HYDROGEN ATOM

Schrodinger equation in 3D spherical polar coordinates:

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi(r,\theta,\phi)+U(r,\theta,\phi)\psi(r,\theta,\phi)=E\psi(r,\theta,\phi)$$

with Coulomb potential $U(r)=\frac{-Ze^2}{4\pi\varepsilon_0 r}$

Rewrite as

$$\underbrace{\left[-\hbar^2\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+2\mu r^2\left[U(r)-E\right]\right]}_{\text{function of } r \text{ only}}\psi(r,\theta,\phi)+\hat{L}^2\psi(r,\theta,\phi)=0$$

function of θ,ϕ only

r is separable ψ is separable

Angular momentum: solutions are spherical harmonic wavefunctions

$$\psi(r,\theta,\phi)=R(r)Y_l^m(\theta,\phi)$$

$$\text{with}\quad \hat{L}^2Y_l^m(\theta,\phi)=\hbar^2l(l+1)Y_l^m(\theta,\phi)\qquad l=0,1,2,...$$

Radial equation for the H atom:

$$\boxed{-\frac{\hbar^2}{2\mu r^2}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right)+\left[\frac{\hbar^2l(l+1)}{2\mu r^2}+U(r)-E\right]R(r)=0}$$

Solutions $R(r)$ are the H atom radial wavefunctions

Simplest case: $l=0$ yields solution

$$R(r)=2\left(\frac{Z}{a_0}\right)^{3/2}e^{-Zr/a_0}$$ exponential decay away from nucleus

with

$$E = -Z^2 e^2 \big/ 8\pi\varepsilon_0 a_0 \quad \text{lowest energy eigenvalue}$$

$$a_0 \equiv \varepsilon_0 h^2 \big/ \pi\mu e^2 \quad \text{Bohr radius}$$

General case: solutions are products of (exponential) x (polynomial)

Energy eigenvalues:

$$E = \frac{-Z^2 e^2}{8\pi\varepsilon_0 a_0 n^2} = \frac{-Z^2 \mu e^4}{8\varepsilon_0^2 h^2 n^2} \qquad n = 1,2,3,...$$

Radial eigenfunctions:

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

where $L_{n+l}^{2l+1}\left(2Zr\big/na_0\right)$ are the *associated Laguerre functions,* the first few of which are:

$n = 1 \quad l = 0 \quad L_1^1 = -1$

$n = 2 \quad l = 0 \quad L_2^1 = -2!\left(2 - Zr\big/a_0\right)$

$\qquad\quad l = 1 \quad L_3^3 = -3!$

$n = 3 \quad l = 0 \quad L_3^1 = -3!\left(3 - 2Zr\big/a_0 + 2Z^2r^2\big/9a_0^2\right)$

$\qquad\quad l = 1 \quad L_4^3 = -4!\left(4 - 2Zr\big/3a_0\right)$

$\qquad\quad l = 2 \quad L_5^5 = -5!$

Normalization:

Spherical harmonics $\quad \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \; \sin\theta \; Y_l^{m*}(\theta,\phi) Y_l^m(\theta,\phi) = 1$

Radial wavefunctions $\quad \int_0^{\infty} dr \; r^2 R_{nl}^*(r) R_{nl}(r) = 1$

TOTAL HYDROGEN ATOM WAVEFUNCTIONS

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_l^m(\theta,\phi)$$

principle quantum number $n = 1,2,3,...$
angular momentum quantum number $l = 0,1,2,...,n-1$
magnetic quantum number $m = 0,\pm1,\pm2,...,\pm l$

ENERGY depends on *n*: $E = -Z^2e^2/8\pi\varepsilon_0 a_0 n^2$

ORBITAL ANGULAR MOMENTUM depends on l: $|L| = \hbar\sqrt{l(l+1)}$

ANGULAR MOMENTUM Z-COMPONENT depends on *m*: $L_z = m\hbar$

Total H atom wavefunctions are normalized and orthogonal:

$$\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta \int_0^{\infty} r^2 dr\ \psi_{nlm}^*(r,\theta,\phi)\psi_{n'l'm'}(r,\theta,\phi) = \delta_{nn'}\delta_{ll'}\delta_{mm'}$$

since components $R_{nl}(r)Y_l^m(\theta,\phi)$ are normalized and orthogonal.

