CHAPTER 8
Atomic Physics

- Allowed solutions to Schrödinger equation for two non-interacting particles accounting for their indistinguishable property
- Bosons and fermions, Pauli's exclusion principle again
- 8.1 Atomic Structure and the Periodic Table

What distinguished Mendeleev was not only genius, but a passion for the elements. They became his personal friends; he knew every quirk and detail of their behavior.

- J. Bronowski

$$\Psi_{n\ell m_\ell m_s} = R_{n\ell} Y_{\ell m_\ell} X_{m_s}$$

Suffices for this chapter, derived results are numerically nearly correct, also we do allow for an inclusion of effects of the fourth dimension (by multiplying what goes on in 3D with the spin wave function)

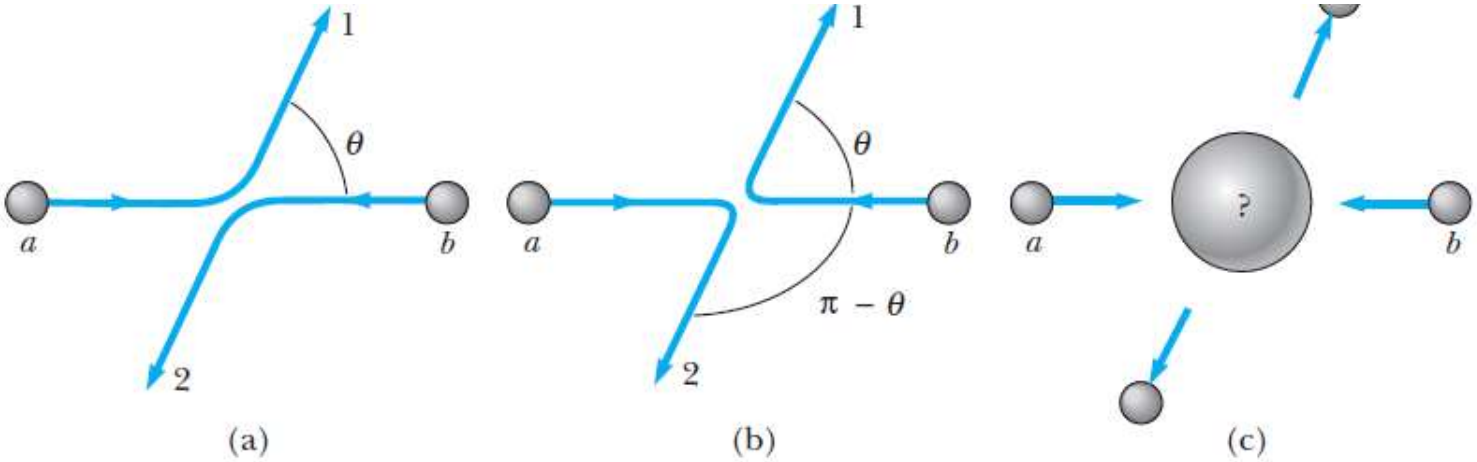


Figure 9.14 The scattering of two electrons as a result of their mutual repulsion. The events depicted in (a) and (b) produce the same outcome for identical electrons but are nonetheless distinguishable classically because the path taken by each electron is different in the two cases. In this way, the electrons retain their separate identities during collision. (c) According to quantum mechanics, the paths taken by the electrons are blurred by the wave properties of matter. In consequence, once they have interacted, the electrons cannot be told apart in any way!

identical particles cannot be told

A consequence of the uncertainty principle

apart in any way—they are truly indistinguishable

There is no path for a quantum mechanical object to follow, uncertainty principle forbids this

The time-independent Schrödinger equation for two particles of mass m

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x_1, x_2)}{\partial x_1^2} - \frac{\hbar^2}{2m}\frac{\partial^2\psi(x_1, x_2)}{\partial x_2^2} + V\psi(x_1, x_2) = E\psi(x_1, x_2)$$

But without spin, so it is not really convincing

if do not interact, however, we can write V as $V_1(x_1) + V_2(x_2)$ But this is not reasonable !

one-dimensional infinite square well solve the Schrödinger equation only inside the well where $V = 0$

Could also have two parts: L_1 and L_2

The single-particle product solutions are

$$\psi_{nm}(x_1, x_2) = \psi_n(x_1)\psi_m(x_2) \qquad 7\text{-}58$$

where $\psi_n(x_1)$ and $\psi_m(x_2)$ are the single-particle wave functions for an infinite square well given by Equation 6-32. Thus, for $n = 1$ and $m = 2$,

$$\psi_{12} = C \sin\frac{\pi x_1}{L_1}\sin\frac{2\pi x_2}{L_2} \qquad 7\text{-}59$$

even if only one part

The probability of finding particle 1 in dx_1 and particle 2 in dx_2 is $|\psi(x_1, x_2)|^2\, dx_1\, dx_2$, which is just the product of the separate probabilities $|\psi(x_1)|^2\, dx_1$ and $|\psi(x_2)|^2\, dx_2$. However, even though we have labeled the particles 1 and 2, if they are identical, we cannot distinguish which is in dx_1 and which is in dx_2. For identical particles, therefore, we must construct the wave function so that the probability density is the same if we interchange the labels:

$$|\psi(x_1, x_2)|^2 = |\psi(x_2, x_1)|^2 \qquad 7\text{-}60$$

Equation 7-60 holds if $\psi(x_1, x_2)$ is either symmetric or antisymmetric on exchange of particles—that is,

$$\psi(x_2, x_1) = +\psi(x_1, x_2) \quad \text{symmetric}$$

$$\psi(x_2, x_1) = -\psi(x_1, x_2) \quad \text{antisymmetric}$$

If that made sense, the particle that we could find at x = ½ L needed to be always the one in state n = 1 (the other particle has zero probability there), if we were to change labels the same condition would apply - so we would violate the condition that quantum mechanical particles are indistinguishable as a consequence of the uncertainly principle, ***so it cannot make sense***

We note that the general wave function of the form of Equation 7-58 and the example (Equation 7-59) are neither symmetric nor antisymmetric. If we interchange x_1 and x_2, we get a different wave function, implying that the particles can be distinguished. These forms are thus *not* consistent with the indistinguishability of identical particles. However, from among all of the possible linear combination solutions of the single product functions, we see that, if ψ_{nm} and ψ_{mn} are added or subtracted, we form symmetric or antisymmetric wave functions necessary to preserve the indistinguishability of the two particles:

$$\psi_S = C\left[\psi_n(x_1)\psi_m(x_2) + \psi_n(x_2)\psi_m(x_1)\right] \quad \text{symmetric}$$

$$\psi_A = C\left[\psi_n(x_1)\psi_m(x_2) - \psi_n(x_2)\psi_m(x_1)\right] \quad \text{antisymmetric}$$

Two basis types of particles, bosons (integer spin) and fermions, (half integer spin)

When n = m for both particles, wavefunction = zero

Pauli Exclusion Principle

There is an important difference between the antisymmetric and symmetric combinations. If n = m, the antisymmetric wave function is identically zero for all x_1 and x_2, whereas the symmetric function is not. More generally, it is found that electrons (and many other particles, including protons and neutrons) can only have antisymmetric *total* wave functions, that is

they are fermions

$$\Psi_{n\ell m_\ell m_s} = R_{n\ell} Y_{\ell m_\ell} X_{m_s} \qquad \textbf{7-61}$$

where $R_{n\ell}$ is the radial wave function, $Y_{\ell m_\ell}$ is the spherical harmonic, and X_{m_s} is the spin wave function

Matter is composed of fermions, half integer spin,

Paraphrasing Winston Churchill: not everybody at the horse races is a crook, but all the crooks are at the horse races: Not all bosons are force particles, but all force particles are bosons

Pauli Exclusion Principle

- To make sense of atomic spectroscopic data of the anomalous Zeeman effect, Pauli proposed his famous exclusion principle: **No two electrons in an atom can have the same set of quantum numbers (n, ℓ, m_ℓ, m_s)**.

- It applies to all particles of half-integer spin, which are called *fermions*, electrons and composite particles (protons and neutrons) in the nucleus are fermions. Each of the latter (composite) particles is composed of three quarks – which are also fermions, spins add up, so no chance for them to become a boson)

The whole periodic table (chemical properties) can be understood by two rules on the basis of the hydrogen atom:

1) The electrons in an atom tend to occupy the lowest energy levels available to them.

2) Pauli exclusion principle.

