The Hydrogen Atom Emission Spectrum
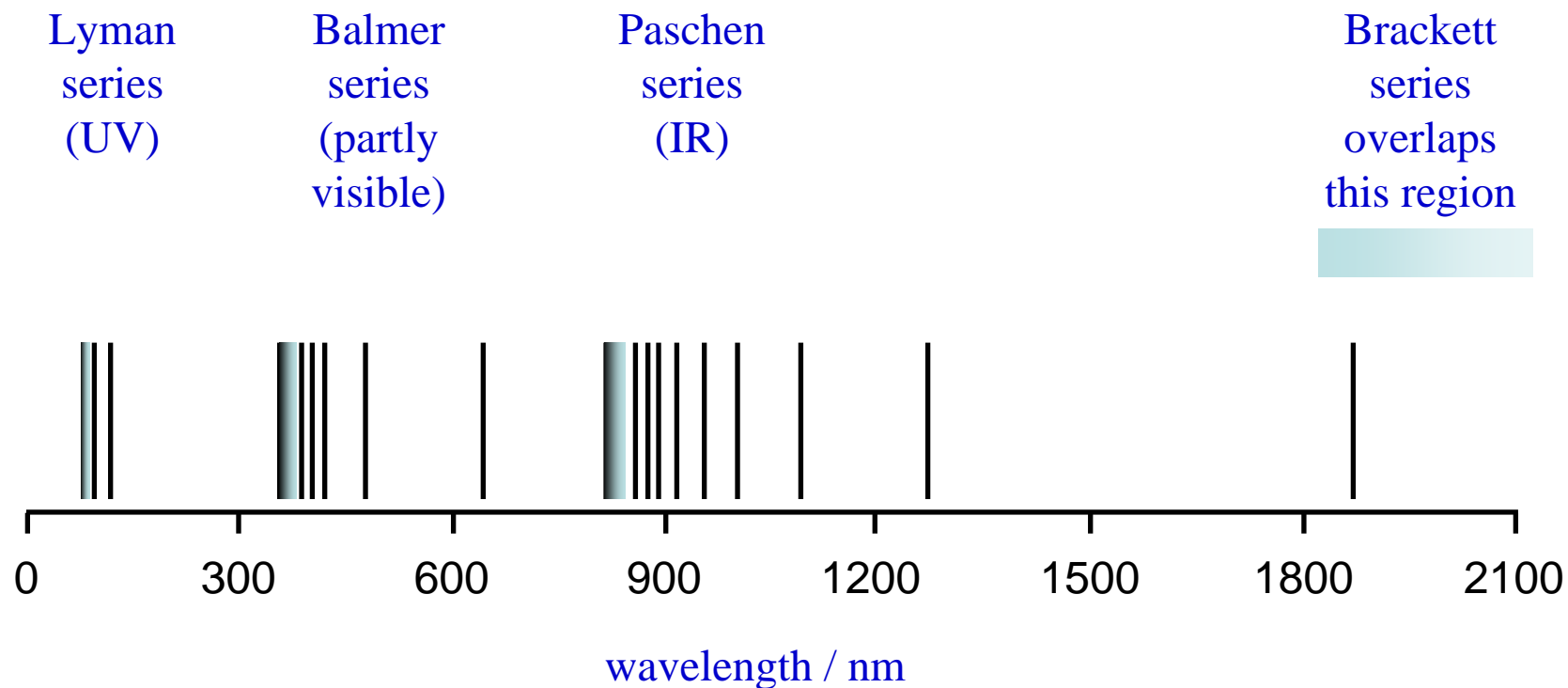
Balmer (1885), Rydberg (1890) and Ritz (1908) analyzed atomic spectra empirically to find relationships between the frequencies of line sequences:

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

Lyman series (UV)   Balmer series (partly visible)   Paschen series (IR)   Brackett series overlaps this region

wavelength / nm

The Bohr Atom

Bohr proposed:

❖ Electrons are 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.

