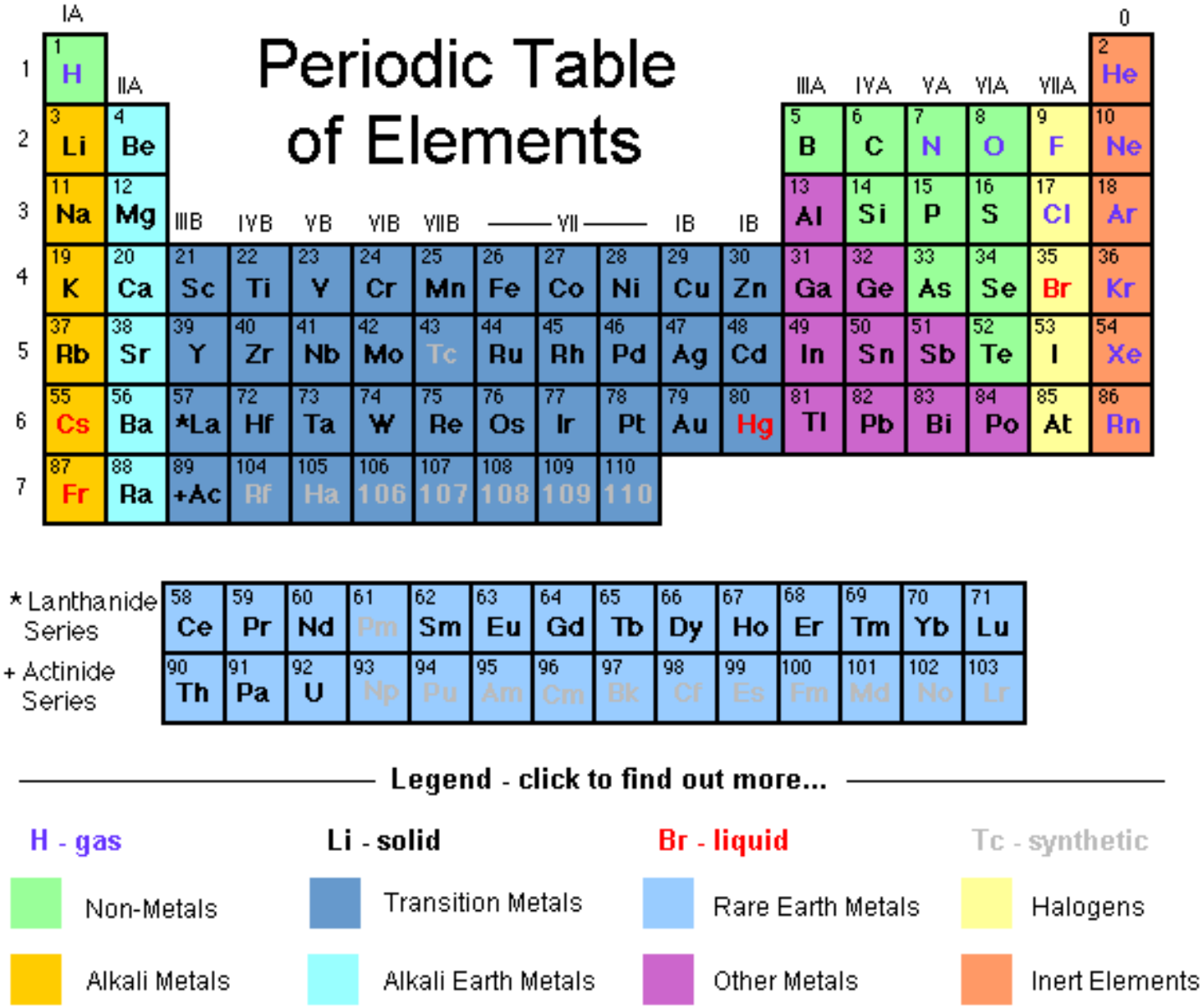
The periodic system of the elements

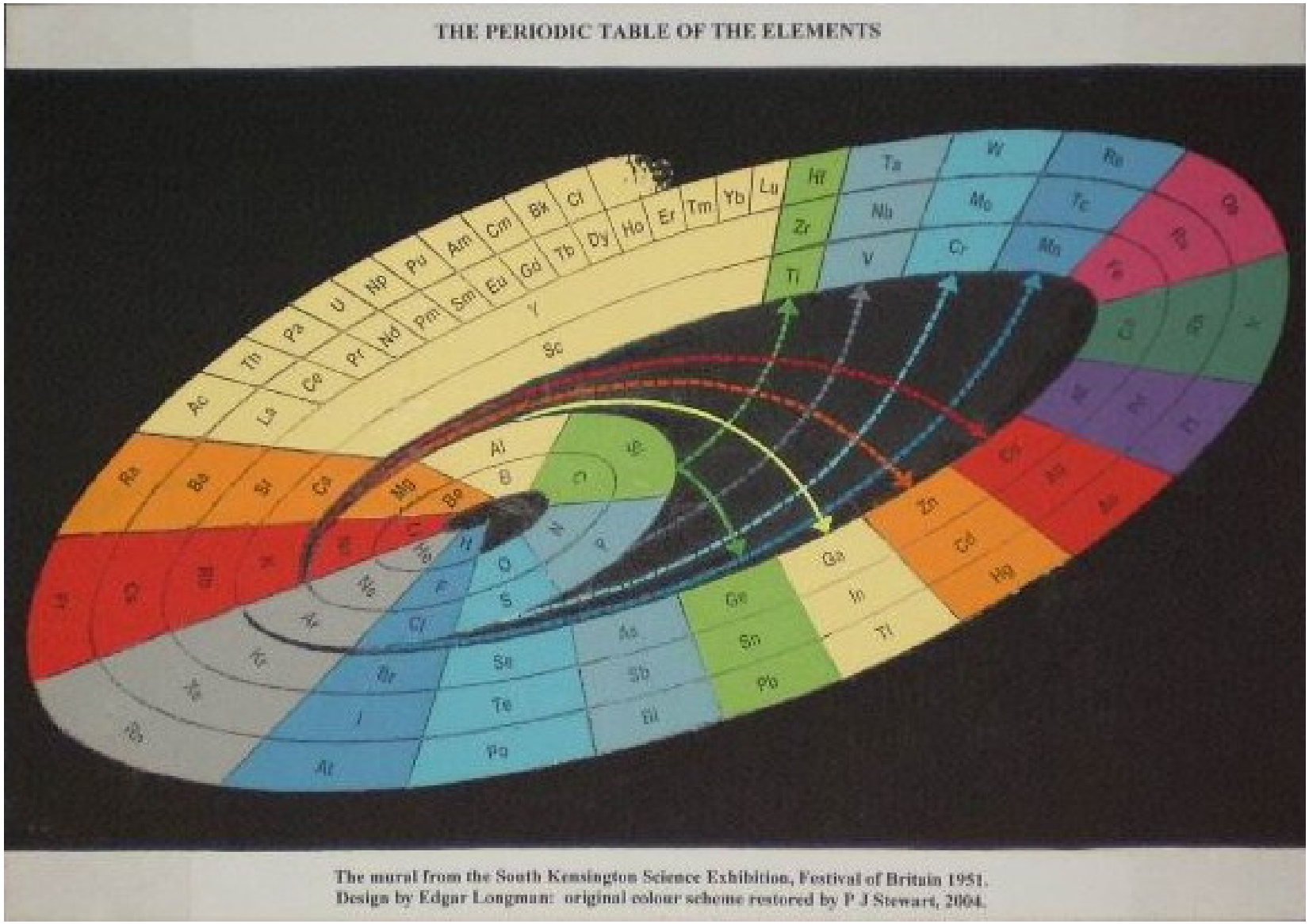
- Study of over 100 elements – daunting task!
- Nature has “provided” the periodic table
- Enables us to correlate an enormous amount of information

Predict

(rather than passively learn)

Chemical Properties !


Periodic Table of Elements
IA
IIA
IIIB
IVB
VB
VIB
VIIB
VII
IB
IB
IIIA
IVA
VA
VIA
VIIA
0
1 H
2 He
3 Li
4 Be
5 B
6 C
7 N
8 O
9 F
10 Ne
11 Na
12 Mg
13 Al
14 Si
15 P
16 S
17 Cl
18 Ar
19 K
20 Ca
21 Sc
22 Ti
23 V
24 Cr
25 Mn
26 Fe
27 Co
28 Ni
29 Cu
30 Zn
31 Ga
32 Ge
33 As
34 Se
35 Br
36 Kr
37 Rb
38 Sr
39 Y
40 Zr
41 Nb
42 Mo
43 Tc
44 Ru
45 Rh
46 Pd
47 Ag
48 Cd
49 In
50 Sn
51 Sb
52 Te
53 I
54 Xe
55 Cs
56 Ba
57 *La
72 Hf
73 Ta
74 W
75 Re
76 Os
77 Ir
78 Pt
79 Au
80 Hg
81 Tl
82 Pb
83 Bi
84 Po
85 At
86 Rn
87 Fr
88 Ra
89 +Ac
104 Rf
105 Ha
106 106
107 107
108 108
109 109
110 110
* Lanthanide Series
+ Actinide Series
58 Ce
59 Pr
60 Nd
61 Pm
62 Sm
63 Eu
64 Gd
65 Tb
66 Dy
67 Ho
68 Er
69 Tm
70 Yb
71 Lu
90 Th
91 Pa
92 U
93 Np
94 Pu
95 Am
96 Cm
97 Bk
98 Cf
99 Es
100 Fm
101 Md
102 No
103 Lr
Legend - click to find out more...
H - gas
Li - solid
Br - liquid
Tc - synthetic
Non-Metals
Transition Metals
Rare Earth Metals
Halogens
Alkali Metals
Alkali Earth Metals
Other Metals
Inert Elements



“the chemical galaxy” alternative scheme

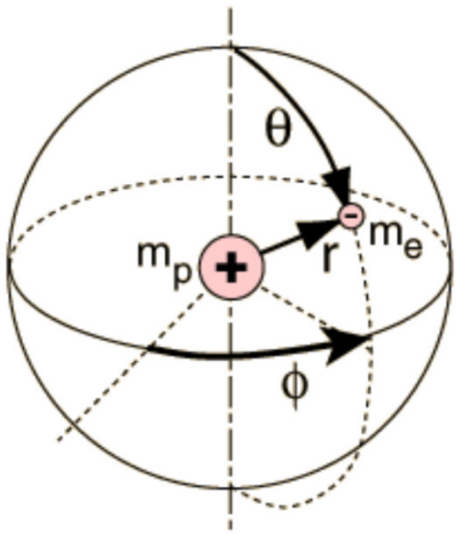
Atomic orbitals

- Schroedinger's wave eqn. *describes one electron systems*, e.g. H, He^{+}, Li^{2+}, where E represents total electronic energy of the wavefunction or orbital ψ

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}+\frac{8\pi^2\mu}{h^2}\left(E+\frac{e^2}{r}\right)\psi=0$$

- Orbitals ***assumed*** to be unchanged for multi-electron atoms
- ***Total electronic energy*** (E) **is governed** ***(or quantized)*** **by four quantum numbers**

1. ***principal (n)*****: dictates orbital energy**
2. ***secondary (l)*****: dictates shape and orientation** *(aka azimuthal or orbital q.n.)*
3. ***magnetic*** (m_l)**: dictates shape and orientation with l**
4. ***spin*** (m_s)**: dictates spin state of the electron**



r	→	n	→	**principal quantum number**
θ	→	l	→	**secondary quantum number**
ϕ	→	m_l	→	**magnetic quantum number**
m_s		→		**spin quantum number**

- In the solution to the Schroedinger equation for the hydrogen atom, ***3 quantum numbers arise from the space geometry of the solution and the 4th arises from electron spin.***
- No two electrons can have an identical set of quantum numbers according to the ***Pauli exclusion principle***, so the ***quantum numbers set limits on the number of electrons which can occupy a given state and therefore give insight into the building up of the periodic table of the elements***.