Hydrogen atom model, Schrödinger plus spin

The principle quantum number has letter codes.

n =	1	2	3	4	..
Letter =	K	L	M	N	…

n = **shells** (e.g.: K shell, L shell, etc.)

n *and* ℓ together for **subshells** (e.g.: 1*s*, 2*p*, 3*d* – where leading number refers to principal quantum number

in each hydrogen-analogous orbital (3D spatial wavefunction-squared) there can only be up to two electrons with opposite spin

Number of sub-shells of each type ($2\ell + 1$)

M shell

L shell

K shell

Since n = 3, three sub-shell types, first is called 3s ($l = 0$), second 3p ($l = 1$), and third 3d ($l = 2$), 18 electrons max when all 9 sub-shells are filled

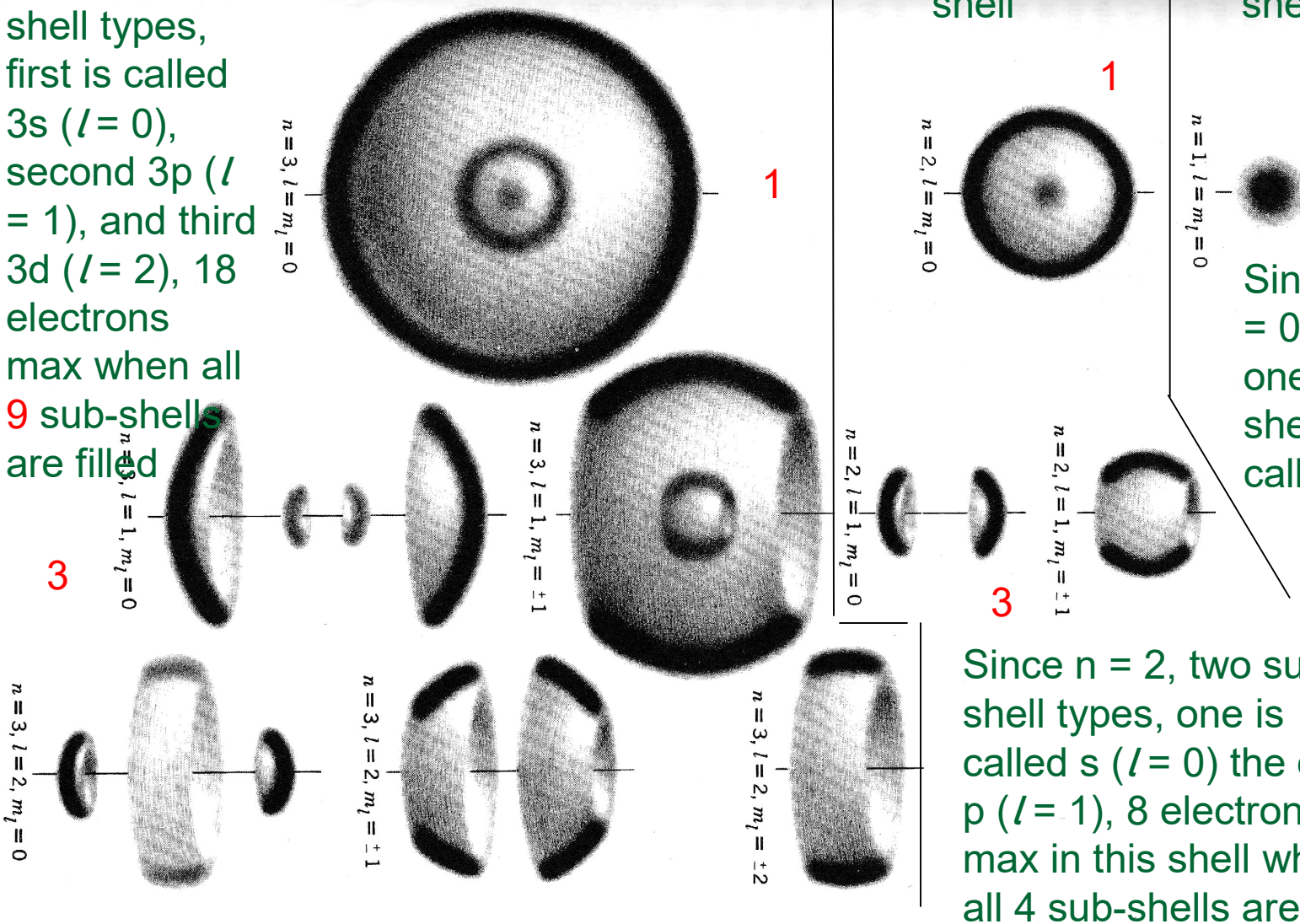


FIGURE 7.10 Representations of $|\psi|^2$ for different sets of quantum numbers. The z axis is the vertical axis. The intensity of each diagram at any point is proportional to the probability of locating an electron in a small volume element at that point.

Since $l = 0$, just one sub shell called s

Since n = 2, two sub-shell types, one is called s ($l = 0$) the other p ($l = 1$), 8 electrons max in this shell when all 4 sub-shells are filled

Filled and half-filled shells and sub-shells result in spherical symmetric electron density distributions for the corresponding atoms, (Unsoeld's theorem)

Atomic Structure

Hydrogen: (n, ℓ, m_ℓ, m_s) = (1, 0, 0, ±½) in ground state. Both spin states with same probability

- In the absence of a magnetic field (and ignoring hyper-fine structure and spin orbit coupling), the state m_s = ½ would be degenerate with the m_s = −½ state. (different wavefunction but same energy)

Helium: (1, 0, 0, ½) for the first electron, (1, 0, 0, −½) for the second electron.

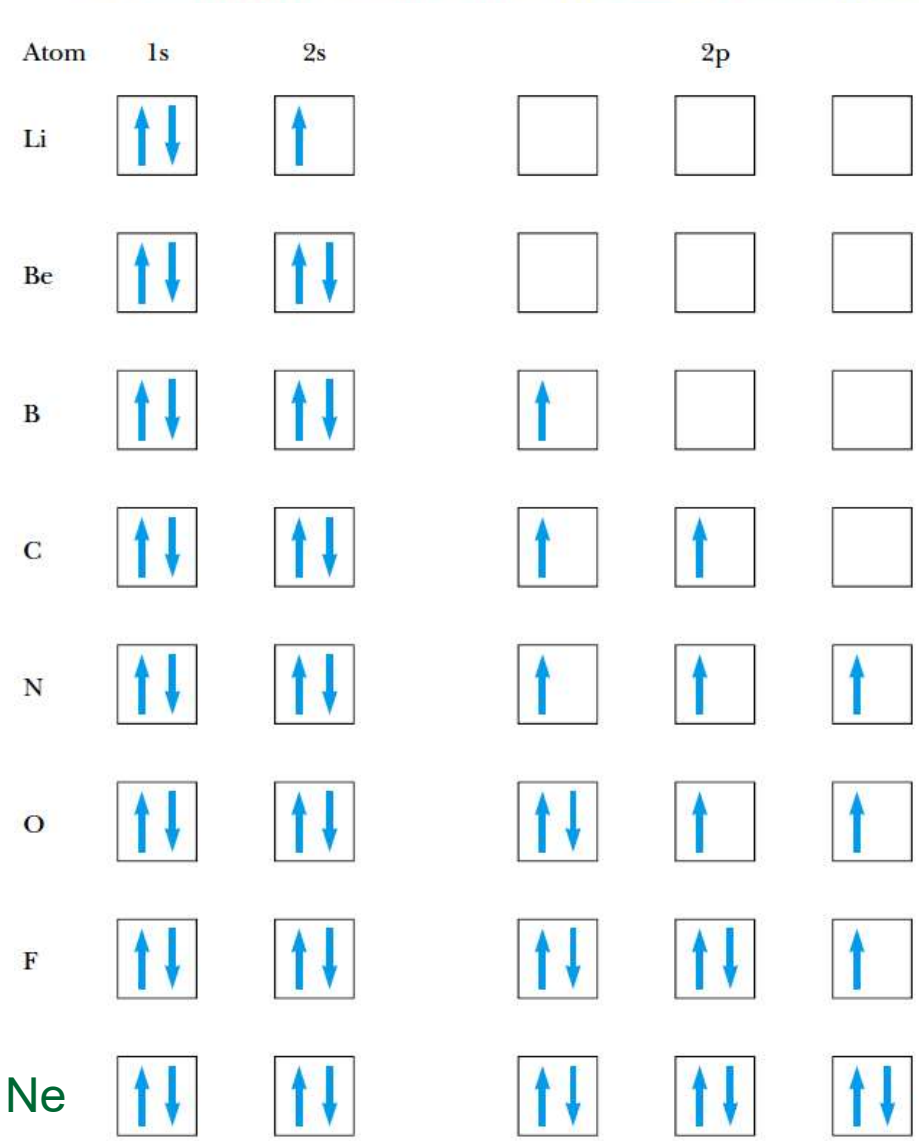
- Electrons have anti-aligned (m_s = +½ and m_s = −½) spins, they are being *paired and* ***spins cancel***, total spin becomes an integer (0), i.e. the whole particle becomes a boson, composed of fermions (which are subject to the Pauli exclusion principle, nuclear spins cancel also, happens at there are two protons and two neutrons).

Electrons for H and He atoms are in the K shell.
H: 1*s* ***He*$^{+:}$ 1s^1 just like H**
He: 1s^2 **Li^{++}: 1s^1 just like H**

There is no sub-shells at all for n = 1, because l = 0, meaning m_l also = 0, so just one set with spatial (3D) quantum numbers (1, 0, 0, ±½)

Number of sub-shells is number of sets with unique spatial (3D) quantum numbers

No more than one electron may occupy a given quantum state specified by a particular set of single-particle quantum numbers n, ℓ, m_ℓ, m_s.



Hund's rule, rather than joining an orbital that is already occupied by one electron, the next electron goes into an orbital all by itself to minimize total energy

→ different hybridizations in crystals

→ Ammonia, NH_3

→ H_20

Figure 9.15 Electronic configurations of successive elements from lithium to neon. The filling of electronic states must obey the Pauli exclusion principle and Hund's rule.

Atomic Structure

How many electrons may be in each shell and subshell?

