PEN205
MODERN PHYSICS

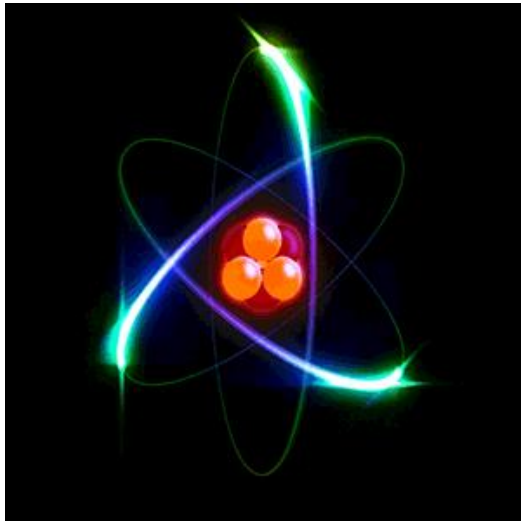
Atomic Physics

Prof. Dr. H. Gül YAĞLIOĞLU – Dr. Öğr. Üyesi Çağıl KADEROĞLU

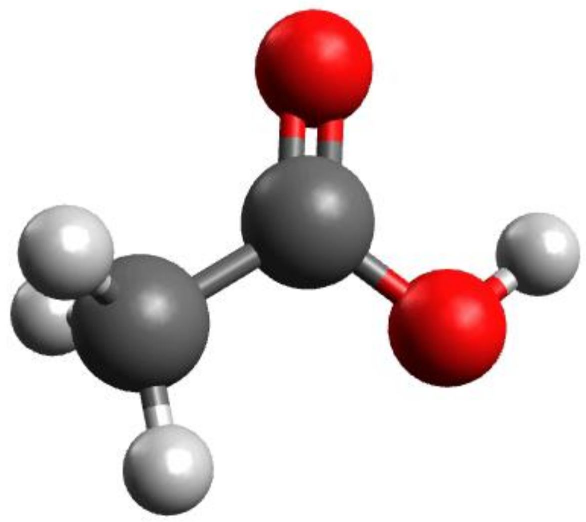
In this chapter, we apply quantum mechanics to atomic systems.

A large portion of the chapter is focused on the application of quantum mechanics to the study of the hydrogen atom.

Understanding the hydrogen atom, the simplest atomic system, is important for several reasons:



- The hydrogen atom is the only atomic system that can be solved exactly.
- Much of what was learned about the hydrogen atom can be extended to such single-electron ions as He^{+} and Li^{2+}.
- The hydrogen atom is an ideal system for performing precise tests of theory against experiment and for improving our overall understanding of atomic structure.
- The quantum numbers that are used to characterize the allowed states of hydrogen can also be used to investigate more complex atoms, and such a description enables us to understand the periodic table of the elements. This understanding is one of the greatest triumphs of quantum mechanics.
- The basic ideas about atomic structure must be well understood before we attempt to deal with the complexities of molecular structures and the electronic structure of solids.



OUTLINE

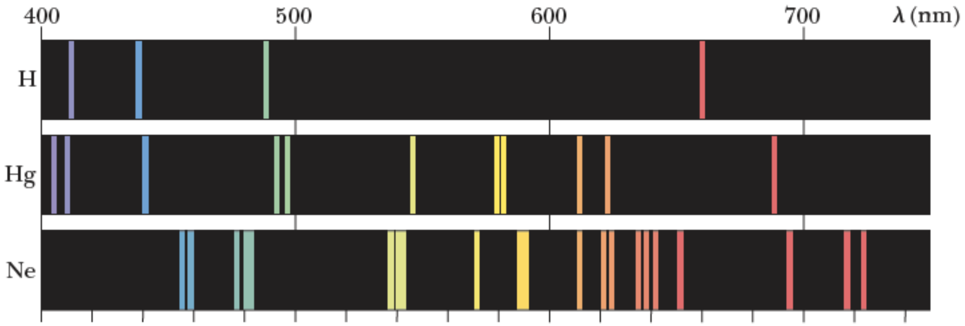
- Atomic Spectra of Gases
- Early Models of the Atom
- The Quantum Model of the Hydrogen Atom
- The Wave Functions for Hydrogen
- Physical Interpretation of the Quantum Numbers
- The Exclusion Principle and the Periodic Table
- More on Atomic Spectra: Visible and X-Ray
- Spontaneous and Stimulated Transitions
- Lasers

Atomic Spectra of Gases

Emission Spectroscopy → when a low-pressure gas undergoes an electric discharge, a discrete line spectrum is observed

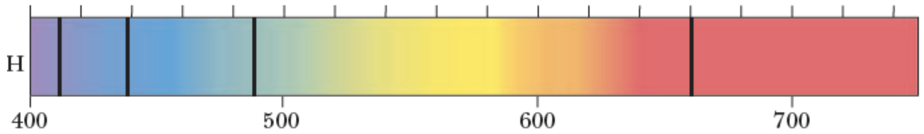
- Electric discharge occurs when the gas is subject to a potential difference that creates an electric field greater than the dielectric strength of the gas.

- Consist of a few bright lines of color on a generally dark background



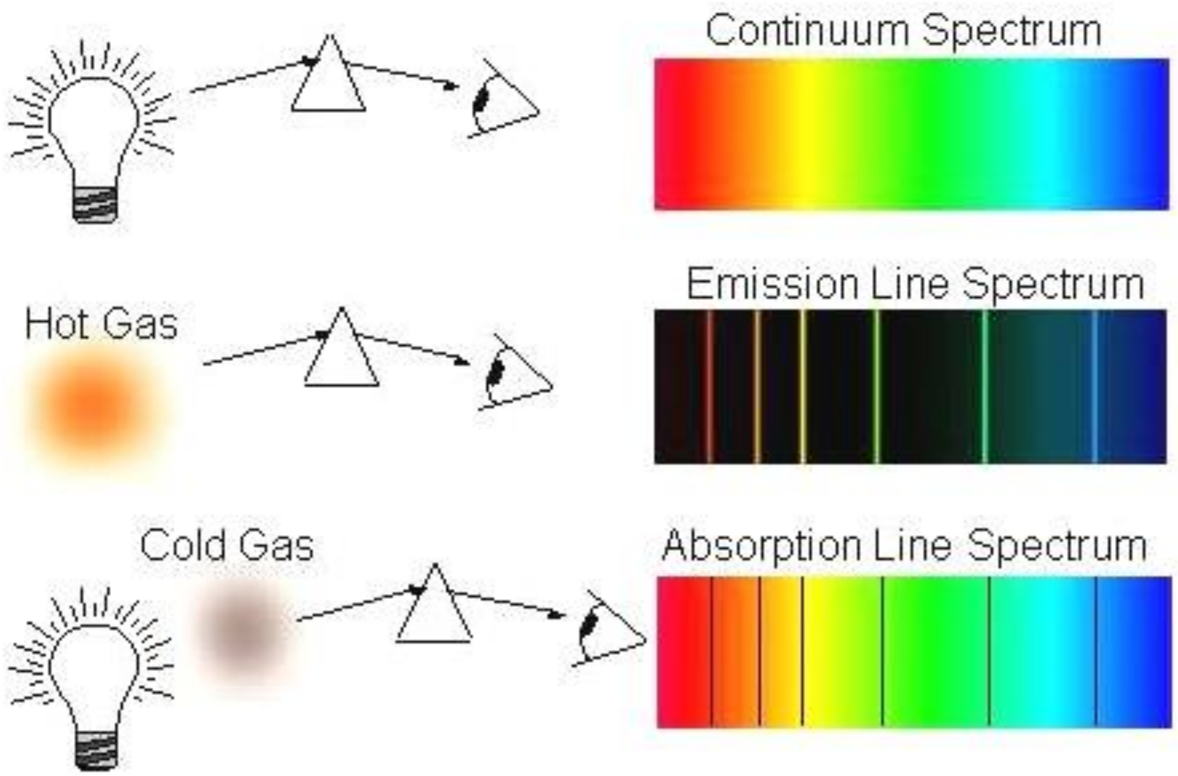
Absorption Spectroscopy → obtained by passing white light from a continuous source through a gas or a dilute solution of the element

- consists of a series of dark lines superimposed on the continuous spectrum of the light source

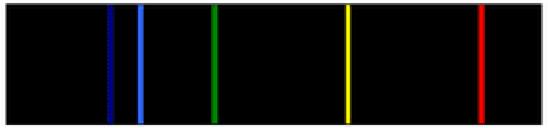


continuous spectrum of radiation emitted by the Sun → atmosphere → absorption lines observed in the solar atmosphere

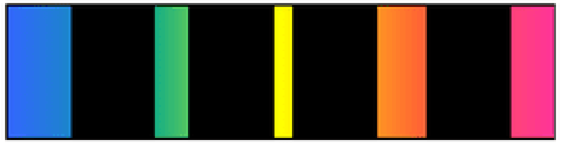
by observation of the various absorption lines in the solar spectrum → **Helium** was discovered (1868)

