5.111 Principles of Chemical Science

Fall 2008

5.111 Lecture Summary #7

Readings for today: Section 1.10 (1.9 in *3rd ed*) – Electron Spin, Section 1.11 (1.10 in *3rd ed*) – The Electronic Structure of Hydrogen.
Read for Lecture #8: Section 1.12 (1.11 in *3rd ed*) – Orbital Energies (of many-electron atoms), Section 1.13 (1.12 in *3rd ed*) – The Building-Up Principle.

Topics:
I. RPD for s-orbitals (continued from Lecture #6)
II. p-orbitals
  A. The shape of p-orbitals
  B. Radial probability distributions
III. Electron spin and the fourth quantum number
IV. Wavefunctions for multielectron atoms

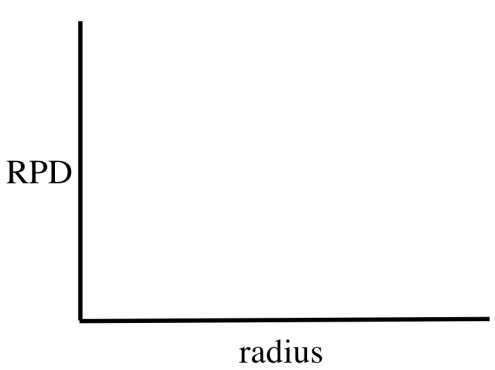
I. RADIAL PROBABILITY DISTRIBUTIONS (RPD) FOR S-ORBITALS

Radial Probability Distribution: The probability of finding an electron in a spherical shell of thickness dr at a distance r from the origin.

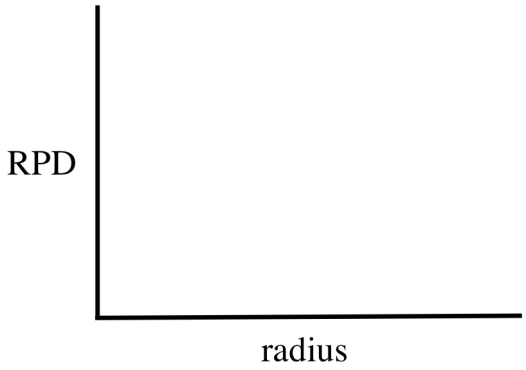
$$\Psi^2 \quad x \quad 4\pi r^2 dr \quad = \quad RPD$$

$$\frac{\text{probability}}{\text{volume}} \quad x \quad \_\_\_\_\_ \quad = \quad \text{probability}$$

Knowing only probability is one of main consequences of Quantum Mechanics. Unlike CM, QM is non-deterministic. The uncertainty principle forbids us from knowing r exactly.



Ψ_{200} (2s)



Ψ_{300} (3s)

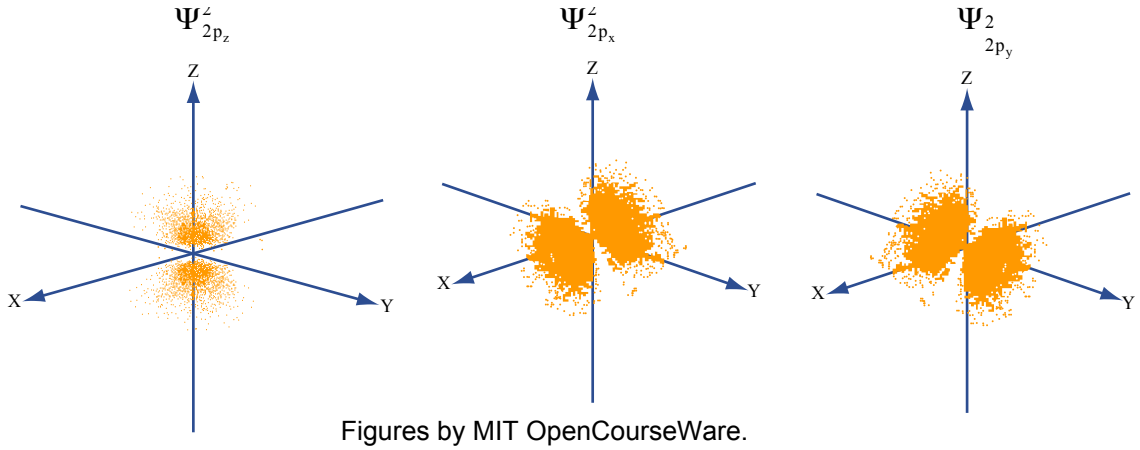
II. P ORBITALS

- For any subshell of $l = 1$, there are three p-orbitals, _____, _____, and _____.
- $m = \pm 1$ states combine to give p_x and p_y orbitals. $m = 0$ is called the p_z orbital.

A. THE SHAPE OF P-ORBITALS

- Unlike s orbitals, p-orbitals have θ, ϕ dependence. P-orbitals _____ spherically symmetrical.
- p orbitals consist of two lobes (of opposite sign) separated by a _____ plane on which $\Psi = 0$ (and $\Psi^2 = 0$).
- There is zero probability of finding a p-electron in a nodal plane. Thus, there is _____ probability of finding a p-electron at the nucleus.

Probability density maps of p orbitals:



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HIGHEST PROB	Along _____	Along ____ axis	Along ____ axis
POSITIVE Ψ	where z is _____	where x is positive	where y is positive
NODAL PLANE	_____ $\theta = 90°$	_____ plane $\phi = 90°$	_____ plane $\phi = 0°$

Nodal planes (planes that have no electron density) arise from angular nodes in the wavefunction.

- Angular nodes: values of _____ or _____ at which Ψ (and Ψ^2) = 0.
- Recall from Lecture #6: Radial nodes are values of **r** at which Ψ (and Ψ^2) = 0.

In general, an orbital has:

n – 1 total nodes

_____ angular nodes

_____ radial nodes

For 2s: _____ = ____ total nodes

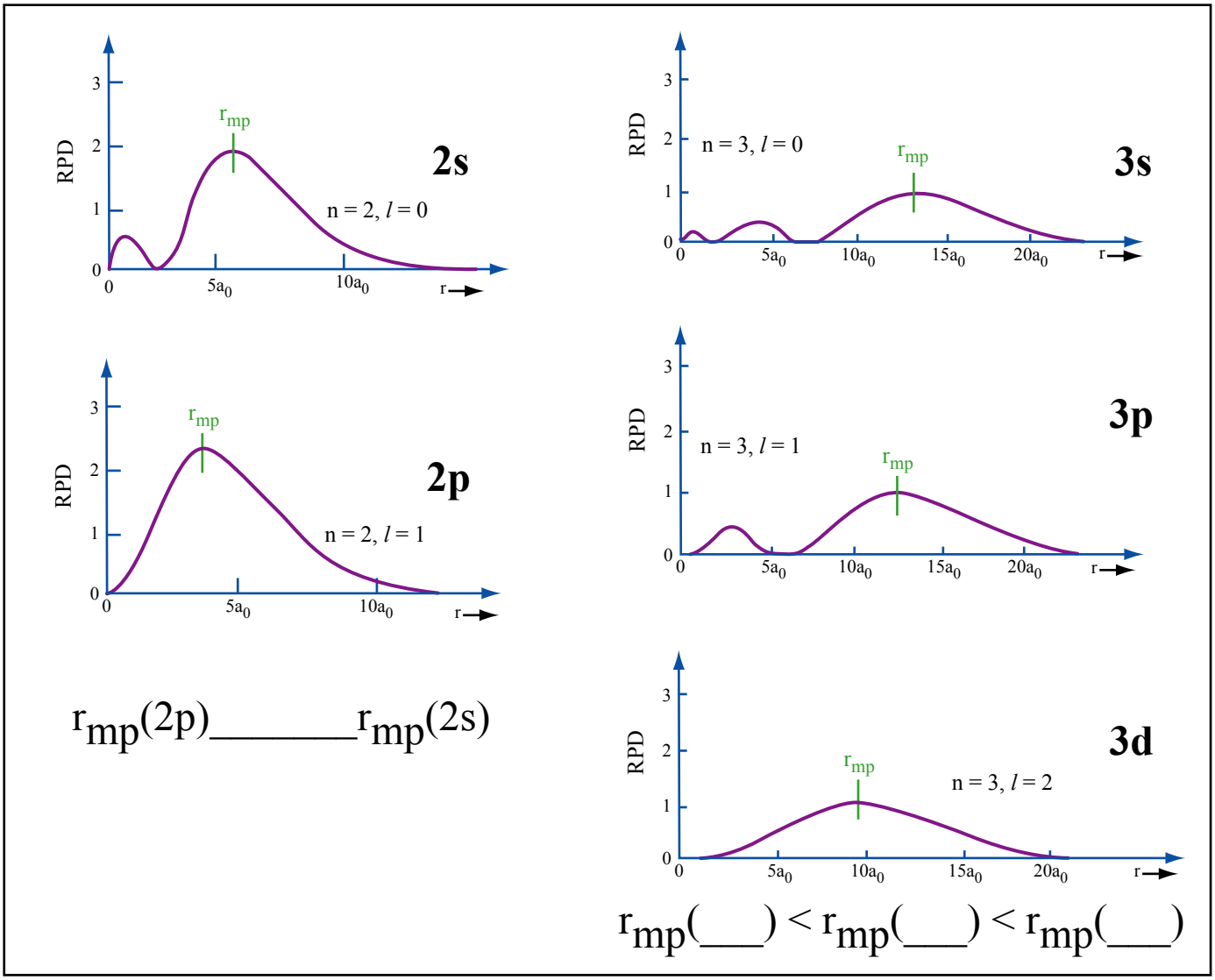
_____ = ____ angular nodes

For 2p: _____ = ____ total nodes

_____ = ____ angular nodes

_____ = ____ radial nodes _____ = ____ radial nodes

B. RADIAL PROBABILITY DISTRIBUTIONS



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Interpreting RPD plots

- As n increases (from 1 to 2 to 3), the orbital r_{mp} "size" _____.
- As *l* increases (from s to p to d) for a given n, the orbital r_{mp} "size"_____.
- Only electrons in s states have a substantial probability of being very close to nucleus. This means that although the "size" of s orbitals is larger than p or d orbitals, s-electrons are the _____ shielded.

III. ELECTRON SPIN AND THE FOURTH QUANTUM NUMBER

From quantum mechanics, a fourth quantum number appears that describes the spin of an electron within an orbital.

Spin magnetic quantum number, _____

There is no classical analogy to spin.

- An electron can have two spin states:
  m_s = _____ (spin up) or m_s = _____ (spin down).

- Similar to the angular momentum quantum number, l, m_s describes the magnitude of an angular momentum. However, m_s completes the description of an _____ and is NOT dependent on the orbital.

The property of electron spin was first proposed by S. Goudsmit and G. Uhlenbeck in 1925 to explain tiny deviations from the expected frequencies of spectral lines:

_____ _____

expected ν observed ν

So we can describe a given orbital using three quantum numbers (n, l, m_l) and a given electron using 4 quantum numbers (n, l, m_l, m_s).

Ψ_{nlm_l} $\Psi_{nlm_lm_s}$

describes an _____ describes an _____

PAULI EXCLUSION PRINCIPLE

No two electrons in the same atom can have the same four quantum numbers. In other words, no two electrons can be in the same orbital and have the same spin.

The Pauli exclusion principle limits an atom to _____ electrons per orbital.

ie. How many *electrons* in a single atom can have the following two quantum numbers: n = 4 and m_l = -2? _____