Lowest few total H atom wavefunctions, for n = 1 and 2 (with $\sigma = Zr/a_0$):

$$n=1 \quad l=0 \quad m=0 \quad \psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\sigma} = \psi_{1s}$$

$$n=2 \quad l=0 \quad m=0 \quad \psi_{200} = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \left(2-\sigma\right)e^{-\sigma/2} = \psi_{2s}$$

$$l=1 \quad m=0 \quad \psi_{210} = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2}\cos\theta = \psi_{2p_z}$$

$$l=1 \quad m=\pm 1 \quad \psi_{21\pm 1} = \frac{1}{\sqrt{64\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2}\sin\theta \; e^{\pm i\phi}$$

or the alternate linear combinations

$$\psi_{2p_x} = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2}\sin\theta \;\cos\phi = \frac{1}{\sqrt{2}}\left(\psi_{21+1}+\psi_{21-1}\right)$$

$$\psi_{2p_y} = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2}\sin\theta \;\sin\phi = \frac{1}{\sqrt{2i}}\left(\psi_{21+1}-\psi_{21-1}\right)$$

The value of l is denoted by a letter: $l = 0,1,2,3...$
s,p,d,f orbitals

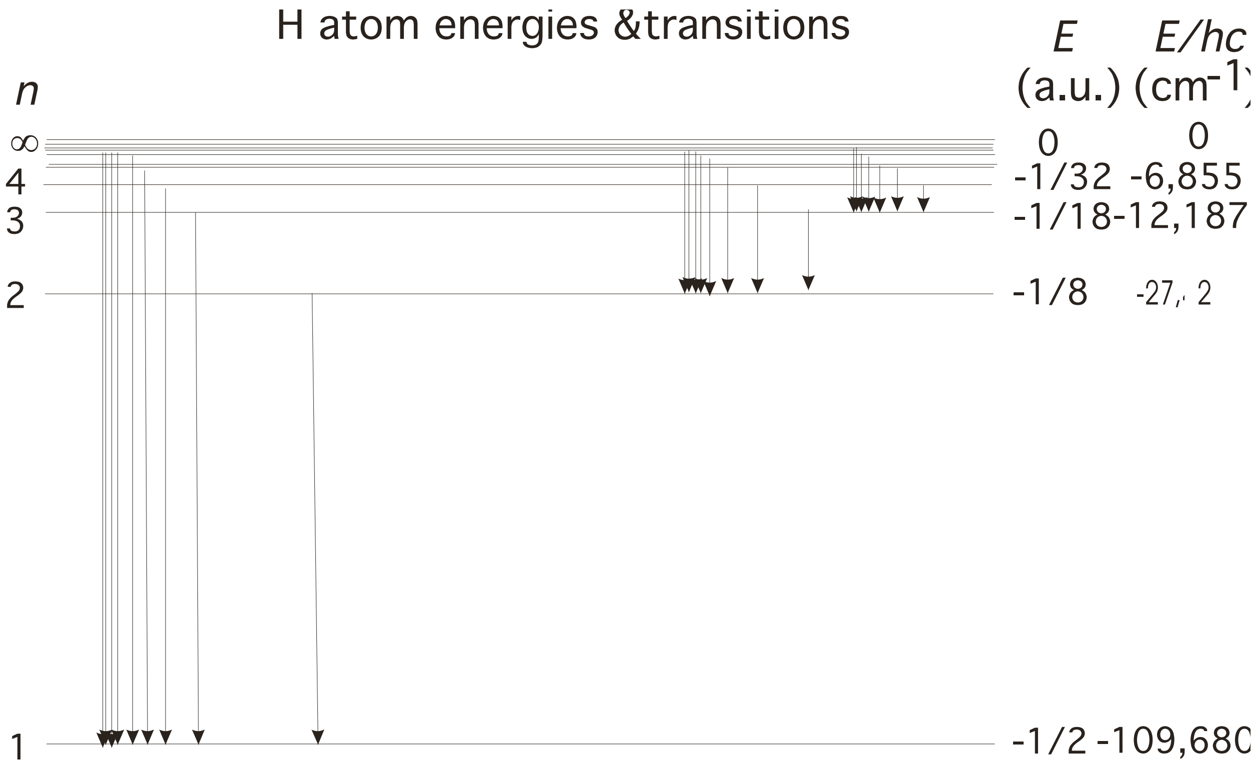
The value of m is denoted by a letter for $l=1$: $m = 0,\ \pm 1$ linear combinations
$p_z,\ p_x, p_y$ orbitals

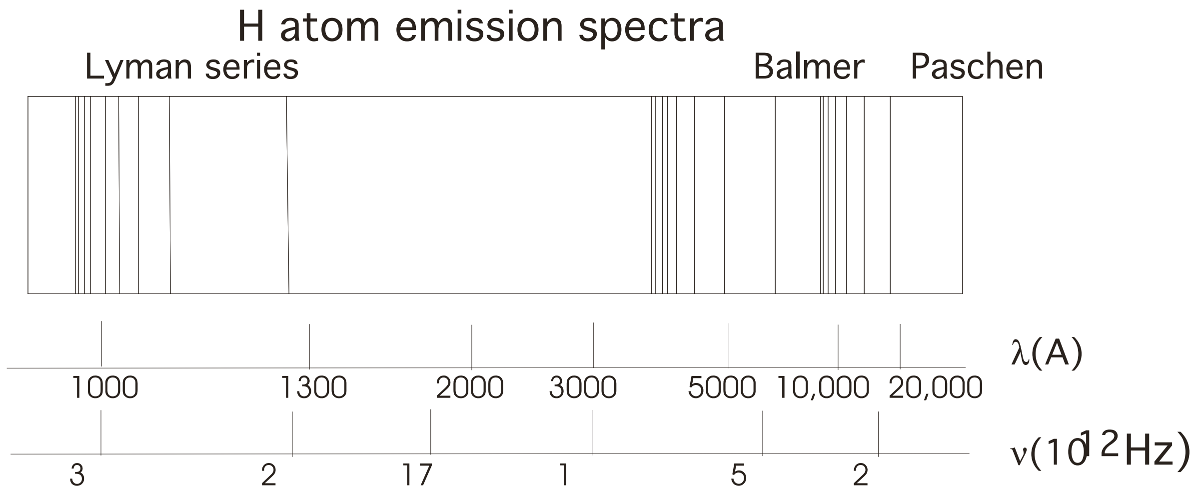
HYDROGEN ATOM ENERGIES

Potential energy of two electrons separated by the Bohr radius:
$U = e^2/4\pi\varepsilon_0 a_0$ _ one “atomic unit” (a.u.) of energy.

H atom energies: $E = -Z^2 e^2/8\pi\varepsilon_0 a_0 n^2 = -Z^2/2n^2$ a.u.

n	E_n (a.u.)
1	-1/2
2	-1/8
3	-1/18
4	-1/32
5	-1/50
	0





DEGENERACIES OF H ATOM ENERGY LEVELS

As *n* increases, the degeneracy of the level increases.
What is the degeneracy g_n of each level as a function of *n*?
Does this help understand the periodic table?

SHAPES AND SYMMETRIES OF THE ORBITALS

S ORBITALS

$$\psi_{1s} = \left(\pi a_0^3\right)^{-1/2} e^{-r/a_0} \qquad \psi_{2s} = \left(32\pi a_0^3\right)\left(2 - r/a_0\right)e^{-r/2a_0}$$

$l = 0$ spherically symmetric

$n - l - 1 = 0$	radial nodes	$n - l - 1 = 1$
$l = 0$	angular nodes	$l = 0$
$n - 1 = 0$	total nodes	$n - 1 = 1$

Electron probability density given by $\left|\psi\left(r,\theta,\phi\right)\right|^2$

Probability that a 1s electron lies between *r* and *r* + *dr* of the nucleus:

$$\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \ \sin\theta \ \psi_{1s}^*\left(r,\theta,\phi\right)\psi_{1s}\left(r,\theta,\phi\right)r^2 dr = 4\pi\left(\pi a_0^3\right)^{-1} e^{-2r/a_0} r^2 dr$$

P ORBITALS: wavefunctions

Not spherically symmetric: depend on θ,ϕ

m = 0 case: $\psi_{210} = \psi_{2p_z} = \left(32\pi a_0^3\right)^{-1/2}\left(r/a_0\right)e^{-r/2a_0}\cos\theta$

