



# **CHEM F111 : General Chemistry**

## **Semester II: AY 2017-18**

Lecture-10, 02-02-2018

# Notice:

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## Doubt clearance session:

Date: 02-02-2018

Time: 17.10 hrs

Venue: Room No 5106

# Notice: Assignment Test-01



**BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE, PILANI**

**II Semester, 2017-2018**

**Course No.: CHEM F111 Course**

**Title: General Chemistry**

**Seating arrangement for Assignment-01 Test**

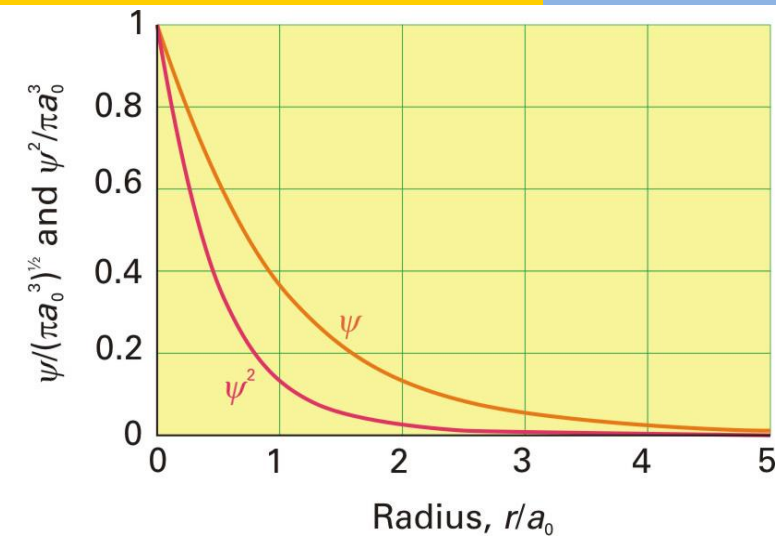
**Date: 08-02-2018**

**Time: 17.30 hrs.**

Tutorial Section	Room No	Invigilator
T-1	3249	Dr. Anil Kumar
T-2	3250	Dr. Paritosh Shukla
T-3	3215	Dr. Shamik Chakraborty
T-4	3156	Dr. Inamur R. Laskar
T-5	3253	Dr. Rajeev Sakhuja
T-6	3158	Dr. Madhushree Sarkar
T-7	3247	Dr. Bibhash R. Sarkar
T-8	3201	Dr. Surojeet Pande
T-9	3248	Dr. Subit K. Saha
T-10	3203	Dr. Saumi Ray
T-11	3160	Dr. Indresh Kumar
T-12	3245	Dr. Ajay K. Sah

**Syllabus: L-08 to L-12 of Course Hand out**

# Summary: Lecture - 09

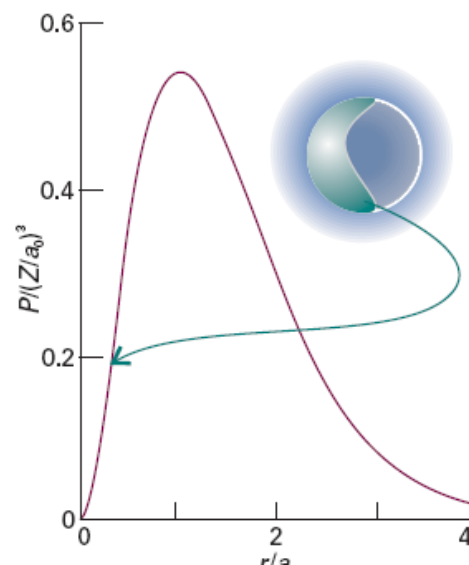
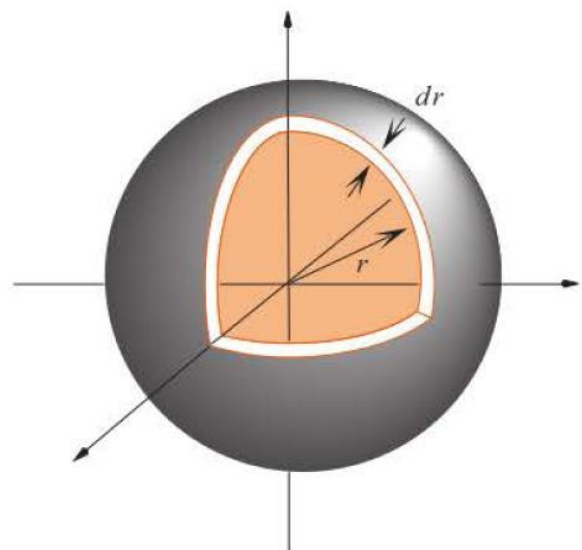
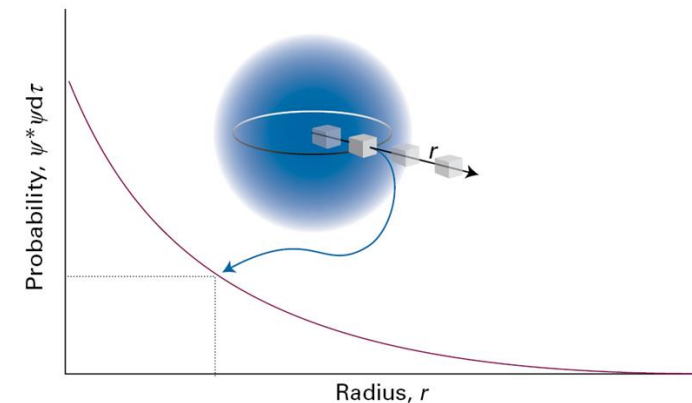