	Total
For each m_ℓ: two values of m_s	2
For each ℓ: $(2\ell + 1)$ values of m_ℓ	$2(2\ell + 1)$

Recall: ℓ = 0 1 2 3 4 5 …

letter = *s p d f g h* …

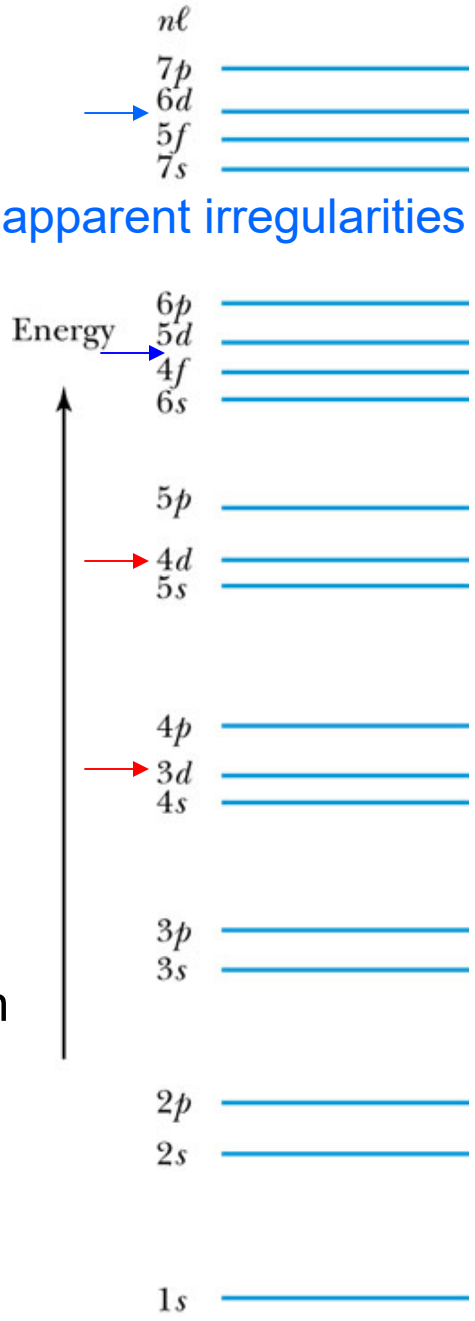
ℓ = 0, (*s* state) can have two electrons.

ℓ = 1, (*p* state) can have six electrons, and so on.

Multiple electrons will interact

Electrons with higher ℓ values are less shielded from the nuclear charge and have higher energy levels than those with lower ℓ values. They have also a larger angular momentum.

4*s* fills before 3*d* – it's due to interactions between the electrons, extra potential energy terms in the Hamiltonian



$$1s < 2s < 2p < 3s < 3p < 4s \sim 3d < 4p < 5s < 4d < 5p < 6s < 4f \sim 5d < 6p < 7s < 6d \sim 5f \ldots$$

Ordering of subshells by energy

Table 9.2 Electronic Configurations of the Elements

Z	Symbol	Ground Configuration	Ionization Energy (eV)	Z	Symbol	Ground Configuration	Ionization Energy (eV)
1	H	$1s^1$	13.595	27	Co	$3d^7 4s^2$	7.86
2	He	$1s^2$	24.581	28	Ni	$3d^8 4s^2$	7.633
3	Li	[He] $2s^1$	5.390	29	Cu	$3d^{10} 4s^1$	7.724
4	Be	$2s^2$	9.320	30	Zn	$3d^{10} 4s^2$	9.391
5	B	$2s^2 2p^1$	8.296	31	Ga	$3d^{10} 4s^2 4p^1$	6.00
6	C	$2s^2 2p^2$	11.256	32	Ge	$3d^{10} 4s^2 4p^2$	7.88
7	N	$2s^2 2p^3$	14.545	33	As	$3d^{10} 4s^2 4p^3$	9.81
8	O	$2s^2 2p^4$	13.614	34	Se	$3d^{10} 4s^2 4p^4$	9.75
9	F	$2s^2 2p^5$	17.418	35	Br	$3d^{10} 4s^2 4p^5$	11.84
10	Ne	$2s^2 2p^6$	21.559	36	Kr	$3d^{10} 4s^2 4p^6$	13.996
11	Na	[Ne] $3s^1$	5.138	37	Rb	[Kr] $5s^1$	4.176
12	Mg	$3s^2$	7.644	38	Sr	$5s^2$	5.692
13	Al	$3s^2 3p^1$	5.984	39	Y	$4d 5s^2$	6.377
14	Si	$3s^2 3p^2$	8.149	40	Zr	$4d^2 5s^2$	6.835
15	P	$3s^2 3p^3$	10.484	41	Nb	$4d^4 5s^1$	6.881
16	S	$3s^2 3p^4$	10.357	42	Mo	$4d^5 5s^1$	7.10
17	Cl	$3s^2 3p^5$	13.01	43	Tc	$4d^5 5s^2$	7.228
18	Ar	$3s^2 3p^6$	15.755	44	Ru	$4d^7 5s^1$	7.365
19	K	[Ar] $4s^1$	4.339	45	Rh	$4d^8 5s^1$	7.461
20	Ca	$4s^2$	6.111	46	Pd	$4d^{10}$	8.33
21	Sc	$3d 4s^2$	6.54	47	Ag	$4d^{10} 5s^1$	7.574
22	Ti	$3d^2 4s^2$	6.83	48	Cd	$4d^{10} 5s^2$	8.991
23	V	$3d^3 4s^2$	6.74	49	In	$4d^{10} 5s^2 5p^1$	5.785
24	Cr	$3d^5 4s$	6.76	50	Sn	$4d^{10} 5s^2 5p^2$	7.342
25	Mn	$3d^5 4s^2$	7.432	51	Sb	$4d^{10} 5s^2 5p^3$	8.639
26	Fe	$3d^6 4s^2$	7.87	52	Te	$4d^{10} 5s^2 5p^4$	9.01

Note the closed subshells for any n at the noble gasses

Note the closed subshells for any n at the noble gasses

Table 9.2 Electronic Configurations of the Elements

Z	Symbol	Ground Configuration	Ionization Energy (eV)	Z	Symbol	Ground Configuration	Ionization Energy (eV)
53	I	$4d^{10}5s^25p^5$	10.454	79	Au	$[Xe, 4f^{14}5d^{10}]\ 6s^1$	9.22
54	Xe	$4d^{10}5s^25p^6$	12.127	80	Hg	$6s^2$	10.434
55	Cs	$[Xe]\ 6s^1$	3.893	81	Tl	$6s^26p^1$	6.106
56	Ba	$6s^2$	5.210	82	Pb	$6s^26p^2$	7.415
57	La	$5d6s^2$	5.61	83	Bi	$6s^26p^3$	7.287
58	Ce	$4f5d6s^2$	6.54	84	Po	$6s^26p^4$	8.43
59	Pr	$4f^36s^2$	5.48	85	At	$6s^26p^5$	9.54
60	Nd	$4f^46s^2$	5.51	86	Rn	$6s^26p^6$	10.745
61	Pm	$4f^56s^2$	5.60	87	Fr	$[Rn]\ 7s^1$	3.94
62	Fm	$4f^66s^2$	5.644	88	Ra	$7s^2$	5.277
63	Eu	$4f^76s^2$	5.67	89	Ac	$6d7s^2$	5.17
64	Gd	$4f^75d6s^2$	6.16	90	Th	$6d^27s^2$	6.08
65	Tb	$4f^96s^2$	6.74	91	Pa	$5f^26d7s^2$	5.89
66	Dy	$4f^{10}6s^2$	6.82	92	U	$5f^36d7s^2$	6.194
67	Ho	$4f^{11}6s^2$	6.022	93	Np	$5f^46d7s^2$	6.266
68	Er	$4f^{12}6s^2$	6.108	94	Pu	$5f^67s^2$	6.061
69	Tm	$4f^{13}6s^2$	6.185	95	Am	$5f^77s^2$	5.99
70	Yb	$4f^{14}6s^2$	6.22	96	Cm	$5f^76d7s^2$	6.02
71	Lu	$4f^{14}5d6s^2$	6.15	97	Bk	$5f^86d7s^2$	6.23
72	Hf	$4f^{14}5d^26s^2$	6.83	98	Cf	$5f^{10}7s^2$	6.30
73	Ta	$4f^{14}5d^36s^2$	7.88	99	Es	$5f^{11}7s^2$	6.42
74	W	$4f^{14}5d^46s^2$	7.98	100	Fm	$5f^{12}7s^1$	6.50
75	Re	$4f^{14}5d^56s^2$	7.87	101	Mv	$5f^{13}7s^2$	6.58
76	Os	$4f^{14}5d^66s^2$	8.71	102	No	$5f^{14}7s^2$	6.65
77	Ir	$4f^{14}5d^76s^2$	9.12	103	Lw	$5f^{14}6d7s^2$	
78	Pt	$4f^{14}5d^86s^2$	8.88	104	Ku	$5f^{14}6d^27s^2$	

Note: The bracket notation is used as a shorthand method to avoid repetition in indicating inner-shell electrons. Thus, [He] represents $1s^2$, [Ne] represents $1s^22s^22p^6$, [Ar] represents $1s^22s^22p^63s^23p^6$, and so on.

