

# Atomic Physics

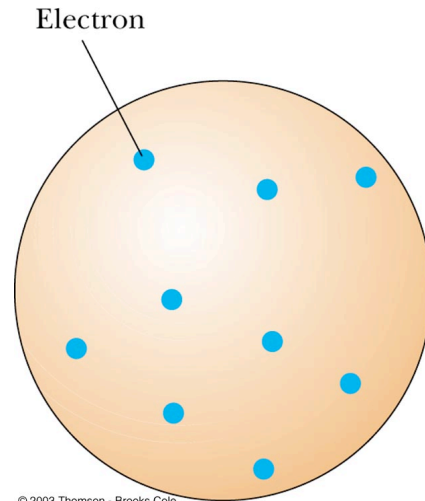
## 28.1 Early Models of the Atom

### The theory:

Thomson “jellybean” model of the atom:

The positive charge occupies most of the volume of the atom

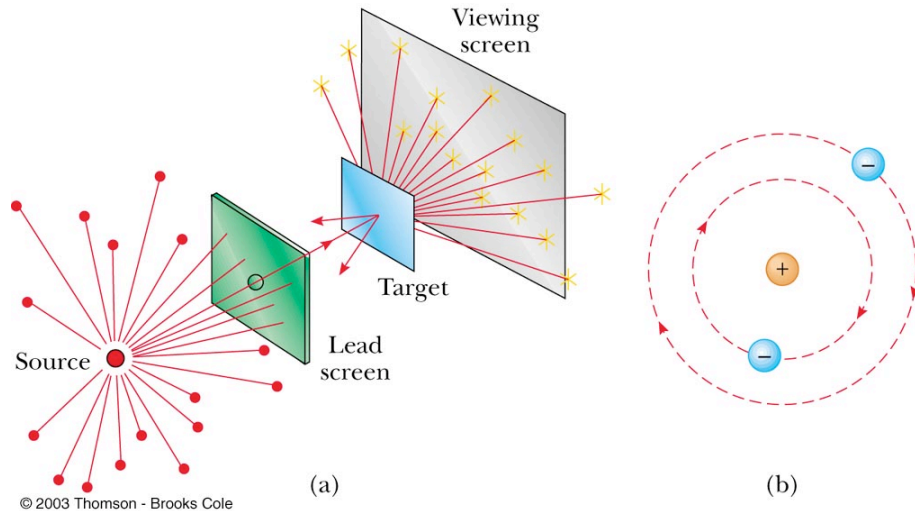
Charged particles shot at this atom should be deflected slightly as they pass through.



### The experiment (Rutherford):

Most of the atom is empty space!

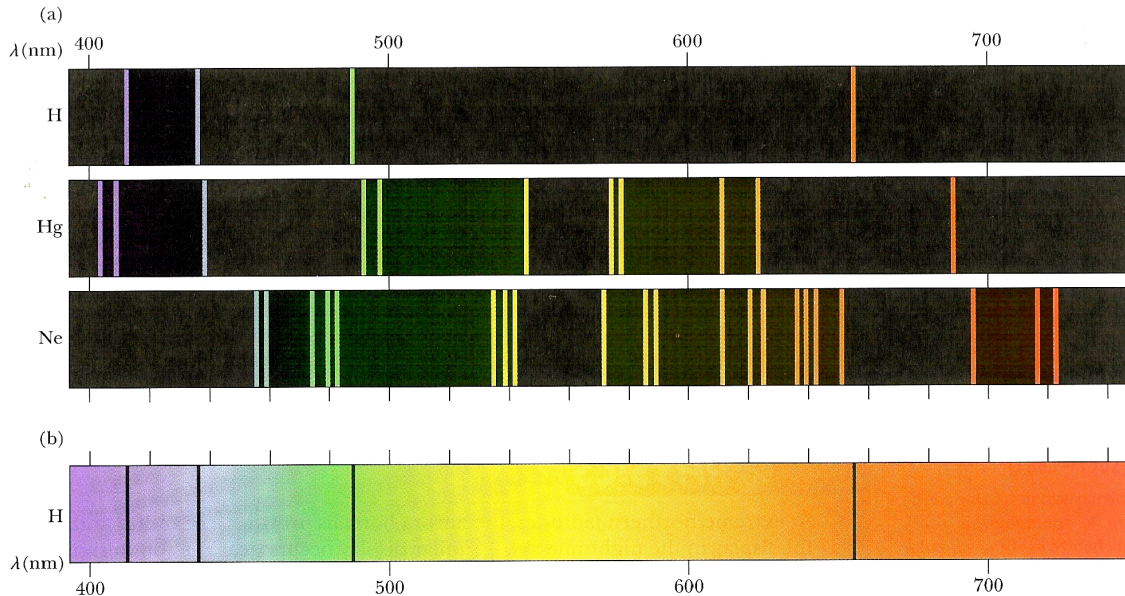
All of the positive charge is concentrated in a very small space!