ψ_{2p_z} independent of ϕ symmetric about z axis

radial nodes	$n - l - 1 = 0$	(note difference from 2s: $R_{nl}\left(r\right)$ depends on l as well as n)
angular nodes	$l = 1$	
total nodes	$n - 1 = 1$	

xy nodal plane – zero amplitude at nucleus

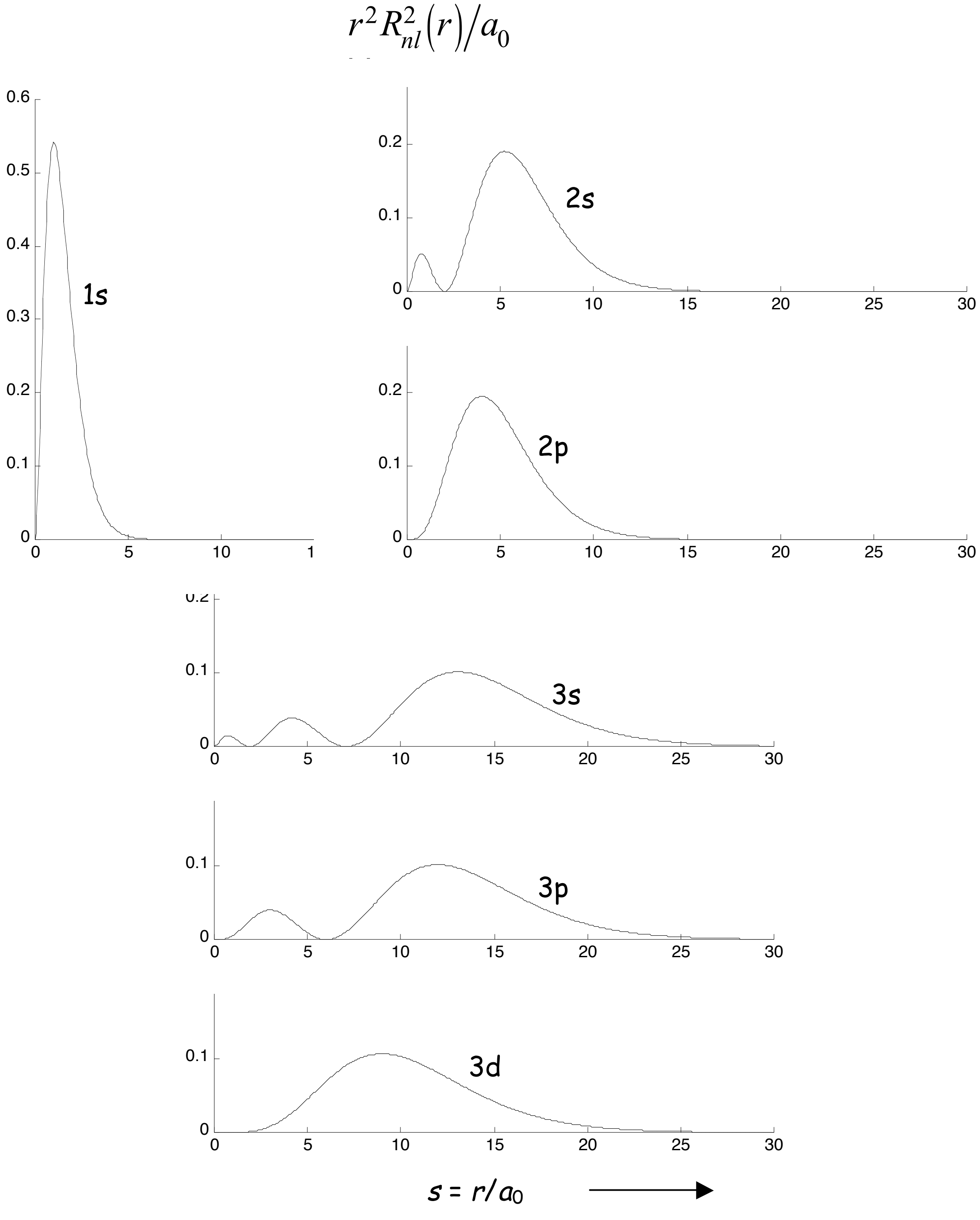
m = ±1 case: Linear combinations give

$$\psi_{2p_x} = \left(32\pi a_0^3\right)^{-1/2}\left(r/a_0\right)e^{-r/2a_0}\sin\theta\cos\phi$$

$$\psi_{2p_y} = \left(32\pi a_0^3\right)^{-1/2}\left(r/a_0\right)e^{-r/2a_0}\sin\theta\sin\phi$$

Equivalent probability distributions

H atom radial probability densities



MAGNETIC FIELD EFFECTS

Electron orbital angular momentum (circulating charge) ⇒ magnetic moment

$$\mu = -\frac{e}{2m_e}\mathbf{L}$$

Magnetic field B applied along z axis interacts with **μ:**
Potential energy

$$U = -\mu \bullet \mathrm{B} = -\mu_z \mathrm{B}_z = \frac{eB_z}{2m_e}\mathrm{L}_z$$

Include in potential part of Hamiltonian operator:

$$\hat{H} = \hat{H}_0 + \frac{eB_z}{2m_e}\hat{L}_z$$

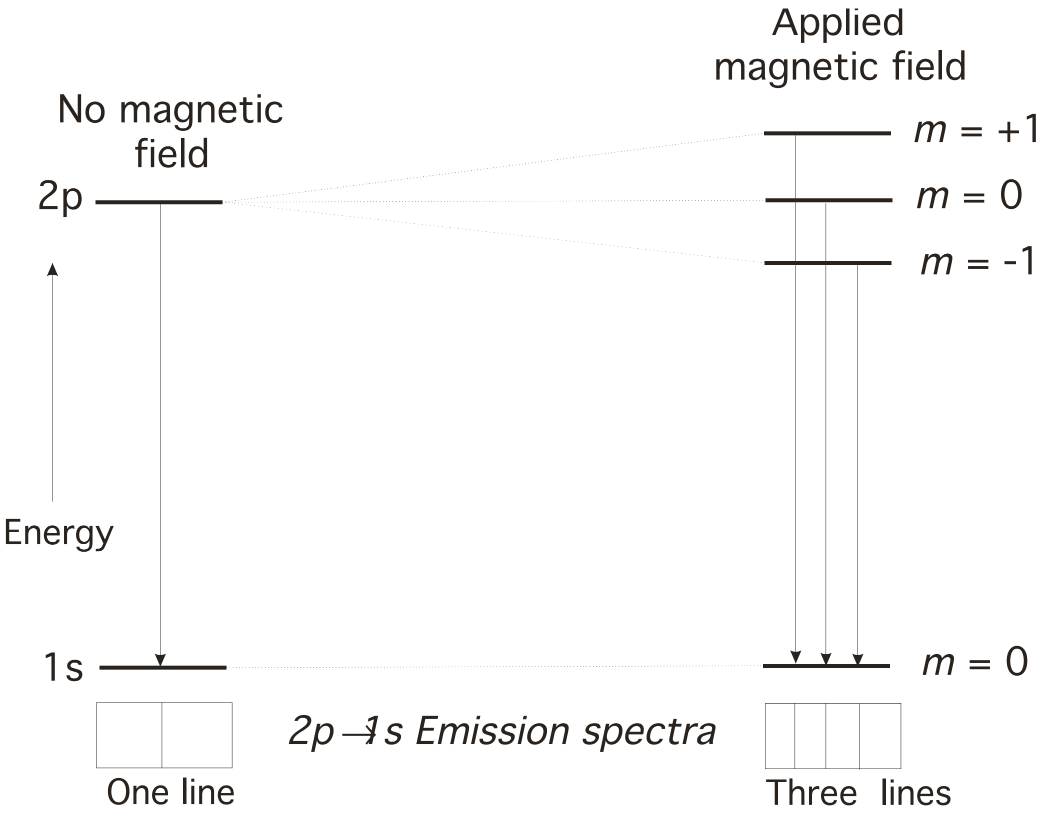
H atom wavefunctions are eigenfunctions of both $\hat{H}_0$ and $\hat{L}_z$ operators eigenfunctions of new $\hat{H}$ operator.

Energy eigenvalues are the sums

$$E = \frac{-Z^2e^2}{8\pi\varepsilon_0 a_0 n^2} + \frac{eB_z}{2m_e}m\hbar$$

Energy depends on magnetic quantum number *m* when a magnetic field is applied.

2p orbitals: m = -1,0,+1 states have different energies
Splitting proportional to applied field B_z.



Complex functions ψ_{21-1} and ψ_{21+1} are eigenfunctions of $\hat{L}_z$ with eigenvalues $\pm m\hbar$.

ψ_{2p_x} and ψ_{2p_y} are eigenfunctions of $\hat{H}_0$ but not of $\hat{L}_z$ $\Rightarrow$ no longer energy eigenfunctions once magnetic field is applied.