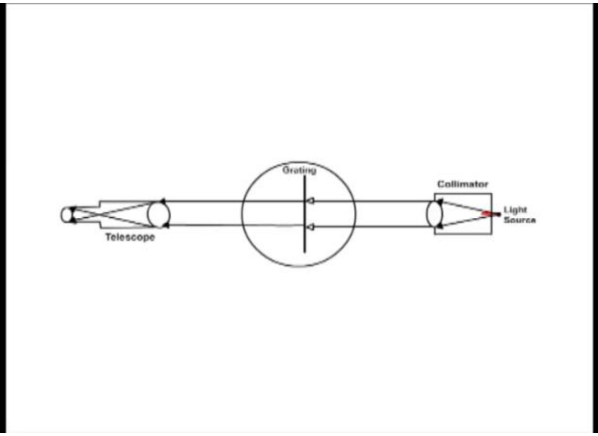


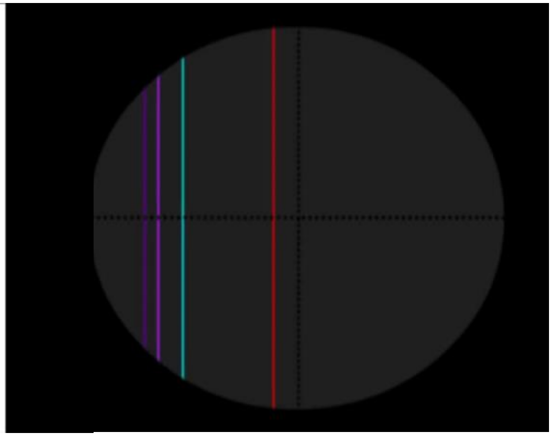
(i) Line spectra - these are emitted from hot monatomic gases - the atoms are not linked to each other in any way.



(ii) Band spectra - these are emitted by gases as well but from ones with more than one atom per molecule.







In your quantum phys. Lab.

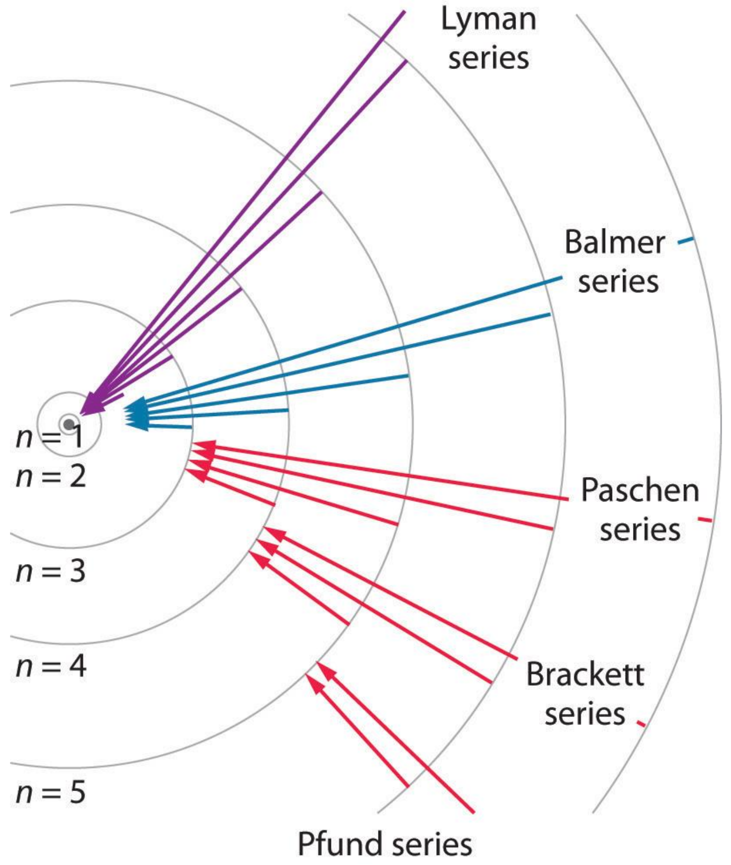
In 1885, Johann Jacob Balmer (1825–1898), found an empirical equation that correctly predicted the wavelengths of four visible emission lines of hydrogen: H_α (red), H_β (blue-green), H_γ (blue-violet), and H_δ (violet)

$$\frac{1}{\lambda} = R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \quad n = 3, 4, 5, \ldots$$ **Balmer series**

$$\frac{1}{\lambda} = R_H\left(1 - \frac{1}{n^2}\right) \quad n = 2, 3, 4, \ldots$$ **Lyman series**

$$\frac{1}{\lambda} = R_H\left(\frac{1}{3^2} - \frac{1}{n^2}\right) \quad n = 4, 5, 6, \ldots$$ **Paschen series**

$$\frac{1}{\lambda} = R_H\left(\frac{1}{4^2} - \frac{1}{n^2}\right) \quad n = 5, 6, 7, \ldots$$ **Brackett series**



No theoretical basis existed for these equations; they simply worked ☺

R_H is a constant now called the **Rydberg constant**
$1.097\,373\,2 \times 10^7\ \text{m}^{-1}$

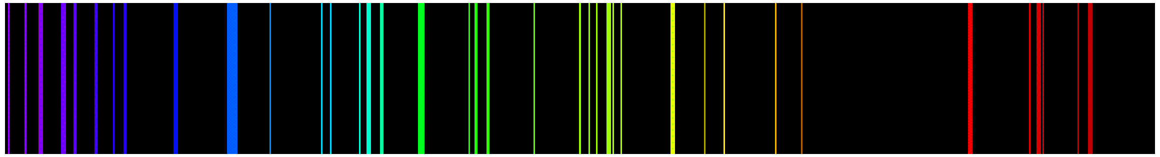
A nice website to see the spectroscopic lines of elements ☺

http://chemistry.bd.psu.edu/jircitano/periodic4.html →

Periodic Table of the Elements

IA 1	IIA 2	IIIB 3	IVB 4	VB 5	VIB 6	VIIB 7	8	VIII 9	10	IB 11	IIB 12	IIIA 13	IVA 14	VA 15	VIA 16	VIIA 17	VIIIA 18
1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.065	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.867	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.409	31 Ga 69.723	32 Ge 72.64	33 As 74.921	34 Se 78.96	35 Br 79.904	36 Kr 83.798
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.906	46 Pd 106.42	47 Ag 107.868	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 I 126.904	54 Xe 131.293
55 Cs 132.905	56 Ba 137.327	71 Lu 174.967	72 Hf 178.49	73 Ta 180.948	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.217	78 Pt 195.078	79 Au 196.967	80 Hg 200.59	81 Tl 204.383	82 Pb 207.2	83 Bi 208.980	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.025	103 Lr (262)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (277)	109 Mt (268)	110 Ds (281)	111 Rg (272)	112 Cn (285)	113 Nh (284)	114 Fl (289)	115 Mc (288)	116 Lv (293)	117 Ts (294)	118 Og (294)

57 La 138.906	58 Ce 140.116	59 Pr 140.908	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.925	66 Dy 162.500	67 Ho 164.930	68 Er 167.259	69 Tm 168.934	70 Yb 173.04
89 Ac 227.028	90 Th 232.038	91 Pa 231.036	92 U 238.029	93 Np 237.048	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)