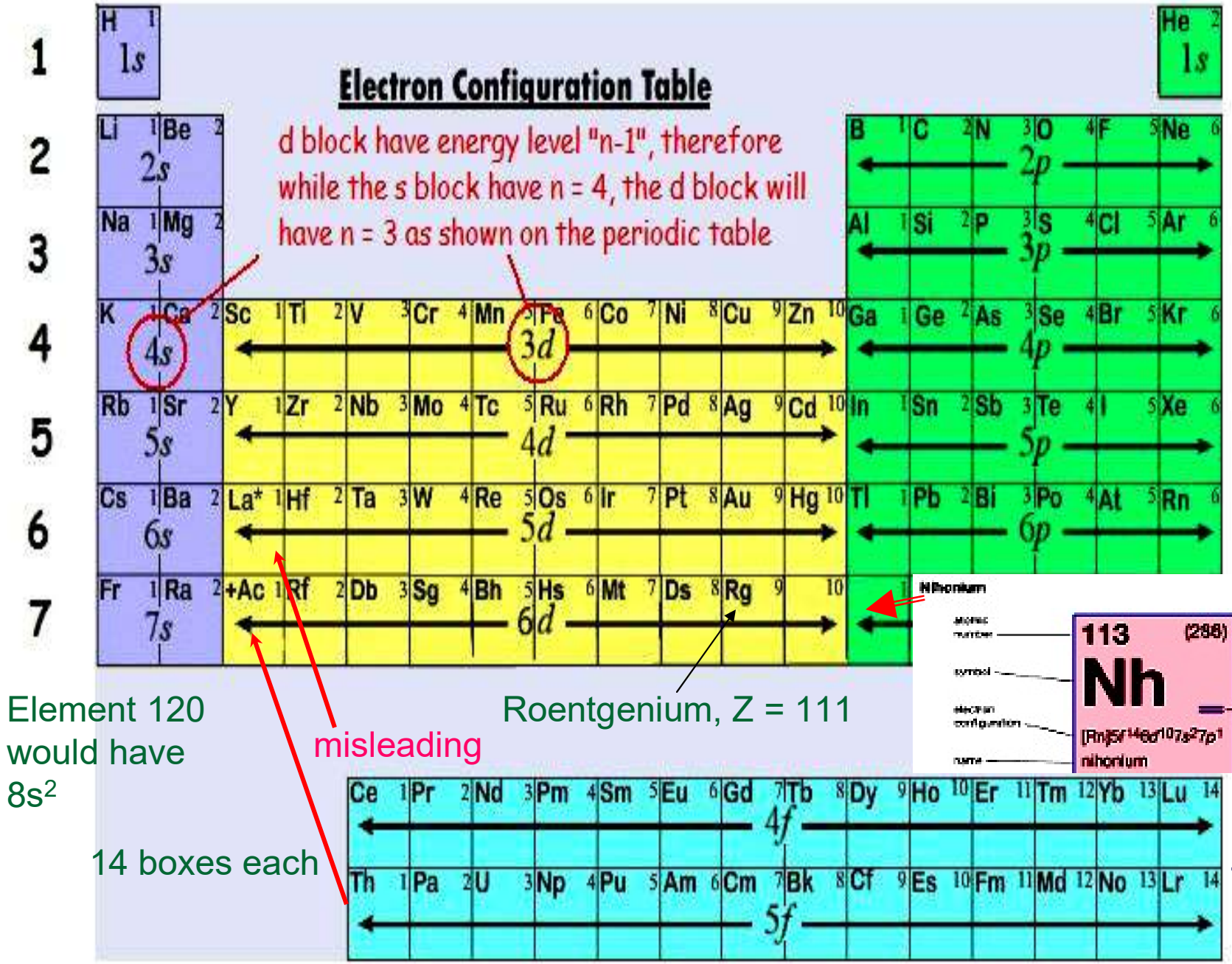
Last of the stable elements

Occur only in U-ores and nuclear reactors

Do not occur naturally on Earth

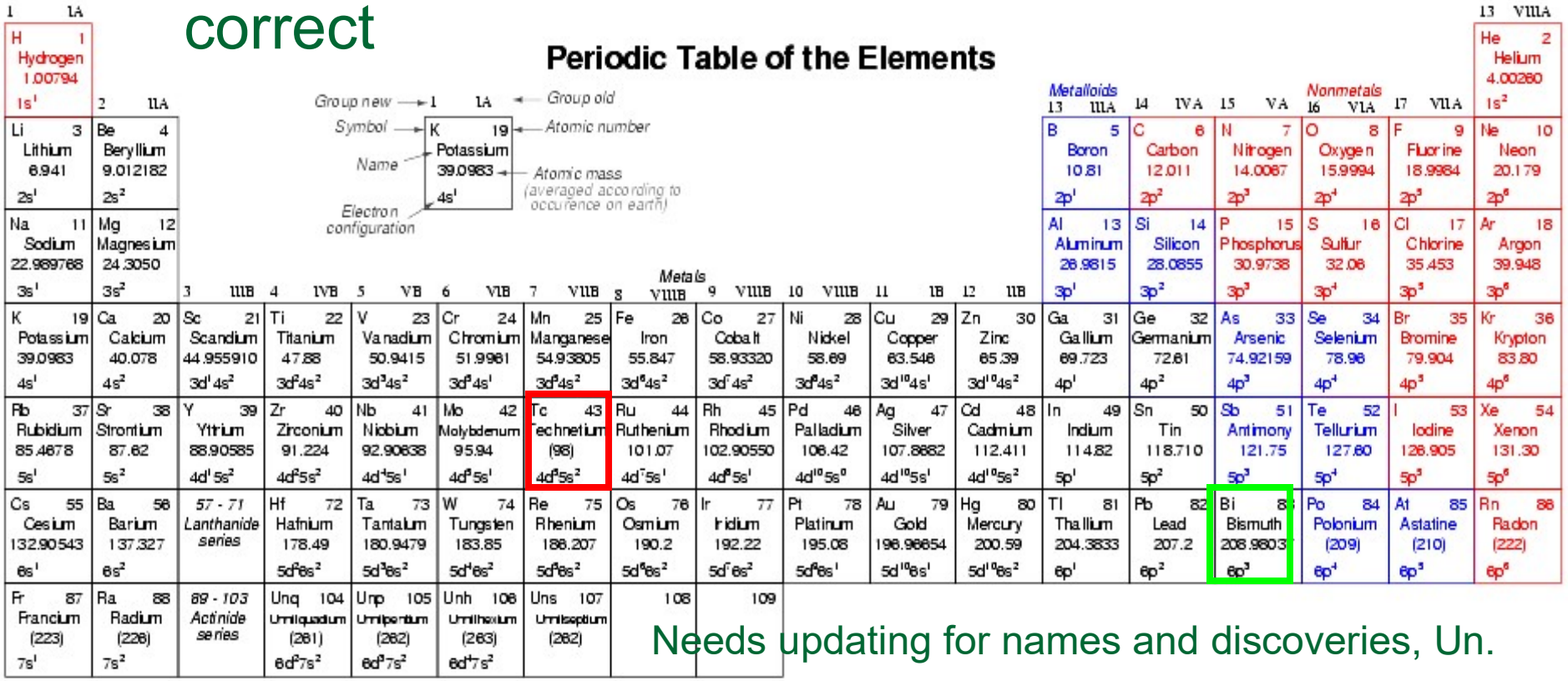
Lr

misleading


Row
1
2
3
4
5
6
7
Electron Configuration Table
d block have energy level "n-1", therefore while the s block have n = 4, the d block will have n = 3 as shown on the periodic table
1s
2s
2p
3s
3p
4s
3d
4p
5s
4d
5p
6s
5d
6p
7s
6d
Nihonium
113
(286)
Nh
[Rn]5f14 6d10 7s2 7p1
nihonium
4f
5f
Element 120 would have 8s2
14 boxes each
misleading
Roentgenium, Z = 111
no Z = 119 yet and beyond

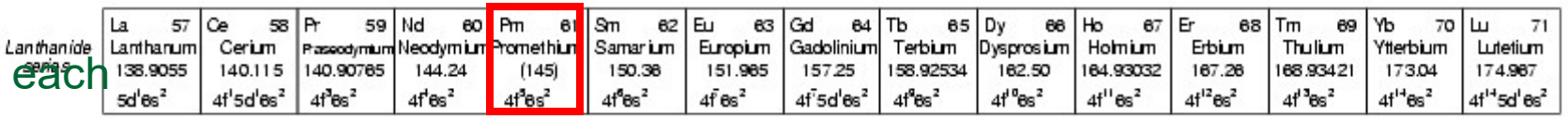
whenever [ ] around atomic mass, radioactive

