

# The Bohr Atom

Balmer (1885), Rydberg (1890) and Ritz (1908) analyzed atomic spectra empirically to find relationships between the frequencies of lines sequences:

$$\nu = T_j - T_k \quad T_j \propto \frac{1}{n^2} \quad n = 1, 2, 3, \dots$$

Bohr proposed

- \* Electrons reside in stationary states (orbits about the nucleus) *without* emission of energy.
- \* Transitions between states result in emission of radiation.
- \* the nuclear electrostatic attraction is exactly balanced by the centrifugal acceleration of the orbiting electron.

$$-\frac{(-Ze)e}{(4\pi\epsilon_0)r^2} = \frac{m_e v^2}{r}$$

- \* Orbital angular momentum is restricted to integral multiples of  $\hbar$ .

$$L = mvr = n\hbar \quad n = 1, 2, 3$$

solving for  $r$ , 
$$r = \frac{n^2 \hbar^2}{mZe^2} (4\pi\epsilon_0)$$

Bohr radius 
$$a_0 = r(n=1, Z=1) = \frac{4\pi\epsilon_0 \hbar^2}{me^2} = 0.529 \text{ \AA}$$

Energies 
$$E_n = T + V = \frac{1}{2}mv^2 - \frac{Ze^2}{(4\pi\epsilon_0)r} = -\frac{mZ^2e^4}{2n^2\hbar^2(4\pi\epsilon_0)^2} = -\frac{\mathcal{R}}{n^2}$$

$$h\nu = \Delta E = E_2 - E_1 = -\mathcal{R} \left[ \frac{1}{n_2^2} - \frac{1}{n_1^2} \right]$$

# The Hydrogen Atom

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2 Z}{(4\pi\epsilon_0)r}$$

$$\hat{H}\psi(r, \theta, \phi) = E\psi(r, \theta, \phi)$$

$$\nabla^2 \psi + \frac{2\mu}{\hbar^2} \left[ \frac{e^2 Z}{(4\pi\epsilon_0)r} + E \right] \psi = 0$$

where 
$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \Lambda^2$$

$Z =$  nuclear charge

$V(r) = 0$  at  $r = \infty$

separation of variables:  $\psi(r, \theta, \phi) = R(r) Y(\theta, \phi)$

$$\left[ \frac{\partial^2 R}{\partial r^2} + \frac{2}{r} \frac{\partial R}{\partial r} \right] Y + \frac{R}{r^2} \Lambda^2 Y + \frac{2\mu}{\hbar^2} \left[ \frac{e^2 Z}{(4\pi\epsilon_0)r} + E \right] R Y = 0$$

Divide by  $R$  and  $Y$  and multiply by  $r^2$  :

$$\frac{r^2}{R} \frac{\partial^2 R}{\partial r^2} + \frac{2r}{R} \frac{\partial R}{\partial r} + \frac{2\mu}{\hbar^2} \left[ \frac{e^2 Z r}{(4\pi\epsilon_0)} + E r^2 \right] = \underbrace{-\frac{1}{Y} \Lambda^2 Y}_{k} = k \quad \text{a constant}$$

$k = l(l+1) \quad l = 0, 1, 2, \dots$   
particle on sphere with

Rewriting the radial part:

$$\left[ \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{l(l+1)}{r^2} + \frac{2\mu}{\hbar^2} \frac{Ze^2}{(4\pi\epsilon_0)r} \right] R = -\frac{2\mu}{\hbar^2} E R$$

Another “well-known” equation.

The solutions,  $R_{nl}$  only exist for  $n = 1, 2, 3, \dots \quad 0 \leq l \leq n-1$

# H Atom Quantum Numbers

The principal quantum number  $n$

determines the energy  $E_n = -\frac{Z^2 \mu e^4}{2\hbar^2 (4\pi\epsilon_0)^2} \cdot \frac{1}{n^2}$

The total wavefunction has  $n-1$  nodes.

The azimuthal quantum number  $l$

describes the total orbital angular momentum:

$$\hat{l}^2 \psi_{nlm} = R_{nl} \hat{l}^2 Y_{lm} = R_{nl} l(l+1)\hbar^2 Y_{lm} = l(l+1)\hbar^2 \psi_{nlm}$$

$l$  is restricted to the values: 0 1 2 ...  $n-1$

and is often designated by letter: s p d

The magnetic quantum number  $m$

describes the z component of the orbital angular momentum:

$$\hat{l}_z \psi_{nlm} = R_{nl} \Theta_{lm} \hat{l}_z \Phi_m = R_{nl} \Theta_{lm} m\hbar \Phi_m = m\hbar \psi_{nlm}$$

$m$  is restricted to the values: 0  $\pm 1$   $\pm 2$  ...  $\pm l$

In a magnetic field, states with different  $m$  will differ in energy, the Zeeman effect.