$$-\frac{(-Ze)e}{(4\pi\varepsilon_0)r^2} = \frac{m_e v^2}{r}$$

❖ Orbital angular momentum is in integral multiples of $\hbar$

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

Solving for r, $\quad r = \dfrac{n^2\hbar^2}{mZe^2}(4\pi\varepsilon_0)$

Bohr radius $\quad a_0 = r$ for $n=1$, $Z=1$

$$= \frac{4\pi\varepsilon_0\hbar^2}{me^2} = 0.529 \ \text{Å}$$

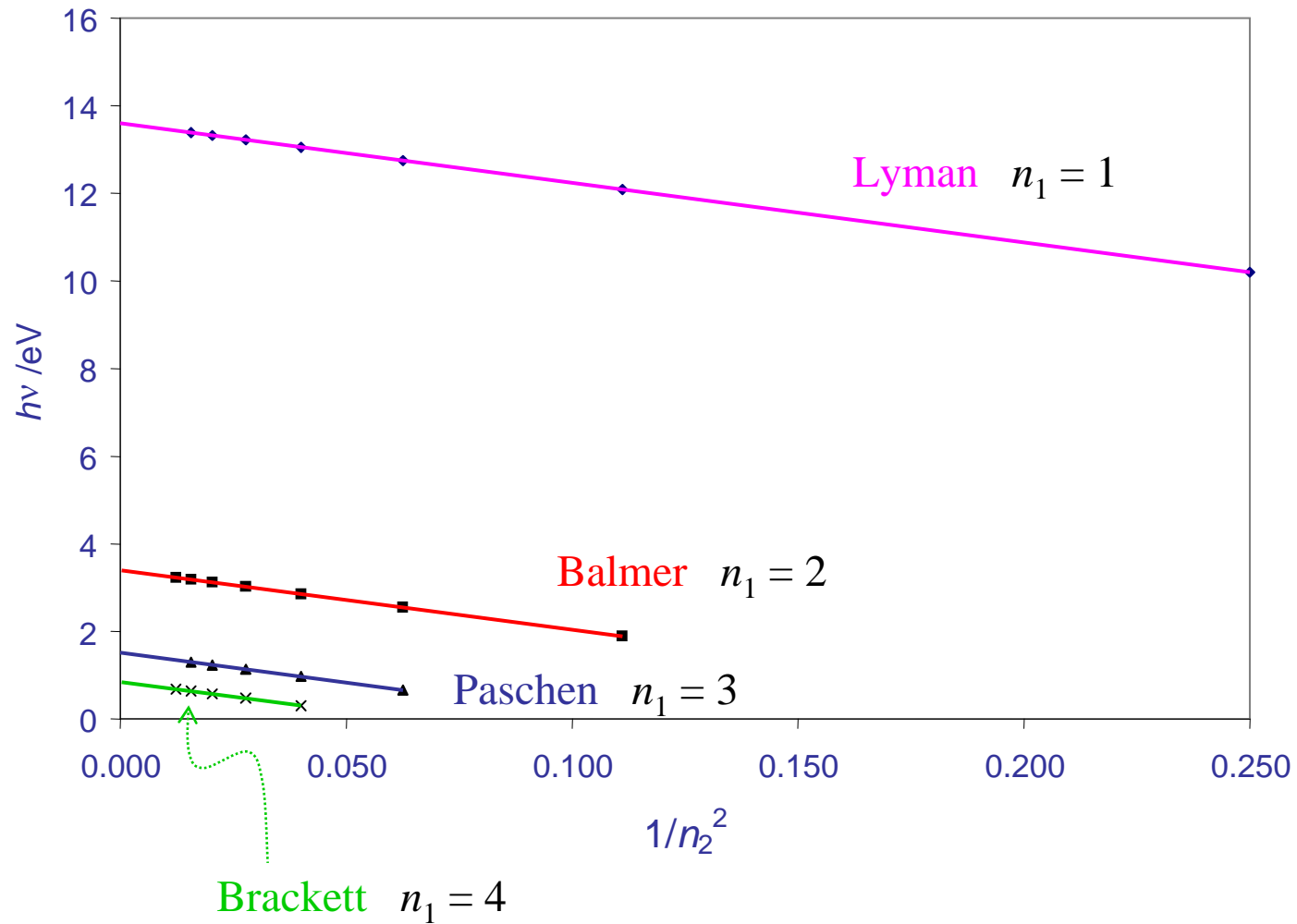Energies $\quad E_n = T + V = \tfrac{1}{2}mv^2 - Ze^2/(4\pi\varepsilon_0 r)$

$$= -\frac{mZ^2e^4}{2n^2\hbar^2(4\pi\varepsilon_0)^2} = -\frac{\mathbb{R}}{n^2}$$