The sensitive volume of the probe:  $4\pi r^2 dr$

Probability:

$$|\psi|^2 \times 4\pi r^2 dr = P(r) dr$$

$$P(r) = 4\pi r^2 |\psi|^2$$



For, H-atom 1s orbital:

$$P(r) = \frac{4Z^3}{a_0^3} r^2 e^{-2Zr/a_0}$$

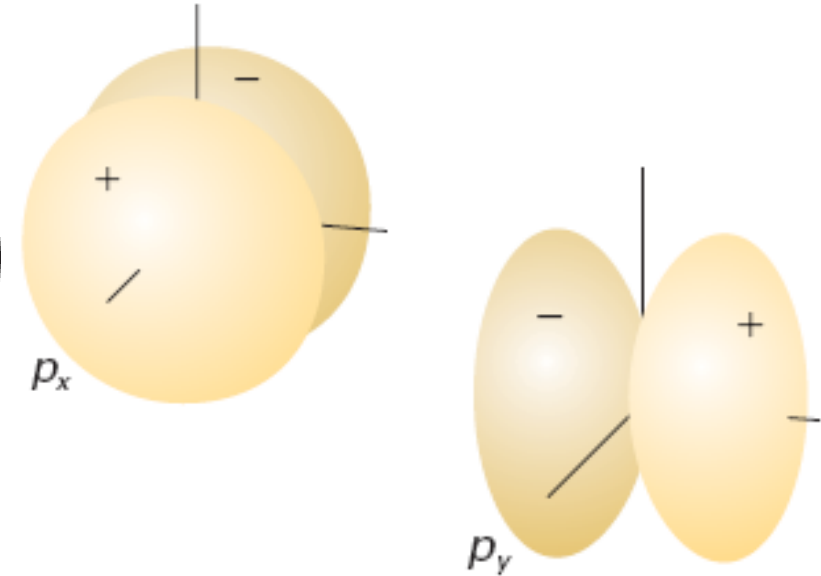
# Summary: Lecture - 09



$$\Psi_{2,1,\pm 1}(r, \theta, \varphi) = \frac{1}{\sqrt{64\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0} \sin \theta \boxed{e^{\pm i\varphi}}$$

**What is your idea about p-orbitals?**

$$\Psi_{p_x} = -\frac{1}{2^{1/2}}(p_{+1} - p_{-1}) = r \sin \theta \cos \phi f(r) = x f(r)$$
$$\Psi_{p_y} = \frac{i}{2^{1/2}}(p_{+1} + p_{-1}) = r \sin \theta \sin \phi f(r) = y f(r)$$



Also an energy eigen function with same energy and eigen function of the angular momentum operator

# Summary: Lecture - 09



$$\int \psi_m^* \psi_n d\tau = \delta_{mn}$$

- ❖ Show that hydrogenlike atomic wave function  $\Psi_{2\ 1\ 0}$  is normalized and it is orthogonal to  $\Psi_{2\ 0\ 0}$ .
- ❖ Show that the PIB wave functions satisfy the relation:  $\int_0^a \psi_n^*(x) \psi_m(x) dx = 0$  for  $m \neq n$

