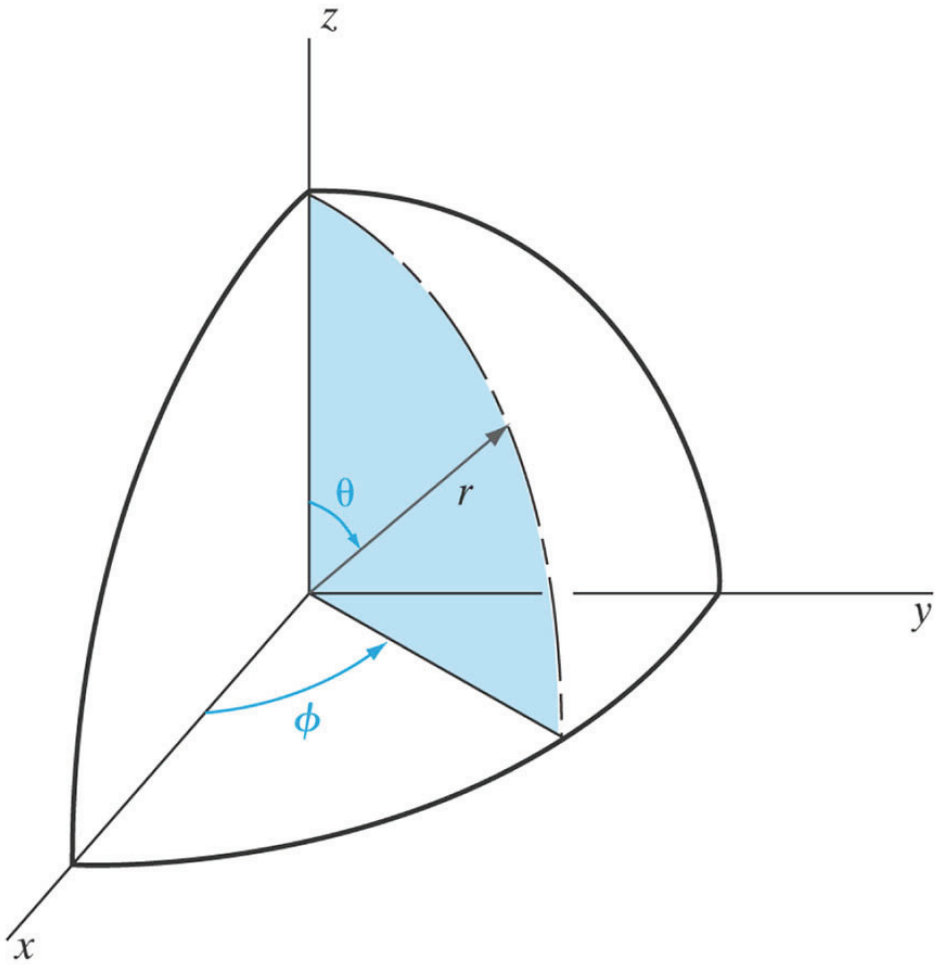
Atomic structure

The Hydrogen Atom

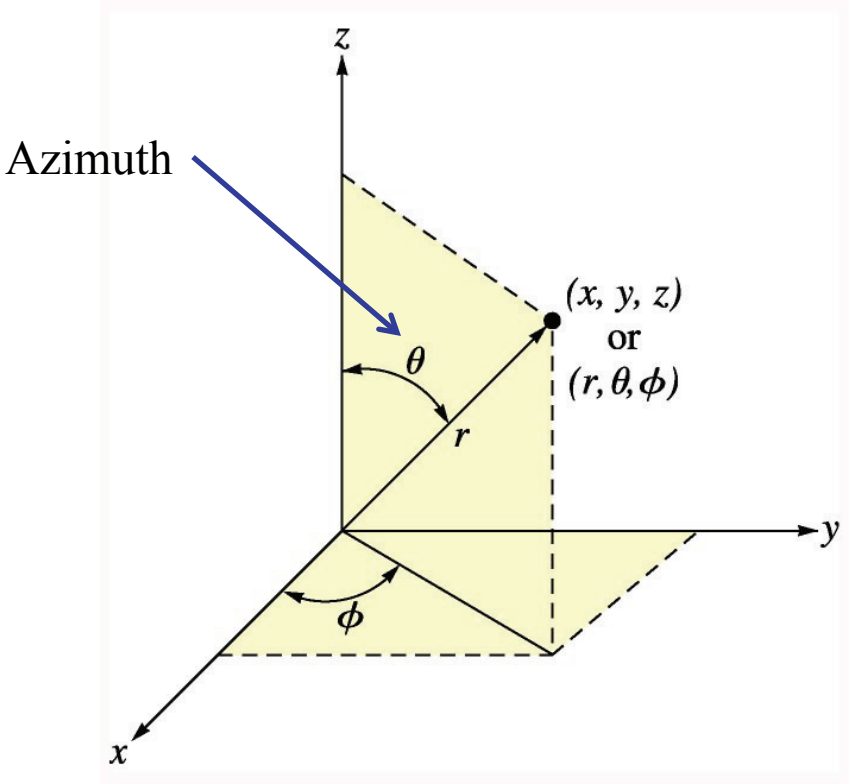
Finding the wave functions for the hydrogen atom requires a solution of the Schrödinger wave equation in ***three dimensions*** for a coulombic potential field.

Since the problem is ***spherically symmetric***, the spherical coordinate system is used in the calculation:



Atomic structure – 2

The radial dependence of the potential suggests that we should from Cartesian coordinates to spherical polar coordinates.



r = interparticle distance
$(0 \leq r \leq \infty)$

θ = angle from z-axis to "x-y plane"
$(0 \leq \theta \leq \pi)$

ϕ = rotation in "x-y plane"
$(0 \leq \phi \leq 2\pi)$

Atomic structure – 3

Potential term $U(x,y,z)$ in the Schrödinger equation written in ***rectangular*** coordinate system must be replaced by $U(r,\theta,\phi)$, representing the Coulomb potential the ***spherical (polar)*** coordinate system which the electron experiences in the vicinity of the proton.

The Coulomb potential varies only with r in spherical coordinates:

$$U(r) = -\frac{q^2}{4\pi\varepsilon_0 r_n}$$

Then, the Schrödinger equation:

$$\nabla^2\Psi(r,\theta,\phi) + \frac{2m}{\hbar^2}\big(E - U(r,\theta,\phi)\big)\Psi(r,\theta,\phi) = 0$$

(Note: the equation above is written in ***rectangular*** coordinate system. To work in ***polar*** coordinate system, it should be transformed.)

Atomic structure – 4

Coulomb potential which the electron experiences in the vicinity of the proton:

$$U(r,\theta,\phi) = U(r) = -\frac{1}{4\pi\varepsilon_0}\frac{q^2}{r}$$

Now, variables in the Schrödinger equation can be separated:

$$\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi)$$

This wave function of an electron in hydrogen atom $\psi(r,\theta,\phi)$ is a product of ***three*** parts. Three separate solutions must be obtained for:

- the ***r***-dependent equation,
- the ***θ***-dependent equation,
- the ***ϕ***-dependent equation.

Atomic structure – 5

The wave functions for the ϕ-dependent equation are ***quantized*** with the following selection rule for the quantum numbers:

$$\mathbf{m} = ..., -3, -2, -1, 0, +1, +2, +3, ...$$

For the r-dependent equation, the ***quantum number*** **n** can be any positive integer (not zero).

For the θ-dependent equation the ***quantum number l*** can be zero or a positive integer.