Transitions $\quad h\nu = \Delta E = E_2 - E_1 = -\mathbb{R}\left[\dfrac{1}{n_2^{\,2}} - \dfrac{1}{n_1^{\,2}}\right]$
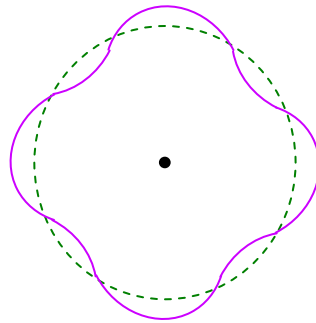
$\mathbb{R}$ is the Rydberg constant

Analysis of the H Atom Spectrum

Lyman $n_1 = 1$

Balmer $n_1 = 2$

Paschen $n_1 = 3$

Brackett $n_1 = 4$

$h\nu\ /\text{eV}$

$1/n_2^{\ 2}$

Why are Bohr orbits Quantized?

Treat the electron in orbit like the 'particle on a ring".

It must satisfy the cyclic boundary condition: $2\pi r = n\lambda$ $\qquad n = 1, 2, 3, ...$

Combining this with the de Broglie relation $\quad p = mv = h/\lambda$

gives the Bohr quantization condition: $\quad L = mvr = \left(\dfrac{h}{\lambda}\right)\left(\dfrac{n\lambda}{2\pi}\right) = n\hbar$

The Hydrogen Atom

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2 Z}{(4\pi\varepsilon_0)r} \quad \text{where} \quad \nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Lambda^2$$

Z = nuclear charge

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

$$\hat{H}\psi(r,\theta,\phi) = E\psi(r,\theta,\phi) \quad \Rightarrow \quad \nabla^2\psi + \frac{2\mu}{\hbar^2}\left[\frac{e^2 Z}{(4\pi\varepsilon_0)r} + E\right]\psi = 0$$

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

$$\left[\frac{\partial^2 R}{\partial r^2} + \frac{2}{r}\frac{\partial R}{\partial r}\right]Y + \frac{R}{r^2}\Lambda^2 Y + \frac{2\mu}{\hbar^2}\left[\frac{e^2 Z}{(4\pi\varepsilon_0)r} + E\right]RY = 0$$

Divide by R and Y and multiply by r^2

$\equiv$ particle on a sphere with $k = l(l+1)$

$$\frac{r^2}{R}\frac{\partial^2 R}{\partial r^2} + \frac{2r}{R}\frac{\partial R}{\partial r} + \frac{2\mu}{\hbar^2}\left[\frac{e^2 Zr}{(4\pi\varepsilon_0)} + Er^2\right] = -\frac{1}{Y}\Lambda^2 Y = k \quad \text{a constant}$$

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

Rewriting the radial part:

$$\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{l(l+1)}{r^2} + \frac{2\mu}{\hbar^2}\frac{Ze^2}{(4\pi\varepsilon_0)r}\right]R = -\frac{2\mu}{\hbar^2}ER$$

Another "well-known" equation.
The solutions, R_{nl} only exist for

$$n = 1, 2, 3, \ldots \quad 0 \leqslant l \leqslant n-1$$

H Atom Quantum Numbers

The principal quantum number n determines the energy $$E_n = -\frac{Z^2 \mu e^4}{2\hbar^2 (4\pi\varepsilon_0)^2} \cdot \frac{1}{n^2}$$

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   ±1   ±2 … ±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.
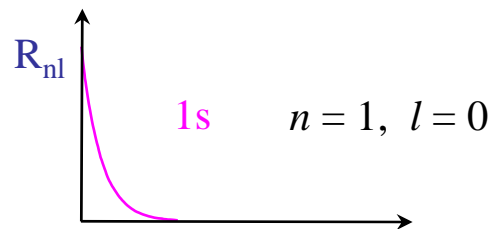
H Atom Radial Wavefunctions