Atomic spectra

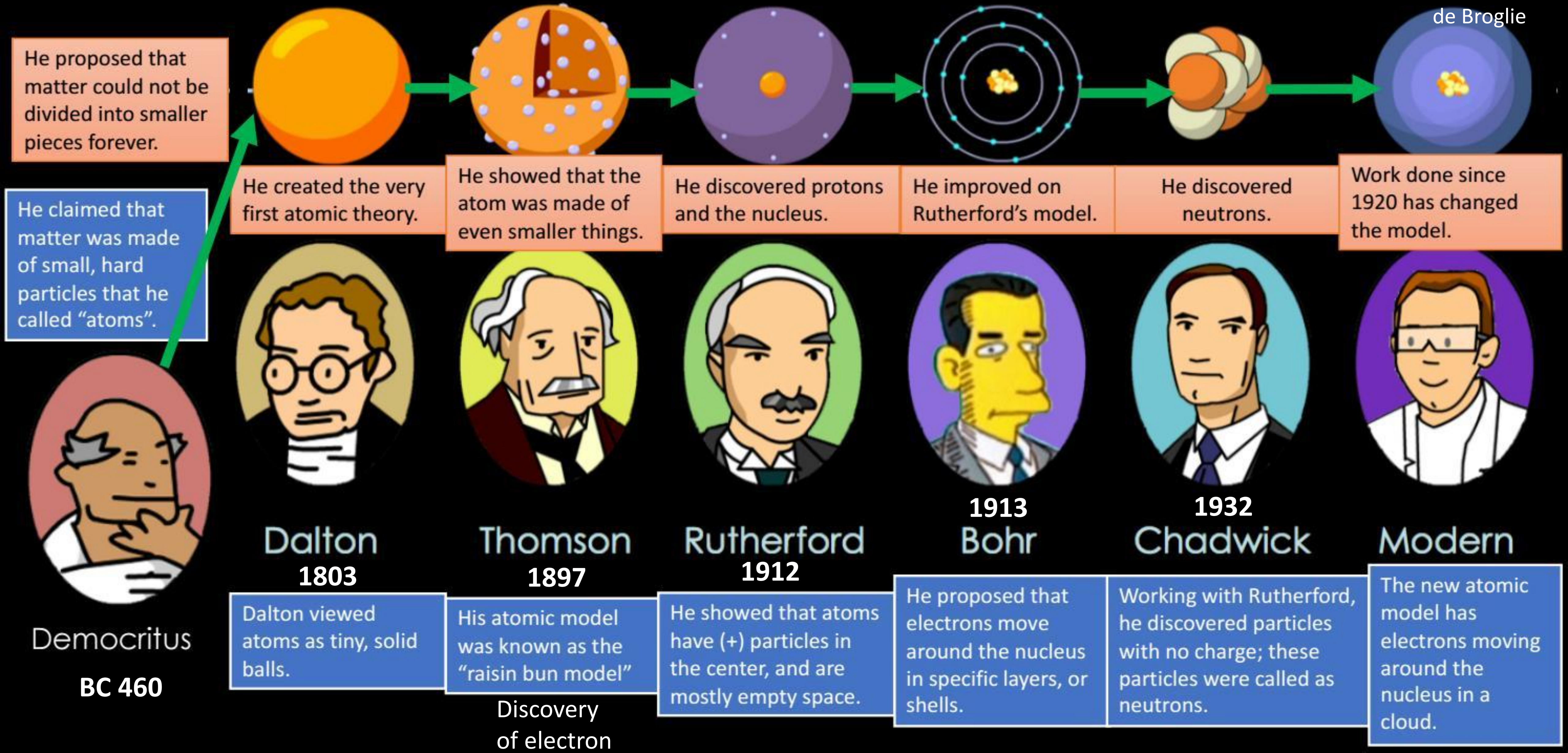
↓

fingerprints of elements

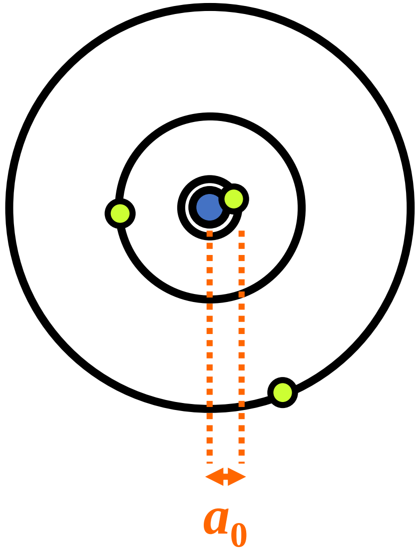
Atomic Model & Theory Timeline

As scientists have learned more and more about atoms, the atomic model has changed.

Einstein,
Planck,
Schrodinger,
Heisenberg,
de Broglie



Let’s remember the details of Bohr’s model



$$r_n = a_0 n^2$$

$$E_n = -k\frac{e^2}{2r_n}$$

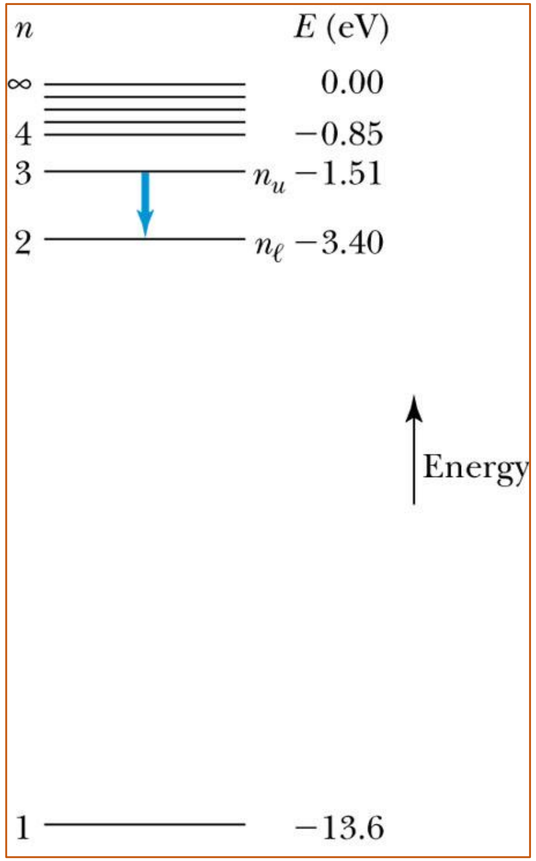
$$E_n = -\underbrace{\frac{ke^2}{2a_0}}_{13.6}\left(\frac{1}{n^2}\right)$$

$$r_1 = a_0 = \frac{\hbar^2}{mke^2} = 0.529\,A^\circ$$

Bohr’s radius

$$E_n = -\frac{13.6}{n^2}\ \text{(eV)}$$

n=1, 2, 3, ...



Bohr radius is the radius of ground state of Hydrogen atom.

The Quantum Model of the Hydrogen Atom

Potential energy function of hydrogen atom

$$U(r) = -k_e \frac{e^2}{r}$$

k_e: Coulomb constant
r: Distance between proton and electron

Let's write this function in time independent Schrodinger wave equation:

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x,y,z)}\left[\frac{\partial^2\psi(x,y,z)}{\partial x^2}+\frac{\partial^2\psi(x,y,z)}{\partial y^2}+\frac{\partial^2\psi(x,y,z)}{\partial z^2}\right] = E - U(r)$$

We won't solve this equation in this class. We will examine the solution of it.

- Solution of the Schrödinger equation gives the energy levels of allowed states in quantum mechanics.

$$E_n = -\left(\frac{k_e e^2}{2a_0}\right)\frac{1}{n^2} = -\frac{13{,}606}{n^2}\ \text{eV} \quad n = 1,2,3,\ldots$$

A negative energy means that the electron and proton are bound together.

For three dimensional quantum mechanics there are three quantum numbers :

The three quantum numbers:

- n: Principal quantum number
- ℓ: Orbital angular momentum quantum number
- m_ℓ: Magnetic (azimuthal) quantum number

The energy levels are: $$E_n = -\frac{E_0}{n^2}$$

➔ The restrictions for the quantum numbers:

- $n = 1, 2, 3, 4, \ldots$
- $\ell = 0, 1, 2, 3, \ldots, n-1$
- $m_\ell = -\ell, -\ell+1, \ldots, 0, 1, \ldots, \ell-1, \ell$

➔ Equivalently:

- $n > 0$
- $\ell < n$
- $|m_\ell| \leq \ell$

Example:
n=1 → l=0, m_l=0
Values are allowed

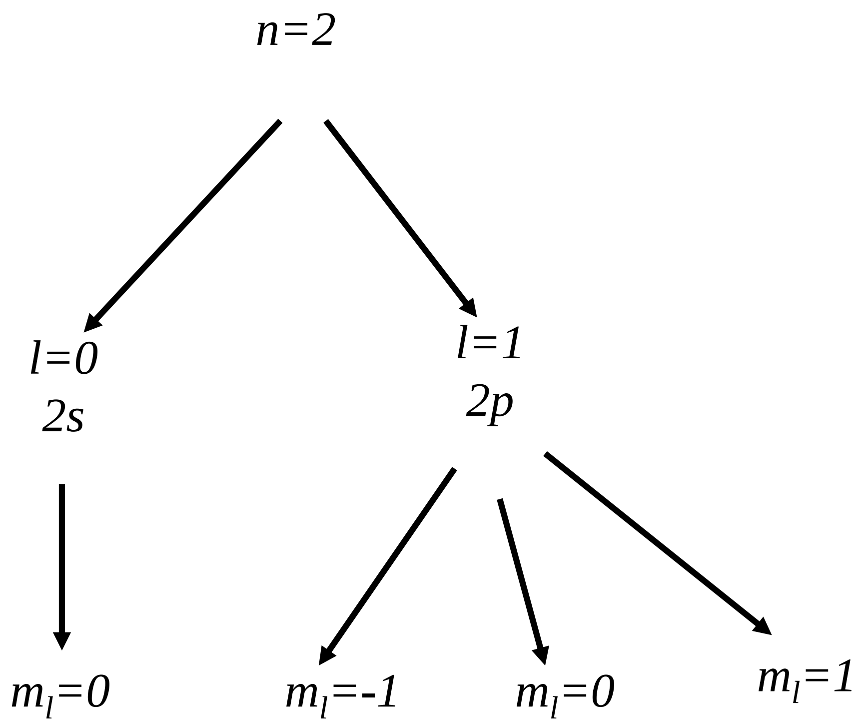
n	Shell symbol	ℓ	Subshell symbol
1	K	0	s
2	L	1	p
3	M	2	d
4	N	3	f
5	O	4	g
6	P	5	h

All states with the same principal quantum number ***n*** are said to form a **shell**, the states with given values of ***n*** and ℓ are said to form a **subshell**.

Example:
$3p$ → $n=3$, $l=1$
$2s$ → $n=2$, $l=0$

Questions:
Does $2d$ state allowed?
Why?

Example: How many allowed energy states are there for n=2 quantum number?