- ***n*** **can be any whole number from one to infinity; 1, 2, 3,….∞.**
- ***l*** **is limited to 0, 1, 2…(≤** ***n*****-1).**
- m_l **is governed by** ***l*** **(hence the subscript) has the values 0, ±1, ±2,….±*l*.**
- m_s **is limited to + ½ or - ½.**
- **Principal quantum number** ***n*** **written as prefix to** ***l***

  e.g. 1s orbital (*n* = 1; *l* = 0 → s orbital)
- ***l*** **is used as shorthand for labeling orbitals.**

- ***l* is often used as shorthand for labeling orbitals:**

  ***l* = 0 → s orbital** *(sharp)*

  ***l* = 1 → p orbital** *(principal)*

  ***l* = 2 → d orbital** *(diffuse)*

  ***l* = 3 → f orbital** *(fundamental)*

  ***l* = 4 → g orbital**

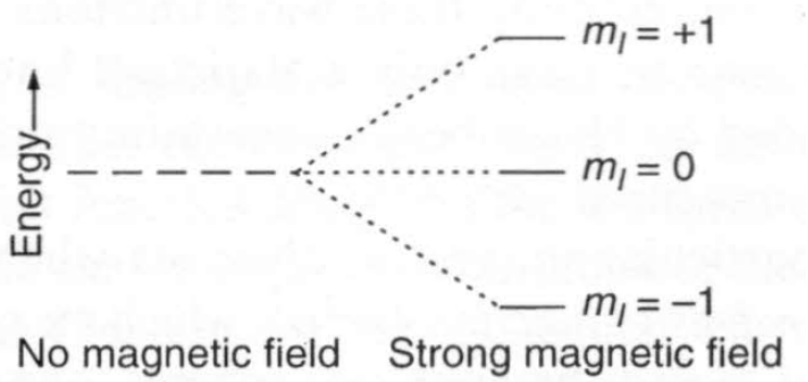
  ***l* = 5 → h orbital**

  ***l* = 6 → i orbital**

  ***l* = 7 → k orbital …l, m, n etc…alphabetically (no j)**

….only s, p, d and f are of chemical significance.

The magnetic quantum number denotes the energy levels available within a subshell



- In the absence of a magnetic field all p orbitals (*l* = 1) are degenerate (equal energy).
- Upon exposure to a magnetic field degeneracy is broken as the ***3 p orbitals are oriented differently in space***.

$l = 0 \rightarrow m_l = 0$

$l = 1 \rightarrow m_l = +1, 0, -1$ (3 p orbitals)

$l = 2 \rightarrow m_l = +2, +1, 0, -1, -2$ (5 d orbitals)…etc.

How many f orbitals exist ?

- ***Example:***

Si : $1s^2\ 2s^2\ 2p^6 3s^2\ 3p^2$

for the $3s^2$ orbital

***n* = 3**

***l* = 0 → s orbital**

$m_l = 0$

for the $3p^2$ orbital

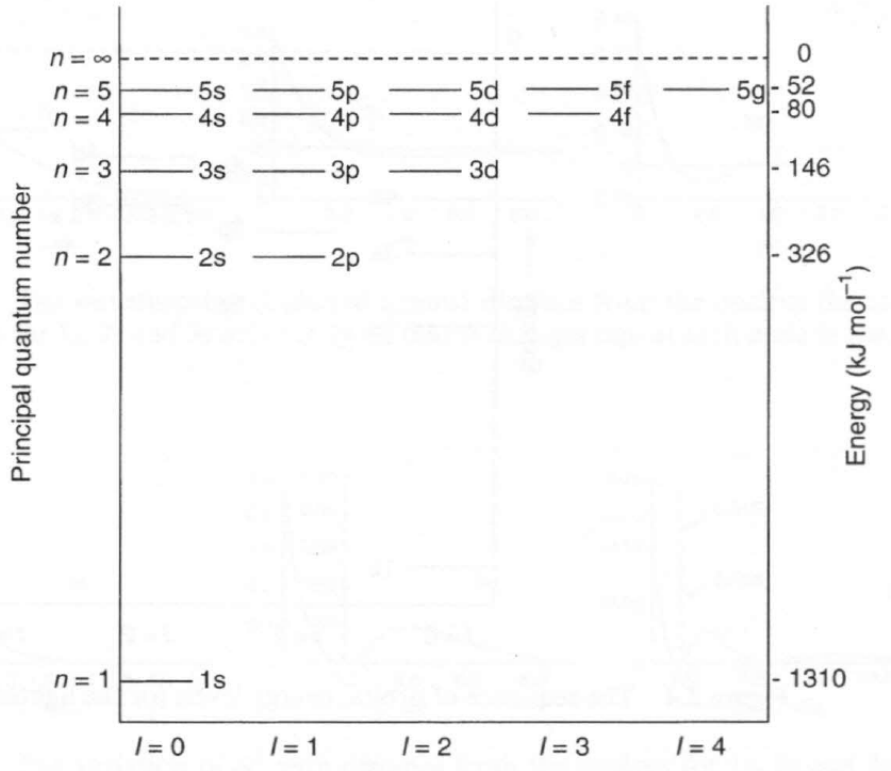
***n* = 3**

***l* = 1 → p orbital**

$m_l = +1, 0, -1$

Which p orbitals are occupied?

H atom energy levels



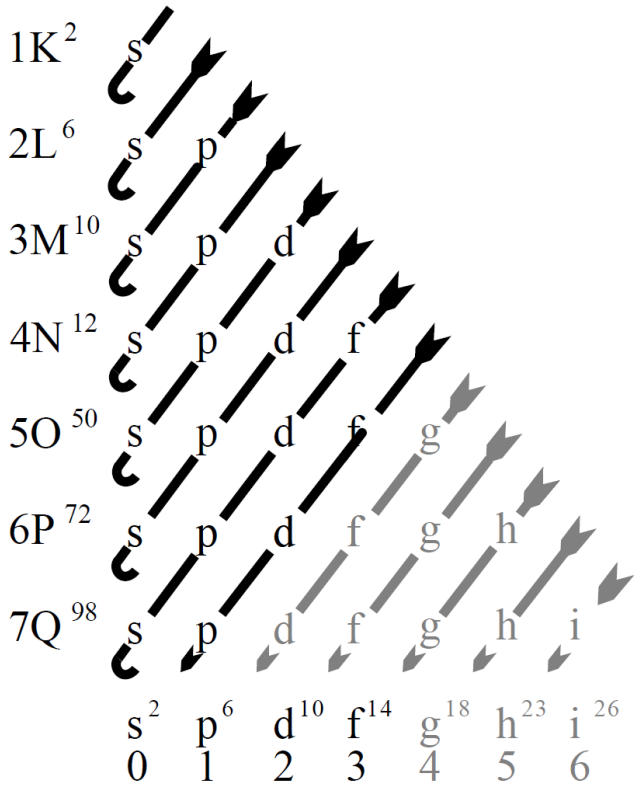
A selection of electronic energy levels in the H atom

- The energy of the *n*th level is equal to $-1310/n^2$ kJmol^{-1}.
- **As *n* increases the orbitals become larger and the electrons are further from the nucleus resulting in a lower electron binding energy *(Coulomb's law)***

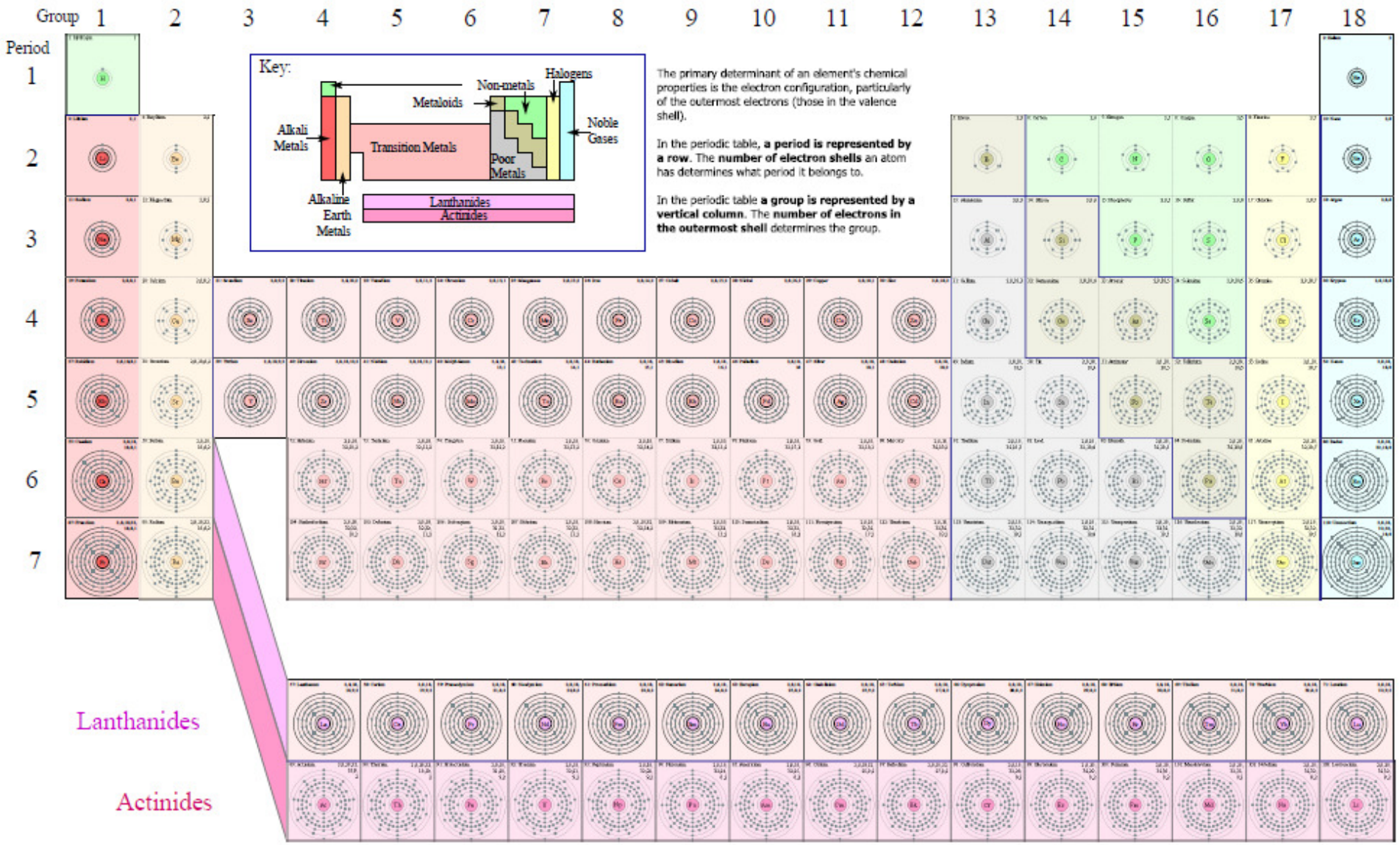
Why are binding energies negative?