Atomic structure – 6

These restrictions are summarized as follows:

Principal quantum number:

$$\mathbf{n} = 1, 2, 3, \ldots$$

Azimuthal quantum number:

$$\boldsymbol{l} = 0, 1, 2, \ldots, (\mathbf{n} - 1)$$

Magnetic quantum number:

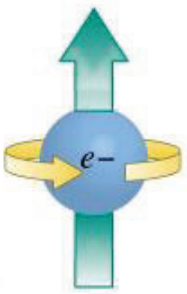
$$\mathbf{m} = -\boldsymbol{l}, \ldots, -2, -1, 0, +1, +2, \ldots, +\boldsymbol{l}$$

Atomic structure – 7

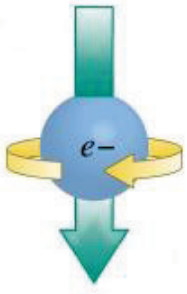
In addition to the three quantum numbers arising from the three parts of the wave equation, there is an important quantization condition on the ***"spin"*** of the electron.

Investigations of electron spin employ the theory of relativity as well as quantum mechanics; therefore, we shall simply state that the intrinsic angular momentum $\boldsymbol{s}$ of an electron with ψ_{nlm} specified is

$$s = \pm\frac{\hbar}{2}$$



"spin up"



"spin down"

That is, in units of $\hbar$, the electron has a spin of ½, and the angular momentum produced by this spin is positive or negative depending on whether the electron is ***"spin up"*** or ***"spin down"***.

Atomic structure – 8

Summary:

Each allowed energy state of the electron in the hydrogen atom is uniquely described by the set of four quantum numbers: **n**, ***l***, **m**, and ***s***.

Using these ***four quantum numbers***, we can identify the various states which the electron can occupy in a hydrogen atom.

The number **n**, called the ***principal quantum number***, specifies the "orbit" of the electron in Bohr terminology.

There is considerable fine structure in the energy levels about the Bohr orbits, for example:

- an electron with **n** = 1 can have only ***l*** = 0 and **m** = 0, but there are two spin states allowed.
- for **n** = 2, ***l*** can be 0 or 1, and **m** can be -1, 0, or +1 with two spins for each state.

Atomic structure – 9

These four quantum numbers with the selection rules precisely describe the structure of ***energy states*** in hydrogen atom.

Electron in a hydrogen atom can occupy ***only*** one of a large number of excited states including the lowest (***ground***) state.

Energy differences between the various states properly account for the observed lines in the hydrogen spectrum.

The Periodic Table – 1

The structure of energy states and quantum numbers arise from solutions to the hydrogen atom problem.

Question: How can we extend the knowledge of hydrogen atom energy structure on description of more complex atoms?

Answer: The ***quantum number selection rules*** are valid for more complicated structures. They can be used to describe the arrangement of atoms in the ***periodic table*** of chemical elements.

The Periodic Table – 2

Pauli exclusion principle.

Wolfgang Pauli

In multi-electron system *only one electron* may occupy a specific discrete energy level.

or in other words:

No two electrons can have the same set of quantum numbers n, *l*, m, *s*.

or in other words:

Only two electrons can have the same three quantum numbers n, *l*, m, and those two must have opposite spin.

The Periodic Table – 3

Pauli exclusion principle is basic to the electronic structure of all atoms in the periodic table

n	***l***	**m**	***s*/ħ**	Allowable states in subshell	Allowable states in complete shell
1	0	0	½	2	2
2	0	0	½	2	8
	1	-1 0 1	½ ½ ½	6	
3	0	0	½	2	18
	1	-1 0 1	½ ½ ½	6	
	2	-2 -1 0 1 2	½ ½ ½ ½ ½	10	

Quantum numbers to n = 3 and allowable states for the electron in a hydrogen atom.

The first four columns show the various combinations of quantum numbers allowed by the selection rules.

The last two columns indicate the number of allowed states (combinations of **n**, ***l***, **m**, and ***s***) for each ***l*** (sub-shell) and **n** (shell, or Bohr orbit).