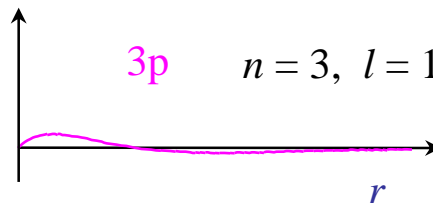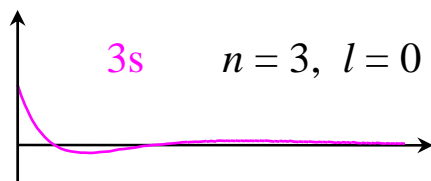The solutions of the radial equation are associated Laguerre functions:
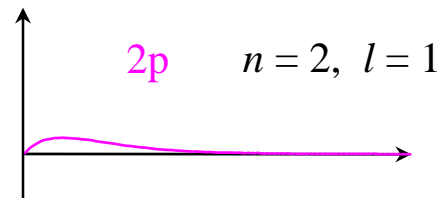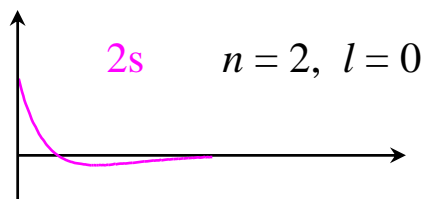
$$R_{nl}(r) = -\left\{ \left[\frac{2Z}{na_0}\right]^3 \cdot \frac{(n-l-1)!}{2n[(n+l)!]^3} \right\}^{1/2} e^{-\rho/2} \rho^l L_{n+l}^{2l+1}(\rho)$$

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

$$\rho = \frac{2\mu Z e^2}{n\hbar^2(4\pi\varepsilon_0)} \cdot r = \frac{2Z}{na_0} \cdot r \qquad a_0 = \frac{\hbar^2(4\pi\varepsilon_0)}{\mu e^2}$$

R_{nl}

1s $n = 1,\ l = 0$

2s $n = 2,\ l = 0$

2p $n = 2,\ l = 1$

number of radial nodes

$$= n - l - 1$$

3s $n = 3,\ l = 0$

3p $n = 3,\ l = 1$

r

total number of nodes

$$= n - 1$$

H Atom Radial Functions

$$R_{10}(r) = \frac{2}{a_0^{3/2}} \exp\left(-\frac{r}{a_0}\right)$$

$$R_{20}(r) = \frac{2}{(2a_0)^{3/2}} \left(1 - \frac{r}{2a_0}\right) \exp\left(-\frac{r}{2a_0}\right)$$

$$R_{21}(r) = \frac{1}{\sqrt{3}(2a_0)^{3/2}} \frac{r}{a_0} \exp\left(-\frac{r}{2a_0}\right)$$

$$R_{30}(r) = \frac{2}{(3a_0)^{3/2}} \left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right) \exp\left(-\frac{r}{3a_0}\right)$$

$$R_{31}(r) = \frac{4\sqrt{2}}{9(3a_0)^{3/2}} \frac{r}{a_0} \left(1 - \frac{r}{6a_0}\right) \exp\left(-\frac{r}{3a_0}\right)$$

$$R_{32}(r) = \frac{2\sqrt{2}}{27\sqrt{5}(3a_0)^{3/2}} \left(\frac{r}{a_0}\right)^2 \exp\left(-\frac{r}{3a_0}\right)$$

Radial Distribution Functions

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

Normalize Y_{00} over the surface area of a sphere of radius r:

$$\int |Y_{00}|^2\,d\tau = \int_0^{2\pi}\int_0^{\pi} Y^*\,Y\,r^2\sin\theta\,d\theta\,d\phi = \frac{1}{4\pi r^2}\int_0^{2\pi}\int_0^{\pi} r^2\sin\theta\,d\theta\,d\phi = 1$$
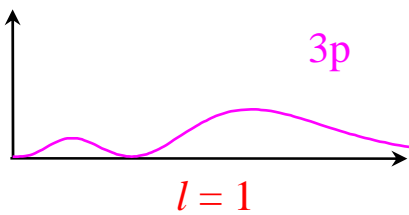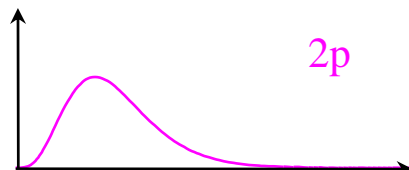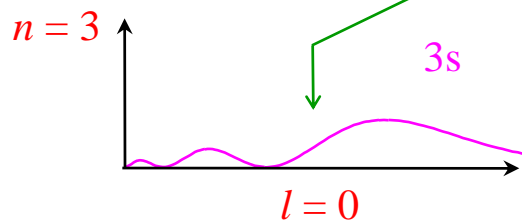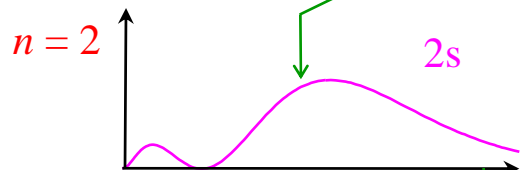
In general, probability density of finding electron
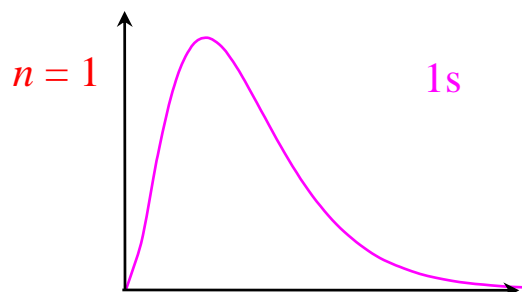
at a point