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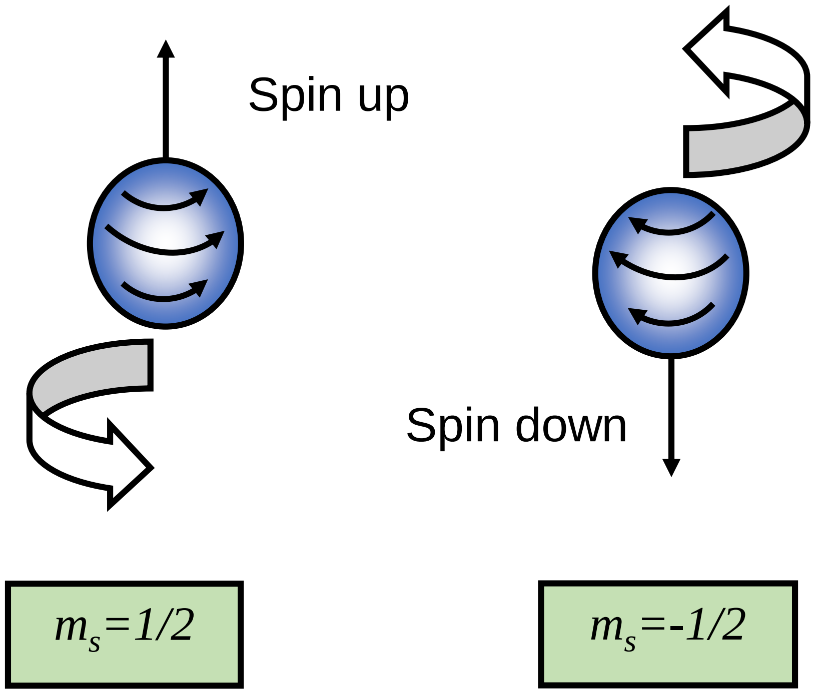
n	Shell symbol	ℓ	Subshel symbol
1	K	0	s
2	L	1	p
3	M	2	d
4	N	3	f
5	O	4	g
6	P	5	h

For n=2, we have for states. Energy of each state is;

$$E_2 = -\frac{13.606\ \text{eV}}{2^2} = -3.401\ \text{eV}$$

Spin magnetic quantum number (m_s)

- Very high resolution spectrometers revealed that spectral lines of gases have **two very closely spaced lines** even in the absence of an external magnetic field.
- In 1925 Samuel Goudsmit and George Uhlenbeck introduced the idea of an electron spinning about its own axis to explain the origin of fine structure. The results of their work introduced yet another quantum number, m_s, called the **spin magnetic quantum number**.



The energy levels for these two cases are close to each other.

Sommerfield and Dirac, later showed that m_s quantum number is not the result of electrons spin, it is the result of electron's relativistic motion.

Example: How many allowed energy states are there for n=2 quantum number?

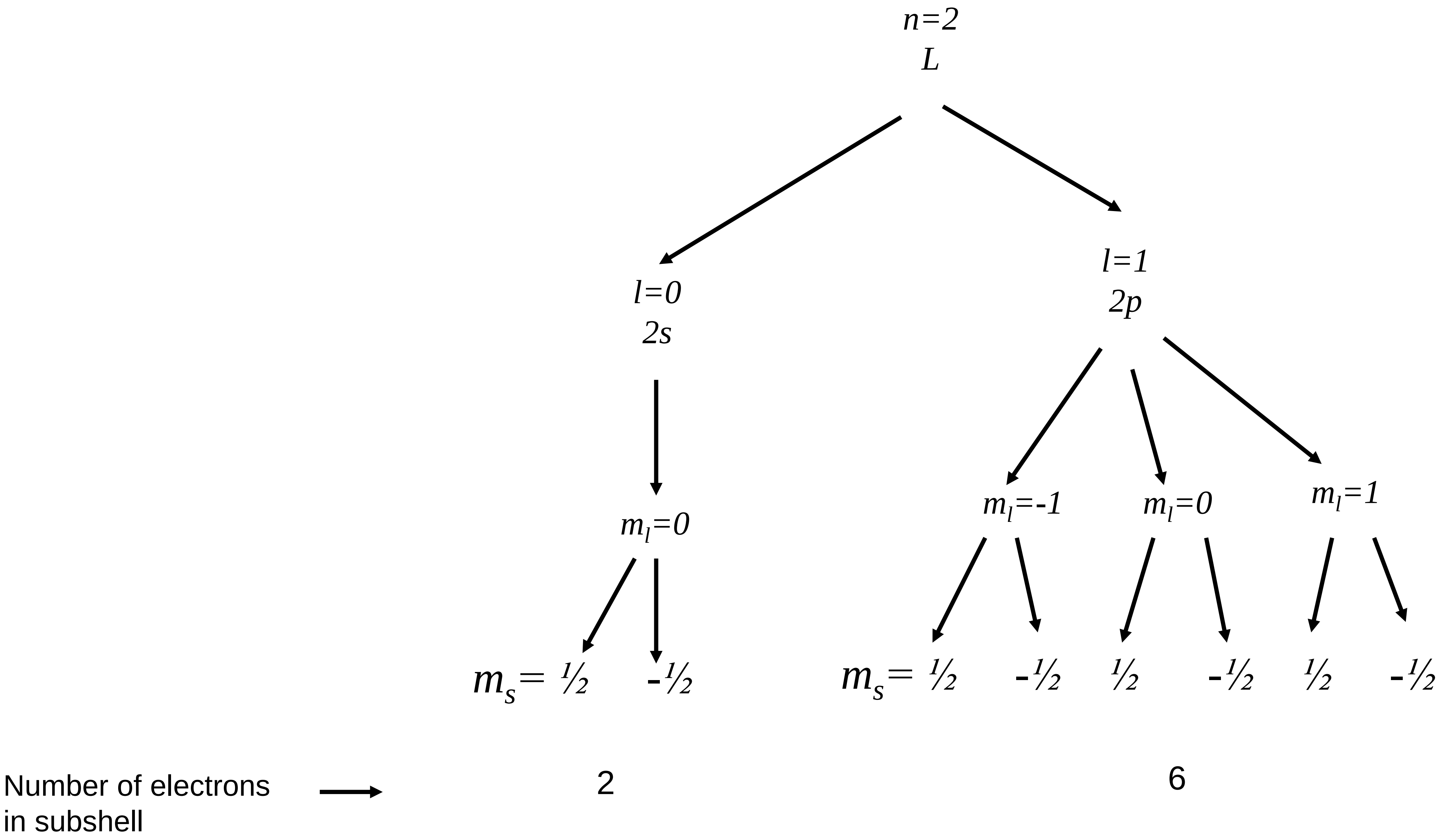


Table 41.2 Quantum States of Electrons in the First Four Shells

n	l	m_l	Spectroscopic Notation	Number of States		Shell
1	0	0	1*s*	2		*K*
2	0	0	2*s*	2	8	*L*
2	1	−1, 0, 1	2*p*	6		
3	0	0	3*s*	2	18	*M*
3	1	−1, 0, 1	3*p*	6		
3	2	−2, −1, 0, 1, 2	3*d*	10		
4	0	0	4*s*	2	32	*N*
4	1	−1, 0, 1	4*p*	6		
4	2	−2, −1, 0, 1, 2	4*d*	10		
4	3	−3, −2, −1, 0, 1, 2, 3	4*f*	14		

The Wave Functions for Hydrogen

If we do not consider electron's spin, the potential energy of Hydrogen atom depends only on the radial distance *r* between electron and the nuclei. Therfore, wave functions representing allowed states depends only *r*.

a_0 :Bohr radius

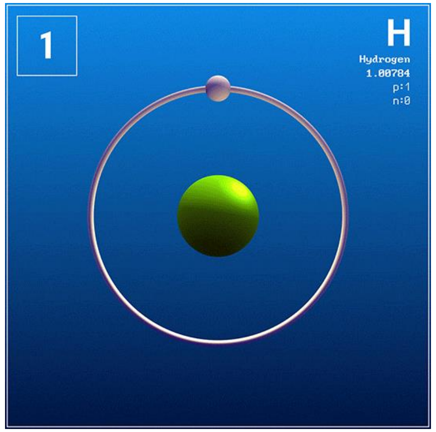
Wave function corresponding 1s state:

$$\psi_{1s}(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

If $r \rightarrow \infty$, $\Psi_{1s} \rightarrow 0$

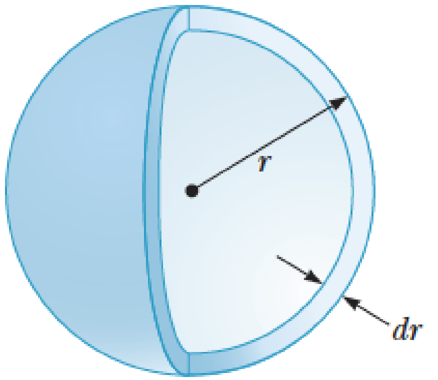
The probability density for the 1s state is;

$$|\psi_{1s}|^2 = \left(\frac{1}{\pi a_0^3}\right) e^{-2r/a_0}$$



because Ψ_{1s} depends only on r , it is **spherically symmetric** →

radial probability density function P(r) : the probability per unit radial length of finding the electron in a spherical shell of radius r and thickness dr.



probability can be written as; $$P(r)\ dr = |\psi|^2\ dV = |\psi|^2\, 4\pi r^2\ dr$$