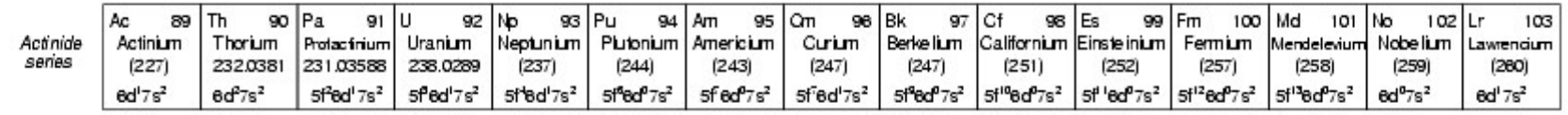
correct



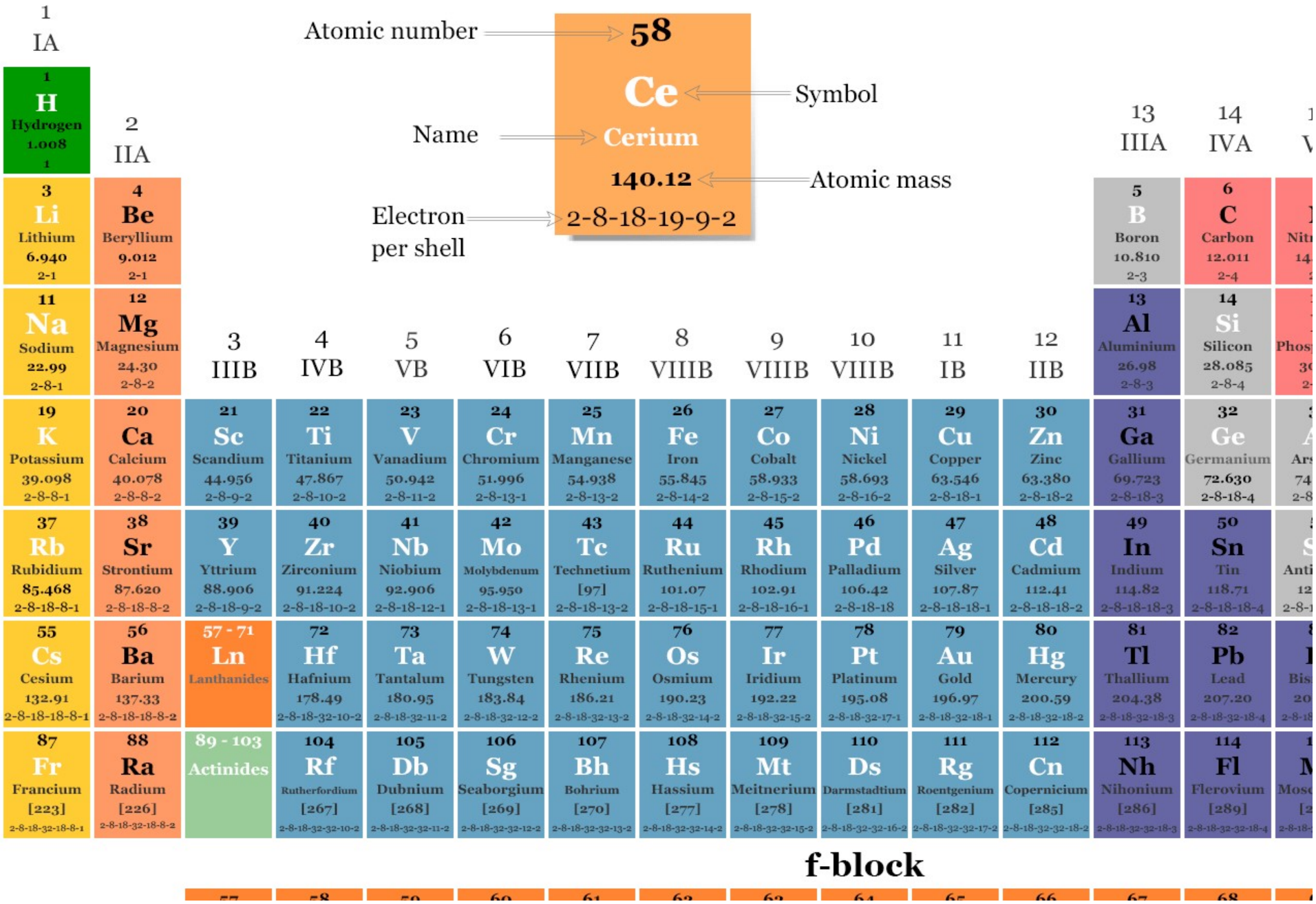
Needs updating for names and discoveries, Un.

15 boxes each

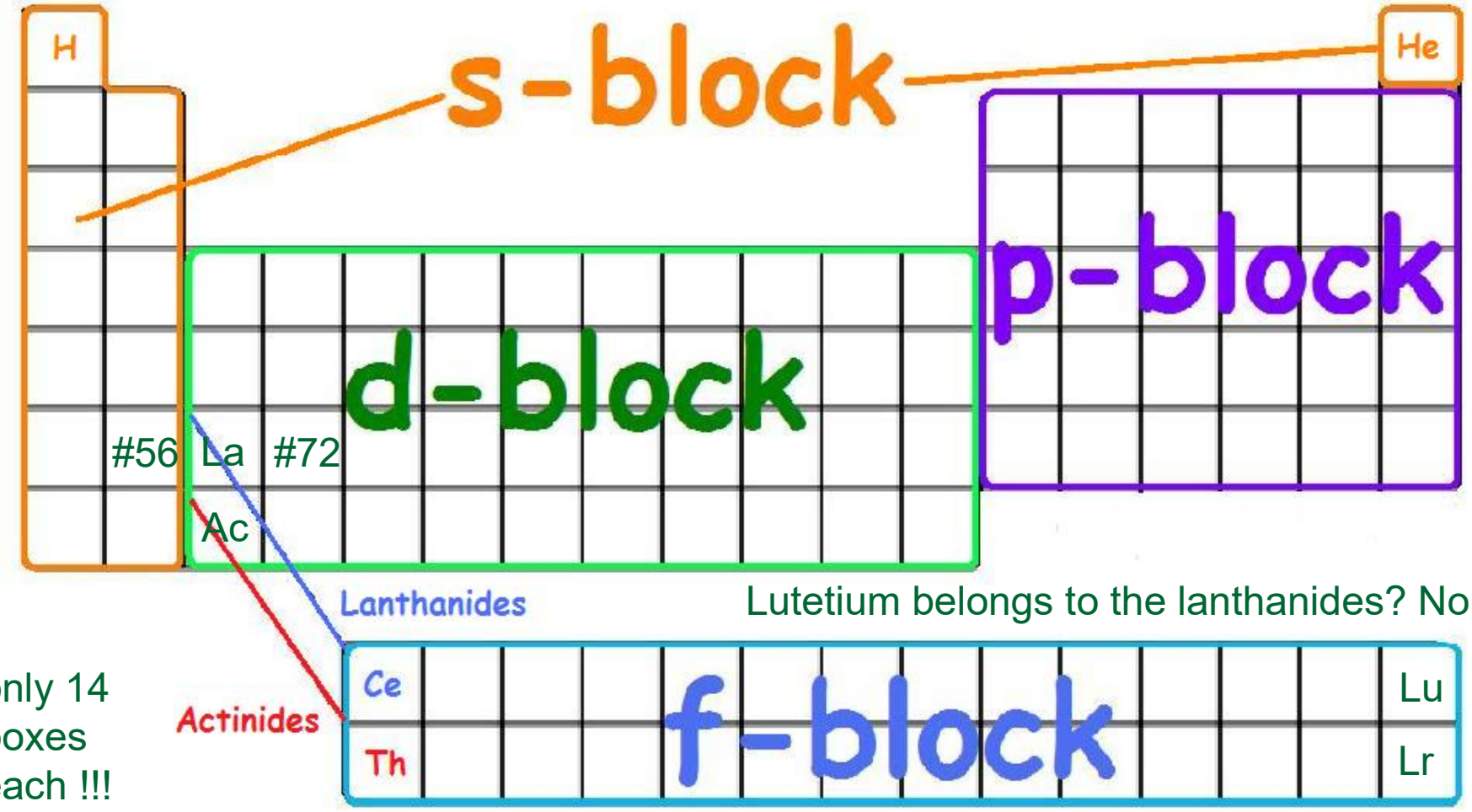




Standard long periodic table, Y and Lu have an analogous electronic structure for outer electrons



15 boxes each??, f means l = 3, max. number of electrons in f-sub-shell $2(2l + 1) = 14$

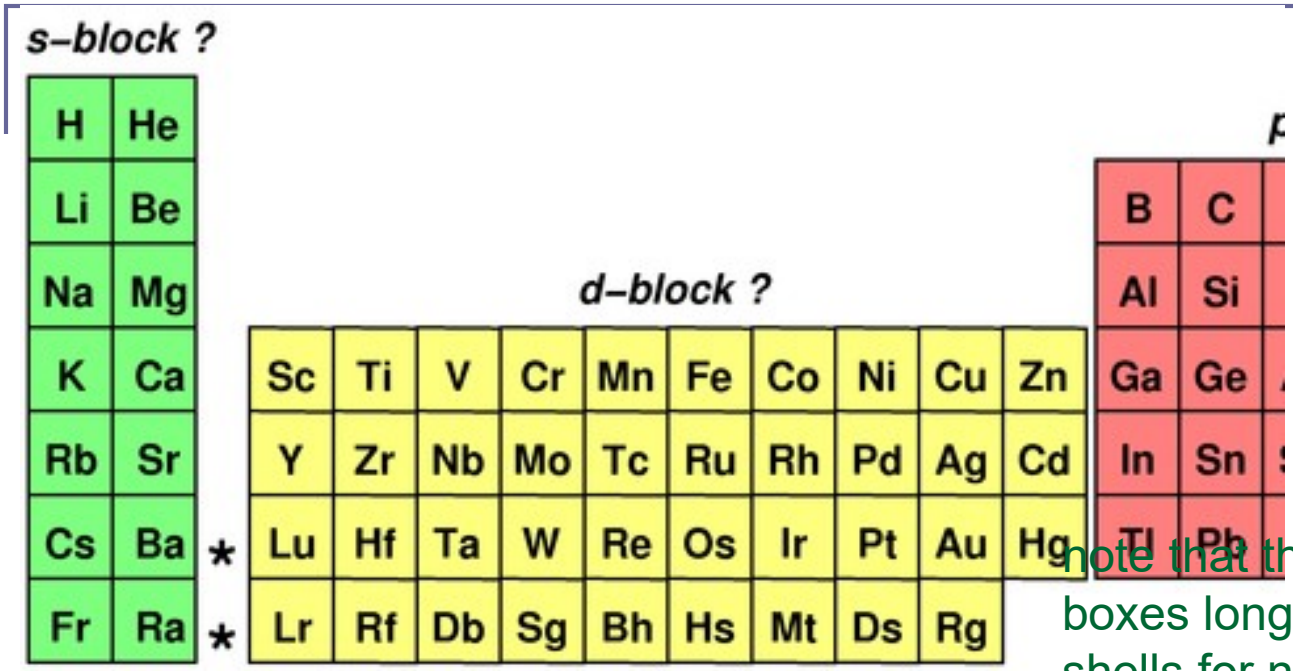


Lutetium belongs to the lanthanides? Nope

only 14 boxes each !!!