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

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

$n = 1$ 1s

$n = 2$ 2s   2p

$n = 3$ 3s   3p

$l = 0$ $l = 1$

How Big is the Hydrogen Atom?

The ground state of the H atom has $n = 1, l = 0, m = 0$ $\qquad \psi_{1s} = \dfrac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$ $\qquad a_0 = \dfrac{\hbar^2 (4\pi\varepsilon_0)}{\mu e^2}$

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

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

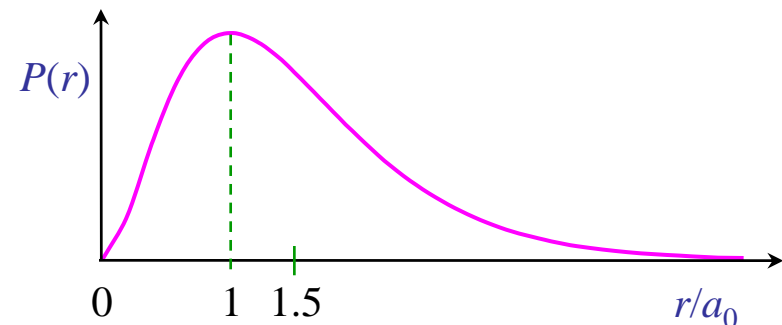has a maximum … $\qquad\qquad 2r e^{-2r/a_0} - \dfrac{2r^2}{a_0} e^{-2r/a_0} = 0$

$\qquad\qquad$ … 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: $\qquad \langle r \rangle_{1s} = \dfrac{1}{\pi a_0^3} \int e^{-r/a_0} r e^{-r/a_0} \, d\tau$

$$= \dfrac{4}{a_0^3} \int_0^\infty r^3 e^{-2r/a_0} \, dr$$

$$= \tfrac{3}{2} a_0$$

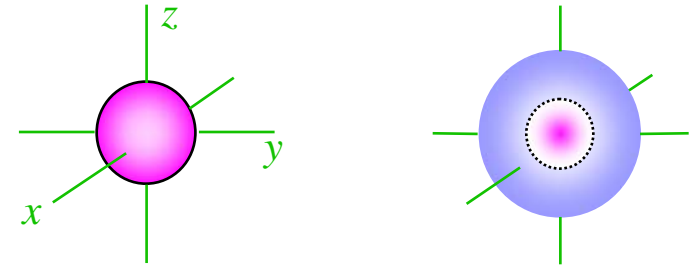$P(r)$ plotted against r/a_0, with axis marks at 0, 1, 1.5

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 ψ_{ns} change according to R_{nl}.
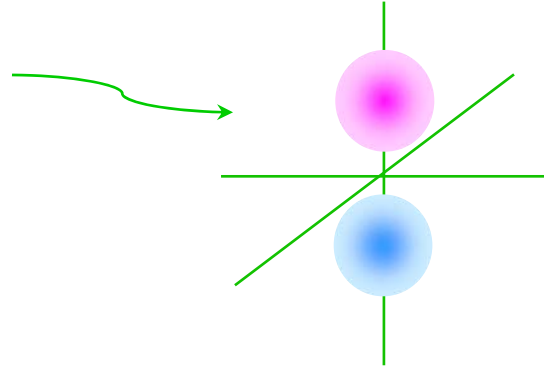
2p orbitals