**This concept would be used in bonding**

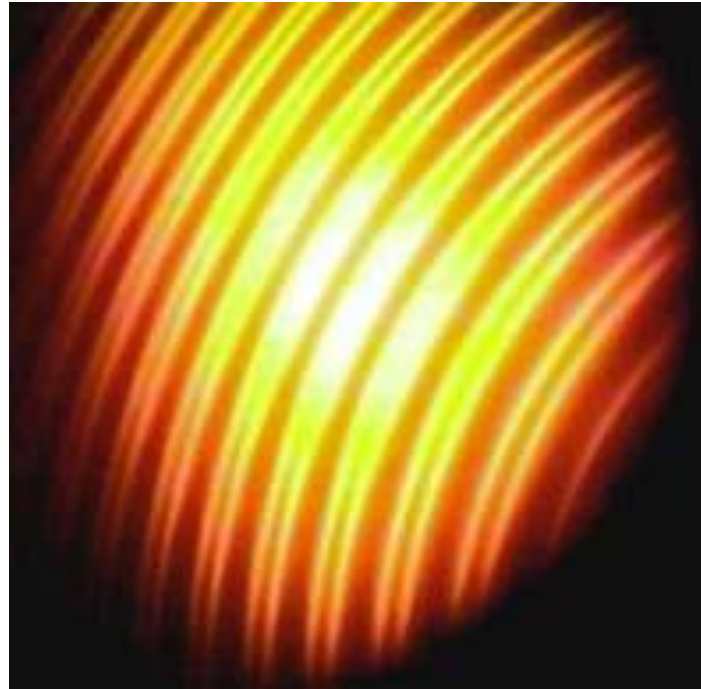
# Do we know all about electrons?



## Sodium Spectrum ( $[\text{Ne}]3s^1$ ):



Double lines at 588.9950  
and 589.5924 nm



Interference pattern  
formed by the sodium  
doublet

Can we explain?

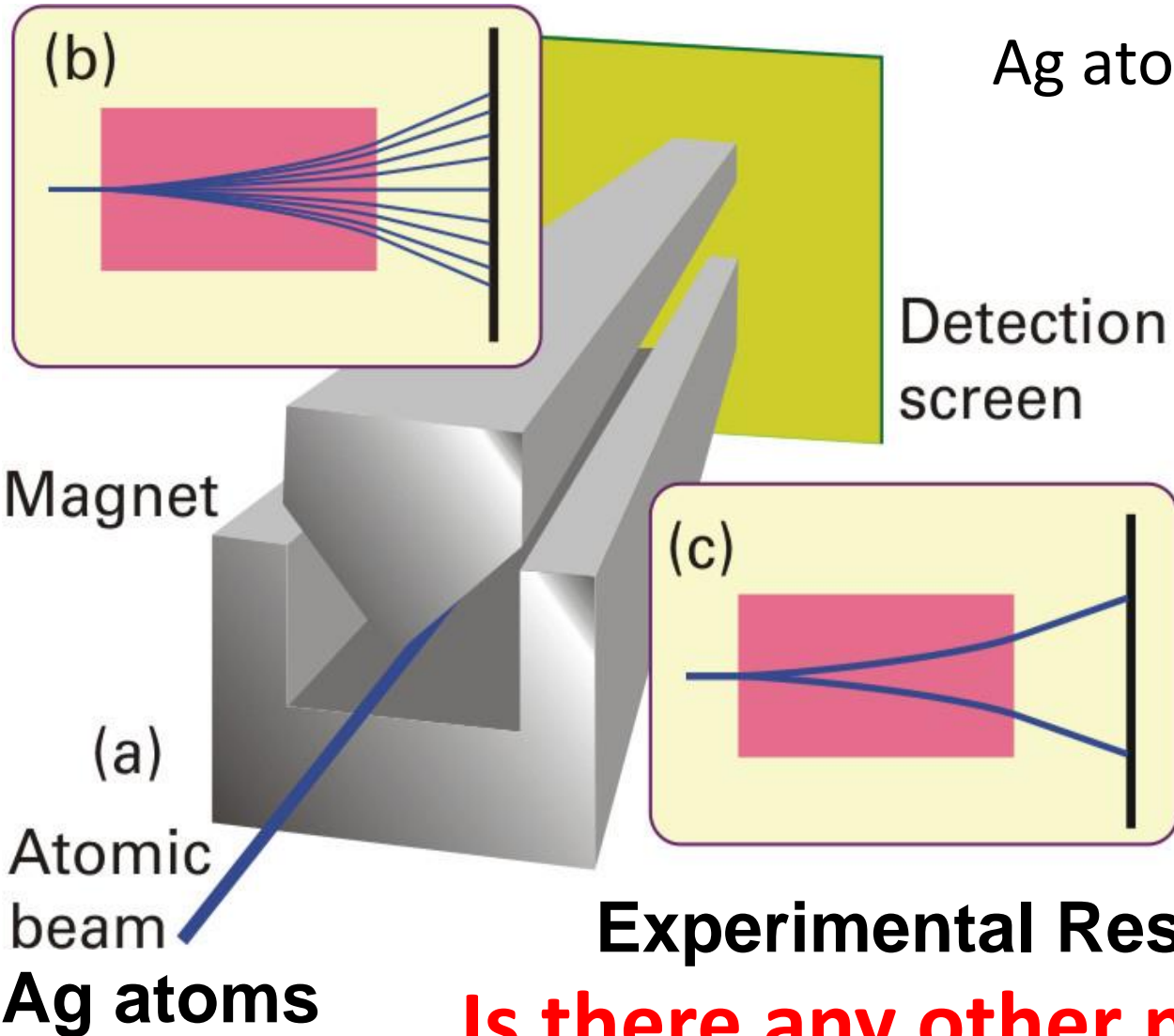
- Energy states.
- Orbital angular momentum states.