Barkla notation

- The existence of electron shells was first observed experimentally via X-ray absorption studies.
- These shells were labeled with the letters *K*, *L*, *M*, *N*, *O*, *P*, and *Q*. The origin of this terminology was alphabetical.
- Still used today for X-ray studies (Siegbahn notation), e.g. EXAFS spectroscopy

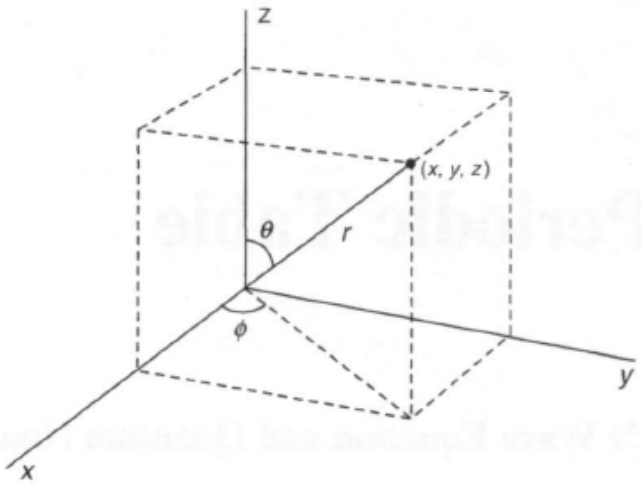


Periodic Table Of Elements Showing Electron Shells



H atom - s orbitals

1. **Spherical in shape, i.e. ψ^2 independent of angular coordinates**
2. The distribution of ψ^2 is not homogeneous for $n > 1$ and has $n - 1$ nodes.
3. Electrons still *penetrate* close to the nucleus for $n > 1$ s orbitals.



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

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

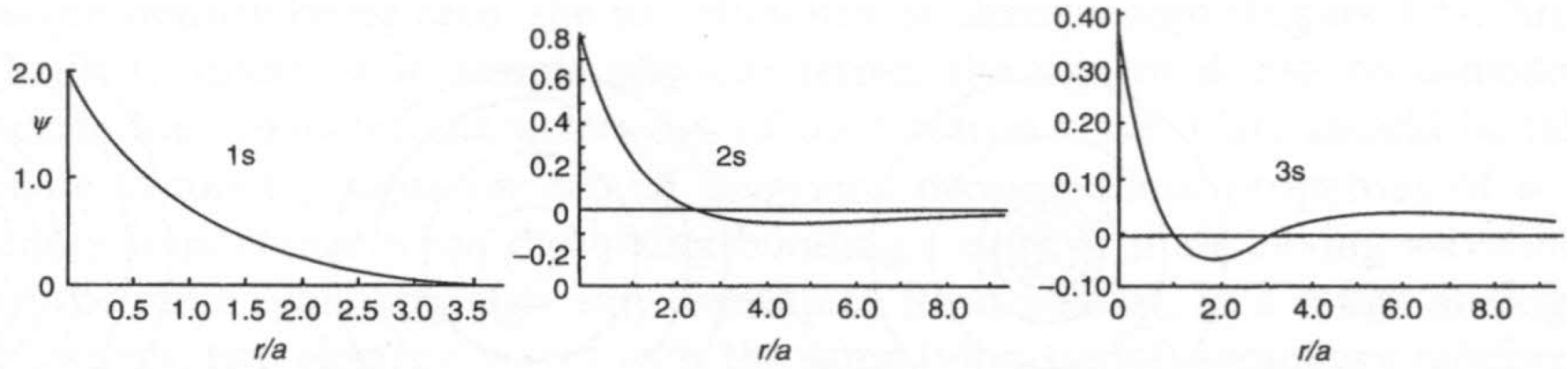
a **= Bohrs radius 0.53 Å**

- Schroedinger and Born suggested that ψ^2 can be used to map atomic orbitals about the nucleus, i.e. **ψ^2 is a measure of electron density**

1. Spherical in shape, i.e. ψ^2 independent of angular coordinates.

2. **The distribution of ψ^2 is not homogeneous for $n > 1$ and has $n - 1$ nodes.**

3. Electrons still *penetrate* close to the nucleus for $n > 1$ s orbitals.

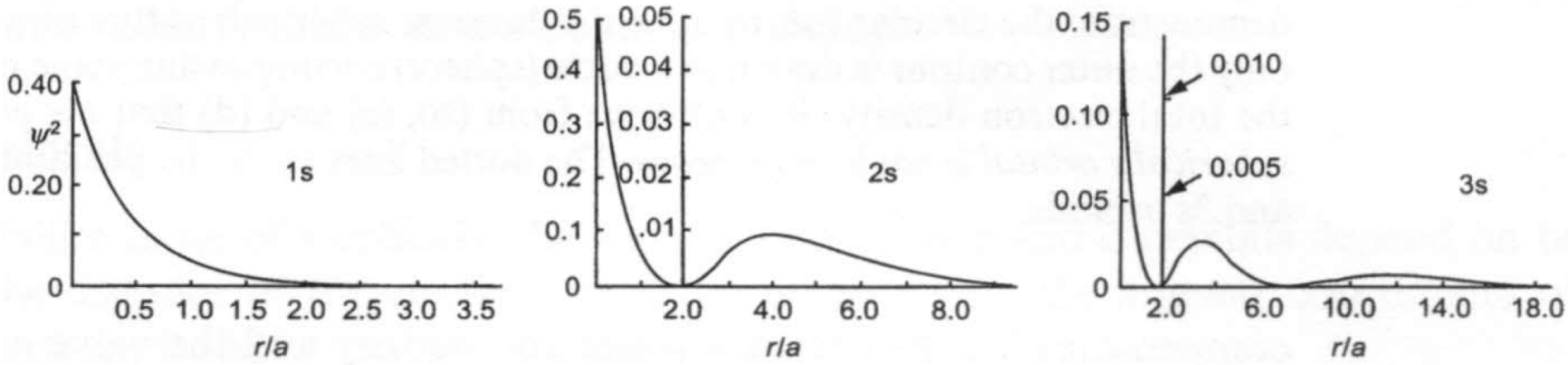


- Plots of **ψ vs. 'distance from the nucleus' (r)** in units of Bohr radius (**a**) for 1s, 2s and 3s orbitals.
- The phase of ψ changes sign where it crosses over ψ = 0 (**node**)

1. Spherical in shape, i.e. ψ^2 independent of angular coordinates.

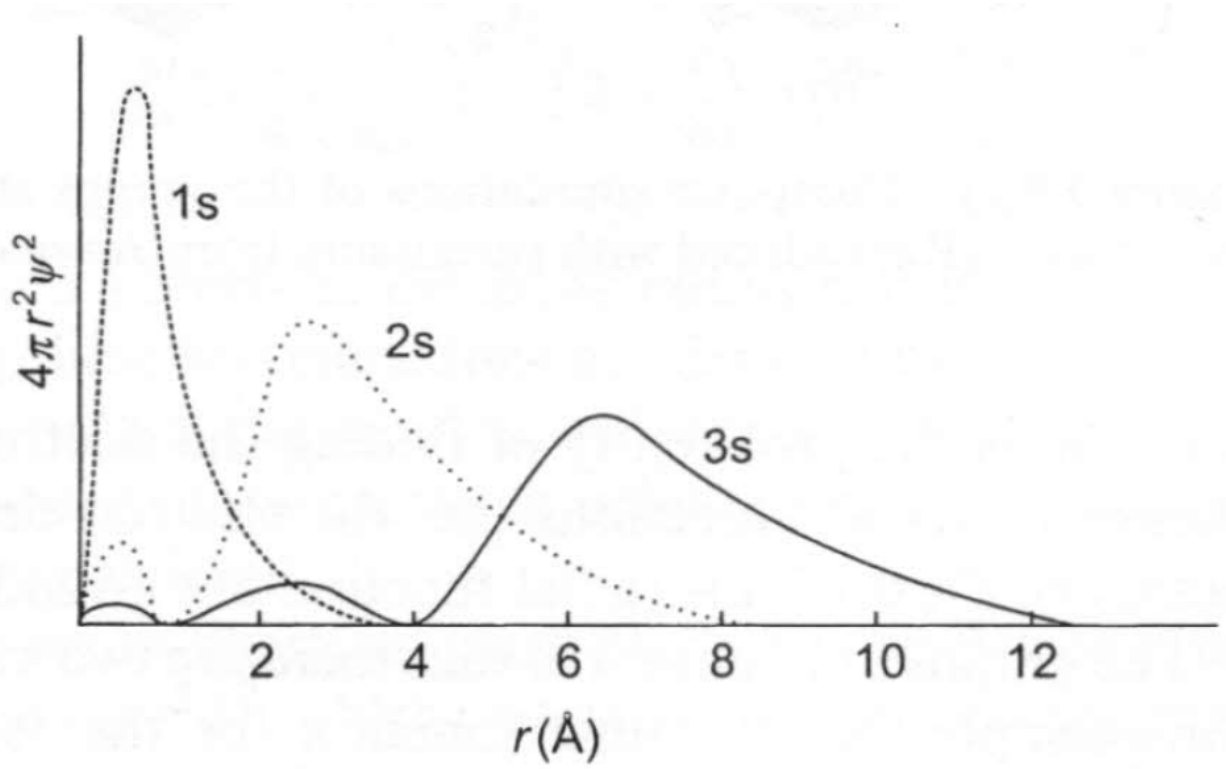
2. The distribution of ψ^2 is not homogeneous for $n > 1$ and has $n - 1$ nodes.