The Periodic Table – 4

Atomic number (Z)	Element	n = 1, l = 0: 1s	2: 0 1 — 2s 2p	3: 0 1 2 — 3s 3p 3d	4: 0 1 — 4s 4p	Shorthand notation
1	H	1				$1s^1$
2	He	2				$1s^2$
3	Li		1			$1s^2\ 2s^1$
4	Be		2			$1s^2\ 2s^2$
5	B		2 1			$1s^2\ 2s^2\ 2p^1$
6	C		2 2			$1s^2\ 2s^2\ 2p^2$
7	N		2 3			$1s^2\ 2s^2\ 2p^3$
8	O		2 4			$1s^2\ 2s^2\ 2p^4$
9	F		2 5			$1s^2\ 2s^2\ 2p^5$
10	Ne	helium core, 2 electrons	2 6			$1s^2\ 2s^2\ 2p^6$
11	Na			1		[Ne] $3s^1$
12	Mg			2		$3s^2$
13	Al			2 1		$3s^2\ 3p^1$
14	Si			2 2		$3s^2\ 3p^2$
15	P			2 3		$3s^2\ 3p^3$
16	S			2 4		$3s^2\ 3p^4$
17	Cl			2 5		$3s^2\ 3p^5$
18	Ar	neon core, 10 electrons		2 6		$3s^2\ 3p^6$
19	K				1	[Ar] $4s^1$
20	Ca				2	$4s^2$
21	Sc			1	2	$3d^1\ 4s^2$
22	Ti			2	2	$3d^2\ 4s^2$
23	V			3	2	$3d^3\ 4s^2$
24	Cr			5	1	$3d^5\ 4s^1$
25	Mn			5	2	$3d^5\ 4s^2$
26	Fe			6	2	$3d^6\ 4s^2$
27	Co			7	2	$3d^7\ 4s^2$
28	Ni			8	2	$3d^8\ 4s^2$
29	Cu			10	1	$3d^{10}\ 4s^1$
30	Zn			10	2	$3d^{10}\ 4s^2$
31	Ga			10	2 1	$3d^{10}\ 4s^2\ 4p^1$
32	Ge			10	2 2	$3d^{10}\ 4s^2\ 4p^2$
33	As			10	2 3	$3d^{10}\ 4s^2\ 4p^3$
34	Se			10	2 4	$3d^{10}\ 4s^2\ 4p^4$
35	Br			10	2 5	$3d^{10}\ 4s^2\ 4p^5$
36	Kr	argon core, 18 electrons		10	2 6	$3d^{10}\ 4s^2\ 4p^6$

Electronic configuration of atoms in the ground state

The Periodic Table – 5

In **1869** Mendeleev and Lothar Meyer (Germany) published nearly identical classification schemes for elements known to date.