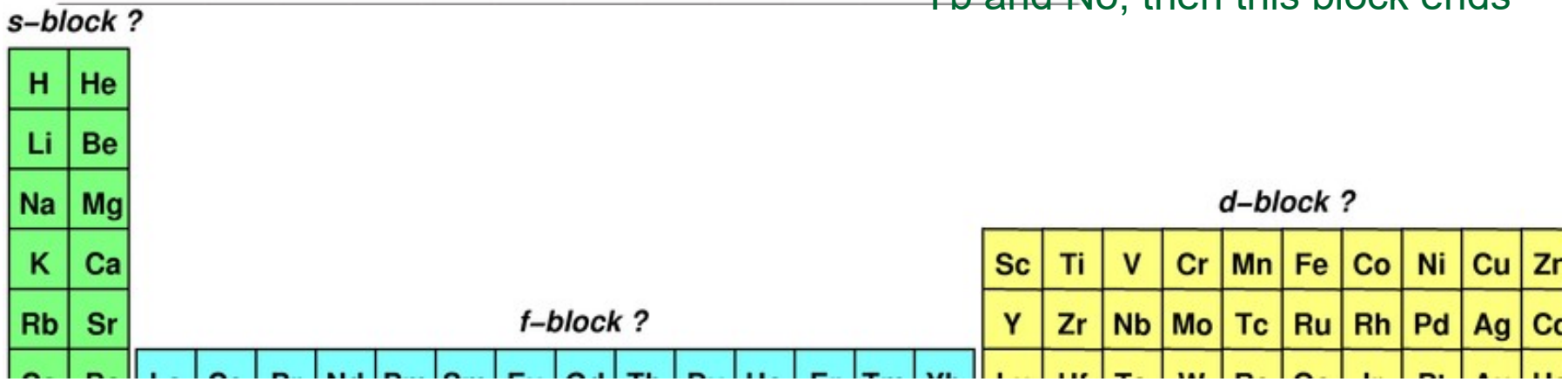
There are 14 = 2(6+1) f-boxes, but both Ce and Th just start with **one** electron in the boxes of the d-block, so it is not obvious if La should be in the same column as Sc and Y, or if Lu and Lr should be in the same column as these two. Actually it is Lu (Lutetium) and Lr (Lawrencium).

Note that La is #57, Lu is # 71 and its next neighbor is Hf with #72

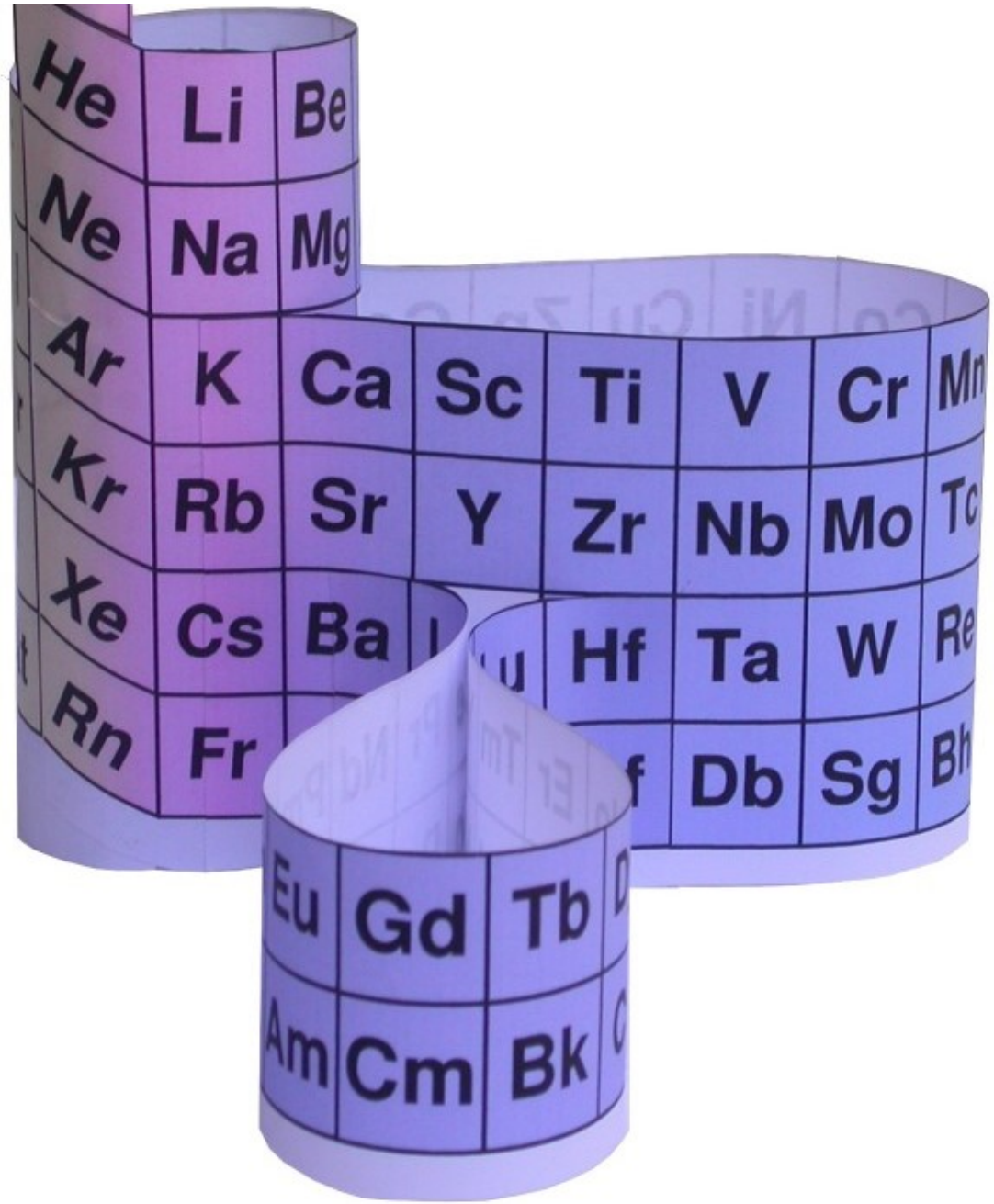


Number of sub-shells of each type ($2\ell + 1$)

note that the f-block is just 14 boxes long, in it the seven f-sub-shells for n = 3 and 4 get filled up, this is achieved when we come to Yb and No, then this block ends



No question marks, this is the more systematic way to show the periodic table


He
Li
Be
Ne
Na
Mg
Ar
K
Ca
Sc
Ti
V
Cr
Mn
Kr
Rb
Sr
Y
Zr
Nb
Mo
Tc
Xe
Cs
Ba
Hf
Ta
W
Re
Rn
Fr
Db
Sg
Bh
Eu
Gd
Tb
Am
Cm
Bk

Groups and Periods in Periodic Table

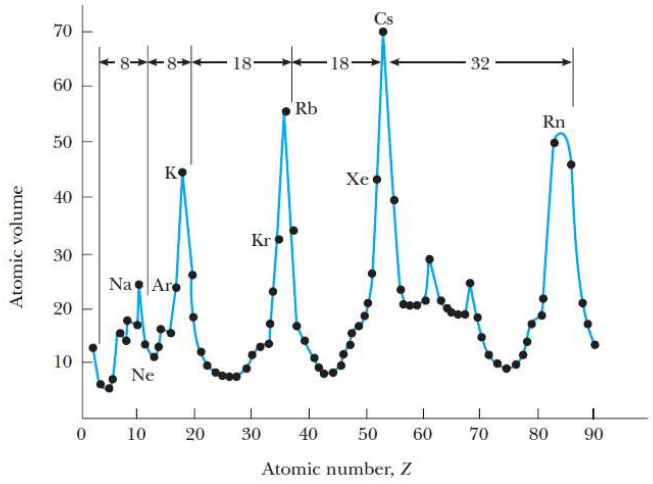
Groups:

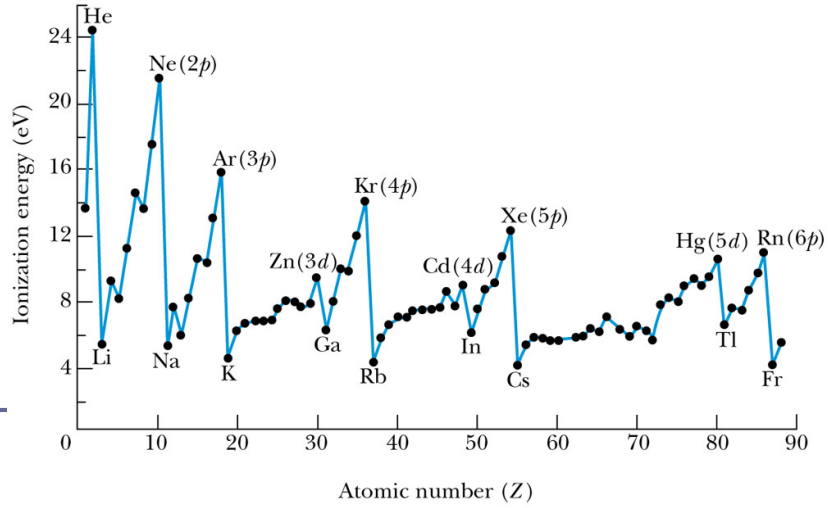
- Vertical columns.
- Same number of electrons in the ℓ orbits.
- Can form similar chemical bonds as these are determined by the outermost (most loosely bound) electrons

Periods:

all atoms have about the same size

- Horizontal rows.
- Correspond to filling of the sub-shells.
- Beginning of each period shows in atomic radii plot, end of each period shows more or less in ionization energy.