The spin quantum number  $s$

is not predicted by this level of theory.

# H Atom Radial Wavefunctions

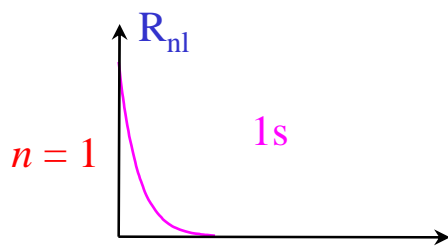
The solutions of the radial equation are **associated Laguerre functions**:

$$R_{nl}(r) = - \left\{ \left[ \frac{2Z}{na_0} \right]^3 \cdot \frac{(n-l-1)!}{2n[(n+l)!]^3} \right\}^{1/2} e^{-\rho/2} \rho^l L_{n+l}^{2l+1}(\rho)$$

where the **Laguerre polynomial** is given by

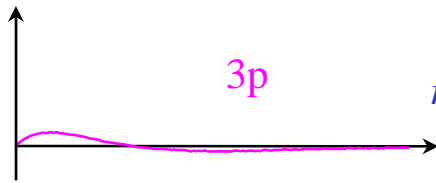
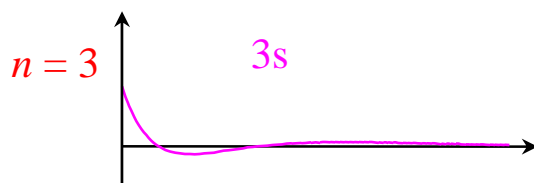
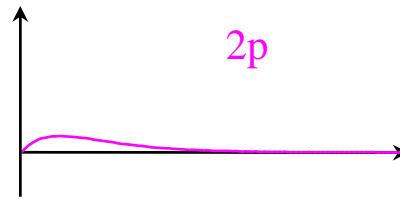
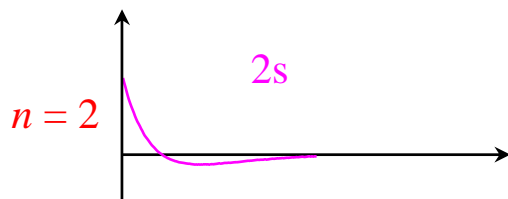
$$L_{n+l}^{2l+1}(\rho) = \sum_{k=0}^{n-l-1} (-1)^{k+1} \frac{[(n+l)!]^2}{(n-l-1-k)!(2l+1+k)!k!} \rho^k$$

with  $\rho = \frac{2\mu Z e^2}{n\hbar^2(4\pi\epsilon_0)} \cdot r = \frac{2Z}{na_0} \cdot r$        $a_0 = \frac{\hbar^2(4\pi\epsilon_0)}{\mu e^2}$



number of radial nodes =  $n - l - 1$

total number of nodes =  $n - 1$



$l = 0$

$l = 1$

# Radial Distribution Functions

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

“Normalize”  $Y_{lm}$  over the surface area of a sphere of radius  $r$ :

$$\int \int |Y_{lm}|^2 d\tau = \int_0^{2\pi} \int_0^{\pi} Y^* Y r^2 \sin \theta d\theta d\phi = 4\pi r^2$$