3. **Electrons still *penetrate* close to the nucleus for $n > 1$ s orbitals.**



Plot of ψ^2 vs *r* for the 1s, 2s and 3s orbitals

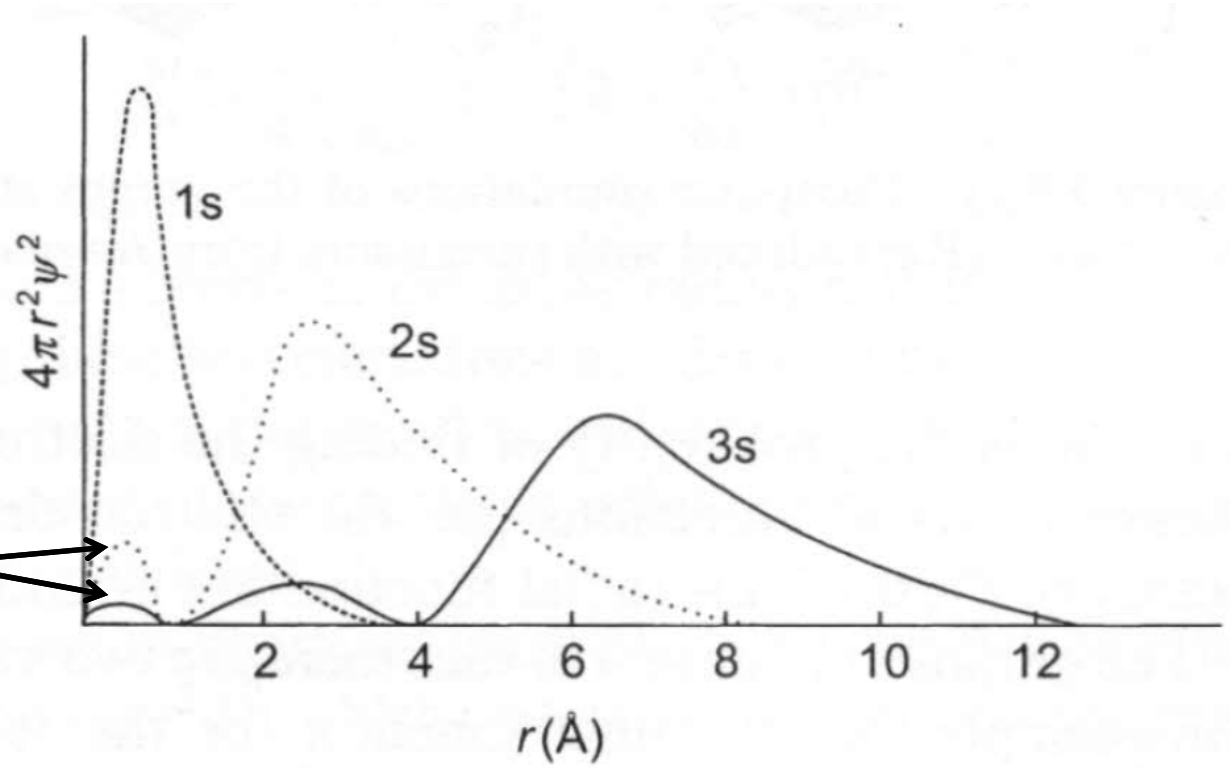
- **ψ^2 represents the electron density, i.e. the probability of finding an electron, at distance r from the nucleus in a particular direction.**
- There is a high electron density at, and close to, the nucleus for all s orbitals. This sharply decreases as r increases (hence second y-axis in plots of 2s and 3s).
- In contrast **ψ^2 is zero at the nucleus for both p, d and f orbitals**.



Plot of radial electron density functions for the 1s, 2s and 3s orbitals of the H atom

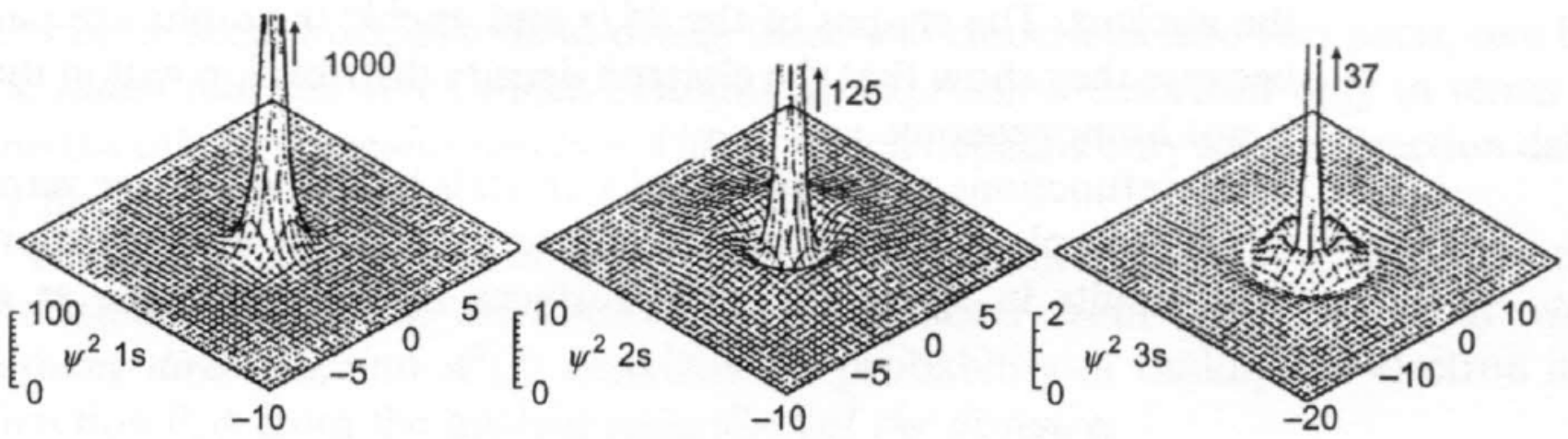
- **The *radial electron density function* is a measure of the electron density ψ^2 at distance *r* from the nucleus within the volume $4\pi r^2$**
- **Maximum radial electron density for 1s occurs at the Bohr radius, r =0.53 Å.**

Note penetration effect of 2s and 3s orbitals

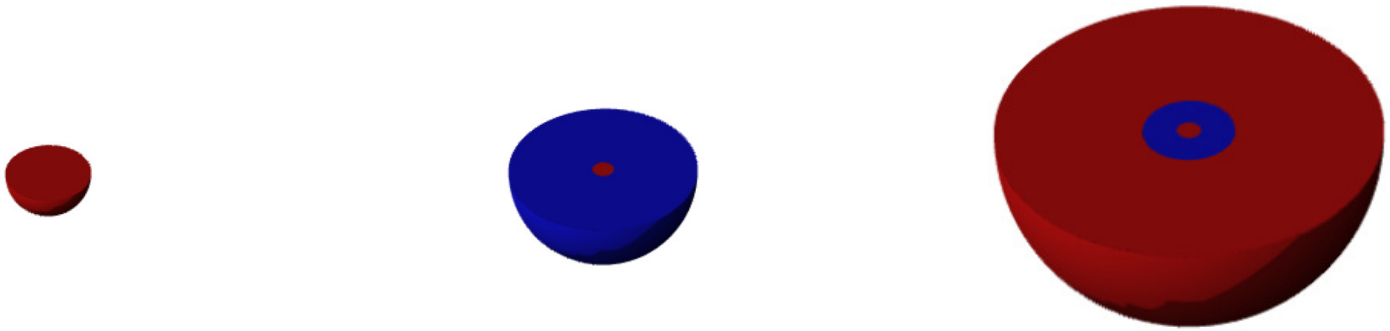


Plot of radial electron density functions for the 1s, 2s and 3s orbitals of the H atom

- The *radial electron density function* is a measure of the electron density ψ^2 at distance *r* from the nucleus within the volume $4\pi r^2$ <u>in all directions</u>
- Maximum radial electron density for 1s occurs at the Bohr radius, r =0.53 Å.

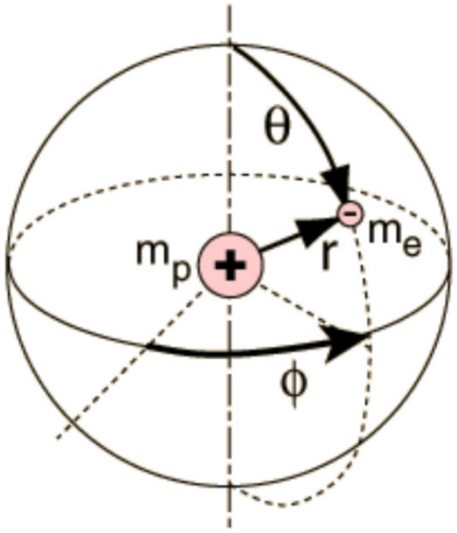


3-D representations of the radial electron density functions of the 1s, 2s and 3s orbitals for the H atom.



H atom - p and d orbitals

- Unlike s orbitals, ψ for orbitals with l > 0 (p, d, f etc.) depends on both distance (r) and angular coordinates (θ, ϕ) of the electron.



r → n → principal quantum number
θ → l → secondary quantum number
ϕ → m_l → magnetic quantum number

m_s → spin quantum number

- **Unlike s orbitals, ψ for orbitals with l > 0 (p, d, f etc.) depends on both distance (*r*) and angular coordinates (θ, ϕ) of the electron.**

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

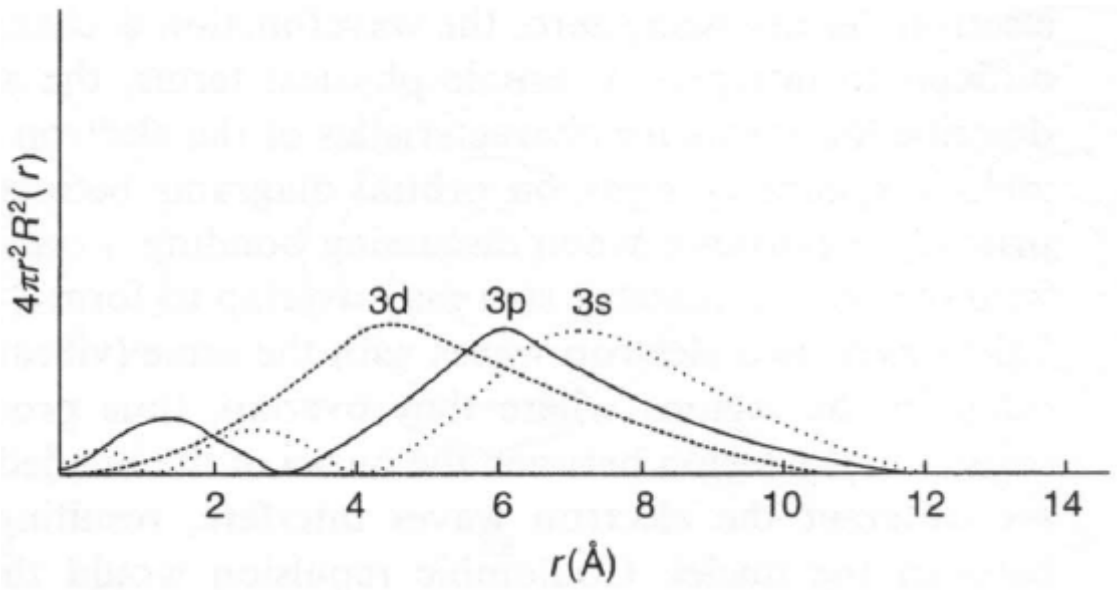
$$\psi_{2s} = \frac{1}{4}\left(\frac{1}{\pi a^3}\right)^{1/2} \left(2 - \frac{r}{a}\right) \exp\left(-\frac{r}{2a}\right)$$

No angular component

$$\psi_{2p_z} = \frac{1}{4}\left(\frac{1}{2\pi a^3}\right)^{1/2} \left[\frac{r}{a} \exp\left(-\frac{r}{2a}\right)\right] (\cos\theta)$$

$$\psi_{3d_{xy}} = \frac{1}{81}\left(\frac{1}{2\pi a^3}\right)^{1/2} \left[\left(\frac{r}{a}\right) \exp\left(-\frac{r}{3a}\right)\right] (\sin^2\theta \sin 2\phi)$$

$$\text{wavefunction} = (\text{a constant}) \times (\text{a radial part}) \times (\text{an angular part})$$



Plot of *radial electron distribution function vs. distance (r)* for 3s, 3p and 3d orbitals of the H atom.