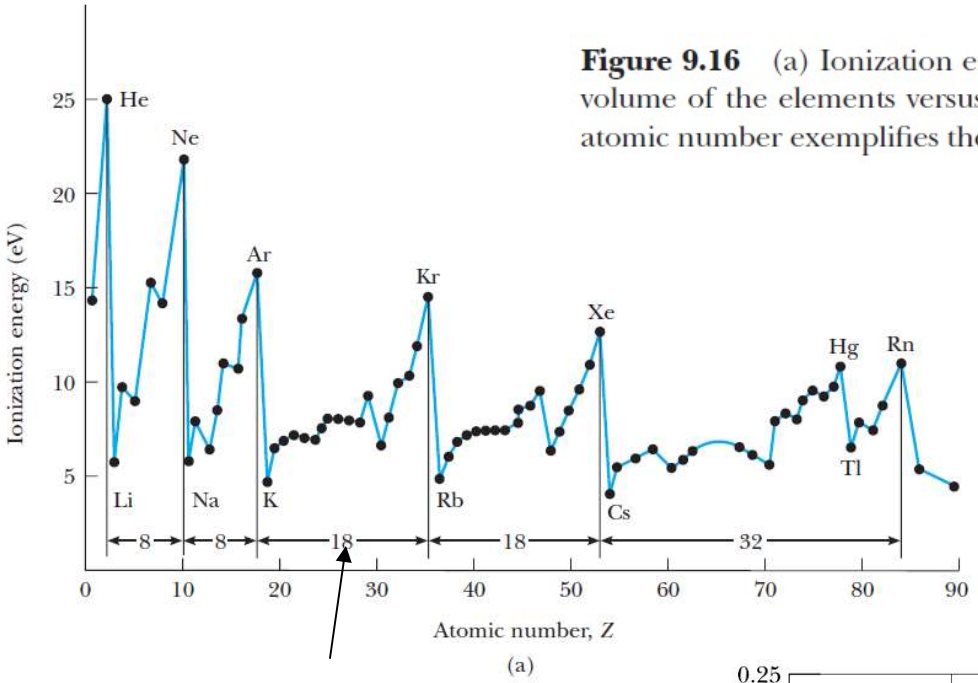
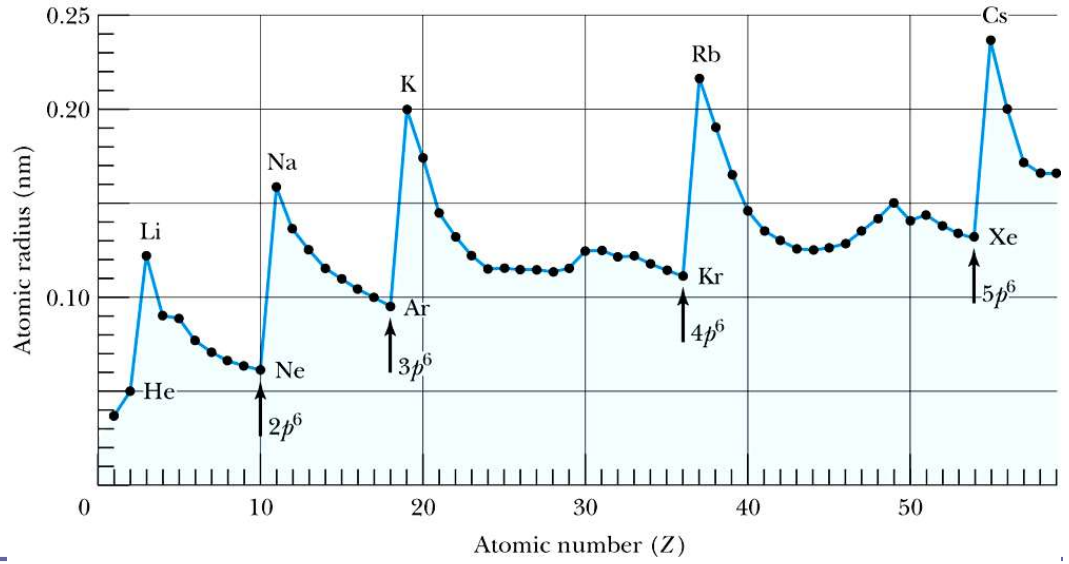


Figure 9.16 (a) Ionization energy of the elements versus atomic number Z. (b) Atomic volume of the elements versus atomic number Z. The recurring pattern with increasing atomic number exemplifies the behavior from which the periodic table gets its name.

32 = 14 + 10 + 6 + 2

18 = 10 + 6 + 2

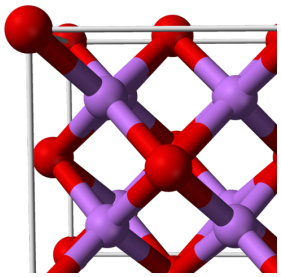


The Periodic Table

Inert Gases:

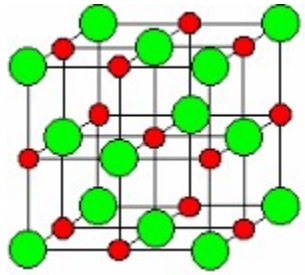
- Last column of the periodic table
- Closed *p* sub-shell except helium (which has closed *s* sub-shell)
- Zero net electronic spin and large ionization energy
- Their atoms interact only very weakly with each other, mono-atomic gasses

Alkalis:



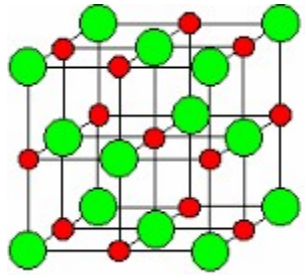
- Single *s* electron outside an inner core, largest atomic radii
- Easily form positive ions with a charge +1e, highly reactive
- Lowest ionization energies
- Form chemical compounds with valence number 1, e.g. Li_2O (lithia, 8 Li cations and 4 O anions per unit cell of a crystal), for molecules: H_2O
- Electrical conductivity in metals is good as the electron joins the free electron cloud easily

Alkaline Earths:



- Two *s* electrons in outer sub-shell
- In chemical compounds with valence number 2, e.g. MgO (magnesia), 4 Mg + 4 O per unit cell of a crystal

The Periodic Table



Halogens:

- Need just one more shared electron to fill outermost subshell
- Form strong ionic bonds with the alkalis, e.g. NaCl
- More stable configurations occur when *p* subshell is completely filled, therefore highly reactive

Transition Metals:

- Three rows of elements in which the 3*d*, 4*d*, and 5*d* are being filled
- Properties primarily determined by the *s* and *p* electrons, rather than by the *d* subshell being filled, which are further inside the atoms
- Initially *d*-shell electrons with unpaired spins, Hund's rule, cause of ferromagnetism
- As the *d* subshell is filled further, the magnetic moments, and the tendency for neighboring atoms to align spins are reduced

The Periodic Table

Lanthanides (*rare earths***)**, starts with La

- Have the outermost $6s^2$ sub-shell completed
- As also occurs in the 3*d* sub-shell, the electrons in the 4*f* sub-shell prefer unpaired electrons (Hund's rule) contribute to ferromagnetic effects

Actinides: *(all radioactive***)**, starts with Ac

Inner sub-shells are being filled while the $7s^2$ sub-shell is completed

- Difficult to obtain chemical data because they are all radioactive (last stable atom is Bi, # 83)
- Commercial usage of U, Pu, Am

Summary

Physical foundations are electronic structures

their consequences are all of chemistry !!!

The **exclusion principle** states that no two electrons can be in the same quantum state; that is, no two electrons can have the same four quantum numbers. The exclusion principle derives from the notion that electrons are identical particles called **fermions.** Fermions are described by wavefunctions that are antisymmetric in the electron coordinates. Wavefunctions that are symmetric in the particle coordinates describe another class of objects called **bosons,** to which no exclusion principle applies. All known particles are either fermions or bosons. An example of a boson is the photon.

Using the exclusion principle and the principle of minimum energy, one can determine the electronic configurations of the elements. This serves as a basis for understanding atomic structure and the physical and chemical properties of the elements.