**State of electrons in an atom is not completely defined yet.**

# Stern Gerlach experiment



**Classically  
expected  
result**



Ag atom  $\rightarrow$  47 electrons  $\rightarrow$  ns1

**Space quantization**

( $2l+1$ ) components  
 $2l+1=2$  and  $l=1/2$   
 $l$  is an integer

**Experimental Result**

**Is there any other magnetic moment?**



# Electron spin



- Sole source of any magnetic moment is due to the intrinsic spin of the electron.
- Experiment provides a way to measure one component of the spin of the electron – determined by the direction of the magnetic field.

$$S_z = \pm \frac{1}{2} \hbar$$

- Spin angular momentum quantum number:  $s = \frac{1}{2}$
- Magnitude of spin angular momentum:

$$\sqrt{s(s+1)} \hbar = \sqrt{3/4} \hbar$$

# Electron spin



Spin quantum number:

$$m_s = \frac{1}{2} (\alpha \text{ state}) \text{ or } -\frac{1}{2} (\beta \text{ state})$$

Thus, component of electron spin along any axis in space (Z-axis) is

$$S_z = \pm m_s \hbar$$

The state of the electron in the hydrogenic atom is fully specified by four quantum numbers:  $n, l, m_l$ , and  $m_s$

$$\Psi(r, \theta, \varphi, \sigma) \equiv \Psi(r, \theta, \varphi) \alpha(\sigma) \text{ or } \Psi(r, \theta, \varphi) \beta(\sigma)$$

# Ground state of H-Atom



$$\left. \begin{aligned} \psi_{1,0,0,\frac{1}{2}}(r,\theta,\varphi) &= \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0} \alpha \\ \psi_{1,0,0,-\frac{1}{2}}(r,\theta,\varphi) &= \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0} \beta \end{aligned} \right\}$$

The complete one electron wave function  $\Psi$  is called a spin orbital

$\alpha$  and  $\beta$  are the spin eigenfunctions and they are orthonormal

$$\int \alpha^* \alpha d\sigma = \int \beta^* \beta d\sigma = 1 \text{ and } \int \alpha^* \beta d\sigma = \int \alpha \beta^* d\sigma = 0$$

Are the spin orbitals orthonormal?