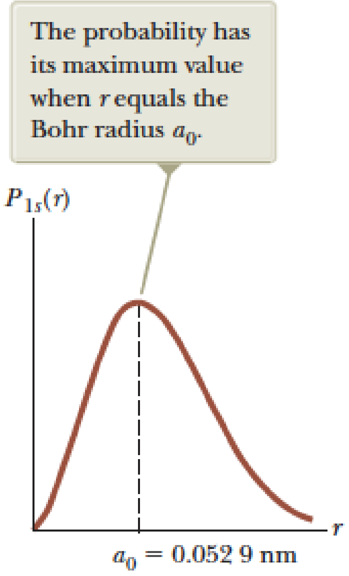
$$|\psi_{1s}|^2 = \left(\frac{1}{\pi a_0^{\ 3}}\right)e^{-2r/a_0}$$

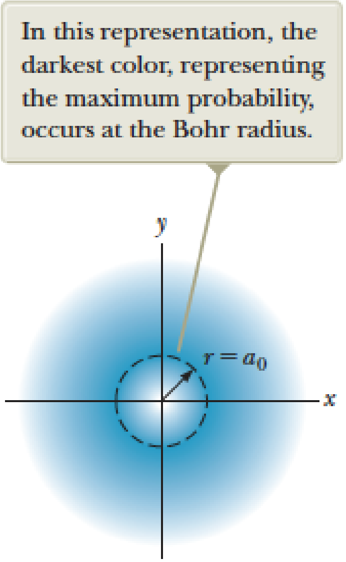
A spherical shell of radius r and infinitesimal thickness dr has a volume equal to $4\pi r^2$ dr.

the radial probability density function for an s state is ; $$P(r) = 4\pi r^2|\psi|^2$$

the radial probability density function for the hydrogen atom in its ground state: $$P_{1s}(r) = \left(\frac{4r^2}{a_0^{\ 3}}\right)e^{-2r/a_0}$$

The probability of finding the electron as a function of distance from the nucleus for the hydrogen atom in the 1s (ground) state.

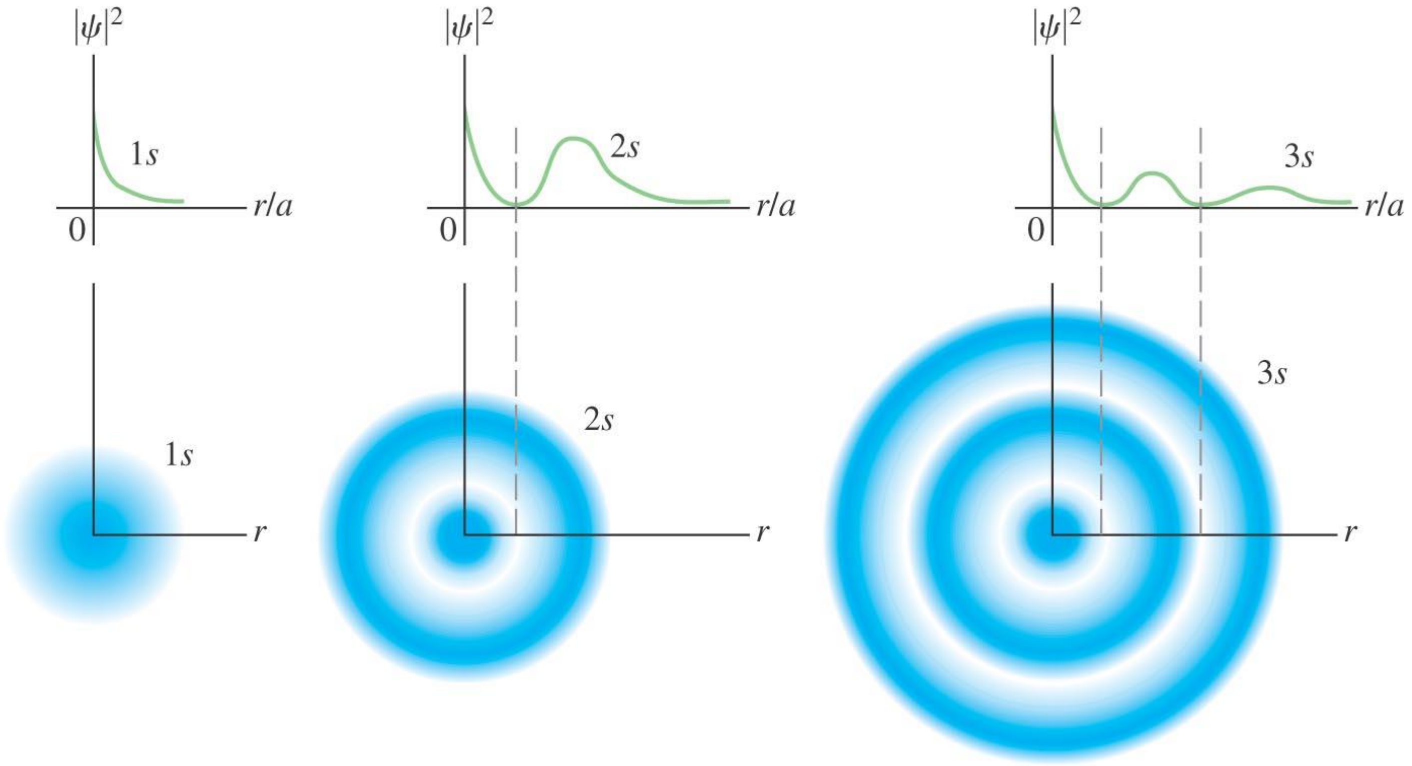


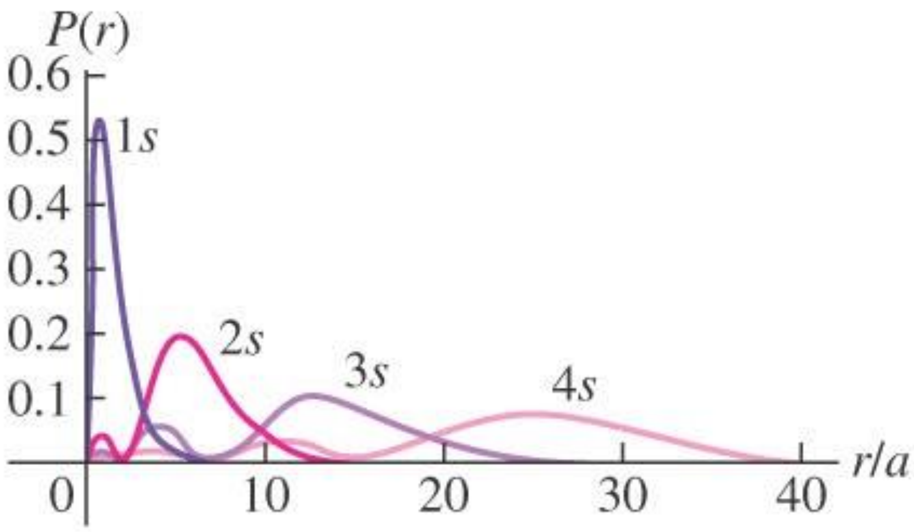


The cross section in the xy plane of the spherical electronic charge distribution for the hydrogen atom in its 1s state

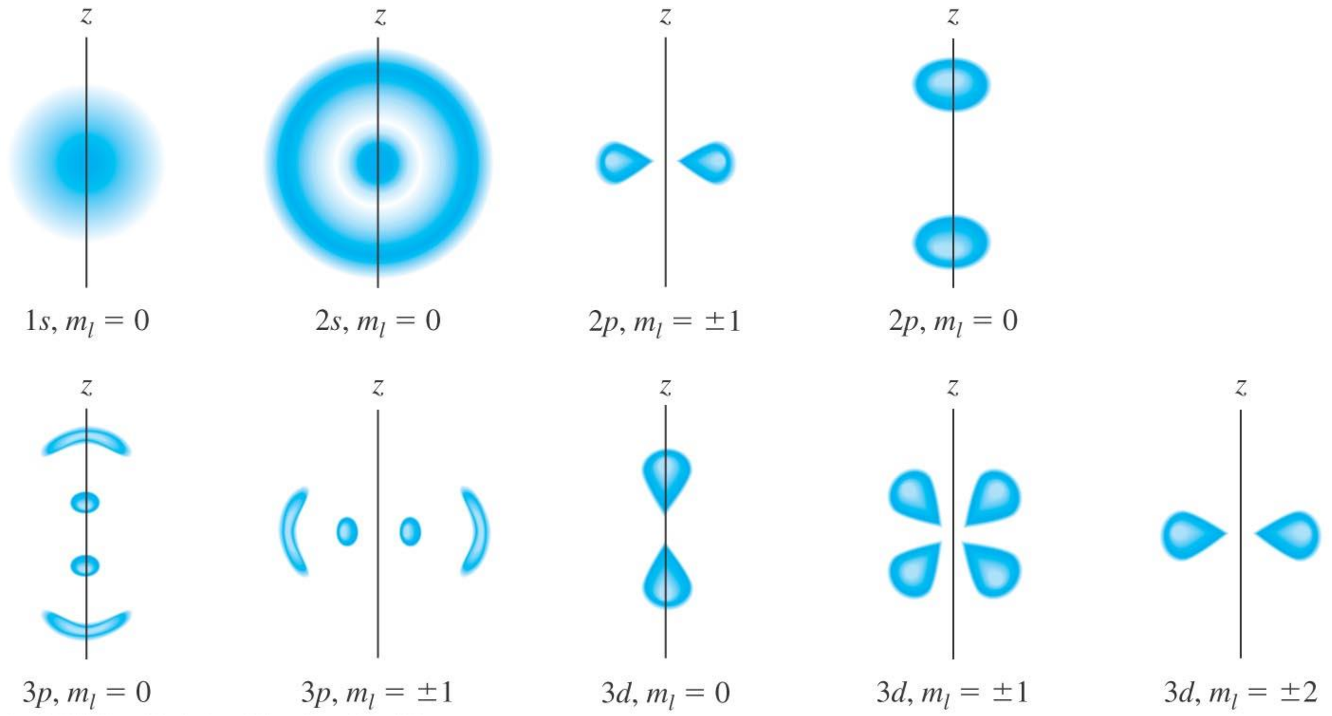
Wave function of the first excited state (2s) of a Hydrogen atom:

$$\psi_{2s}(r) = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2 - \frac{r}{a_0}\right)e^{-r/a_0}$$





All *s* states have spherical symmetric wave functions but the other states do not have.



