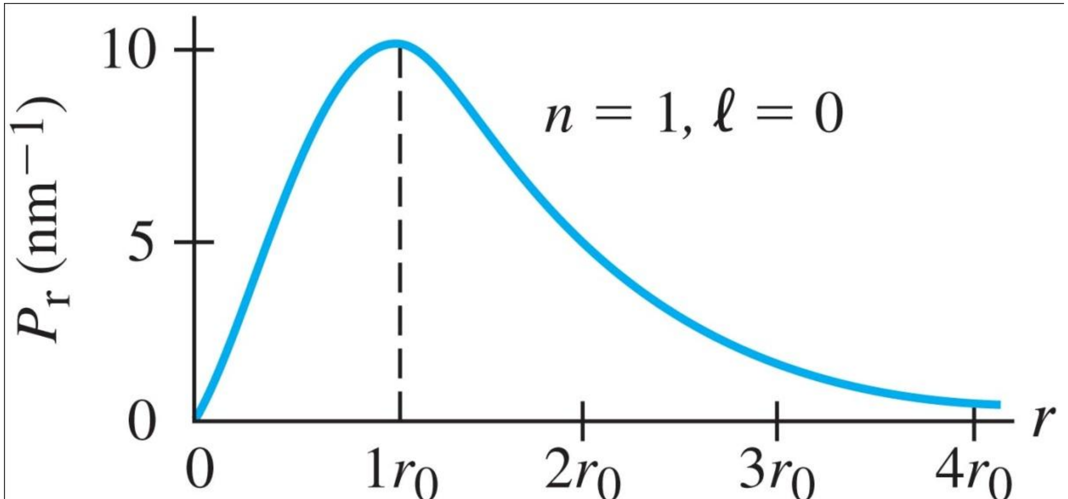
$$|\psi|^2 dV = 4\pi r^2 |\psi|^2 dr = P_r dr \quad \textbf{with} \quad P_r = 4\pi r^2 |\psi|^2$$

Probability to find electron at position *r*

Hydrogen Atom Wave Functions

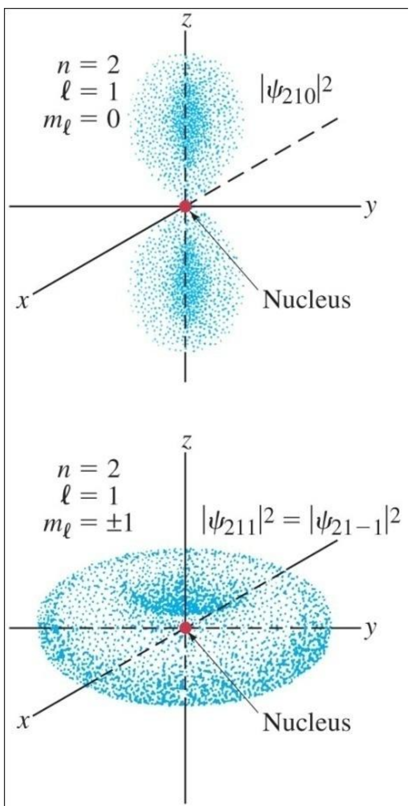
The ground state is spherically symmetric; the probability of finding the electron at a distance between *r* and *r* + *dr* from the nucleus is:

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



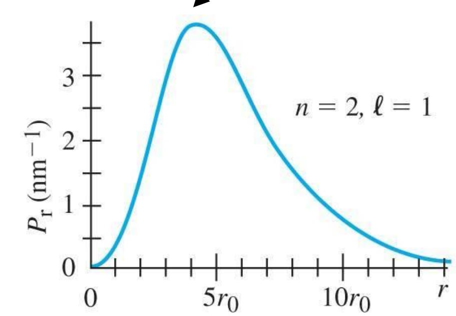
Hydrogen Atom Wave Functions

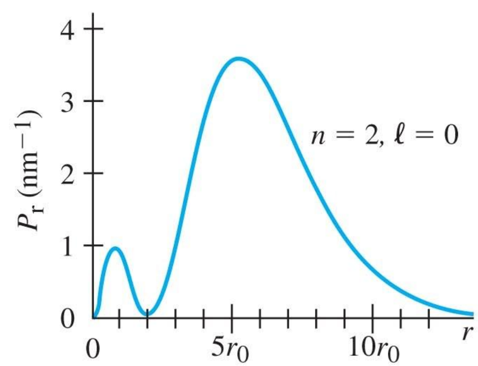
This figure shows the three probability distributions for n = 2 and ℓ = 1 (the distributions for m = +1 and m = -1 are the same), as well as the radial distribution for the n = 2 states.



(a)

most probable





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:

$$\Psi_{nlm}(\vec{r},t) = R_{nl}(r)\,\Upsilon_{lm}(\theta,\phi)$$

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

Traditional nomenclature for orbitals

$\ell = 0$ **; s-orbitals**

$\ell = 2$ **; d-orbitals**

$\ell = 1$ **; p-orbitals**

$\ell = 3$ **; f-orbitals**

Intermezzo

Quantum analog of electromagnetic radiation

Classical electric dipole radiation $\longrightarrow$ Transition dipole moment

Classical oscillator $\longrightarrow$ 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:

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

Intermezzo

Selection rules

Wave functions Ψ have well defined parity

$$\Psi(-x) = \Psi(x) \qquad \text{even}$$

$$\Psi(-x) = -\Psi(x) \qquad \text{odd}$$

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

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

because: $f(-x) = \Psi_f^*(-x)(-x)\Psi_i(-x)$

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

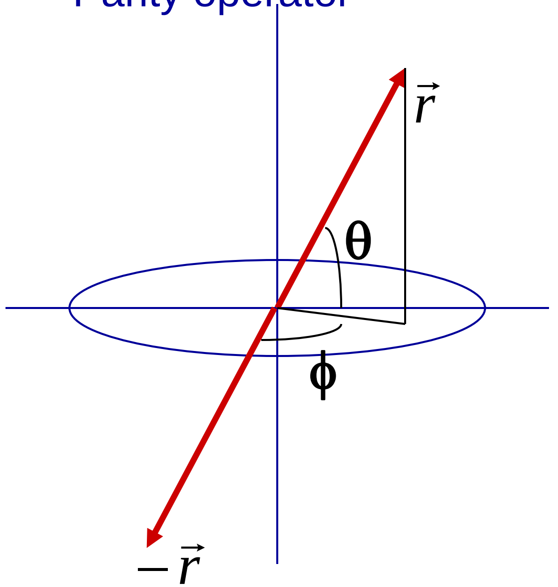
Electric dipole radiation connects states of opposite parity !

Intermezzo

Selection rules

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

Parity operator



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

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

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

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 may occur but with much lower probability.

"selection rules, related to symmetry (parity)"

Transitions from ground state $\ell = 0$ **to excited state** $\ell = 1$

From s-orbitals to p-orbitals

Selection rules in Hydrogen atom

Intensity of spectral lines given by

$$|\mu_{fi}|^2 = |\int \Psi_f^* \vec{\mu} \Psi_i|^2 = |\langle \Psi_f | -e\vec{r} | \Psi_i \rangle|^2$$

1) Quantum number n
   no restrictions

2) Parity rule for ℓ

$$\Delta\ell = odd$$

3) Laporte rule for ℓ

   Angular momentum rule:

$$\vec{\ell}_f = \vec{\ell}_i + \vec{1} \quad \text{so} \quad \Delta\ell \le 1$$

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