The modern model of the atom is born. But:

1. Does not explain why there are spectral lines.
2. Classical electrodynamics rears its ugly head: orbiting electrons should continuously radiate light, lose energy, and fall into the nucleus. They don't.

## 28.2 Atomic Spectra

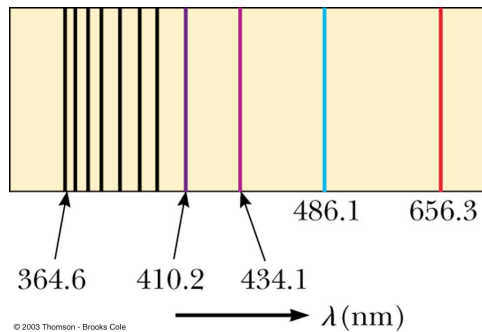


Each element has its own characteristic “fingerprint”.

A heated gas emits emission lines.

The same gas, when placed between a bright continuous background source and the observer produces absorption lines at those same wavelengths.

### Balmer & the Hydrogen Atom



$$\frac{1}{\lambda} = R_H \left( \frac{1}{2^2} - \frac{1}{n^2} \right) \quad \text{where } n = 3, 4, 5, \dots \text{ and}$$

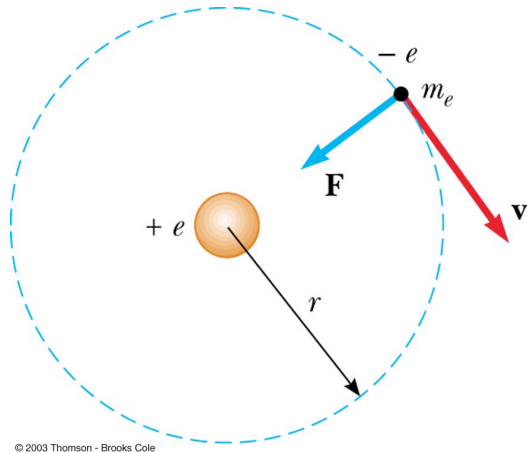
$$R_H = 1.0973732 \times 10^7 \text{ m}^{-1} \quad \text{Rydberg constant}$$

### Example: Problem #4

The “size” of the atom in Rutherford’s model is about  $1.0 \times 10^{-10} \text{ m}$ . (a) Determine the speed of an electron moving in a circle around the proton using the attractive electrical force between an electron and a proton separated by this distance. (b) Does this speed suggest that Einsteinian relativity must be considered when studying the atom? (c) Compute the de Broglie wavelength of the electron as it moves about the proton. (d) Does this wavelength suggest that wave effects, such as diffraction and interference, must be considered when studying the atom?

### 28.3 The Bohr Theory of Hydrogen

1913 – Bohr postulates a “semi-classical” description of how the H atom works.