- **p and d orbitals are more diffuse than s orbitals**, therefore less penetrating.
- ***Penetration effect*** for orbitals of the same *n* value:

s > p > d > f

- There are

  n – 1 nodes in an s orbital

  n – 2 nodes in a p orbital

  n – 3 nodes in a d orbital…..for a given principal quantum number n.

- Neither plotting the ***angular function*** *or* the ***radial function*** vs $4\pi r^2 \psi^2$ can represent the whole orbital as in doing so the other component is ignored.

- Typically, the derivative of the angular function is represented in the majority of texts.

	s (l=0)	p (l=1)			d (l=2)					f (l=3)						
	m=0	m=0	m=±1		m=0	m=±1		m=±2		m=0	m=±1		m=±2		m=±3	
	s	p_z	p_x	p_y	d_{z^2}	d_{xz}	d_{yz}	d_{xy}	$d_{x^2-y^2}$	f_{z^3}	f_{xz^2}	f_{yz^2}	f_{xyz}	$f_{z(x^2-y^2)}$	$f_{x(x^2-3y^2)}$	$f_{y(3x^2-y^2)}$
n=1																
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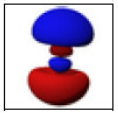
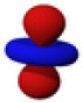
n=3																
n=4																
n=5										...	...	...	...	...	...	...
n=6					...	...	...	...	...	...	...	...	...	...	...	...
n=7		...	...	...	...	...	...	...	...	...	...	...	...	...	...	...

http://en.wikipedia.org/wiki/Atomic_orbital

Multi-electron atoms: s, p and d orbitals

- Consider

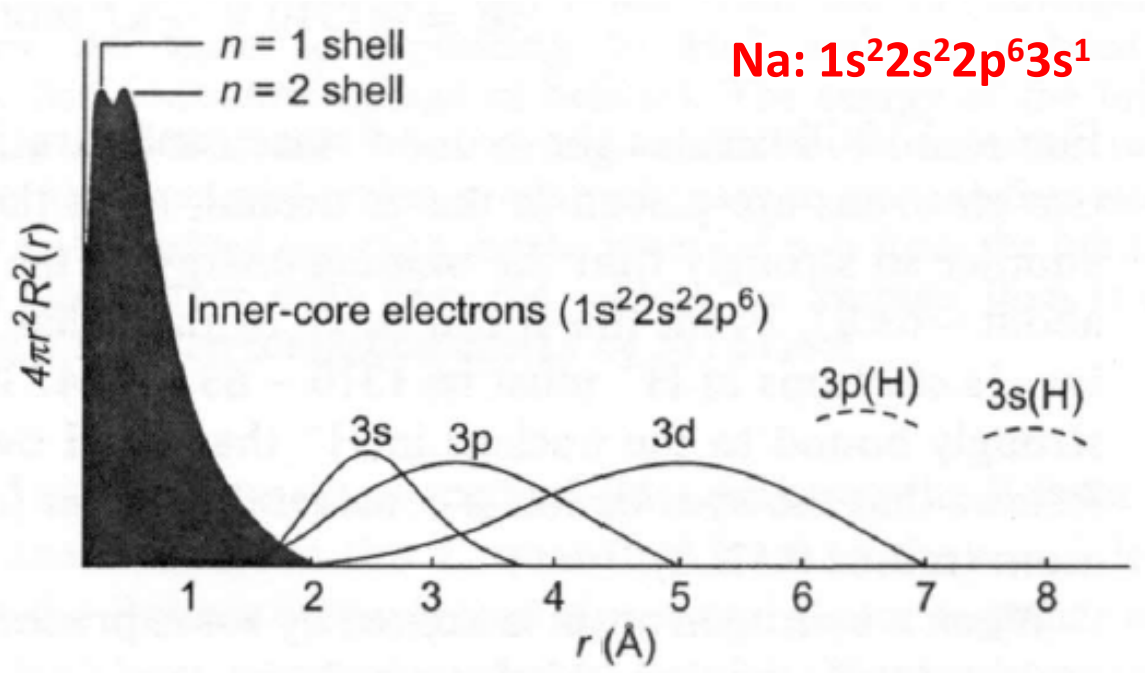
  Na: $1s^2 2s^2 2p^6 3s^1$

- **Inner shell electrons experience greater positive charge (greater attraction) and are held closer to the nucleus**

- In *absence of* this ***penetration effect*** the outermost $3s^1$ electron would experience an attraction from the +11 nuclear charge moderated by the ten inner-shell electrons in the n = 1 and n = 2 shells.

- Thus the ten $1s^2 2s^2 2p^6$ electrons serve to repel the outermost $3s^1$ electron shielding it from the +11 charge such that it experiences an ***effective nuclear charge*** of *ca*. +1

Shielding and penetration effect: *effective nuclear charge*

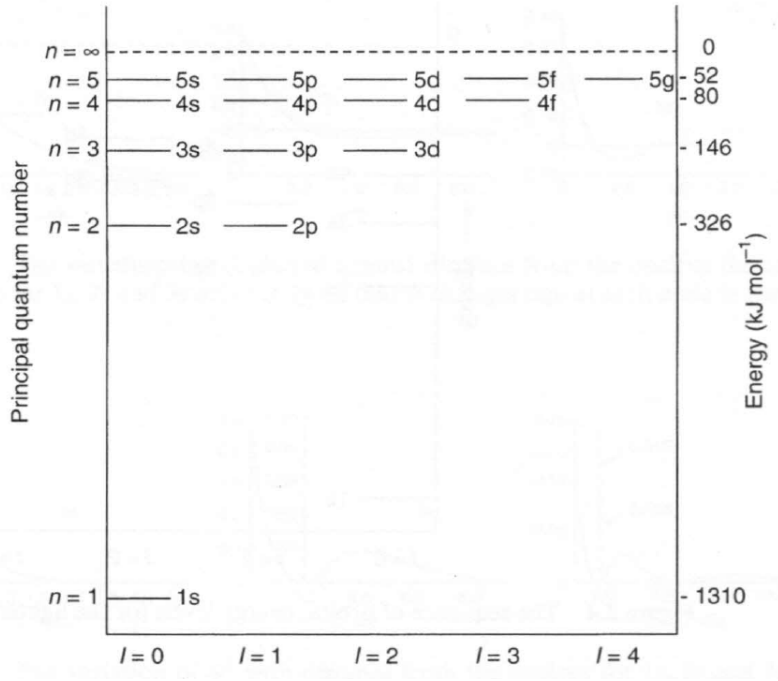


A plot of radial electron density functions for the Na atom

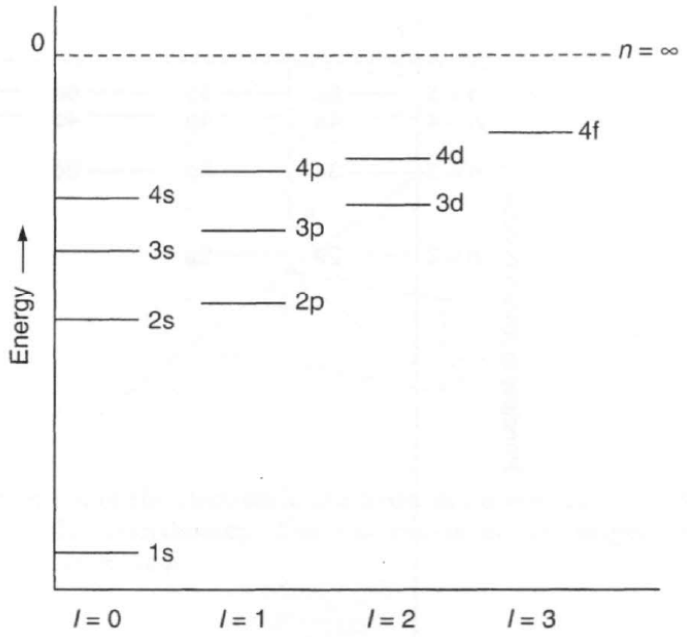
- The smallest orbitals are those bound stronger to the nucleus
- Note the difference in penetration effect for the 3s, 3p and 3d orbitals.
- **Due to penetration an effective nuclear charge of > + 1 is experienced by 3s and 3p**.

Multi-electron atom energy levels

- Effect of the penetration effect on orbital energies for a multi-electronic atom.



A selection of electronic energy levels in the H atom



A generic sequence of orbital energy levels for the lighter elements other than the H atom

Filling up the periodic table

Aufbau principle

- The orbitals of lower energy are filled in first with the electrons and only then the orbitals of high energy are filled
- Madelung rule: electron shells fill up on the order of the quantum number sum '$n + l$'

Pauli exclusion principle

- no two electrons can have the same four quantum numbers, i.e. if n, l, and m_l are the same, m_s must be different such that the electrons have opposite spins

Hunds rule of maximum multiplicity

- For a given electron configuration, the term with maximum multiplicity (2S + 1) has the lowest energy

Aufbau (building-up) principle

The orbitals of lower energy are filled in first with the electrons and only then the orbitals of high energy are filled

- For the H atom there is no energy difference between orbitals with the same principal quantum number *n*.
- This is not true for the outer electrons of other atoms.
- Each added electron is subject to the electric field created by the positive charge of atomic nucleus *and* the negative charge of other electrons that are bound to the nucleus.
- **Orbitals with the highest angular momentum are further from the nucleus, however, orbitals with a low angular momentum (*s*- and *p*-orbitals) have are closer to the nucleus and feel on average a stronger nuclear charge.**
- **This explains why 4*s* orbitals are filled before even 3*d* orbitals**.

