

Lecture #4 (Ch. 13) Electron Spin, Selection Rules and Polyelectronic Atoms

I. QM Picture of Hydrogenic Atoms: Eigenstates (energy states)

II. Electron Spin

III. Spectral Transitions & Selection Rules

IV. Polyelectronic atoms

I. QM Picture of Hydrogenic Atoms: Eigenstates (energy states)

Orbitals = 1-e wavefunctions of Hydrogenic atoms

3 Q no.s used to specify orbital: principle (n), azimuthal (orbital angular = l), and magnetic quantum no. (m_l , the projection of l along magnetic field axis.)

In Hydrogenic atom, energy only depends on n , since only 1 e, thus same n , but diff l & m_l value

n, l, m_l . **RULES:** n (principle, $n \uparrow \rightarrow E \uparrow$), l (azimuthal) up to $n-1$ (spdf), magnetic m_l ($2l+1$ values from $-l, -l+1, 0, \dots, l-1, l$). n^2 orbitals per n shell. Shapes of s,p,d,f orbitals.

Note $n-1$ nodes in graphs ($n-(l+1)$ radial nodes plus l angular nodes (nodal planes) = $n-1$)

Example: If the principle quantum number is 4 and the azimuthal is 2, what is the subshell designation. List the possible values of m (magnetic quantum number)

Answer: 4d, since 0=s, 1=p, 2=d and the values of m range from $-l$ to $+l = -2, -1, 0, 1, 2$

S-orbitals

S orbitals ($n = 1, l = 0, m_l = 0$) have form:

$$\psi = \frac{e^{-r/a_0}}{\sqrt{\pi a_0^3}}$$

There is no angular dependence thus function is **spherically symmetric**.

Volume element between r and $r+\delta r$ spheres is: $4\pi r^2 \delta r = \delta V$

The probability of finding the electron between r and $r+dr$ is $\psi^2 \times \delta V = 4\pi r^2 \delta r \times \psi^2$

$4\pi r^2 \psi^2$ = radial distribution fn.

Shell Probability: What's probability of finding electron between a_0 and $(a_0 + 1 \text{ pm})$

Use this for illustration 13.3 in which $\delta r = 1 \text{ pm}$, $a_0 = 52.9 \text{ pm}$, and ψ is given by the above expression, thus the probability of an S-orbital electron between a_0 and $a_0 + 1 \text{ pm}$:

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

Note that max value of ψ is 0 when $r = 0 \rightarrow \psi = \frac{1}{\sqrt{\pi a_0^3}}$ however maximum value of $4\pi r^2 \psi^2$

= $P(r)$ the radial distribution function occurs at $r = a_0$ for 1S orbital

P & d orbitals

P orbitals have $l = 1$

Existence of **nodal plane** for all orbitals with $l > 0$ (p,d,f...) is due to nonzero orbital angular momentum being interpreted as the electron circulating about the nucleus, so it should not be at the nucleus.

The units of angular momentum are in units of \hbar : angular momentum = $\sqrt{l(l+1)} \hbar$

d orbitals have $l = 2$.

II. Electron Spin

There is a **magnetic moment** associated with an orbiting or spinning electric charge and is proportional to the **angular momentum** given by LH Rule for e (RH rule for pos charge). Orbital angular momentum **l**, spin angular momentum **s**. Spin angular momentum is inherent QM property with no **classical analogue**.

a-electron spin in direction such that $m_s = +\frac{1}{2}$ **b-electron** spin in direction such that $m_s = -\frac{1}{2}$

Stern-Gerlach experiment proved e-spin exists with Ag atoms (47 electrons, no orbital angular momentum) split into 2 beams in mag field, due to α & β spin interacting differently with mag field.

Fermions - particles with half integral spin such as electrons, neutrons, protons (constitute matter)

Bosons - particles with integral spin, such as photons. (particles that transmit forces)

III. Spectral Transitions & Selection Rules

Conservation of angular momentum occurs in chem rxn & physical processes. Since photon's spin is 1, for hydrogenic atoms the transition between diff't l levels must change by 1 **selection rule $\Delta l = \pm 1$** . i.e. $3s \rightarrow 2p$ **allowed**, $2s \rightarrow 1s, 4s \rightarrow 3d, 4f \rightarrow 3p$ **forbidden**. Also **$\Delta m_l = 0, \pm 1$** found from transition dipole moment matrix elements utilizing time dependent **H**. Of course **Δm_s** can be any value consistent with **Δl** ,

[i.e. to what nl levels can 3d electrons connect via an optical transition:](#)

IV. Polyelectronic Atoms

Polyelectronic schrodinger eqn can't be solved exactly (4 solvable models: PIB, RR, HO, Hydrogenic atoms) because of many interparticle e-e e-p potential terms. **POSSIBLE QUIZ QUESTION**

E-levels and their allowed transitions between them may be summarized by a **Grotrian diagram** in which the transition intensities are proportional to line thicknesses..

s,p,d, etc of a given shell no longer degenerate.

A. Orbital Approximation

Understand difference between overall wavefunction for atom (**$\Psi = f(\psi(1), \psi(2), \psi(3))$**). and individual 1-electron wavefns (orbitals) for each electron $\{\psi(1), \psi(2), \psi(3)..\}$.

Orbital Approximation: 1st approx'n to **$\Psi = \psi(1) \psi(2) \psi(3)...$** , thus by noting the orbital occupation (electronic configuration) the approx overall wavefn **Ψ** is determined.

B. Aufbau Principle

When determining the ground state e-config we add electrons energetically, **Aufbau principle**, gauided by the **Pauli Principle** (no 2 electrons 4 quan nos:) and **Hunds Rules** (electons entering same subshell fill separate ml orbitals prior to pairing).

For example : the electron configuration of B is: $1s^2 2s^2 2p^1$ DRAW Orbital occupancy DIAGRAM
Can you determine the structure of N with its corresponding Orbital occupancy diagram: