<u>Q</u>  <u>Reaction Profile</u>   What is it?
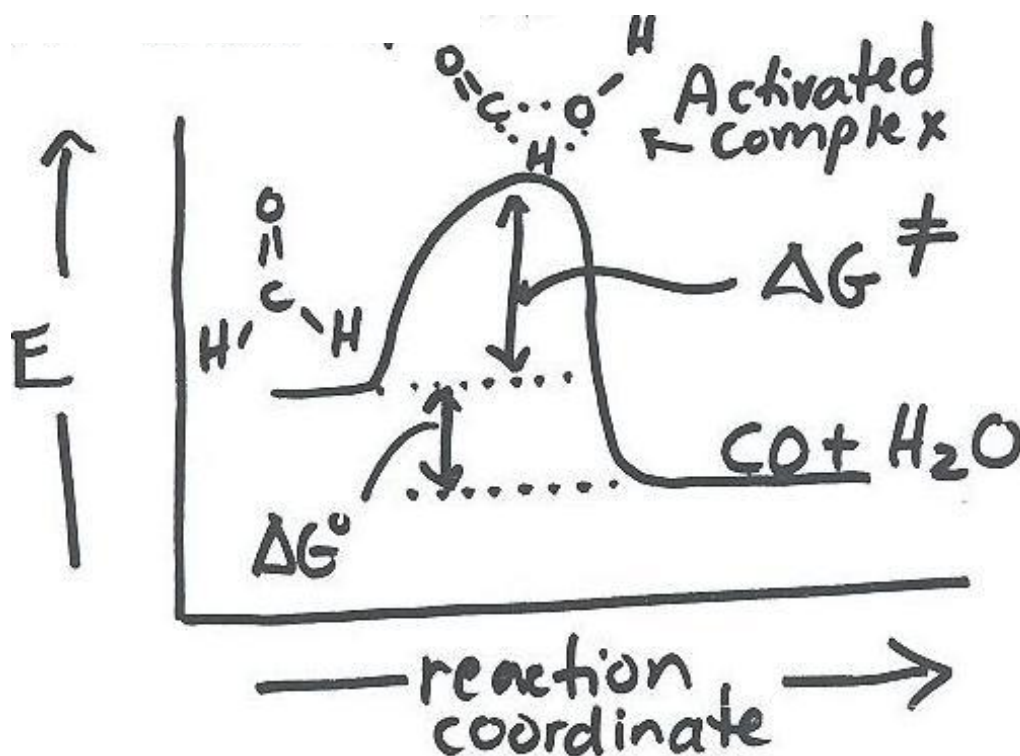<u>A</u>  It is a graph of free energy, G, versus the pathway of the reaction.
(The pathway is the change in bond distances during the conversion from reactants to products)

ex. Decomposition of formic acid

<u>Q</u>  Based on the reaction profile, how can one increase the rate of a reaction?

<u>A</u>  For one thing, we cannot change the value of the Equilibrium constant, K, unless we change the reaction conditions (temp., pressure, solvent etc.,) but we can alter the rate without changing the reaction conditions by adding a catalyst.

<u>A Catalyst lowers the $\Delta G^{\neq}$, Activation Energy</u>

<u>Two Ways:</u>
1. catalysts can assist in forming the activated complex
2. catalysts can provide an entirely different pathway by <u>temporarily</u> binding to the reactants.

Continuing with the review…..

# Electronic Structure
## Chapter 2

### Atomic Electronic Structure

The (a) number and (b) distribution of electrons around an atom.

These two features essentially dictate the properties of the atom.

First hints about the electronic structure of atoms came from experimental work carried out in late 1800's & early 1900's.

Absorption and Emission of radiation from atoms was well-documented but not at all understood.

- Not until 1913, were any theories advanced that could even explain the emission spectrum of Hydrogen.

This was when Rydberg realized that the emission lines had specific wave numbers, but he could not reconcile this relationship with classical physics which said: the $e^-$ would spiral into the nucleus and emit a continuum of energies.

- In 1913, Bohr broke from classical physics and said there are <u>Discrete</u>, <u>Quantized Levels</u> where an electron can reside in an atom.  He related the angular momentum mvr to an  integer value (Quantized Value)

$$mvr = \frac{nh}{2p}$$

m is the mass
v is velocity
r is radius
h  is Planck's const.
n  is an integer value
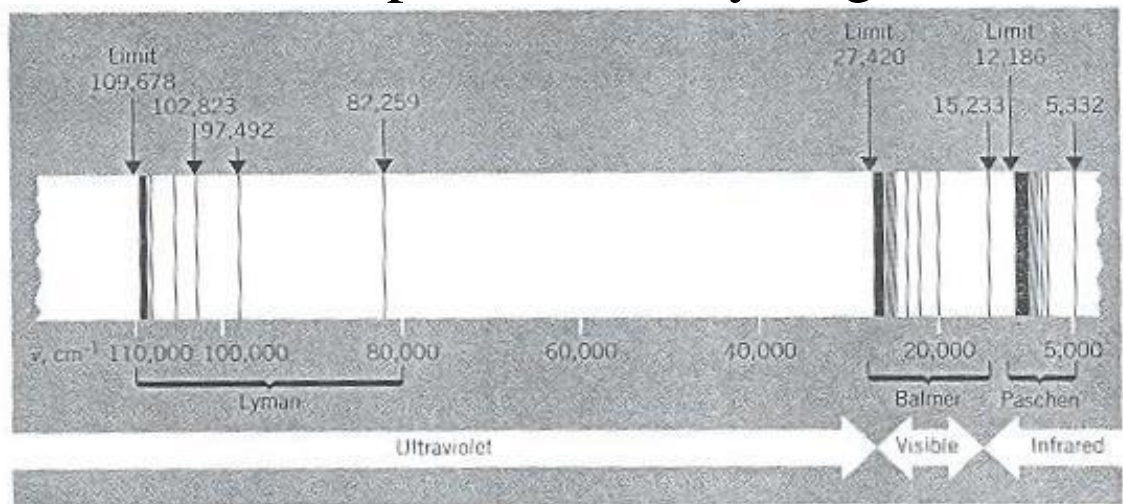
# Emission Spectrum of Hydrogen



**Figure 2-1** The emission spectrum of atomic hydrogen as recorded on a strip of film. Each line represents an emission frequency. Three series of lines are shown. Within each series, the lines converge to a limit. Two more well-defined series occur for atomic hydrogen in the infrared (IR) region, but they are not shown here.
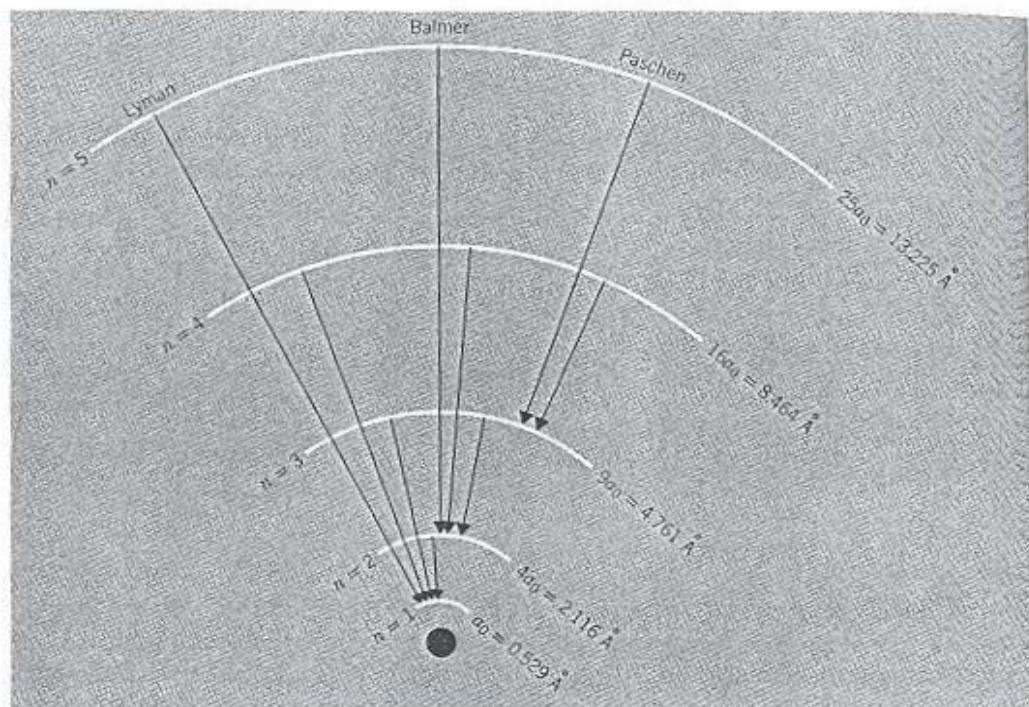


**Figure 2-2** A diagram of the Bohr orbits and the corresponding energies for an electron in the hydrogen atom. Each arc represents a portion of an orbit. The transitions that give rise to the three series of spectroscopic lines of Fig. 2-1 are indicated.

Bohr orbits and the transitions associated with emissions from higher orbits to orbits $n = 1$, $n = 2$, $n = 3$.

Q  Is the Bohr atom model capable of being extended to other atoms besides H?
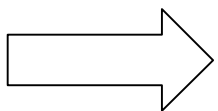
A  NO

Q  Why?

A  Electrons are not discrete particles with precisely defined positions and velocities.

Bohr himself used the idea put forth by Max Planck that electromagnetic energy (photons or any wave) is quantized:

$$E = h\nu$$

Planck's constant

⟹  Electrons have the same wave-like properties that photons have.

# Dawn of Dual Particle-Wave Theories
$\implies$ **Wave Mechanics**

## Two important players:

De Broglie

$$l = h/mv$$

Particle-Wave
Equation

{ All particles with velocities, v, and mass, m can be described by a wavelength

Schrödinger

$$H\Psi = E\Psi$$
Wave equation

{ Proposed a general mathematical expression for an electron

The Theory of Wave Mechanics is the method of operator algebra

H  - Hamiltonian operator defines a series of operations to perform

Ψ   - Wave function describes the e⁻ in terms of its wave properties

$$\Psi = R(r) \quad \Theta(\theta) \, \Phi(\varphi)$$

$\underbrace{\qquad}$ Radial     $\underbrace{\qquad}$ angular

Wave functions have two components:
The physical manifestation of Ψ is what we call an orbital. Orbitals have:
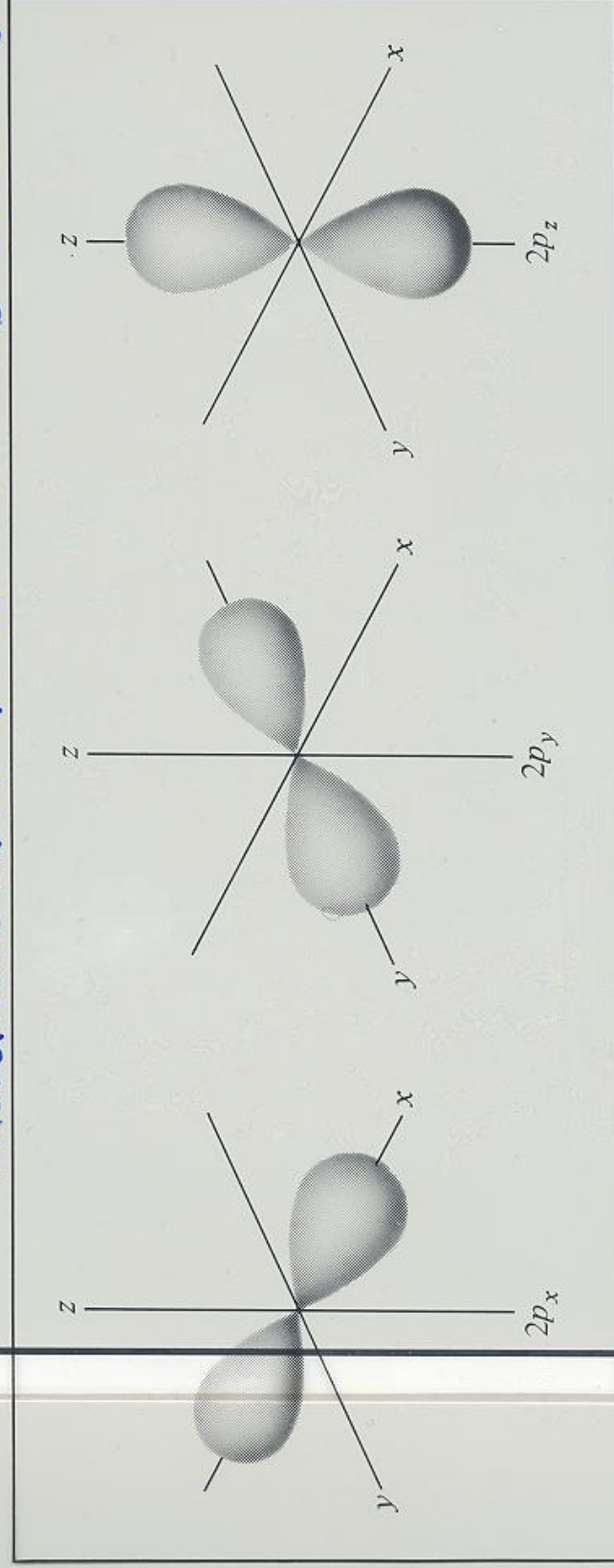    1) <u>shape</u> determined by angular part
    2) <u>extension</u> determined by radial part
       <u>or size</u>

The most simplistic way that these two are depicted is in the form of boundary surface diagrams (our usual meaning of an orbital)
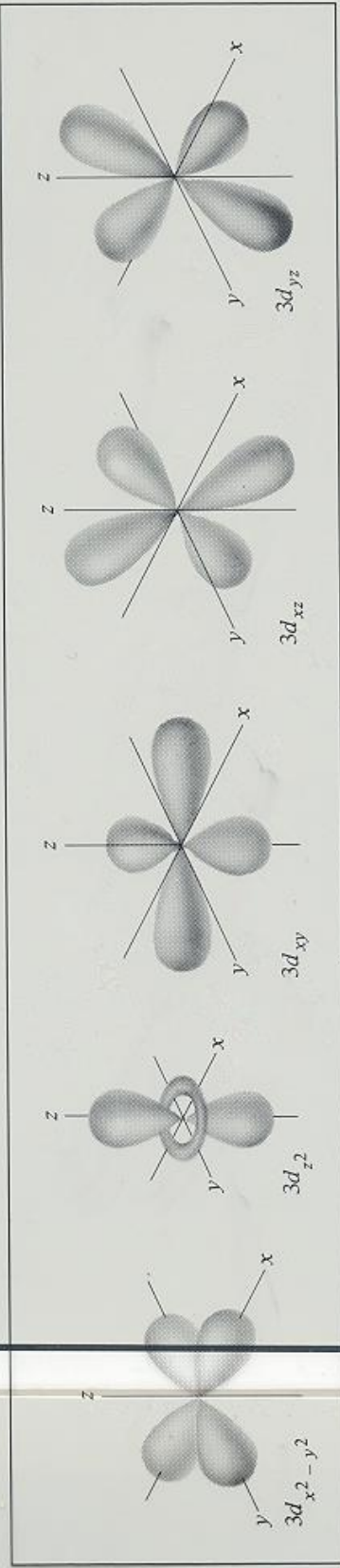
Figure 7.25

Boundary surface Diagrams

Three p orbitals

identical in shape (probabilities) and energies



2$p_x$    2$p_y$    2$p_z$

Figure 7.26

# Boundary surface Diagrams

## five d orbitals



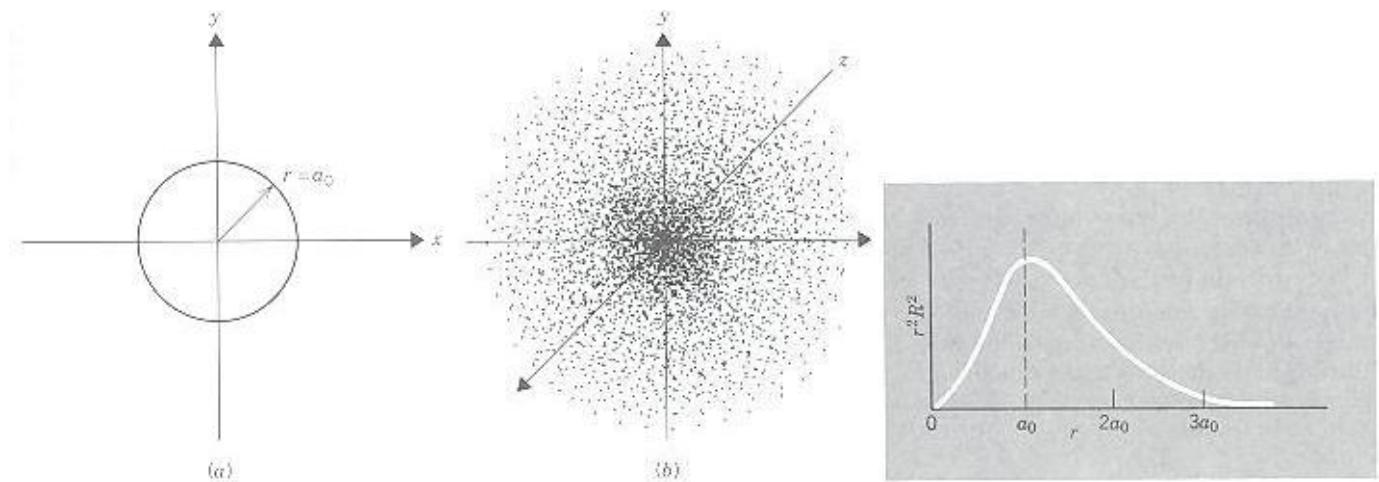$3d_{z^2}$   $3d_{xy}$   $3d_{xz}$   $3d_{yz}$   $3d_{x^2-y^2}$

although it looks different, the $d_{z^2}$ orbital is identical in all aspects to the other forms

The square of $\Psi$, $\Psi^2$, gives a measure of the e⁻ density in various regions.

<u>Q</u>  How does the Bohr model compare to the wave function model?

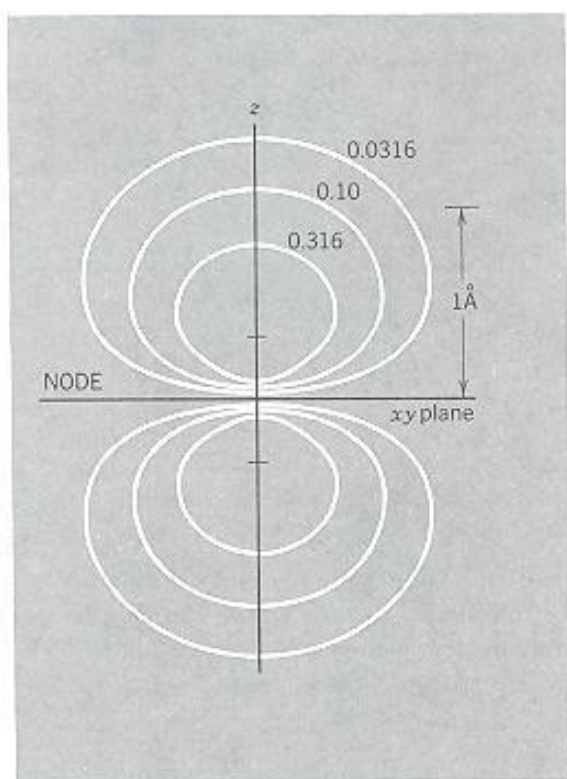<u>A</u>  The precise orbit of an e⁻ in a Bohr orbit is the place where the e⁻ density probability is the highest:



Bohr model          dot density          e⁻ density
                      diagram              probability
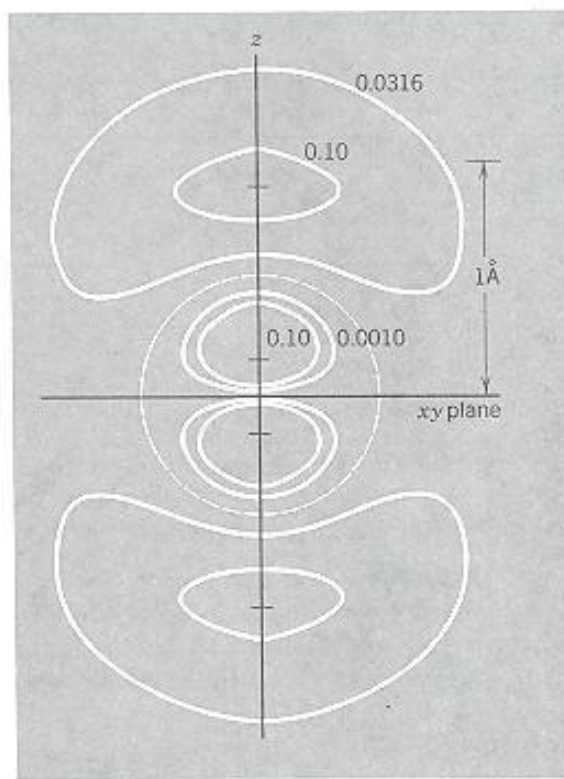                                           function

Another way to show how the e⁻ density (or probability for finding the e⁻) varies in an orbital is a contour map:
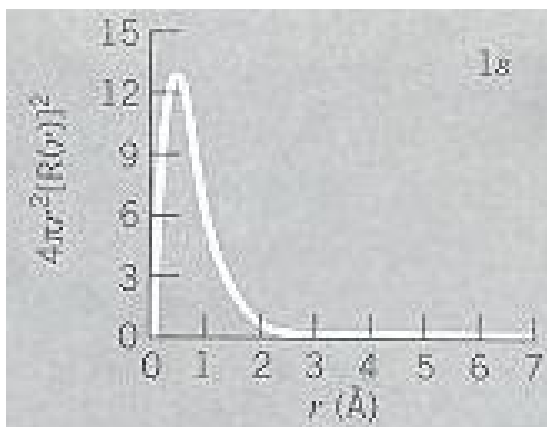
2p                                    3p



There are major differences that arise because of the function $4\pi r^2[R(r)]^2$ which is the e⁻ density probability function.
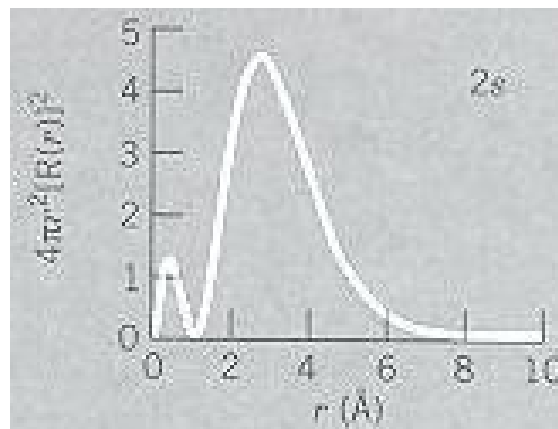
# e⁻ density probability functions

$$4\pi r^2 [R(r)]^2 \quad (r^2[R(r)]^2 \text{ for short})$$

1s                                                                2s
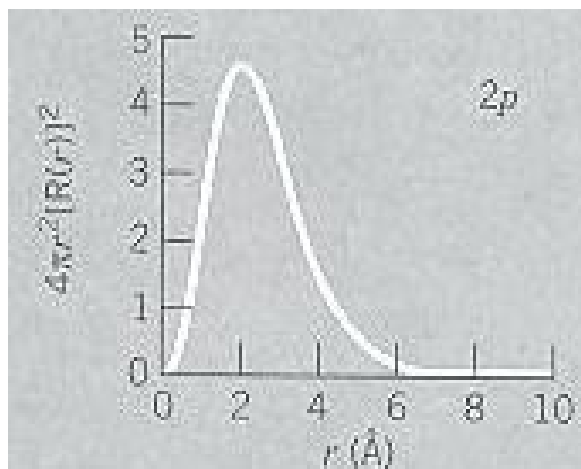
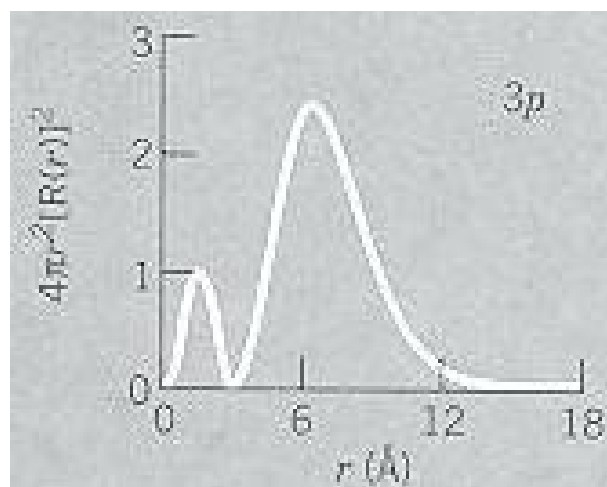

no probability of the e⁻
at the nucleus

2p                                                                3p



for a 2p orbital the e⁻ density increases to a
maximum then drops off.     3p is different

## Summary of Quantum numbers for an electron:

n    principal Q.N    n can be $0 \to \infty$
     n determines the size of the orbitals

$\ell$    orbital Q. N.    $\ell = 0,1,2\ldots(n\text{-}1)$
     determines the shape of orbitals

$m_\ell$   $_{+}\ell\ldots o\ldots\text{-}\ell$   $\ell{=}1$    $m_\ell =_{\pm}1, 0$ etc.,

$m_s$   $_{\pm}$ ½ for each election

## Four Q.N.'s in all:
| | | |
|---|---|---|
| n = 1 shell | $\ell{=}0$ | 1s |
| n = 2 shell | $\ell{=}0$ | 2s |
| | $\ell{=}1$ | 2p |
| n = 3 shell | $\ell{=}0$ | 3s |
| | $\ell{=}1$ | 3p |
| | $\ell{=}2$ | 3d |

*etc.,*

# Electronic Configuration

The term used to describe the manner in which electrons are arranged in an atom
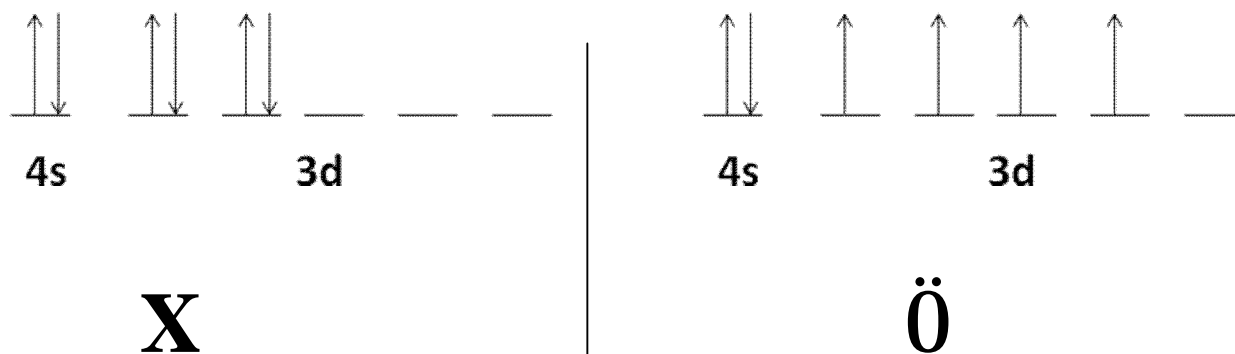
1.) <u>Aufbau Principle:</u>
Add electrons from the lowest to the highest levels

2.) <u>Hund's Rule of maximum multiplicity:</u>
Add electrons in orbitals of the same energy (degenerate set) with same spin before pairing spins.

e.g. $1s^2 s^2 2p^6 3s^2 3p^6 4s^2 3d^4$ is:

4s              3d                    4s              3d

**X**                                    **Ö**

## Pauli Exclusion Principle:

No two electrons can have the same 4 Quantum numbers (in other words, if two electrons are in the same shell (n), same set of orbitals ($\ell$), and same exact orbital ($m_\ell$), then they would have different values of $m_s$ (spins) + ½ for one and - ½ for the other

$$m_\ell = \quad \overline{\phantom{-1}} \quad \overline{\phantom{0}} \quad \overline{\phantom{+1}}$$
$$m_\ell = \quad -1 \quad 0 \quad +1$$
$$2p$$

Both electrons:

$$n=2$$
$$\ell=1$$
$$m_\ell = -1$$

but $m_s$ = + ½ for one
and $m_s$ = - ½ for other

Orbital energies in the H atom

4s ——     4p ——     4d – – –     4f – – –

3s ——     3p ——     3d – – –

2s ——     2p ——

1s ——
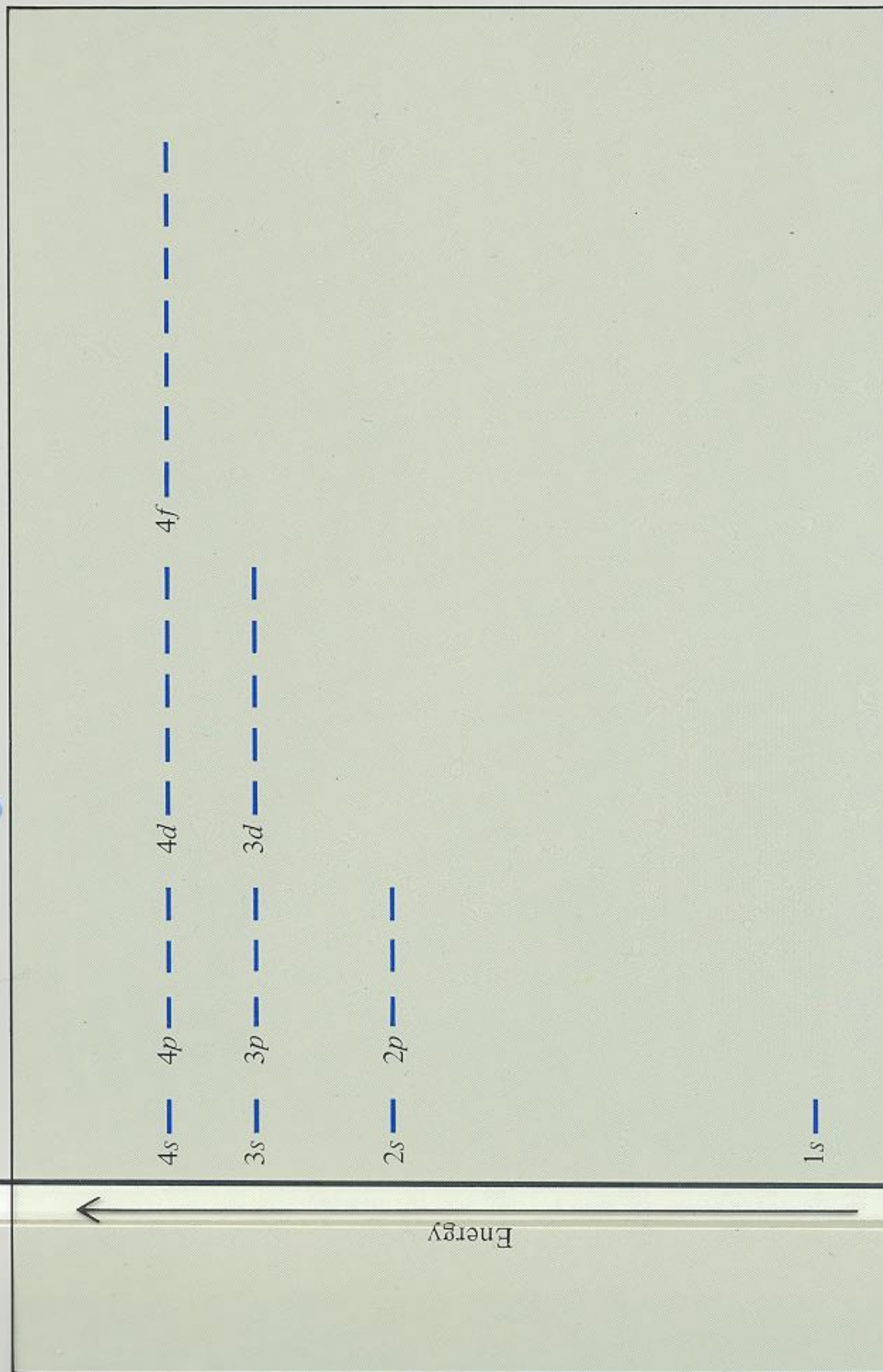
Energy →

Figure 7.27

Figure 7.28

Orbital energy levels in a many-electron atom

Energy ↑

5s —

4s —          4p — — —

3s —          3p — — —          4d — — —

2s —          2p — — —          3d — — —

1s —
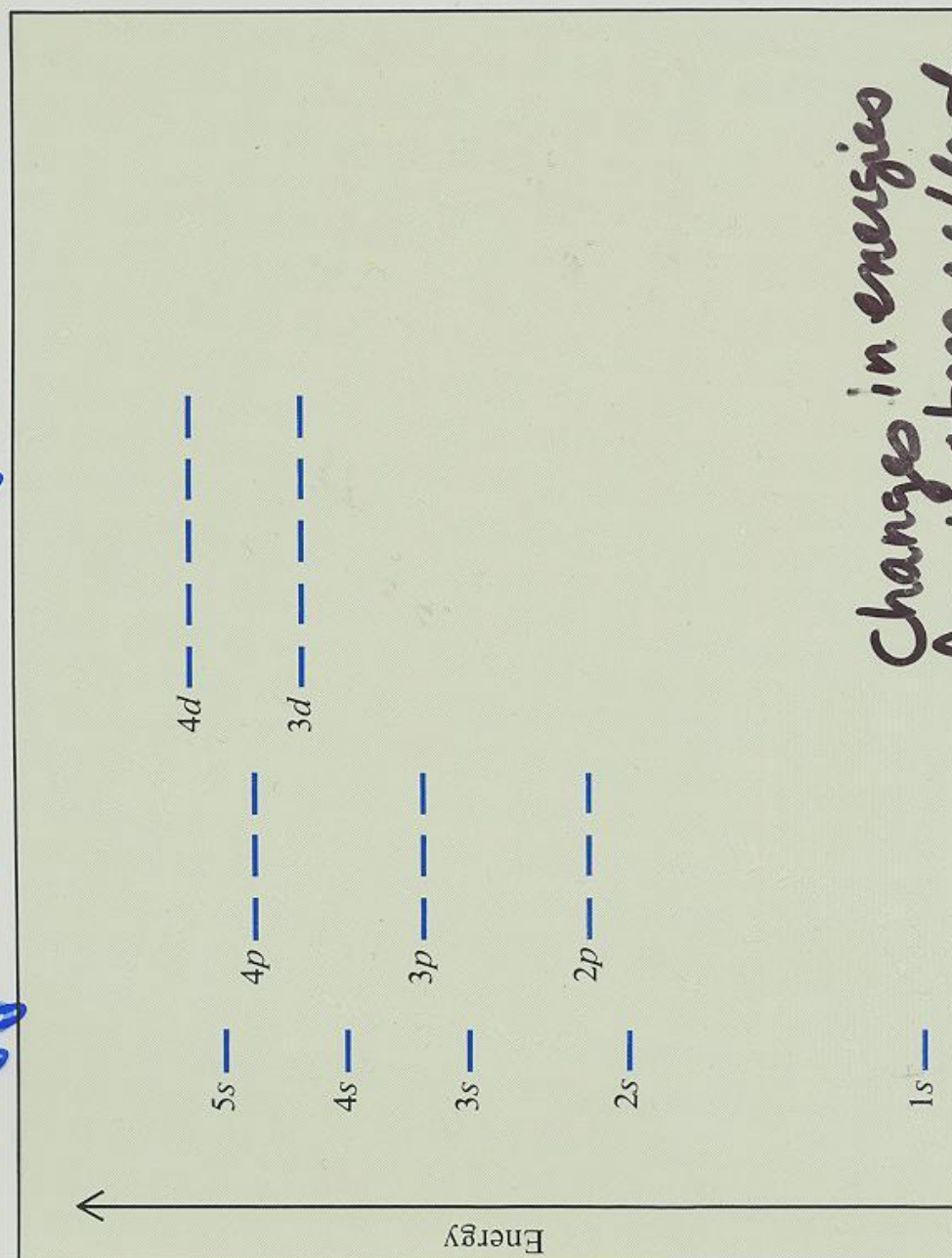
Change in energies
from H atom reflect
e⁻ repulsions and
relative shapes of
orbitals