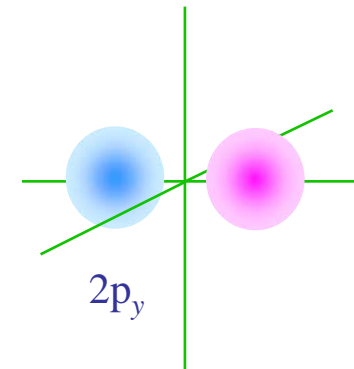$$Y_{10} \propto \cos\theta$$
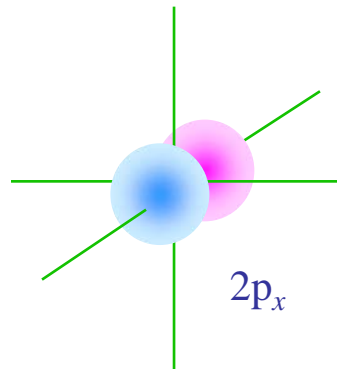
$$Y_{11} \propto \sin\theta\, e^{i\phi}$$

$$Y_{1-1} \propto \sin\theta\, e^{-i\phi}$$
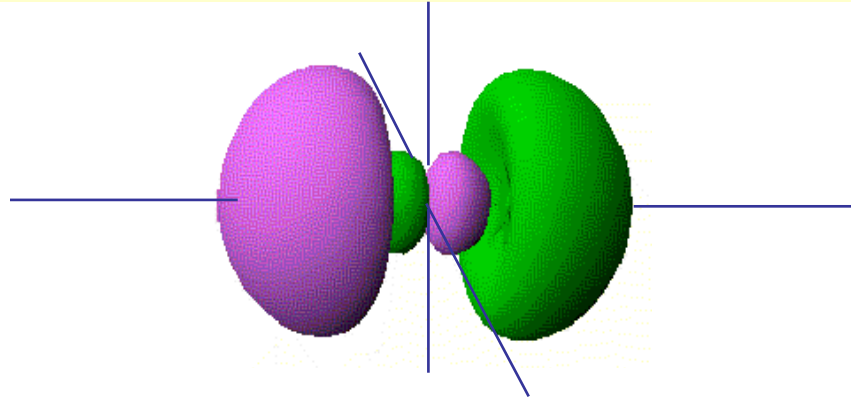
Construct a pair of real functions:

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

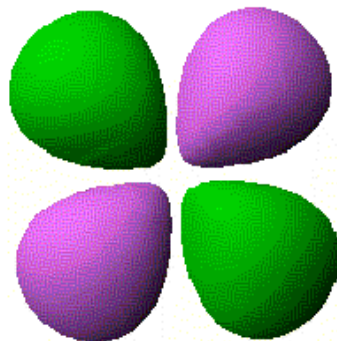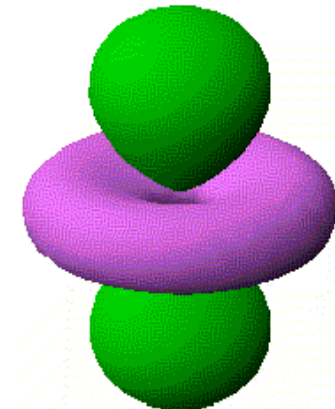$$\left|2p_y\right\rangle \propto \tfrac{1}{2i}(Y_{11} - Y_{1-1}) \propto \sin\theta\sin\phi$$

$2p_x$

$2p_y$

Shapes of H Atom Orbitals (cont.)

3p orbitals

3d orbitals

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

$$\left| 3d_{xz} \right\rangle \propto \tfrac{1}{2}(Y_{2\,1} + Y_{2-1}) \propto \sin\theta\cos\theta\cos\phi$$

$$\left| 3d_{yz} \right\rangle \propto \tfrac{1}{2i}(Y_{2\,1} - Y_{2-1}) \propto \sin\theta\cos\theta\sin\phi$$

$$\left| 3d_{x^2-y^2} \right\rangle \propto \tfrac{1}{2}(Y_{2\,2} + Y_{2-2}) \propto \sin^2\theta\cos 2\phi$$
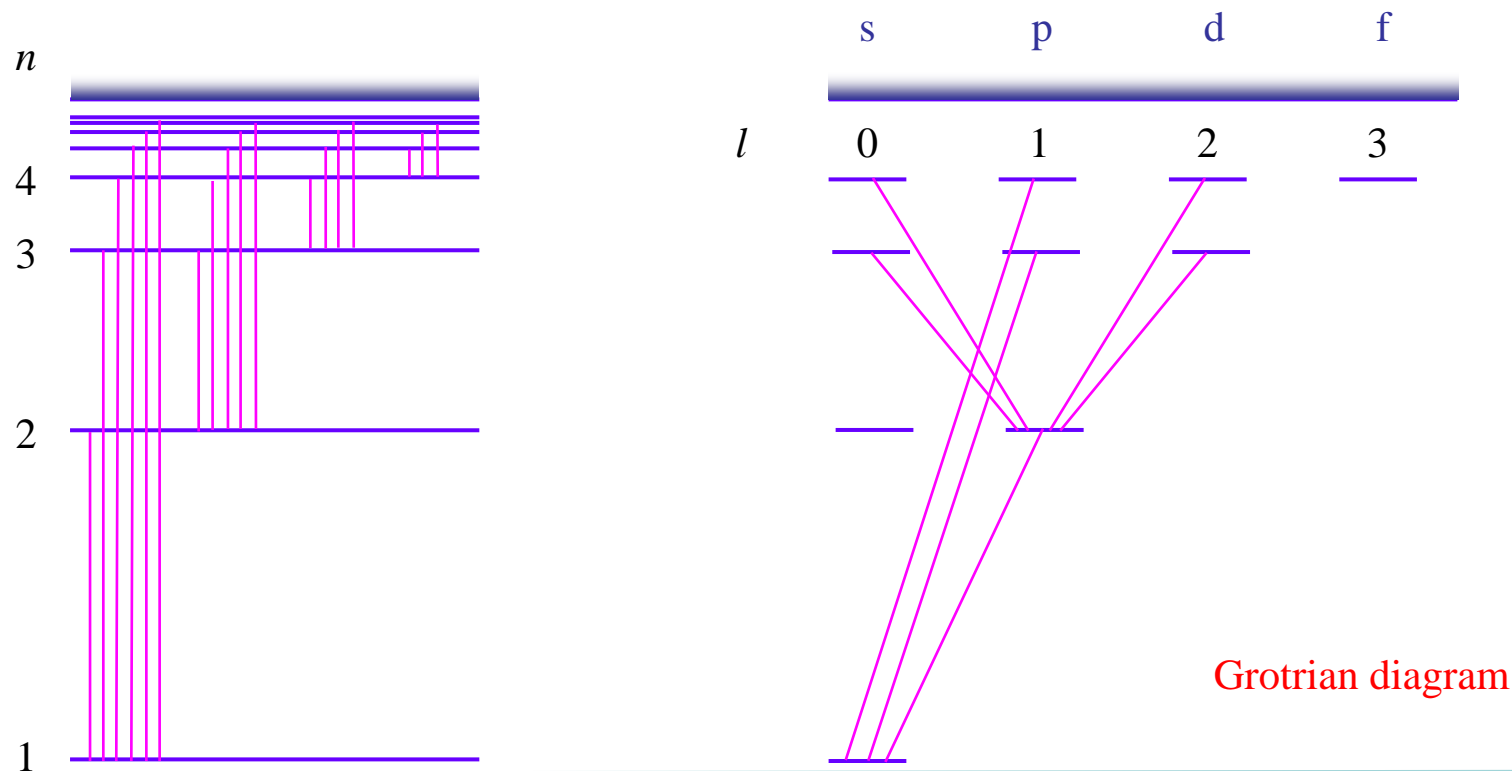
$$\left| 3d_{xy} \right\rangle \propto \tfrac{1}{2i}(Y_{2\,2} - Y_{2-2}) \propto \sin^2\theta\sin 2\phi$$

The Spectrum of Atomic Hydrogen

$$E_n = -\frac{R_H}{n^2}$$ where R_H is known as the Rydberg constant: $$R_H = \frac{\mu e^4}{2\hbar^2(4\pi\varepsilon_0)^2} = \frac{\mu e^4}{8h^2\varepsilon_0^2}$$ J

Spectral transitions are governed by selection rules: $\Delta n =$ any integer, $\Delta l = \pm 1$, $\Delta m = 0$

photons have angular momentum

Grotrian diagram

The Spectra of Hydrogen-like Atoms

Li atom

Hydrogen-like: (core) ns[1]

e.g. Alkali metal atoms, Be$^+$, 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.

(core = 1s^2)