What if there are more than one electron?

Helium has a nuclei with 2p and two electrons.

Due to complexity of potential interactions, Schrödinger equation can not be solved but the approximate solution can be found in terms of single particle wave functions:

$$\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N,t) = \Psi_1(\vec{r}_1,t)\,\Psi_2(\vec{r}_2,t)\cdots\Psi_N(\vec{r}_N,t)$$

The Exclusion Principle and the Periodic Table

- the state of a hydrogen atom is specified by four quantum numbers: n, l, m_l, m_s
- the number of states available to other atoms may also be predicted by this same set of quantum numbers.

these four quantum numbers can be used to describe all the electronic states of an atom, regardless of the number of electrons in its structure.

How many electrons can be in a particular quantum state?

Pauli answered this important question in 1925;

No two electrons can ever be in the same quantum state; therefore, no two electrons in the same atom can have the same set of quantum numbers.

Pauli's Exclusion Principle

Wolfgang Pauli

Pauli's Exclusion Principle

If this principle were not valid, an atom could radiate energy until every electron in the atom is in the lowest possible energy state and therefore the chemical behavior of the elements would be grossly modified.
Nature as we know it would not exist.

orbital : the atomic state characterized by the quantum numbers : n, ℓ, m_ℓ

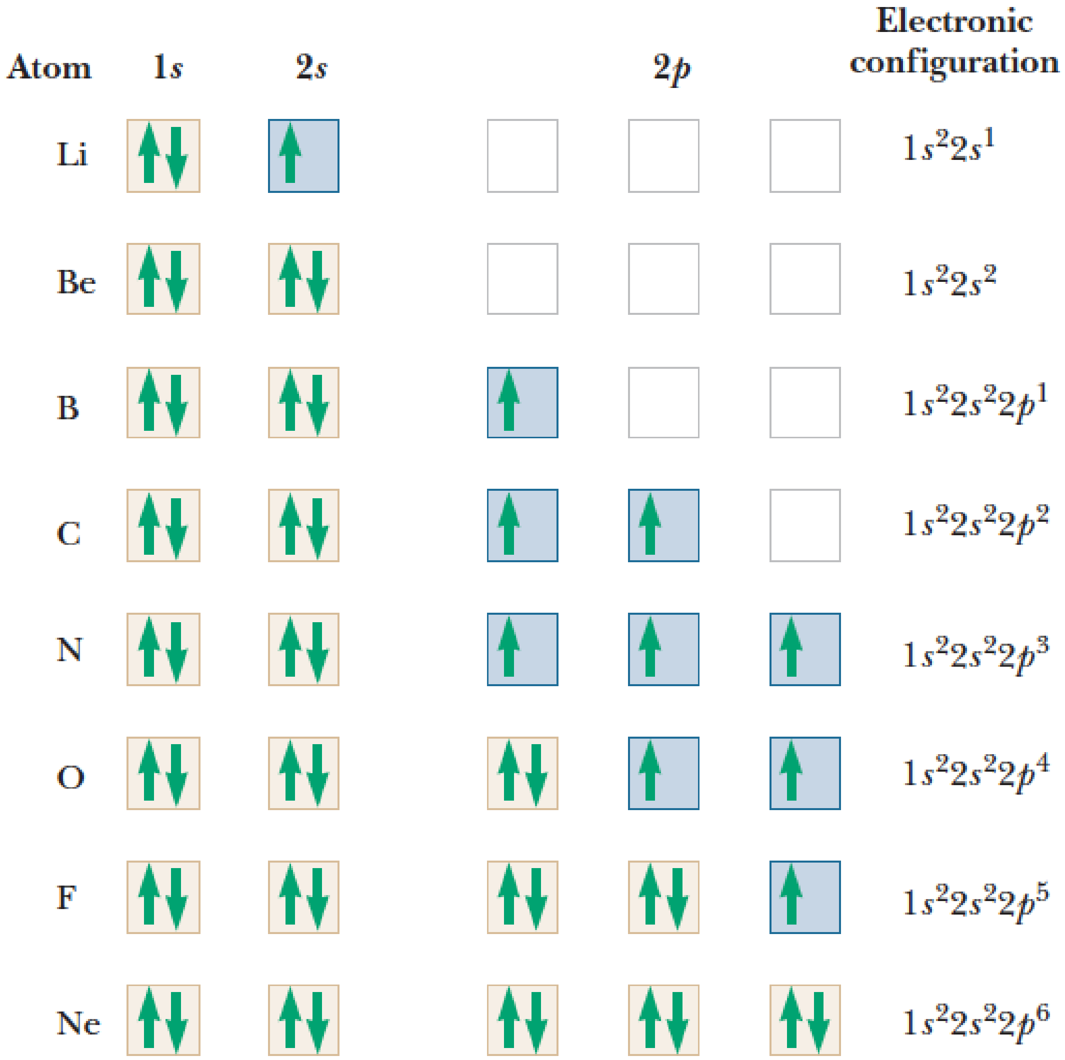
According to exclusion principle → only two electrons can be present in any orbital.

spin magnetic quantum number of these electrons are: $m_s = +\frac{1}{2}$ ↑ , $m_s = -\frac{1}{2}$ ↓

Because each orbital is limited to two electrons, the number of electrons that can occupy the various shells is also limited!

Shell	n	1	2				3								
Subshell	ℓ	0	0	1			0	1			2				
Orbital	m_ℓ	0	0	1	0	−1	0	1	0	−1	2	1	0	−1	−2
	m_s	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓
		1s	2s	2p			3s	3p			3d				

- $n > 0$
- $\ell < n$
- $|m_\ell| \leq \ell$



n	Shell symbol	ℓ	Subshel symbol
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3	M	2	d
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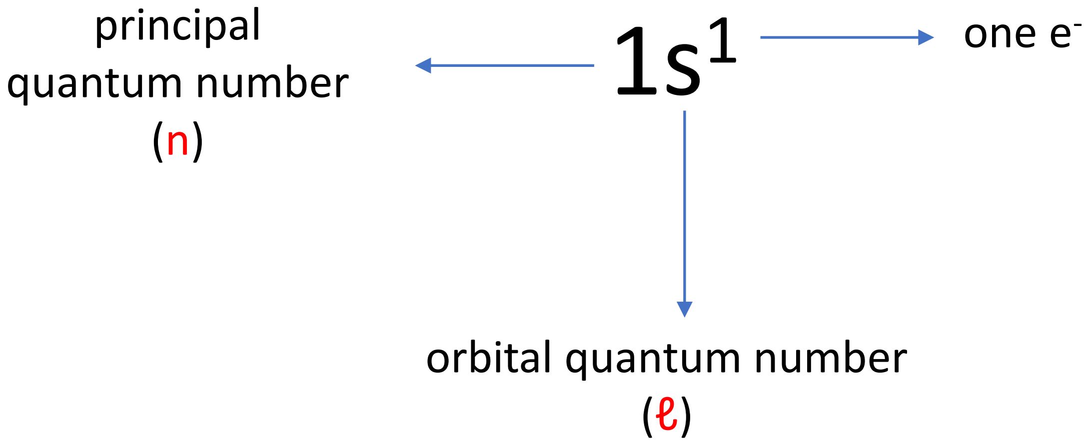
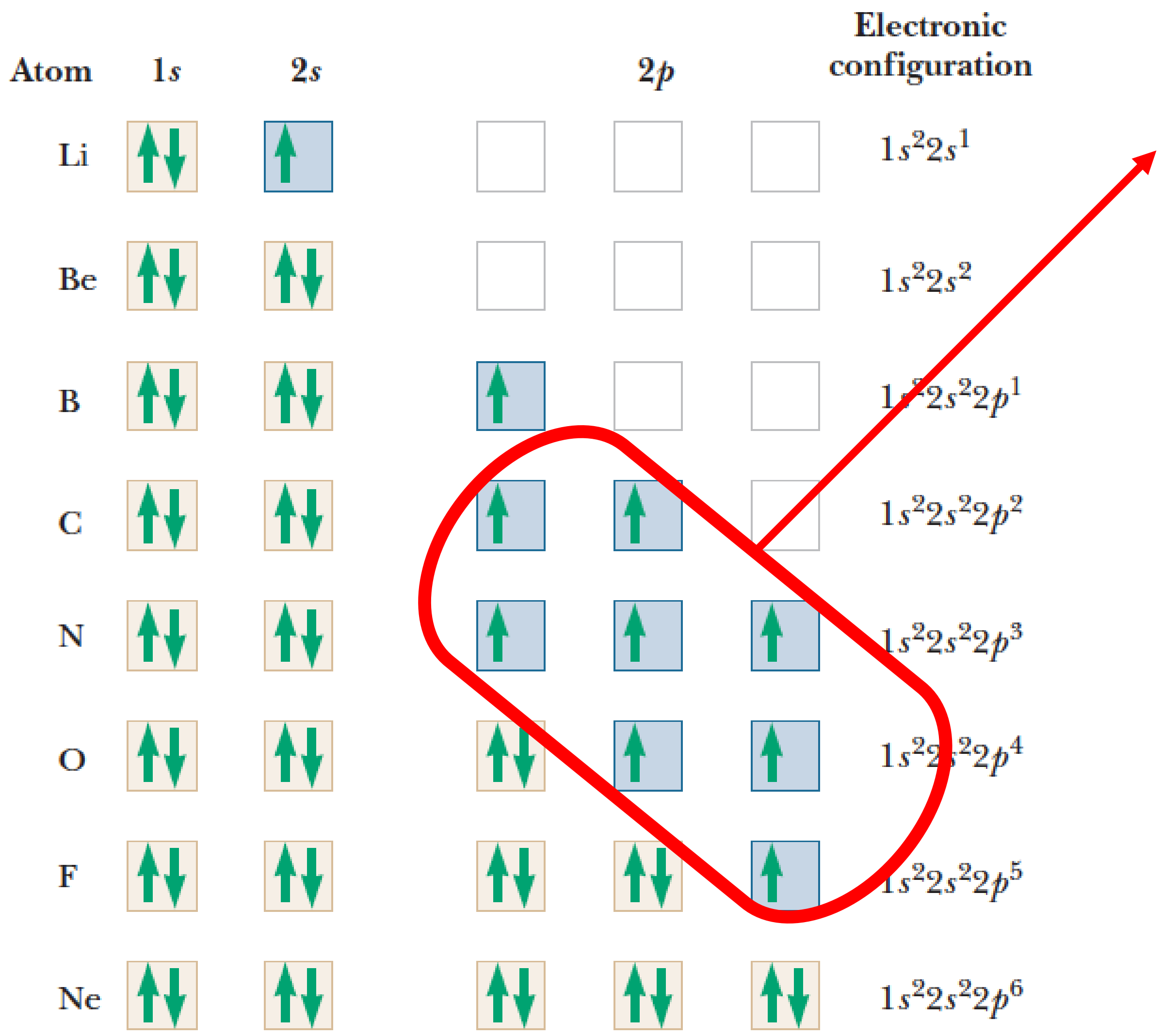
5	O	4	g
6	P	5	h





Carbon has 6 electrons.

Do they go into the same orbital with paired spins (↑ ↓)

or

do they occupy different orbitals with unpaired spins (↑ ↑)

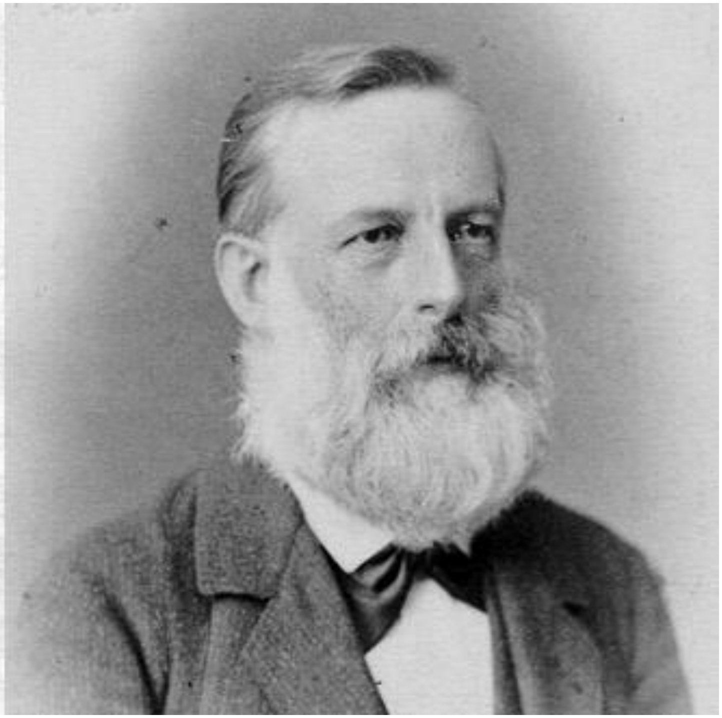
According to experiments → most stable one is (↑ ↑)

Hund's Rule

when an atom has orbitals of equal energy, the order in which they are filled by electrons is such that a maximum number of electrons have unpaired spins.

Some exceptions to this rule occur in elements having subshells that are close to being filled or half-filled.

4 werthig	3 werthig	2 werthig	1 werthig
—	—	—	—
—	—	—	—
C = 12,0	N = 14,04	O = 16,00	Fl = 19,0
16,5	16,96	16,07	16,46
Si = 28,5	P = 31,0	S = 32,07	Cl = 35,46
$\frac{89,1}{2}$ = 44,55	44,0	46,7	44,51
—	As = 75,0	Se = 78,8	Br = 79,97
$\frac{89,1}{2}$ = 44,55	45,6	49,5	46,8
Sn = 117,6	Sb = 120,6	Te = 128,3	J = 126,8
89,4 = 2.44,7	87,4 = 2.43,7	—	—
Pb = 207,0	Bi = 208,0	—	—



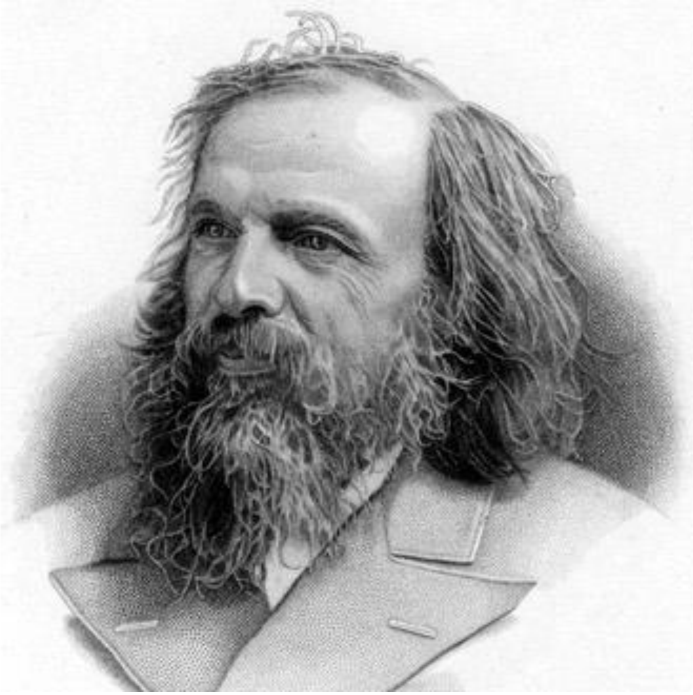
Julius Lothar Meyer

1860s – 1870s

Invention of Periodic Table

…before quantum mechanics…

Dimitri Mendeleev



ОПЫТЪ СИСТЕМЫ ЭЛЕМЕНТОВЪ,

ОСНОВАННОЙ НА ИХЪ АТОМНОМЪ ВѢСѢ И ХИМИЧЕСКОМЪ СХОДСТВѢ.

			Ti=50	Zr=90	?=180.
			V=51	Nb=94	Ta=182.
			Cr=52	Mo=96	W=186.
			Mn=55	Rh=104,4	Pt=197,4
			Fe=56	Ru=104,4	Ir=198.
			Ni=Co=59	Pl=106,6	Os=199.
H=1			Cu=63,4	Ag=108	Hg=200.
	Be=9,4	Mg=24	Zn=65,2	Cd=112	
	B=11	Al=27,4	?=68	Ur=116	Au=197?
	C=12	Si=28	?=70	Sn=118	
	N=14	P=31	As=75	Sb=122	Bi=210?
	O=16	S=32	Se=79,4	Te=128?	
	F=19	Cl=35,5	Br=80	I=127	
Li=7	Na=23	K=39	Rb=85,4	Cs=133	Tl=204.
		Ca=40	Sr=87,6	Ba=137	Pb=207.