53

Knowledge of Atomic Structure is so important, because it allows us to understand the periodic relationships among elements.

Concepts that follow from Electronic Structure:

1. The interpenetrations of atomic orbitals which depends on size & shape (in other words, how they fit together)

2. Because of their interpenetration, we order the orbitals in the Aufbau way: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p…

3. Because of the different interpenetrations and orientations of the orbitals, the electrons experience different nuclear charges.

and finally….**MAIN POINT!!!**

4. Properties Such as:
   - Ionization Energies
   - Atomic & Ionic Sizes
   - Electron Affinities
   - Electronegativities

   Reflect on the Electronic Configuration of a group (column) and a period (row)

---

## Ionization Energy or Enthalpy
$\Delta H_{ion}$ in kJ/mol – First Ionization Energy

*Three trends are noticeable:*
1. Maximum at Noble Gases
2. Minimum at alkali metals (closed-shell is favored)
3. The increase in going from alkali metal to noble gas. (e.g. Na to Ar for example) is not regular → there are two "dips

<u>Q.</u>  Why?

<u>A.</u>  Because of differences in shielding of s  &
      p orbitals

<u>Shielding</u>
When you put electrons in orbitals with the
same Quantum number, n, (same shell), as you
keep adding more, they are less shielded from
the positive charge of the nucleus.

The leads to it being more difficult to remove
electrons (higher I.E.)
<u>in other words</u>…

The Effective Nuclear Charge increases as you
go across a row

Ar

Cl

P S

Si

$P^4 \rightarrow P^3$
half-filled

Mg

Na

Al

↑

first p
electron is
being added
(less shielded)
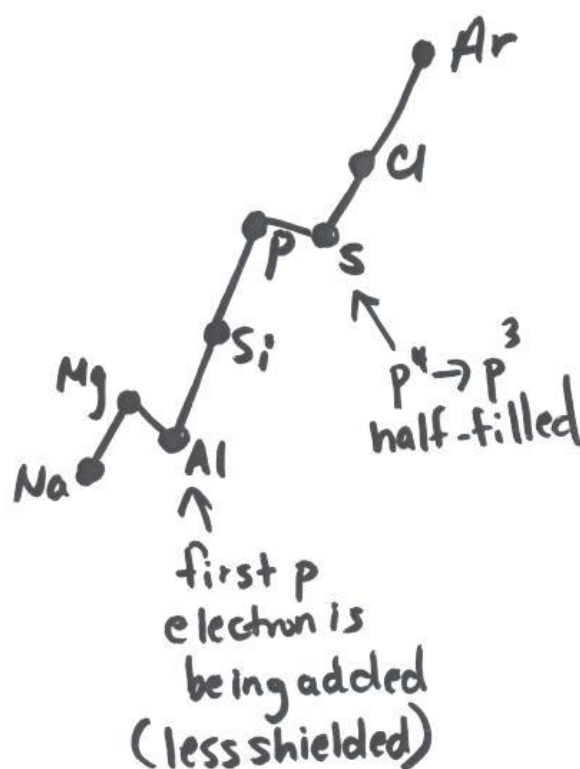
Q. Why do the changes at Al and S happen?

A. Because    Na is $2s^1$
              Mg is $2s^2$
- Al is $2s^2 2p^1$ - it is favored to lose the one p electron to go back to a filled sub-shell
-S is $2s^2 2p^4$ - it is easier to lose an electron to get it back to the stable half-filled sub-shell $2s^2 2p^3$