- The *aufbau principle* is governed by ***Madelung's rule***:

When considering consecutive neutral atoms the electron shells fill up on the order of the quantum number sum '$n + l$'

For electrons in states of equal '$n + l$' the order of filling goes with increasing n.

- The rule is based on the total number of nodes in the atomic orbital '$n + l$' which is related to the energy.
- This rule is obeyed remarkably well over the whole periodic table.

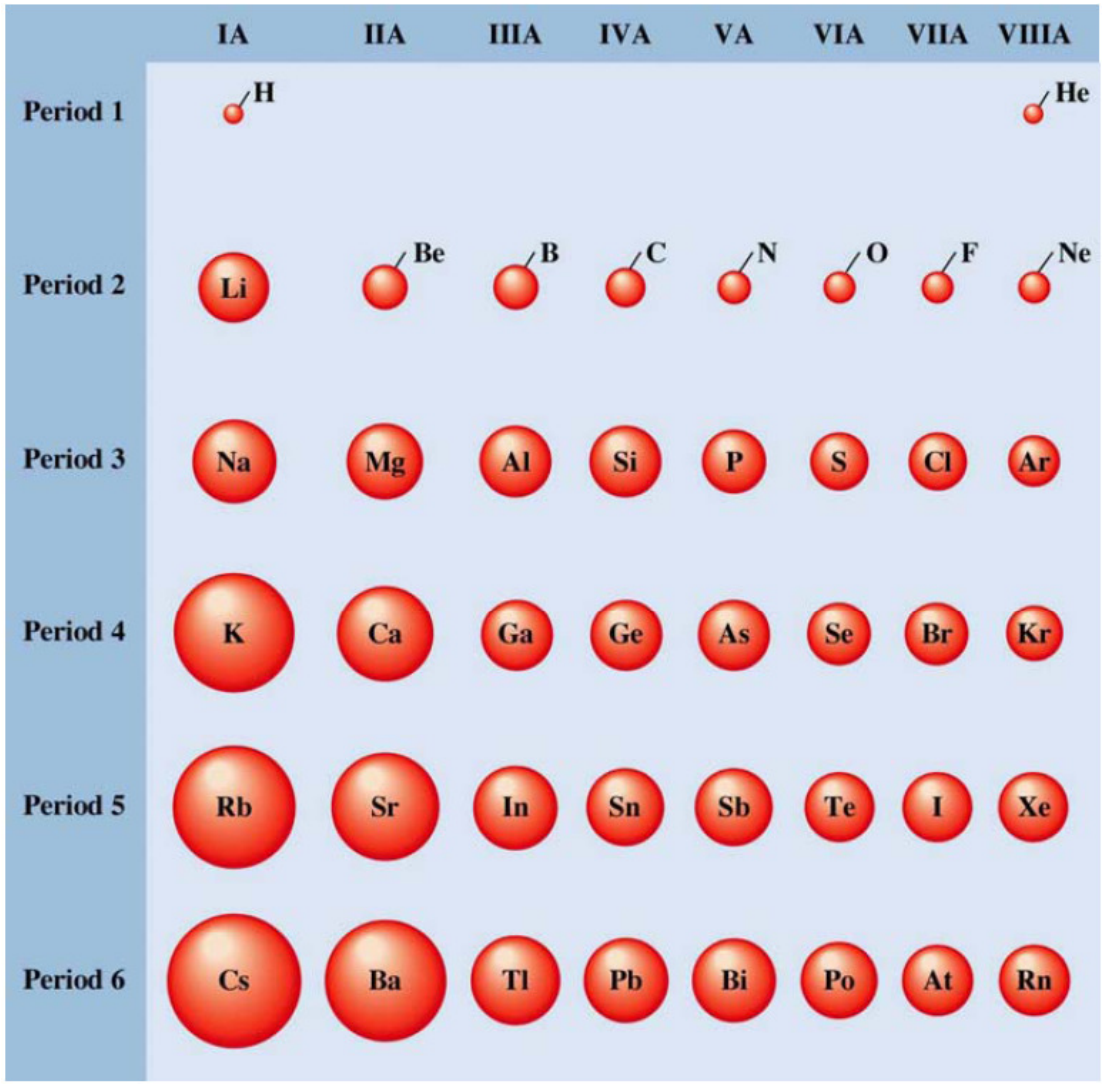
4s '$n + l$' = 4 **vs.** **3d** '$n + l$' = 5

- **4*s* orbitals are filled before 3*d* orbitals**.

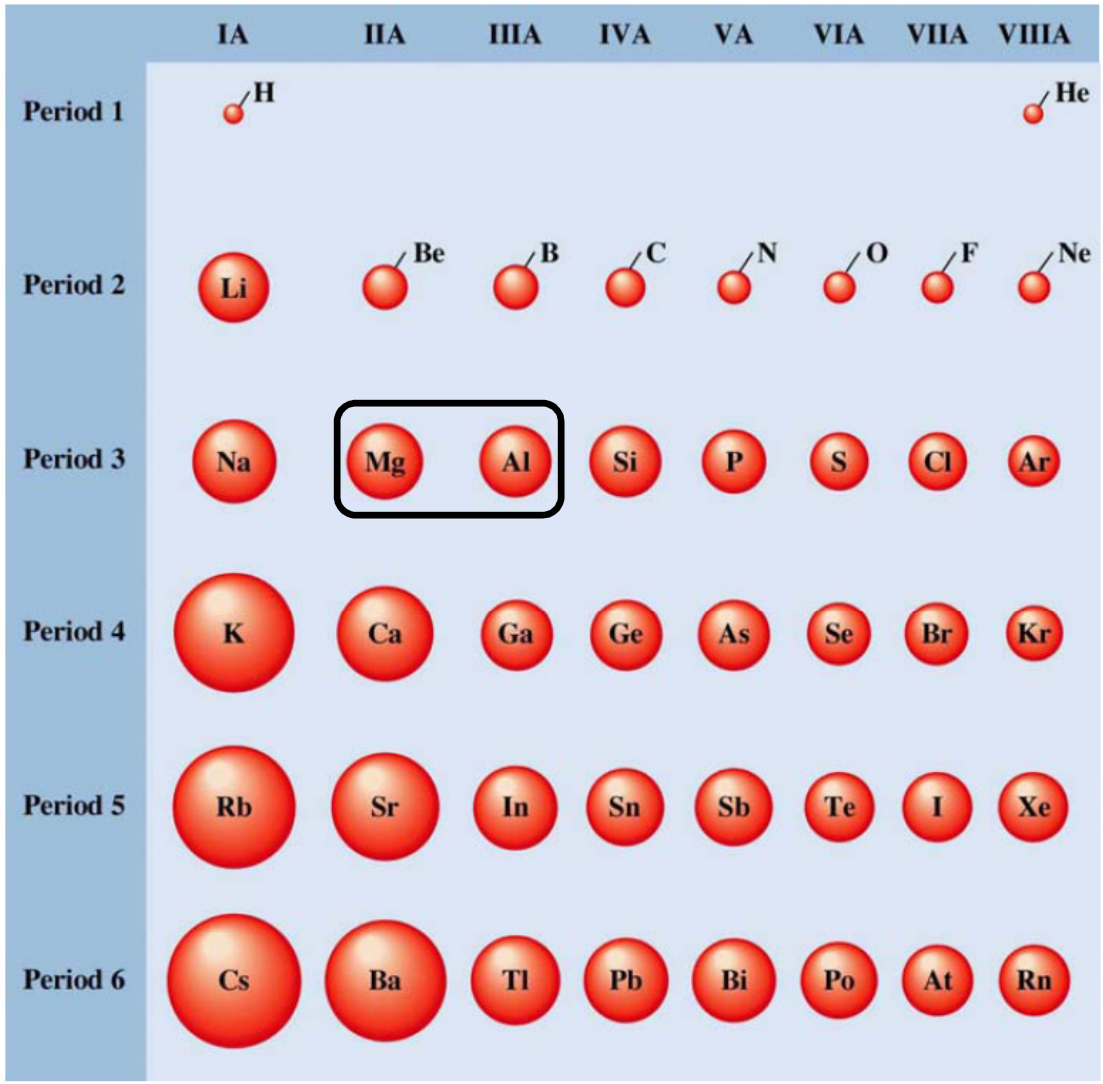
Hunds rule of maximum multiplicity

For a given electron configuration, the term with maximum multiplicity (2S + 1) has the lowest energy

- A greater total spin state (2s + 1) forces the unpaired electrons to reside in different spatial orbitals manifested in a lower energy state,
- The different occupied spatial orbitals decrease the screening of electron-nuclear attractions.
- As a result of Hund's rule, constraints are placed on the way atomic orbitals are filled using the *aufbau principle*. Before any two electrons occupy an orbital in a subshell, other orbitals in the same subshell must first each contain one electron.
- Also, the electrons filling a subshell will have parallel spin before the shell starts filling up with the opposite spin electrons (after the first orbital gains a second electron).



An illustration of the periodic trend in main group atomic radii



An illustration of the periodic trend in main group atomic radii

Molecular orbitals

- In molecules, the situation becomes more complex, as each molecule has a different orbital structure.

- The ***molecular orbitals are labeled according to their symmetry (MO theory)***, rather than the atomic orbital labels used for atoms and monoatomic ions.

- For example, the electron configuration of the dioxygen molecule:

$$\mathbf{O_2 : 1\sigma_g^2\ 1\sigma_u^2\ 2\sigma_g^2\ 2\sigma_u^2\ 1\pi_u^4\ 3\sigma_g^2\ 1\pi_g^{*2}}$$