Probability density of finding electron

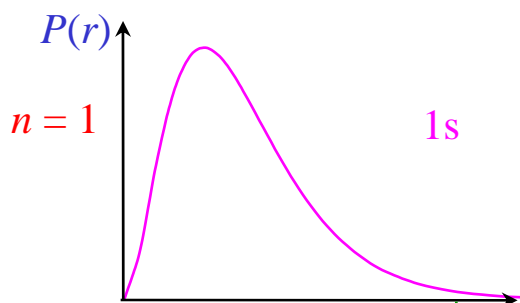
at a point

$$P(r, \theta, \phi) = |\Psi|^2 d\tau = R^2 r^2 \sin \theta d\theta d\phi$$

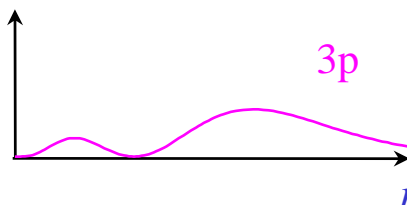
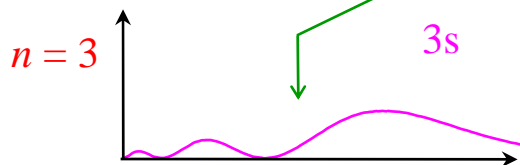
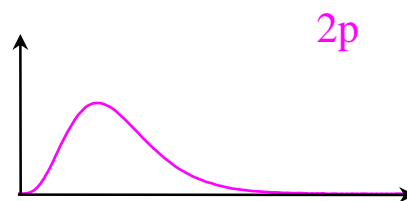
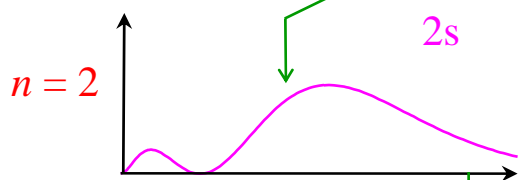
at a distance  $r$

$$P(r) = R^2 dr \int_0^{2\pi} \int_0^{\pi} Y^2 r^2 \sin \theta d\theta d\phi$$

$$= 4\pi r^2 R^2 dr$$



radial distribution function



$l = 0$

$l = 1$

# How Big is the Hydrogen Atom?

The ground state of the H atom has  $n = 1, l = 0, m = 0$

$$\psi_{1s} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \quad a_0 = \frac{\hbar^2(4\pi\epsilon_0)}{\mu e^2}$$

The radial distribution function  $P(r) = 4\pi r^2 \psi_{1s}^2$

$$= \frac{4}{a_0^3} r^2 e^{-2r/a_0}$$

has a maximum ...

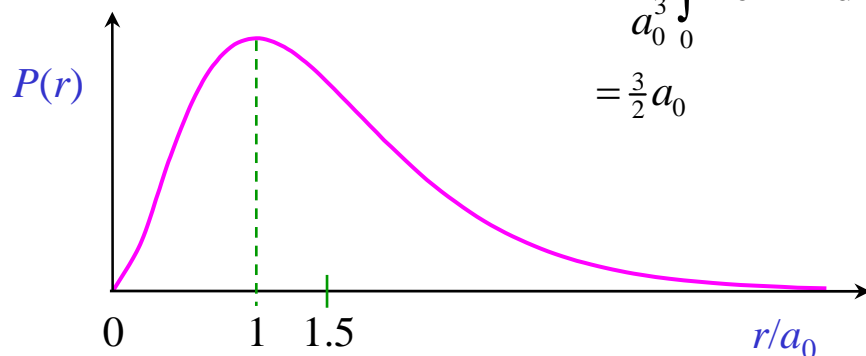
$$2re^{-2r/a_0} - \frac{2r^2}{a_0} e^{-2r/a_0} = 0$$

... at  $r = a_0$

The **Bohr radius**  $a_0$  is the **most probable** radius at which the electron can be found.

This is *not* the same as the **average distance** of the electron from the nucleus, which is the **expectation value**:

$$\begin{aligned} \langle r \rangle_{1s} &= \frac{1}{\pi a_0^3} \int e^{-r/a_0} r e^{-r/a_0} d\tau \\ &= \frac{4}{a_0^3} \int_0^\infty r^3 e^{-2r/a_0} dr \\ &= \frac{3}{2} a_0 \end{aligned}$$

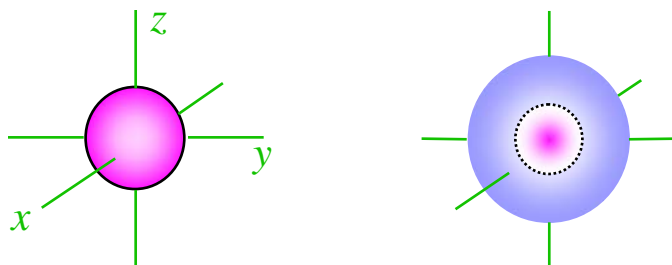


# Shapes of H Atom Orbitals

s orbitals

$$Y_{lm} = Y_{00} = \frac{1}{\sqrt{4\pi}} \quad \text{i.e. spherical symmetry,}$$

but the amplitude and sign of  $\psi_{ns}$  change according to  $R_{nl}$ .