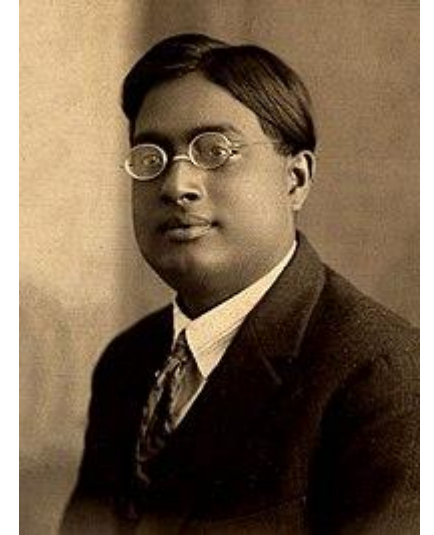
Are the spin orbitals eigen functions of the  $\hat{H}$  for H-atom?

**Spin is strictly a non-classical concept**

# Spin of fundamental particles

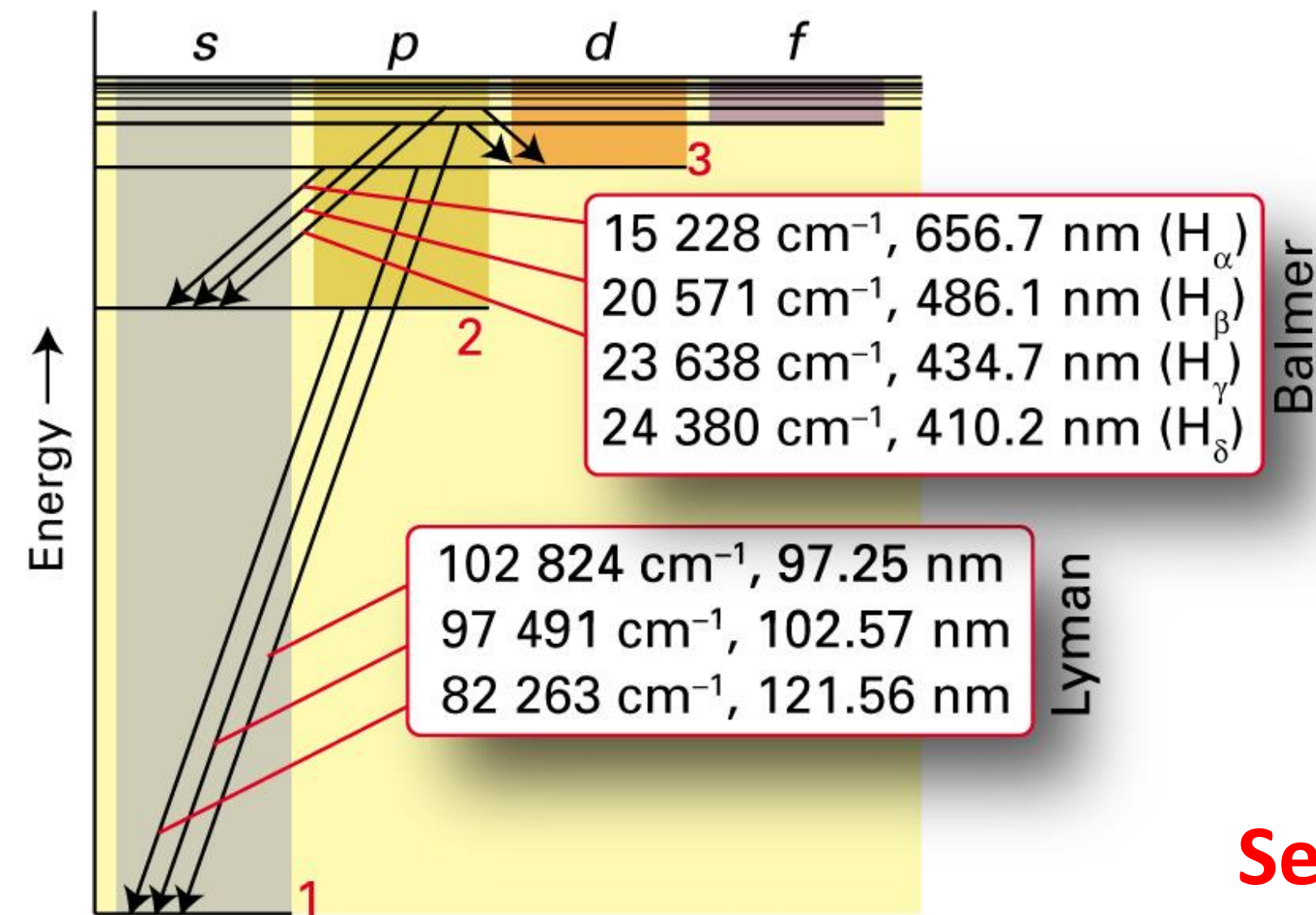


- All fundamental particles have characteristic spin values.
- Protons and Neutrons are also spin  $\frac{1}{2}$  particles like electrons.
- Photons are spin 1 particles.
- All particles may be classified as **BOSONS** (spin quantum number is zero or a positive integer, ie.,  $s = 0, 1, 2, \dots$ )
- **FERMIONS** (spin quantum number is a positive half-integer, ie.,  $s = \frac{1}{2}, \frac{3}{2}, \dots$ )



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# Spectral Transitions



Grotrian Diagram for H-atom

Observation:

- Not all transitions between all available orbitals do occur.
- $2s \rightarrow 1s$  does not happen
- $3d \rightarrow 1s$  does not happen

**Selection rule??**

# Selection rule – one electron atom



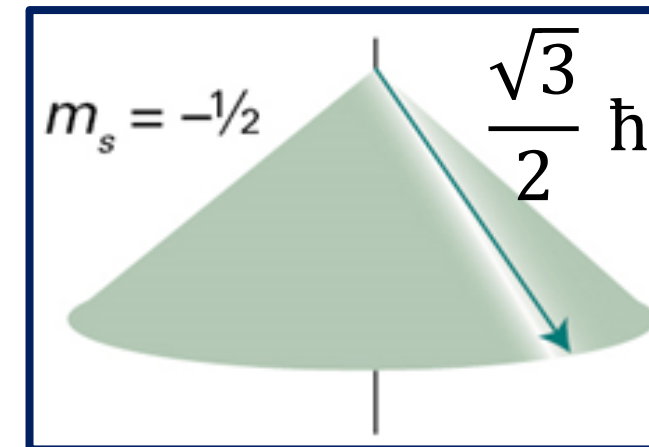
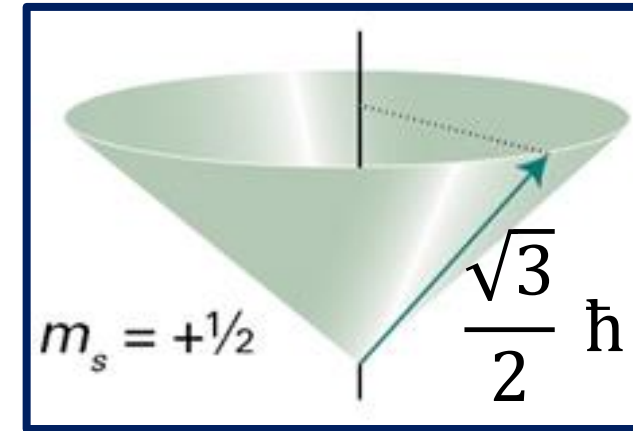
For the one electron atom, the selection rule is just the statement of the conservation of angular momentum, keeping in mind that a photon carries (spin) angular momentum of magnitude corresponding to spin quantum number  $s = 1$ .

**Selection rule:  $\Delta l = \pm 1$  and  $\Delta m_l = 0, \pm 1$**

# Spin – one electron: Summary



- Stern-Garlach experiment: Intrinsic spin of electron
- Spin quantum number:  $s = \frac{1}{2}$ ;
- Spin magnetic quantum number:  $m_s = \pm \frac{1}{2}$
- Magnitude of spin angular momentum:  $\sqrt{s(s+1)} \hbar$
- Z-component of spin angular momentum:  $S_z = \pm \frac{1}{2} \hbar$
- Possible spin states with  $s = \frac{1}{2}$  is two ( $\alpha, \beta$ )
- Spin multiplicity:  $(2s + 1)$



# What about other atoms?

innovate

achieve

lead

## The Periodic Table

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57-71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89-103	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
			57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
			89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr



# Many-Electron Atoms



Let us discuss He atom:

Form of Hamiltonian Operator??