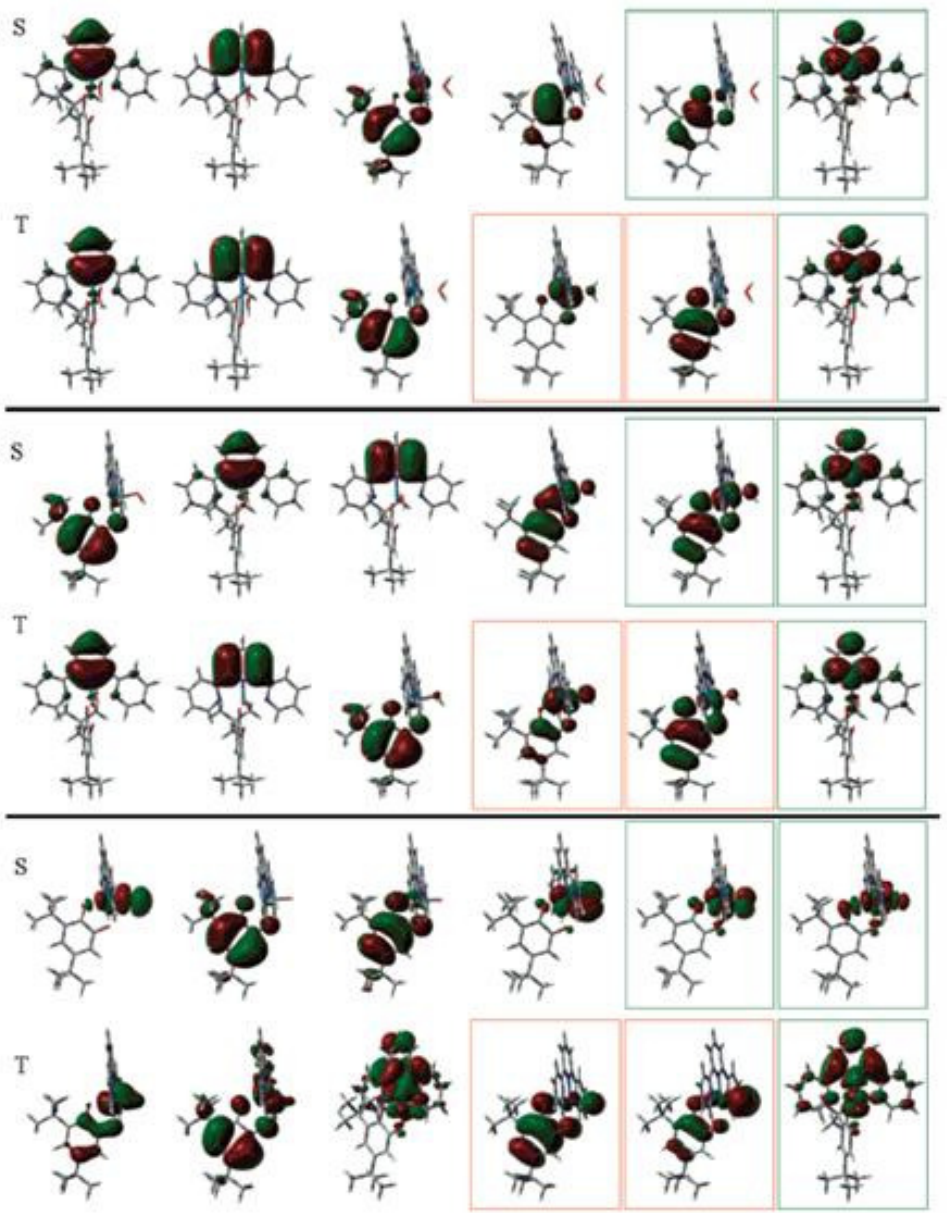
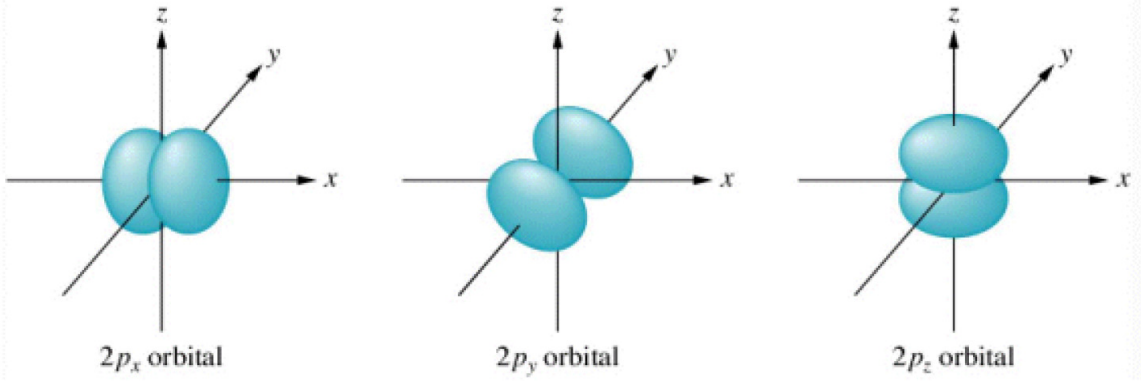
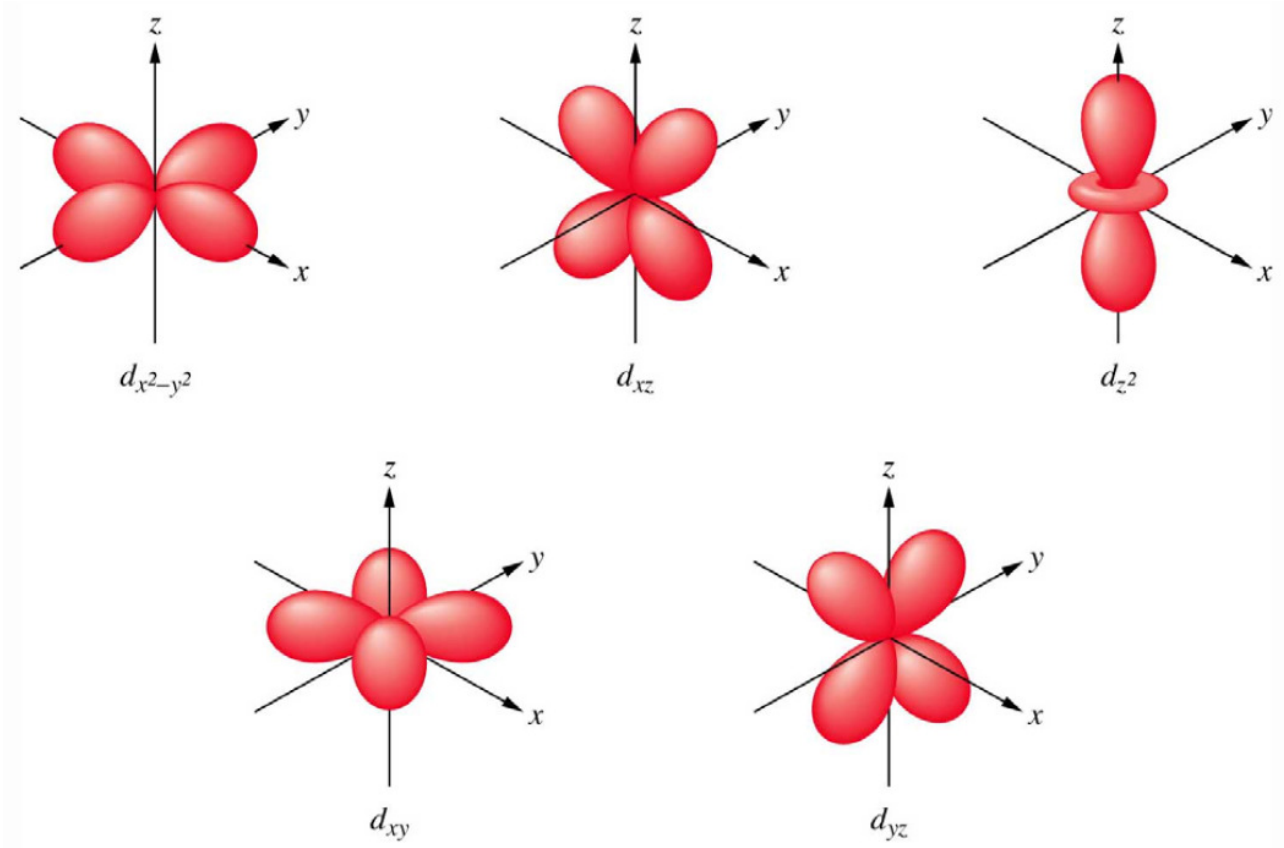


Illustration of the ***molecular orbitals for a transition metal complex*** calculated by density functional theory (DFT) methods.





ψ angular component of the 2p and 3d atomic orbitals for the H atom

Binding energies: the Hydrogen atom

- The solution of the Schroedinger wave equation for a 1e system such as the H atom gives:

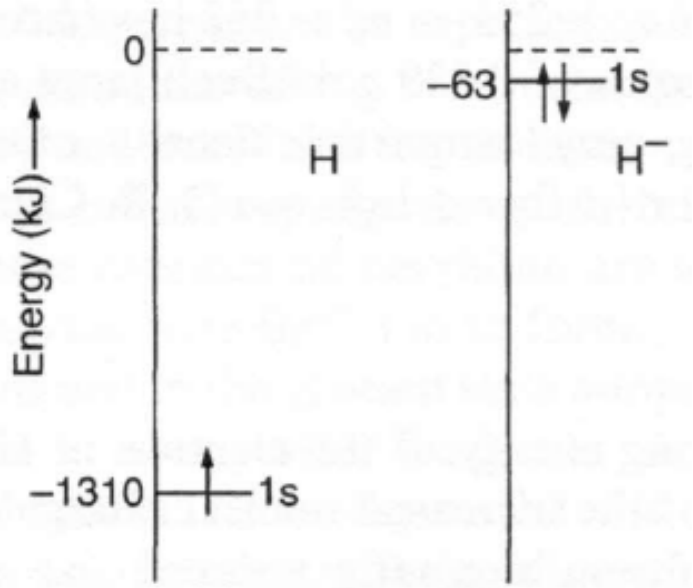
$$E = -\frac{2\pi^2 me^4 Z^2}{h^2} \times \frac{1}{n^2}$$

  - ***e* is the electronic charge**
  - ***Z* is the nuclear charge**
  - ***n* is the principal quantum number**

- Thus for the H atom where $Z = 1$
  the binding energy of the 1s electron = -1310 kJmol^{-1}

$$E = -1310 \times \frac{1}{n^2}\,\mathrm{kJ(mol\ H)^{-1}}$$

Hydrogen vs Hydride



Ground state electronic structures of the H atom and the hydride ion H^-

- **When 2e are place in the H atom, as in H^-, they repel each other so strongly that the binding energy of the electrons falls from -1310 $kJmol^{-1}$ to -63 $kJmol^{-1}$.**
- Thus the repulsion energy of the 2e amounts to 1310 – 63 = 1247 kJ.
- **This repulsion effect increases the size of the atom from 0.53 Å for H to 1.5 Å for H^-.**

Helium Atom

- He is a much smaller atom than H due to the increased nuclear charge.
- Binding energy four times that found for H atom due to increased nuclear charge