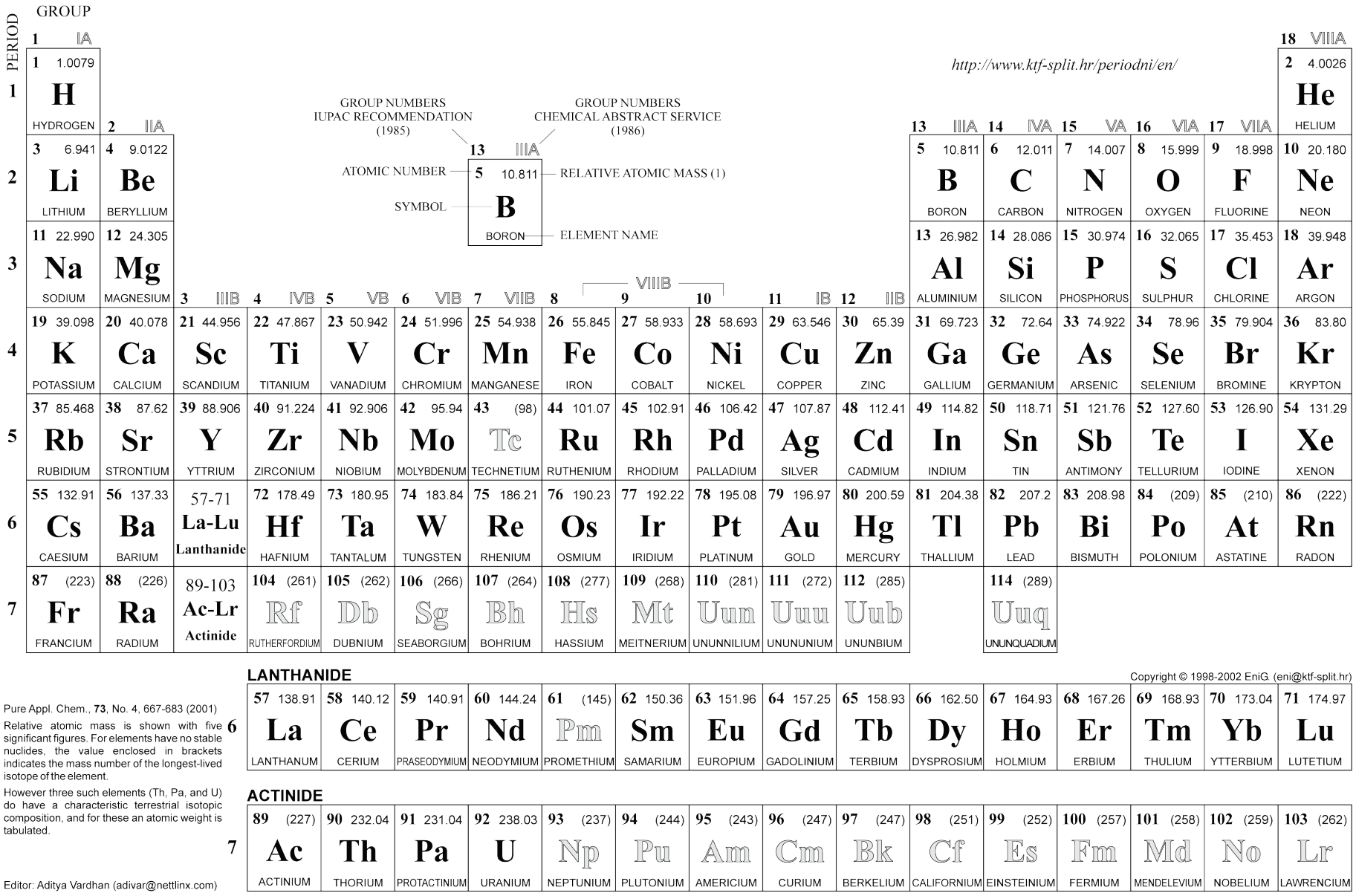
The periodic table is base on the similarity of properties and reactivities exhibited by certain elements.

Later, Henri Moseley (England, 1887-1915) established that each elements has a unique atomic number (***Z***), which is how the current periodic table is organized.

Dmitri Mendeleev.

Row	Group I — R_2O	Group II — RO	Group III — R_2O_3	Group IV RH_4 RO_2	Group V RH_3 R_2O_5	Group VI RH_2 RO_3	Group VII RH R_2O_7	Group VIII — RO_4
1	H = 1							
2	Li = 7	Be = 9.4	B = 11	C = 12	N = 14	O = 16	F = 19	
3	Na = 23	Mg = 24	Al = 27.3	Si = 28	P = 31	S = 32	Cl = 35.5	
4	K = 39	Ca = 40	— = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56, Co = 59, Ni = 59, Cu = 63
5	(Cu = 63)	Zn = 65	— = 68	— = 72	As = 75	Se = 78	Br = 80	
6	Rb = 85	Sr = 87	?Yt = 88	Zr = 90	Nb = 94	Mo = 96	— = 100	Ru = 104, Rh = 104, Pd = 106, Ag = 108
7	(Ag = 108)	Cd = 112	In = 113	Sn = 118	Sb = 122	Te = 125	I = 127	
8	Cs = 133	Ba = 137	?Di = 138	?Ce = 140				
9								
10			?Er = 178	?La = 180	Ta = 182	W = 184		Os = 195, Ir = 197, Pt = 198, Au = 199
11	(Au = 199)	Hg = 200	Tl = 204	Pb = 207	Bi = 208			
12				Th = 231		U = 240		

The Periodic Table – 6



(1) Pure Appl. Chem., **73**, No. 4, 667-683 (2001)

Relative atomic mass is shown with five significant figures. For elements have no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.

However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

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