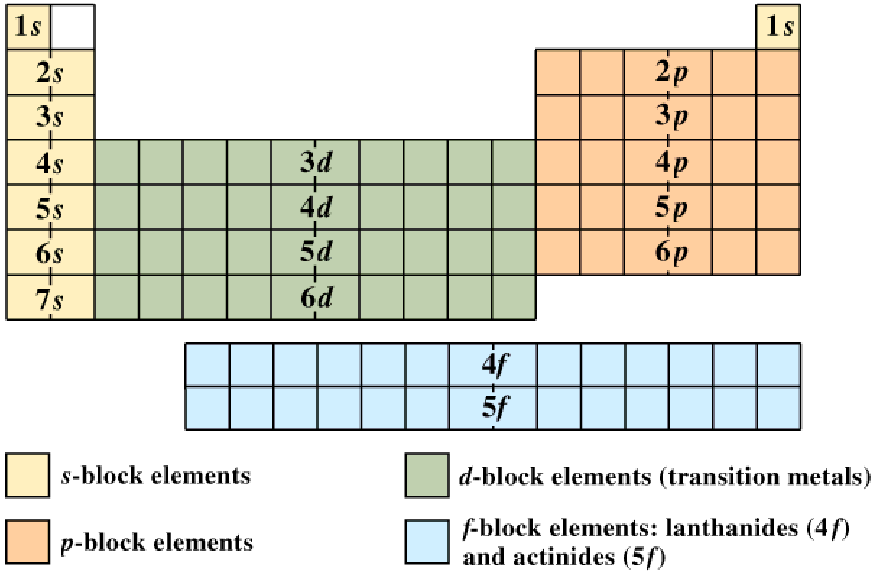
Modern Periodic Table

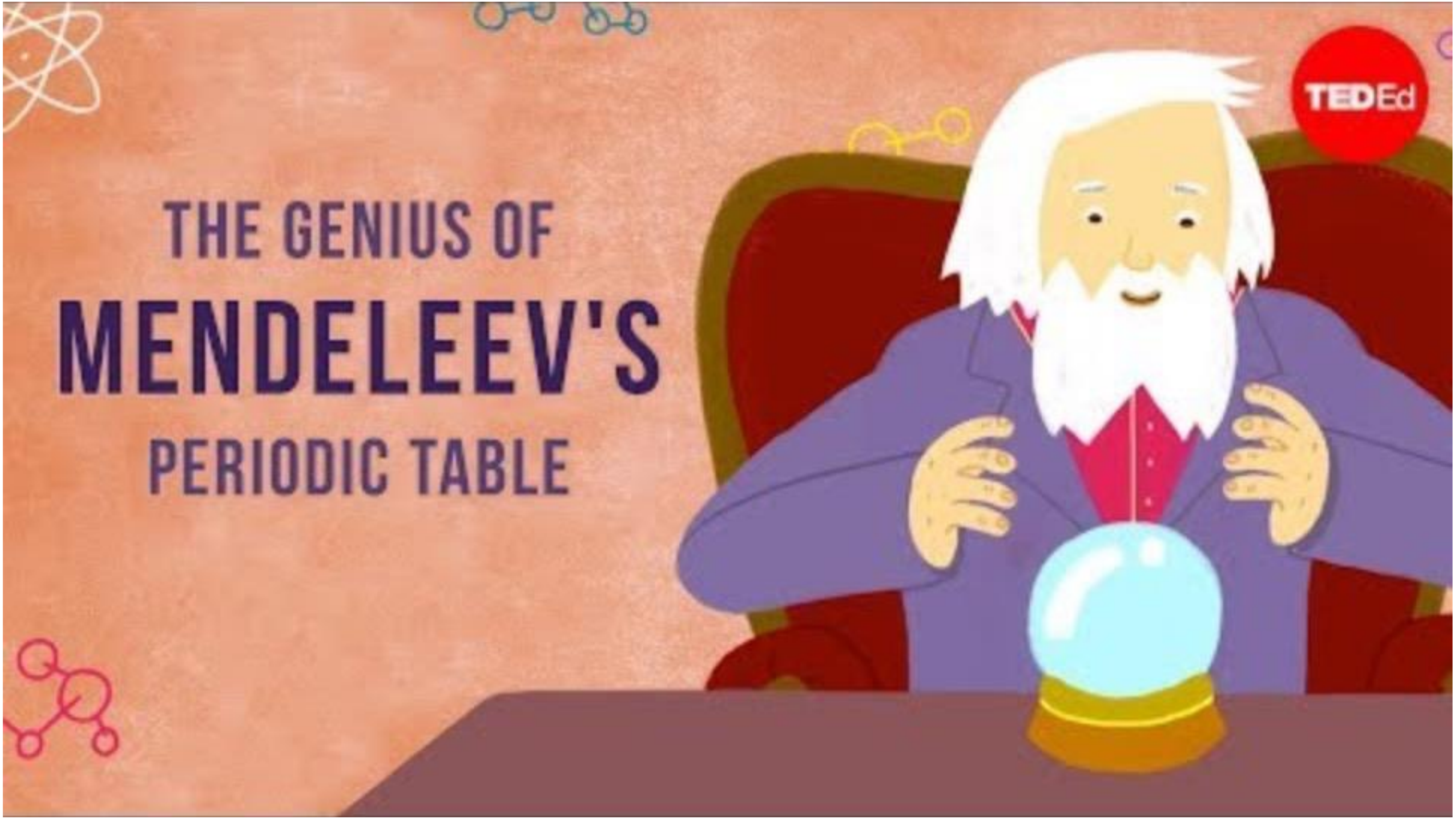
Group I	Group II	Transition elements										Group III	Group IV	Group V	Group VI	Group VII	Group 0
H 1 $1s^1$																H 1 $1s^1$	He 2 $1s^2$
Li 3 $2s^1$	Be 4 $2s^2$											B 5 $2p^1$	C 6 $2p^2$	N 7 $2p^3$	O 8 $2p^4$	F 9 $2p^5$	Ne 10 $2p^6$
Na 11 $3s^1$	Mg 12 $3s^2$											Al 13 $3p^1$	Si 14 $3p^2$	P 15 $3p^3$	S 16 $3p^4$	Cl 17 $3p^5$	Ar 18 $3p^6$
K 19 $4s^1$	Ca 20 $4s^2$	Sc 21 $3d^14s^2$	Ti 22 $3d^24s^2$	V 23 $3d^34s^2$	Cr 24 $3d^54s^1$	Mn 25 $3d^54s^2$	Fe 26 $3d^64s^2$	Co 27 $3d^74s^2$	Ni 28 $3d^84s^2$	Cu 29 $3d^{10}4s^1$	Zn 30 $3d^{10}4s^2$	Ga 31 $4p^1$	Ge 32 $4p^2$	As 33 $4p^3$	Se 34 $4p^4$	Br 35 $4p^5$	Kr 36 $4p^6$
Rb 37 $5s^1$	Sr 38 $5s^2$	Y 39 $4d^15s^2$	Zr 40 $4d^25s^2$	Nb 41 $4d^45s^1$	Mo 42 $4d^55s^1$	Tc 43 $4d^55s^2$	Ru 44 $4d^75s^1$	Rh 45 $4d^85s^1$	Pd 46 $4d^{10}$	Ag 47 $4d^{10}5s^1$	Cd 48 $4d^{10}5s^2$	In 49 $5p^1$	Sn 50 $5p^2$	Sb 51 $5p^3$	Te 52 $5p^4$	I 53 $5p^5$	Xe 54 $5p^6$
Cs 55 $6s^1$	Ba 56 $6s^2$	57–71*	Hf 72 $5d^26s^2$	Ta 73 $5d^36s^2$	W 74 $5d^46s^2$	Re 75 $5d^56s^2$	Os 76 $5d^66s^2$	Ir 77 $5d^76s^2$	Pt 78 $5d^96s^1$	Au 79 $5d^{10}6s^1$	Hg 80 $5d^{10}6s^2$	Tl 81 $6p^1$	Pb 82 $6p^2$	Bi 83 $6p^3$	Po 84 $6p^4$	At 85 $6p^5$	Rn 86 $6p^6$
Fr 87 $7s^1$	Ra 88 $7s^2$	89–103**	Rf 104 $6d^27s^2$	Db 105 $6d^37s^2$	Sg 106 $6d^47s^2$	Bh 107 $6d^57s^2$	Hs 108 $6d^67s^2$	Mt 109 $6d^77s^2$	Ds 110 $6d^97s^1$	Rg 111	Cn 112	113	Fl 114	115	Lv 116	117	118

*Lanthanide series	La 57 $5d^16s^2$	Ce 58 $5d^14f^16s^2$	Pr 59 $4f^36s^2$	Nd 60 $4f^46s^2$	Pm 61 $4f^56s^2$	Sm 62 $4f^66s^2$	Eu 63 $4f^76s^2$	Gd 64 $5d^14f^76s^2$	Tb 65 $5d^14f^86s^2$	Dy 66 $4f^{10}6s^2$	Ho 67 $4f^{11}6s^2$	Er 68 $4f^{12}6s^2$	Tm 69 $4f^{13}6s^2$	Yb 70 $4f^{14}6s^2$	Lu 71 $5d^14f^{14}6s^2$
**Actinide series	Ac 89 $6d^17s^2$	Th 90 $6d^27s^2$	Pa 91 $5f^26d^17s^2$	U 92 $5f^36d^17s^2$	Np 93 $5f^46d^17s^2$	Pu 94 $5f^67s^2$	Am 95 $5f^77s^2$	Cm 96 $5f^76d^17s^2$	Bk 97 $5f^86d^17s^2$	Cf 98 $5f^{10}7s^2$	Es 99 $5f^{11}7s^2$	Fm 100 $5f^{12}7s^2$	Md 101 $5f^{13}7s^2$	No 102 $5f^{14}7s^2$	Lr 103 $5f^{14}6d^17s^2$

elements in a column have similar chemical properties

Electron configuration and the periodic table

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