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Electron orbits in circular orbit under Coulomb attraction

Only certain orbits are stable. *While in this electron orbit, the atom does not emit electromagnetic radiation*

Radiation is emitted when the electron jumps from one orbit to another, and the energy of the emitted photon is the difference in energy of the 2 levels

$$E_i - E_f = hf$$

The allowed orbits are those where the angular momentum of the electron is given by

$$mvr = n\hbar \quad \text{where } n = 1, 2, 3, \dots \quad \text{and } \hbar = h/2\pi$$

The total energy is  $E = KE + PE = \frac{1}{2}m_e v^2 - k_e \frac{e^2}{r}$  where  $k_e$  is the Coulomb constant

We also have  $\underbrace{k_e \frac{e^2}{r^2}}_{\text{Coulomb force}} = m_e \underbrace{\frac{v^2}{r}}_{\text{orbital acceleration}}$  so  $\frac{1}{2}m_e v^2 = \frac{k_e e^2}{2r}$

$$\text{So } E = -\frac{k_e e^2}{2r}$$

Now, let's look at what happens due to the condition of the angular momentum having fixed values.

$$\underbrace{v^2 = \frac{n^2 \hbar^2}{m_e^2 r^2}}_{\text{angular momentum restriction}} \quad \text{and also} \quad \underbrace{v^2 = \frac{k_e e^2}{m_e r}}_{\text{orbital acceleration}}$$

$$\text{So } r_n = \frac{n^2 \hbar^2}{m_e k_e e^2} \quad n = 1, 2, 3, \dots$$

The smallest allowed orbit occurs when  $n=1$ , and it is called the **Bohr radius**:

$$a_0 = \frac{\hbar^2}{m_e k_e e^2} = 0.0529 \text{ nm}$$

The radii of the rest of the orbits will simply be  $r_n = n^2 a_0 = n^2 (0.0529 \text{ nm})$

Substituting the equation for the radii into the energy equation gives:

$$E_n = -\frac{m_e k_e^2 e^4}{2\hbar^2} \left( \frac{1}{n^2} \right) = -\frac{13.6}{n^2} \text{ eV}$$

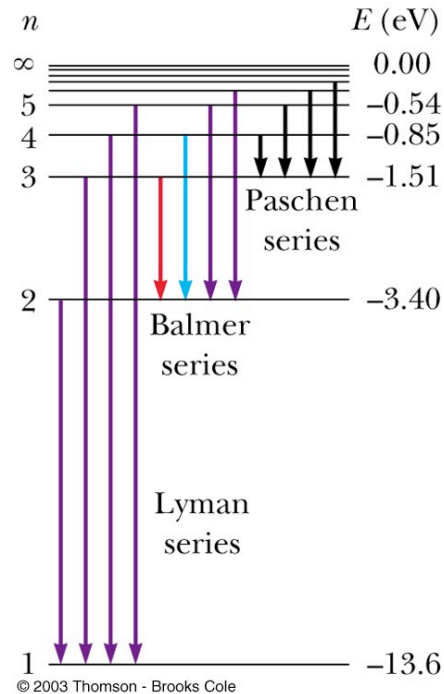
According to Bohr, the frequency emitted by the atom when it goes from an initial energy state to a final energy state is then just

$$f = \frac{E_i - E_f}{h} = \frac{m_e k_e^2 e^4}{4\pi\hbar^3} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad \text{and}$$

$$\frac{1}{\lambda} = \frac{f}{c} = \frac{m_e k_e^2 e^4}{4\pi c \hbar^3} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = R_H \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

The Balmer lines are just the special case where  $n_f = 2$ , but transitions from any orbit to any other orbit will also give rise to a series of spectral lines.

Furthermore, the case where  $n_f = \infty$  gives the energy required to ionize the atom. For the ground state, it is 13.6 eV.



**Example: Problem #14**

A hydrogen atom initially in its ground state ( $n = 1$ ) absorbs a photon and ends up in the state for which  $n = 3$ . (a) What is the energy of the absorbed photon? (b) If the atom eventually returns to the ground state, what photon energies could the atom emit?

## 28.4 Modification of the Bohr Theory

### Successes of the Bohr Model:

- Explained all of the series of emission lines of H
- Predicted the correct value of  $R_H$
- Predicted the correct size of H
- Predicted the correct energy levels of H

It also worked for other “hydrogenic” atoms – those with a single electron

$$E_n = -\frac{m_e k_e^2 Z^2 e^4}{2\hbar^2} \left( \frac{1}{n^2} \right) \quad n = 1, 2, 3, \dots$$

$$\text{and} \quad \frac{1}{\lambda} = \frac{m_e k_e^2 Z^2 e^4}{4\pi c \hbar^3} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

### Example: Problem #27

(a) Find the energy of the electron in the ground state of doubly ionized lithium, which has an atomic number  $Z = 3$ . (b) Find the radius of its ground-state orbit. (Note: this is just Example 28.3 done for lithium instead of helium).

**Did not work well with multi-electron atoms: modifications needed!**

TABLE 28.1		Shell and Subshell Notations	
$n$	Shell Symbol	$\ell$	Subshell Symbol
1	K	0	<i>s</i>
2	L	1	<i>p</i>
3	M	2	<i>d</i>
4	N	3	<i>f</i>
5	O	4	<i>g</i>
6	P	5	<i>h</i>
⋮		⋮	

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$n$  principle quantum number

$\ell$  orbital quantum number where  $\ell = 0, 1, 2, n - 1$ . (elliptical orbits)

So,

$$n = 1 \rightarrow \ell = 0$$

$$n = 2 \rightarrow \ell = 0, 1$$

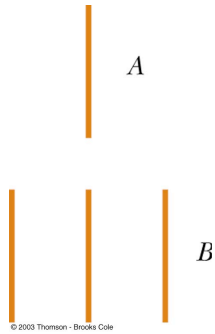
$$n = 3 \rightarrow \ell = 0, 1, 2$$

etc.

All states with given  $n$  form a *shell*

All states with a given  $n$  and  $\ell$  form a subshell

Maximum number of electrons per subshell is  $2(2\ell + 1)$



*Zeeman splitting* of spectral lines in strong magnetic fields requires yet another quantum number, the *orbital magnetic quantum number*

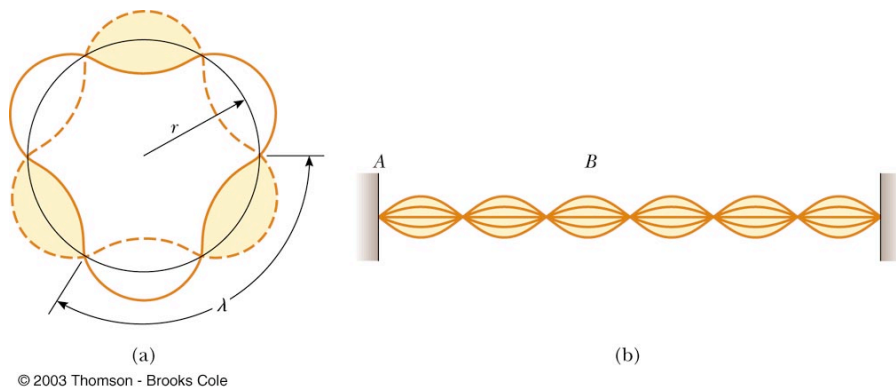
$$m_\ell \quad \text{where } m_\ell = -\ell, (-\ell + 1) \dots -1, 0, 1, 2, \dots (\ell - 1), \ell$$

*Fine structure splitting* requires yet another one, the spin magnetic quantum number  $m_s$

### 28.5 De Broglie Waves and the Hydrogen Atom

Okay, *why* did Bohr's postulate for "quantized angular momentum" actually work for explaining the H atom? *DeBroglie suggested that the electron's wave pattern must be such that an integral number of waves would fit in the orbit, similar to a standing wave (but with its tail in its mouth!).*

In this interpretation, the  $n=1$  level contains 1 whole wave, the  $n=2$  level has 2 whole waves, etc.



$$2\pi r = n\lambda \quad n = 1, 2, 3, \dots \quad \text{deBroglie's postulate}$$

$$\text{but } \lambda = \frac{h}{p} = \frac{h}{m_e v} \quad \text{so } 2\pi r = n \frac{h}{m_e v}$$

$$\text{hence } m_e v r = n\hbar$$

#### **Example: Problem #31**

Determine the wavelength of an electron in the third excited orbit of the hydrogen atom, with  $n = 4$ .

## 28.6 Quantum Mechanics and the Hydrogen Atom

Mathematically (without making any *ad hoc* assumptions), the full-blown solution to the wave equation automatically yields:

- the principle quantum number  $n$  which determines the energies of the orbits
- the orbital quantum number  $\ell$
- the orbital magnetic quantum number  $m_\ell$
- the rules that govern the values that these quantum numbers can have.

**TABLE 28.2** Three Quantum Numbers for the Hydrogen Atom

Quantum Number	Name	Allowed Values	Number of Allowed States
$n$	Principal quantum number	1, 2, 3, . . .	Any number
$\ell$	Orbital quantum number	0, 1, 2, . . . , $n - 1$	$n$
$m_\ell$	Orbital magnetic quantum number	$-\ell, -\ell + 1, . . . , 0, . . . , \ell - 1, \ell$	$2\ell + 1$

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$n = 1$	$\ell = 0$	<b>1s</b>	$m_\ell = 0$
$n = 2$	$\ell = 0$	<b>2s</b>	$m_\ell = 0$
	$\ell = 1$	<b>2p</b>	$m_\ell = -1$
			$m_\ell = 0$
$m_\ell = 1$			
$n = 3$	$\ell = 0$	<b>3s</b>	$m_\ell = 0$
	$\ell = 1$	<b>3p</b>	$m_\ell = -1$
			$m_\ell = 0$
			$m_\ell = 1$
	$\ell = 2$	<b>3d</b>	$m_\ell = -2$
			$m_\ell = -1$
$m_\ell = 0$			
$m_\ell = 1$			
$m_\ell = 2$			

## 28.7 The Spin Magnetic Quantum Number

The splitting of the yellow sodium line into two separate lines of slightly different energies indicates that one more quantum number was required. This is the so-called spin

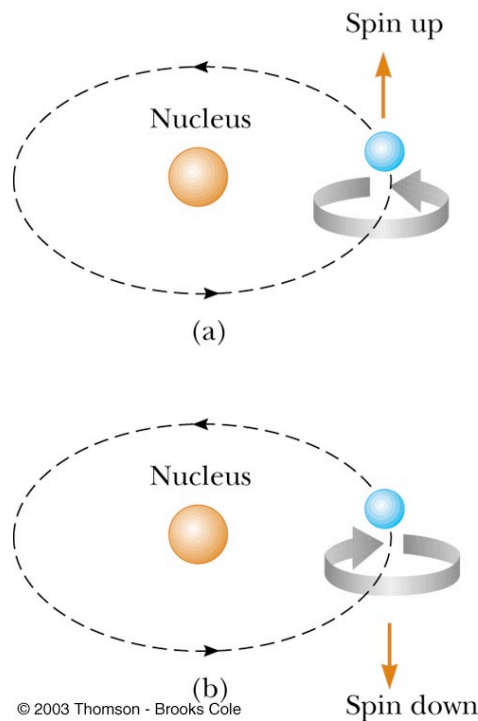
quantum number  $m_s = \pm \frac{1}{2}$ .

We can (incorrectly) visualize it as the electron having some rotational spin that is either “up” or “down”.

Each of these would have a slightly different energy.

(Imagine of the nucleus and the electron each were little magnets with a N and S pole. They would like to be oppositely-aligned, and would require work to make the N poles point the same way)

The H atom produces a photon with  $\lambda = 21\text{cm}$  when it spontaneously flips from one state to the other. On the average this takes millions of years to do.....



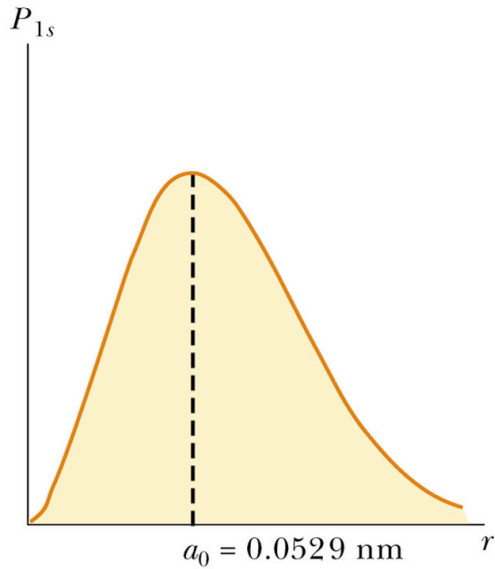
### **Example: Problem #34**

List the possible sets of quantum numbers for electrons in the 3d subshell.



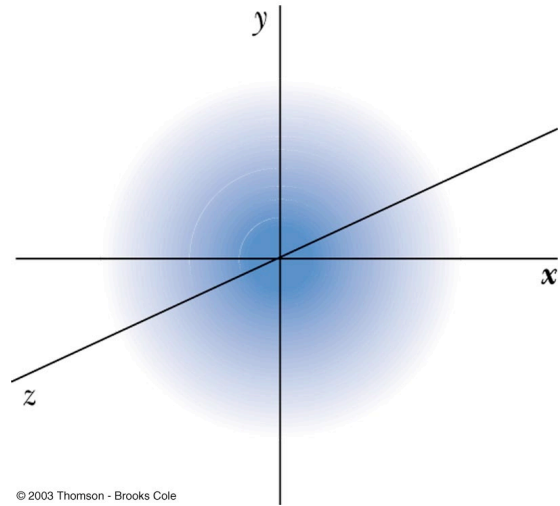
## 28.8 Electron Clouds (read)

We no longer think of the electrons as particles orbiting in specific orbits. Rather, the wave function  $\Psi$  (or more specifically its square) tells us the probability distribution of the electron.



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$\Psi^2$  reaches its maximum value for the  $n = 1$  orbital at the Bohr radius  $a_0$



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We can view all of the  $s$  orbitals as fuzzy spherical shells

## 28.9 The Exclusion Principle and the Periodic Table

Okay, atoms can have many energy levels. Why are there different elements? Why do they have different chemical properties? Why don't all atoms have all of their electrons in the  $1s$  orbital?

**Pauli Exclusion Principle:** *No two electrons can ever be in the same quantum state; that is, no two electrons in the same atom can have exactly the same values for  $n$ ,  $\ell$ ,  $m_\ell$ , and  $m_s$ .*

Each possible substate with 4 quantum numbers can only hold 1 electron! So in an atom with many electrons, the lower levels sequentially “fill up”, forcing the rest into higher substates.

**TABLE 28.3** Number of Electrons in Filled Subshells and Shells

Shell	Subshell	Number of Electrons in Filled Subshell	Number of Electrons in Filled Shell
K ( $n = 1$ )	$s(\ell = 0)$	2	2
L ( $n = 2$ )	$s(\ell = 0)$	2	8
	$p(\ell = 1)$	6	
M ( $n = 3$ )	$s(\ell = 0)$	2	18
	$p(\ell = 1)$	6	
	$d(\ell = 2)$	10	
N ( $n = 4$ )	$s(\ell = 0)$	2	32
	$p(\ell = 1)$	6	
	$d(\ell = 2)$	10	
	$f(\ell = 3)$	14	

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The Atomic Number which defines the element, is the number of protons in the nucleus. For a neutral atom, this must be equal to the number of electrons it has. The more it has, the higher will be the substates that contain these electrons. *The chemical properties are governed by the number of electrons in the outermost substate only.*