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

$$\Rightarrow \hat{H} = \hat{H}_1^{(0)} + \hat{H}_2^{(0)} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \quad \hat{H}_i^{(0)} \text{ is the H-atom Hamiltonian for the } i^{\text{th}} \text{ electron}$$

- We can not solve Schrödinger equation exactly.
- We need to adopt approximations.

# Orbital approximation – He atom



Start with H-atom like wave function with an effective nuclear charge:

$$\Phi(1, 2) = \Psi_1(1) \Psi_2(2) \Rightarrow \Phi_{He, 1s^2} = \Psi_{H, 1s}(1) \Psi_{H, 1s}(2)$$

Interelectronic repulsion is neglected

$$\psi(1, 2) = (8/\pi a_0^3)^{1/2} e^{-2r_1/a_0} (8/\pi a_0^3)^{1/2} e^{-2r_2/a_0}$$

Electronic configuration is  $1s^2$

What about Li?

Can all 3 electrons occupy 1s orbital ?

# Pauli exclusion principle



- No more than two electrons may occupy a given orbital, and if two electrons do occupy one orbital, then their spins must be paired.
- The two electrons with paired spins ( $\uparrow\downarrow$ ) have zero net spin angular momentum.
- This principle forms the basis of the electronic structure of atoms, chemical periodicity, and molecular structure.

# Pauli principle



When the labels of any two identical fermions ( $\frac{1}{2}$  integer spin) are exchanged, the total wave function (including spin) changes sign.  
(ANTISYMMETRIC under interchange of any two electrons)

Fermions  $\psi(2,1) = -\psi(1,2)$

$$\psi_{1,0,0,\frac{1}{2}}(r,\theta,\varphi) = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \boxed{e^{-Zr/a_0}} \boxed{\alpha}$$

Spatial part                      Spin part

**What would be the form of He-atom wave function?**

# Antisymmetric wave function



First consider the spatial part of the wave function.

$$\psi(1,2) = \phi(1) \phi(2) \Rightarrow \text{symmetric}$$

Pauli principle:  $\psi(1,2) = -\psi(2,1)$  (MUST FOLLOW!)

*Thus, spin part must be antisymmetric*

Since each electrons has two possible spin states – four possible spin functions:

$$\alpha(1)\alpha(2), \beta(1)\beta(2), \alpha(1)\beta(2), \alpha(2)\beta(1)$$

Violate the principle of indistinguishability of identical particles in quantum mechanics

# Antisymmetric wave function



We can consider normalized linear combination:

$$\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) \pm \beta(1)\alpha(2)]$$

Spin orbitals:

$$\psi(1,2) = \phi(1)\phi(2) \alpha(1)\alpha(2)$$

$$\psi(1,2) = \phi(1)\phi(2) \beta(1)\beta(2)$$

$$\psi(1,2) = 2^{-1/2} \phi(1)\phi(2) \{ \alpha(1)\beta(2) + \beta(1)\alpha(2) \}$$

$$\psi(1,2) = 2^{-1/2} \phi(1)\phi(2) \{ \alpha(1)\beta(2) - \beta(1)\alpha(2) \}$$

Symmetric

Anti-symmetric

# Pauli exclusion principle



Approximate wave function for He ground state:

$$\psi(1,2) = 2^{-1/2} \phi(1)\phi(2) \{ \alpha(1)\beta(2) - \beta(1)\alpha(2) \}$$



Spin orbitals

- Two electrons can not occupy the same spin orbital
- No two electrons in an atom can have the same values for all their quantum number:  $n, l, m_l, m_s$

Distinguishability of identical particles in classical & quantum mechanics

# Shielding and penetration



The third electron in Li must enter the  $n = 2$  shell, but the 2s or the 2p?

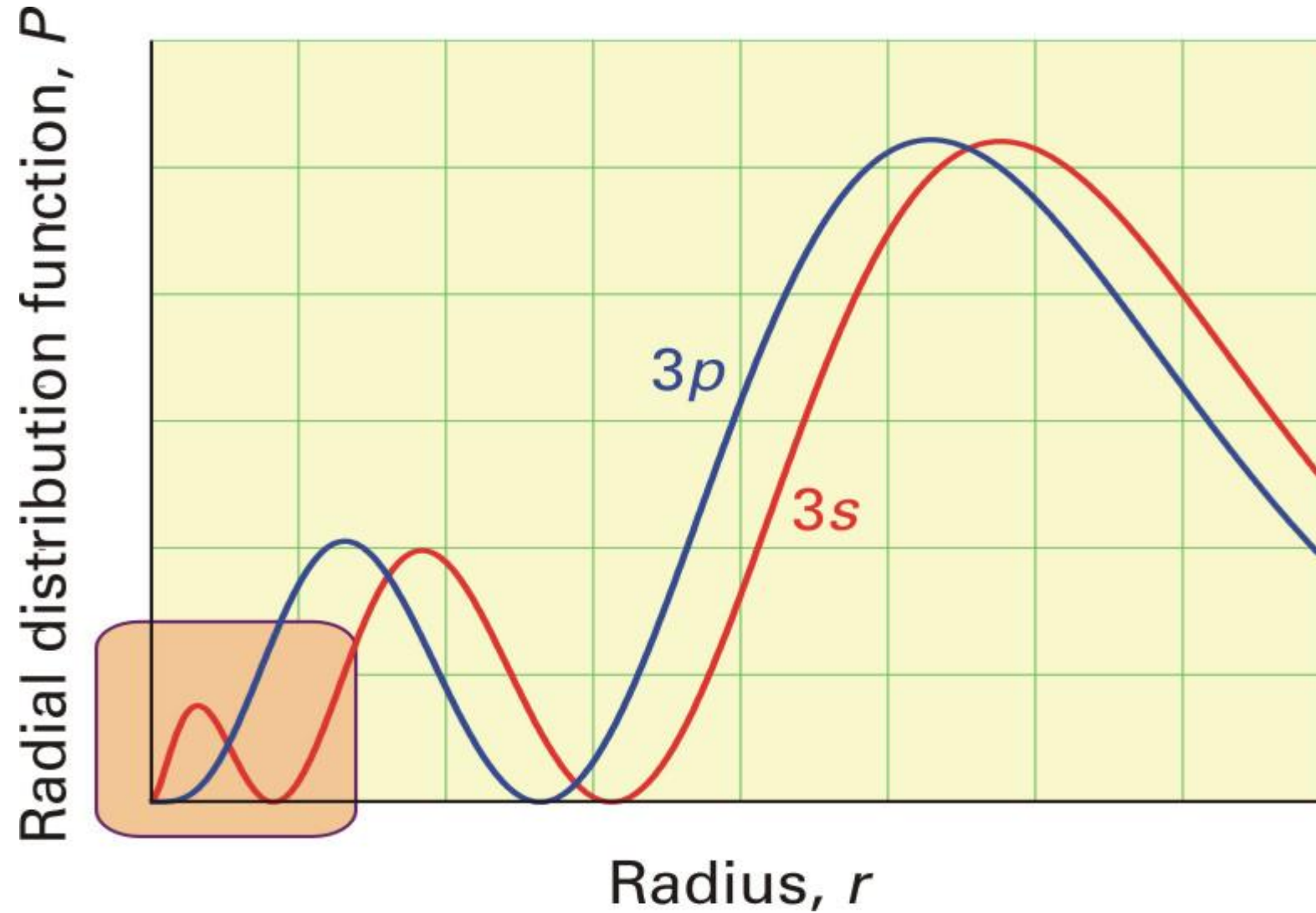
## Shielding:

In a many electron atom, each electron is shielded from the nucleus by the others, and to a first approximation, each electron may be thought of as experiencing an effective nuclear charge.

The effective nuclear charge experienced by an electron will be determined by its probability density distribution, and this in turn by its wave function.



# Penetration



# Order of occupation



- The greater penetration of an 's' electron compared to a 'p' electron of the same shell implies that it experiences a greater effective nuclear charge. In turn, the effective nuclear charge experienced by the 'p' electron will be greater than that for a 'd' electron in the same shell.
- In general therefore, in the same shell of a many-electron atom, the order of energies of the orbitals is  $s < p < d < f$ . The ground electronic configuration of Li is therefore  $1s^2 2s^1$ , or  $[\text{He}] 2s^1$
- The individual orbitals of a given subshell remain degenerate because they all have the same radial characteristics and so experience the same effective nuclear charge.

# Topics for self study

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- Aufbau principle
- Hund's rule
- Periodic table
- Effective nuclear charge
- Atomic radius
- Ionization energy
- Electron affinity