All atoms in crystals are of about the same size, 0.1 – 0.5 nm diameter, in fact, their size is inferred on how much space they take up in crystals

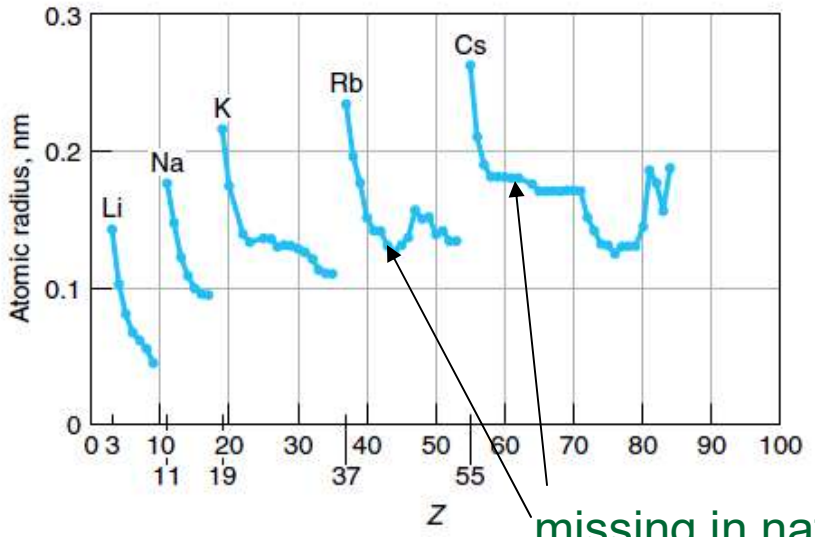


Figure 7-21 The atomic radii versus Z shows a sharp rise following the completion of a shell as the next electron must have the next larger n. The radii then decline with increasing Z, reflecting the penetration of wave functions of the electrons in the developing shell. The recurring patterns here and in Figure 7-20 are examples of the behavior of many atomic properties that give the periodic table its name.

missing in nature

Periodic physical and chemical properties of atoms are due to periodic electronic structures, chemical properties depend strongly on the outermost electrons, ferromagnetic properties are due to unpaired spins in d and f orbitals (Hund's rule)

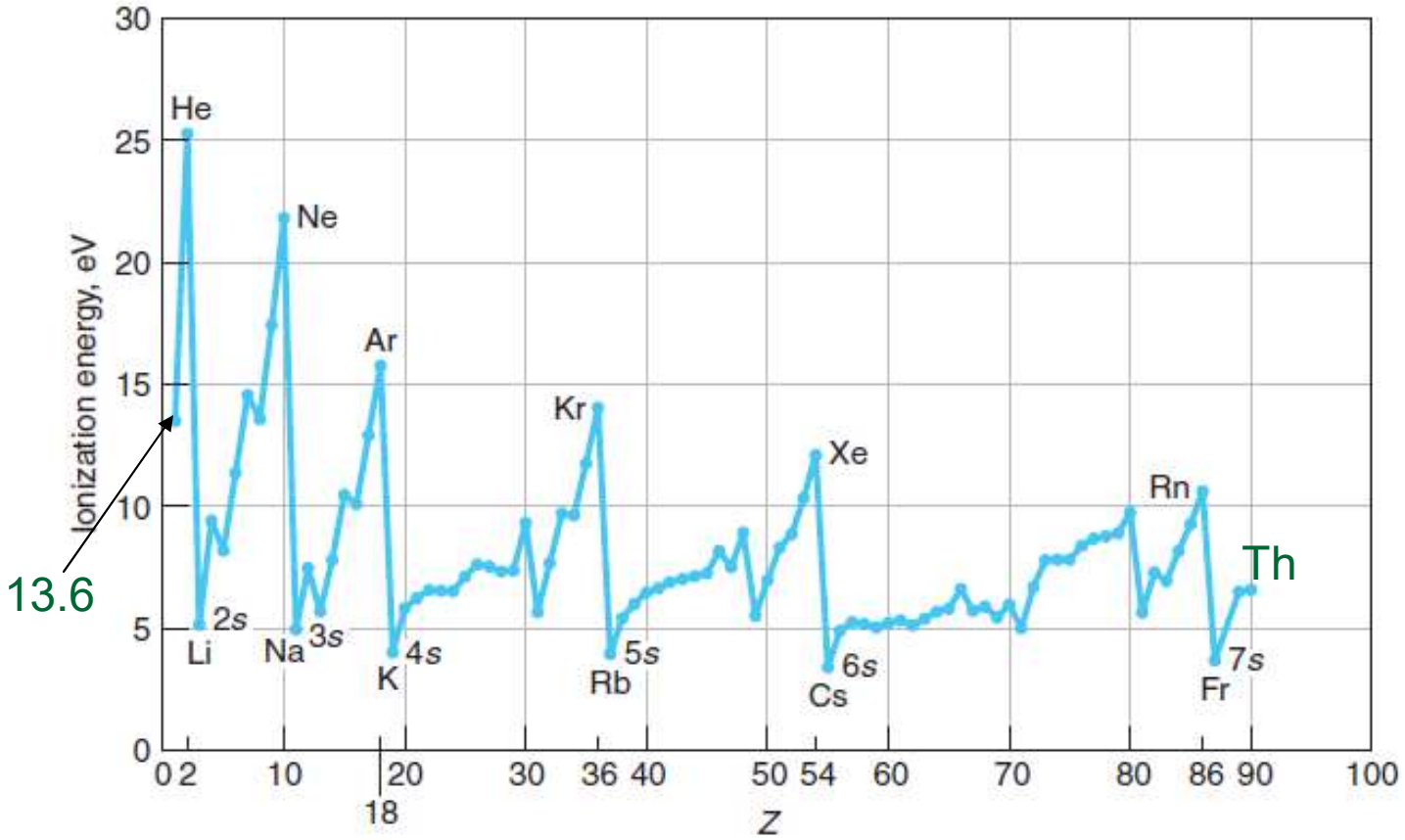
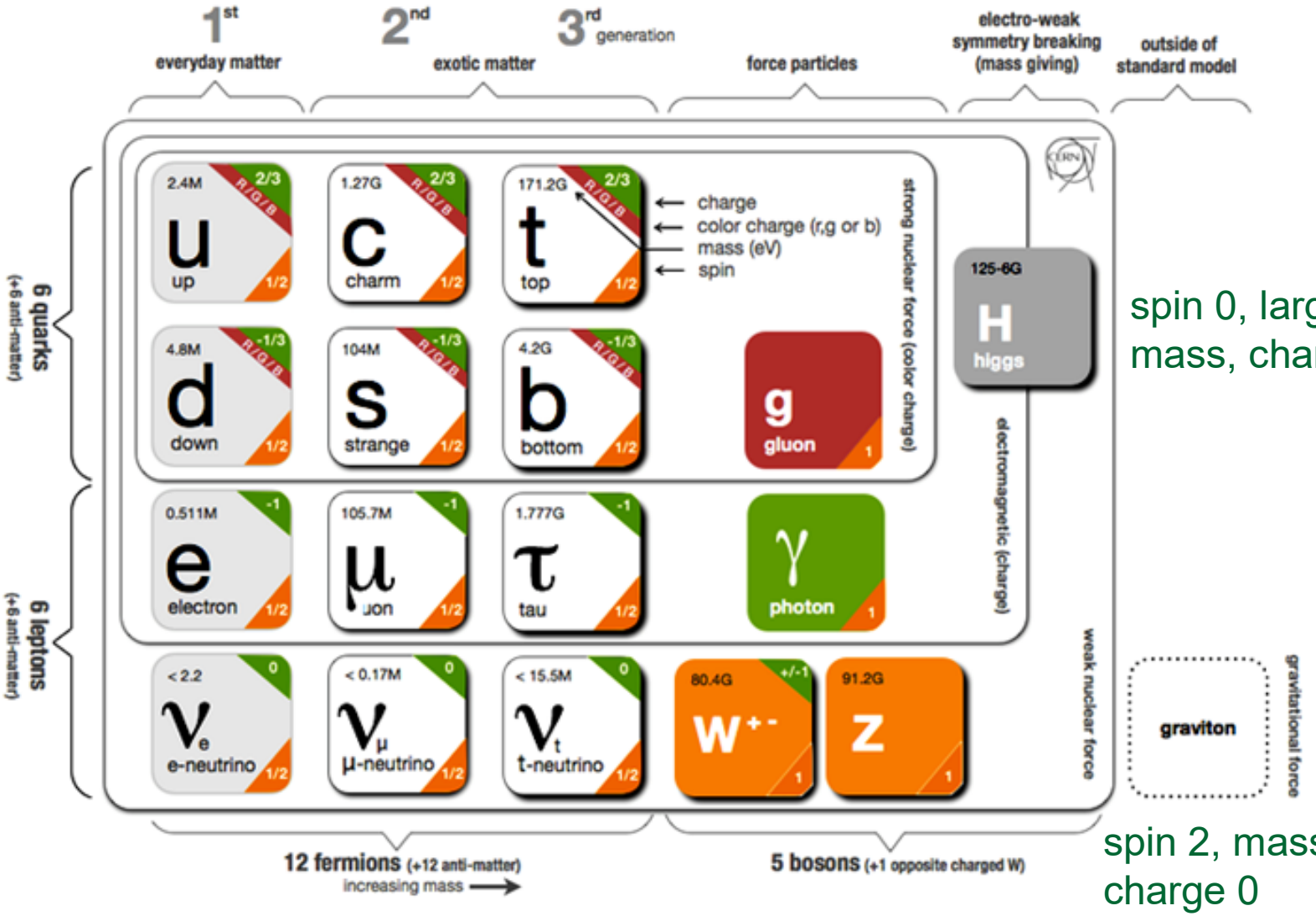


Figure 7-20 First ionization energy vs. Z up to $Z = 90$. The energy is the binding energy of the last electron in the atom. This energy increases with Z until a shell is closed at Z values of 2, 10, 18, 36, 54, and 86. The next electron must go into the next higher shell and hence is farther from the center of core charge and thus less tightly bound. The ionization potential (in volts) is numerically equal to the ionization energy (in eV).

Fermions have spin ½



spin 0, large mass, charge 0

spin 2, mass 0, charge 0

proton: two up one down quark, spin ½
neutron: one up two down quark, spin ½

Bosons have integer spin, 0, 1, 2