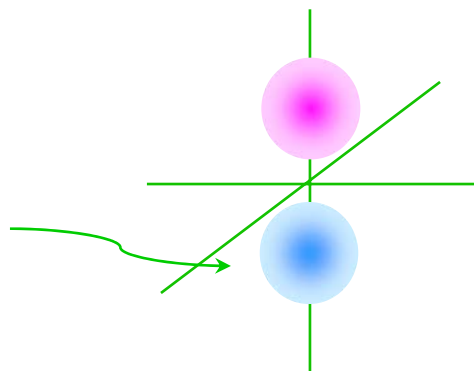


2p orbitals

$$Y_{10} \propto \cos \theta$$

$$Y_{11} \propto \sin \theta e^{i\phi}$$

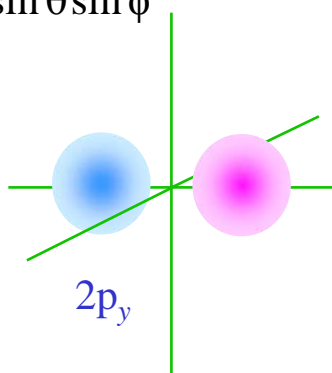
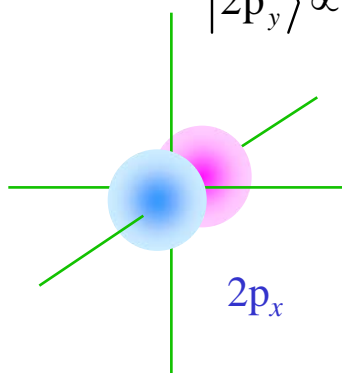
$$Y_{11} \propto \sin \theta e^{-i\phi}$$



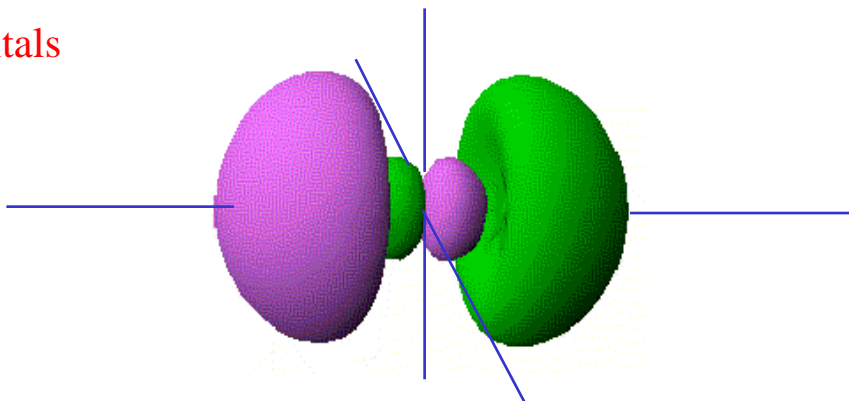
Construct a pair of real functions:

$$|2p_x\rangle \propto \frac{1}{2}(Y_{11} + Y_{1-1}) \propto \sin \theta \cos \phi$$

$$|2p_y\rangle \propto \frac{1}{2i}(Y_{11} - Y_{1-1}) \propto \sin \theta \sin \phi$$

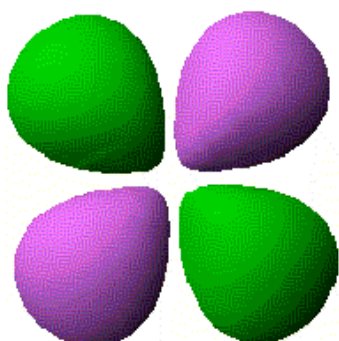
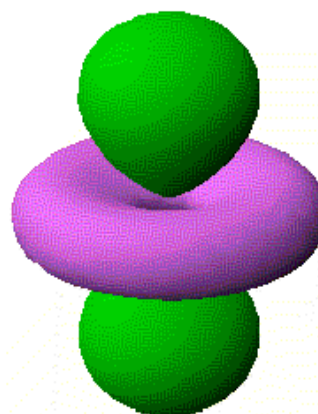


### 3p orbitals



### 3d orbitals

$$Y_{lm} = Y_{20} \propto (3\cos^2 \theta - 1)$$



$$|3d_{xz}\rangle \propto \frac{1}{2}(Y_{21} + Y_{2-1}) \propto \sin \theta \cos \theta \cos \phi$$

$$|3d_{yz}\rangle \propto \frac{1}{2i}(Y_{21} - Y_{2-1}) \propto \sin \theta \cos \theta \sin \phi$$

$$|3d_{x^2-y^2}\rangle \propto \frac{1}{2}(Y_{22} + Y_{2-2}) \propto \sin^2 \theta \cos 2\phi$$

$$|3d_{xy}\rangle \propto \frac{1}{2i}(Y_{22} - Y_{2-2}) \propto \sin^2 \theta \sin 2\phi$$



# The Spectrum of Atomic Hydrogen

$$E_n = -\frac{R_H}{n^2}$$

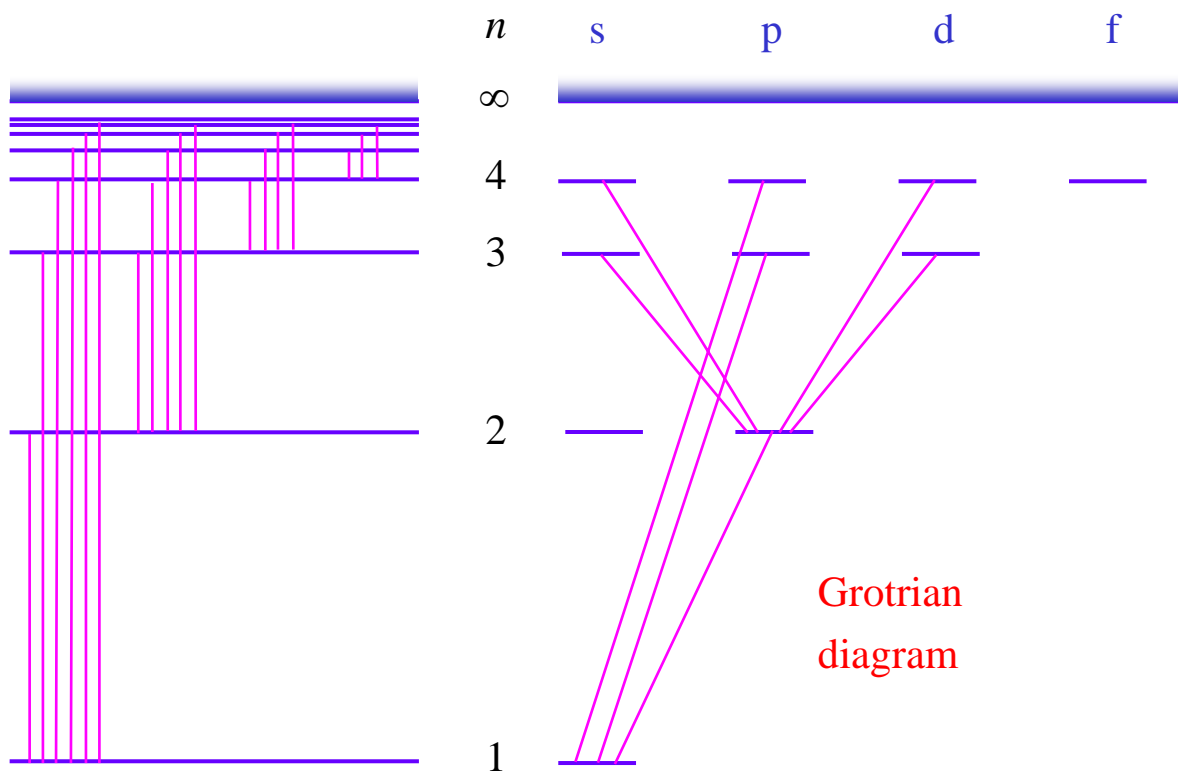
where  $R_H$  is known as the

**Rydberg constant:** 
$$R_H = \frac{\mu e^4}{2\hbar^2(4\pi\epsilon_0)^2} = \frac{\mu e^4}{8h^2\epsilon_0^2} \text{ J}$$

Spectral transitions are governed by **selection rules**:

$$\Delta n = \text{any integer}, \quad \Delta l = \pm 1, \quad \Delta m = 0$$

photons have angular momentum



# The Spectra of Hydrogen-like Atoms

Hydrogen-like: (core)  $ns^1$

e.g. Alkali metal atoms,  $\text{Be}^+$ ,  $\text{B}^{++}$ , ...

The core electrons influence the characteristic spectrum arising from the single outermost electron by **shielding** the nuclear charge to some extent. The orbital energies depend on  $l$  as a result of differing **penetration** of the core.

Li atom