**TABLE 28.4** Electronic Configuration of Some Elements

Z	Symbol	Ground-State Configuration	Ionization Energy (eV)	Z	Symbol	Ground-State Configuration	Ionization Energy (eV)
1	H	$1s^1$	13.595	19	K	[Ar] $4s^1$	4.339
2	He	$1s^2$	24.581	20	Ca	$4s^2$	6.111
3	Li	[He] $2s^1$	5.390	21	Sc	$3d4s^2$	6.54
4	Be	$2s^2$	9.320	22	Ti	$3d^24s^2$	6.83
5	B	$2s^22p^1$	8.296	23	V	$3d^34s^2$	6.74
6	C	$2s^22p^2$	11.256	24	Cr	$3d^54s^1$	6.76
7	N	$2s^22p^3$	14.545	25	Mn	$3d^54s^2$	7.432
8	O	$2s^22p^4$	13.614	26	Fe	$3d^64s^2$	7.87
9	F	$2s^22p^5$	17.418	27	Co	$3d^74s^2$	7.86
10	Ne	$2s^22p^6$	21.559	28	Ni	$3d^84s^2$	7.633
11	Na	[Ne] $3s^1$	5.138	29	Cu	$3d^{10}4s^1$	7.724
12	Mg	$3s^2$	7.644	30	Zn	$3d^{10}4s^2$	9.391
13	Al	$3s^23p^1$	5.984	31	Ga	$3d^{10}4s^24p^1$	6.00
14	Si	$3s^23p^2$	8.149	32	Ge	$3d^{10}4s^24p^2$	7.88
15	P	$3s^23p^3$	10.484	33	As	$3d^{10}4s^24p^3$	9.81
16	S	$3s^23p^4$	10.357	34	Se	$3d^{10}4s^24p^4$	9.75
17	Cl	$3s^23p^5$	13.01	35	Br	$3d^{10}4s^24p^5$	11.84
18	Ar	$3s^23p^6$	15.755	36	Kr	$3d^{10}4s^24p^6$	13.996

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**Example: Problem #36**

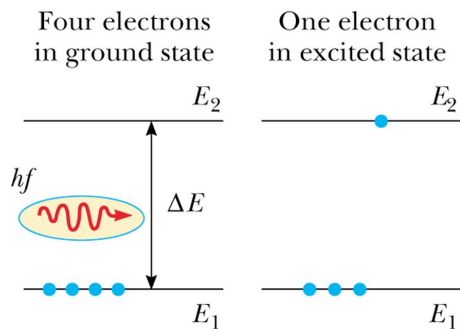
(a) Write out the electronic configuration of the ground state for oxygen ( $Z = 8$ ). (b)

Write out values for the set of quantum numbers  $n$ ,  $\ell$ ,  $m_\ell$ , and  $m_s$  for each of the electrons in oxygen.

## 28.11 Atomic Transitions (read) – The Truth about Transitions

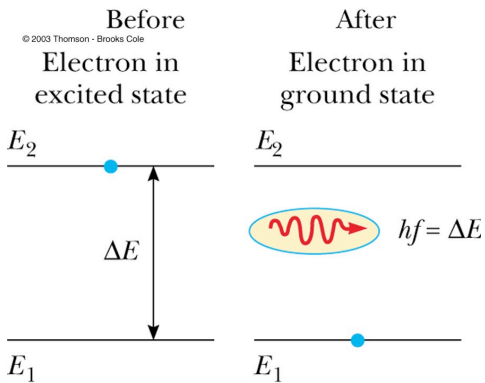
Almost all electronic transitions that occur in atoms that involve photons fall into one of three categories:

- *Stimulated absorption*
- *Spontaneous Emission*
- *Stimulated Emission*



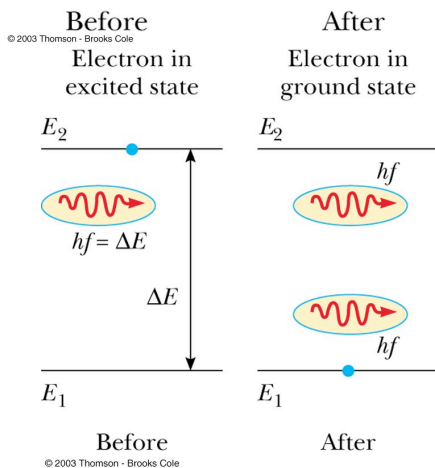
### *Stimulated absorption*

Here a photon is absorbed by the atom is the energy  $hf$  of the photon is equal to that required to make the electron jump to a higher energy level where  $\Delta E = hf$ .



### *Spontaneous emission*

Most atoms can remain in an excited energy state for about  $10^{-8}$  sec before spontaneously dropping back to a lower state, emitting a photon with  $hf = \Delta E$  in the process.



### *Stimulated emission*

In this process, first discussed by Einstein, occurs when a photon passing by an atom in an excited state with  $\Delta E = hf$  of that photon, causes another photon of the same energy to be emitted. This is the process that is operating in lasers.

The rate coefficients of these three processes are the “Einstein A and B coefficients”.