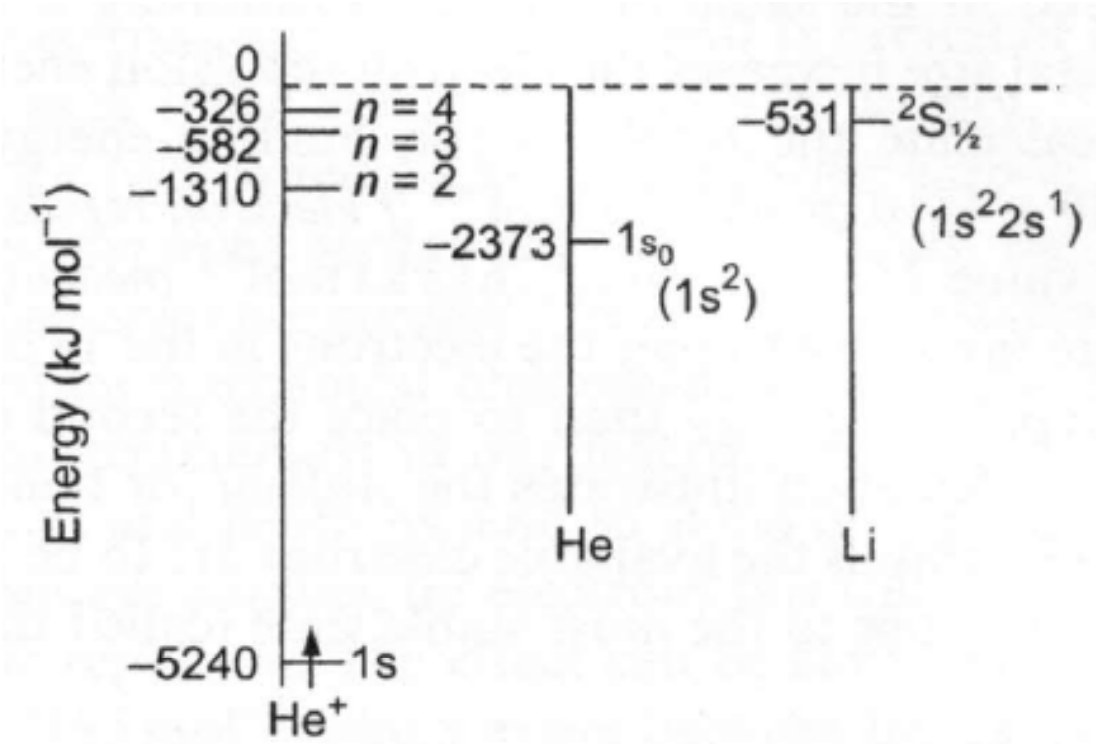
  (Z = 2; *E* = -5240 kJmol^{-1})

- First ionization energy = 2373 kJmol^{-1}
  - ➢ electron-electron repulsion energy = (binding energy – ionization energy)

    = (5240 – 2373) kJmol^{-1} = 2867 kJmol^{-1}

First ionization energies:

H : 1s^1	**H$^-$: 1s^2**	**He : 1s^2**
1310 kJmol^{-1}	**63 kJmol^{-1}**	**2373 kJmol^{-1}**



- Energy level diagrams for He^+, He and Li.
- The **$2s^1$ electron of Li is shielded** (by the inner $1s^2$ electron pair) from the overall nuclear charge (3+) thus it is relatively far from the nucleus in comparison to other 1s electrons found across the periodic table.
- **This gives rise to a low first ionization energy of 531 $kJmol^{-1}$ for Li**.

Ionization potentials and electron affinities

- The ***first ionization energy*** of an atom is the **minimal energy needed to remove the highest energy, outermost electron from the neutral atom** (equals minus the energy of the highest occupied orbital).
- It is *always a positive value, e.g.* +531 kJmol^{-1} for Li
- Trends in ionization potentials:
  - increase with atomic number within a given period
  - follows the trend in size, as it is more difficult to remove an electron that is closer to the nucleus.
  - decrease down the group (for the same reason)
- The ***electron affinity*** **(*E.A.*) *is the energy required to add an electron* to a neutral atom in the gaseous state to form a negative ion**.
- The electron affinity for various elements varies in value, but in general, it follows the same trend as the ionization potential.

First Short Period (#2)

- Li, Be, B, C, N, O, F, Ne

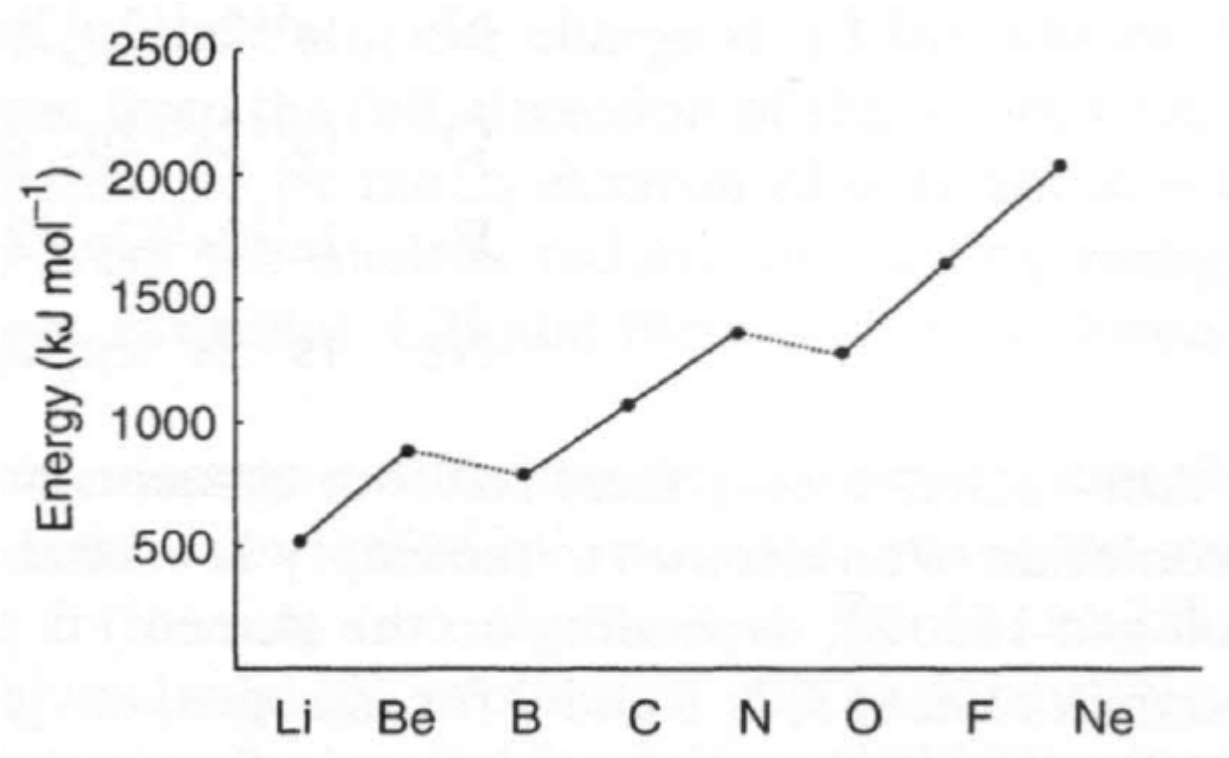
  Li: $1s^2 2s^1$

- Relatively low first ionization energy = 531 $kJmol^{-1}$ therefore Li^+ very common oxidation state, e.g. LiCl, LiOH, BuLi

  Be: $1s^2 2s^2$

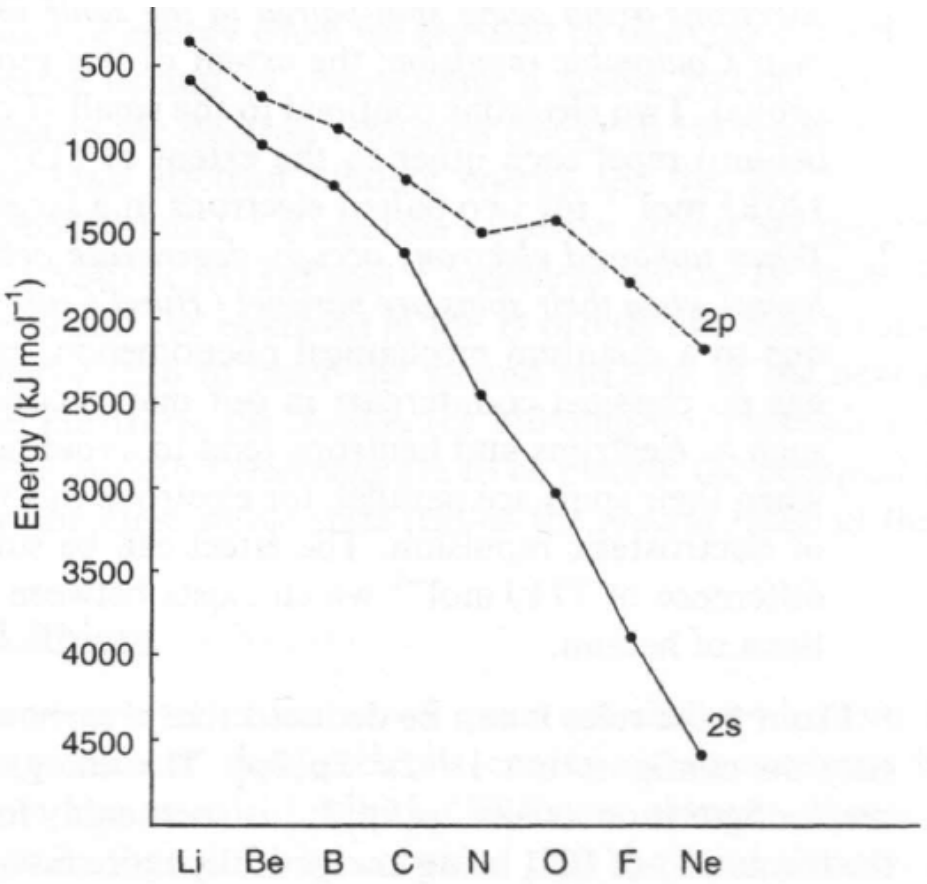
- Outer shell now full thus increased ionization energies. Be^{2+} salts not common.

  (first = 900 $kJmol^{-1}$; second = 1756 $kJmol^{-1}$)



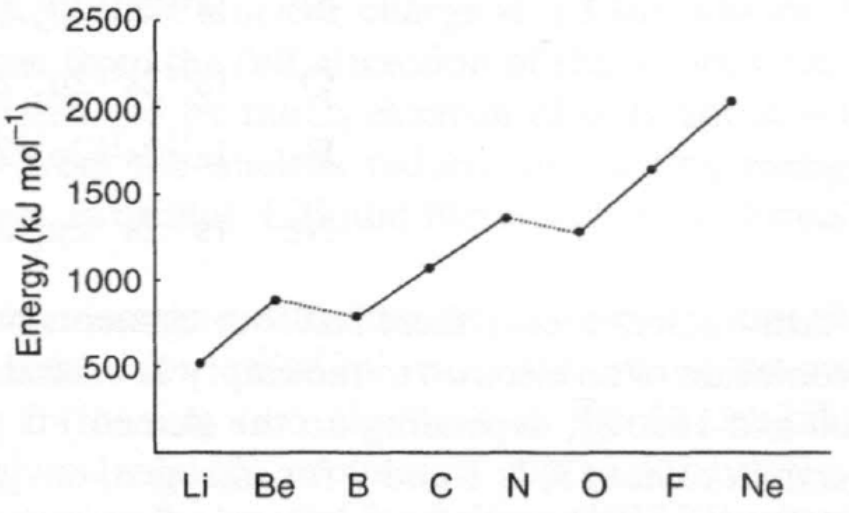
The variation in first ionization energies across the first period

- **Ionization energy increase with atomic number within a given period**

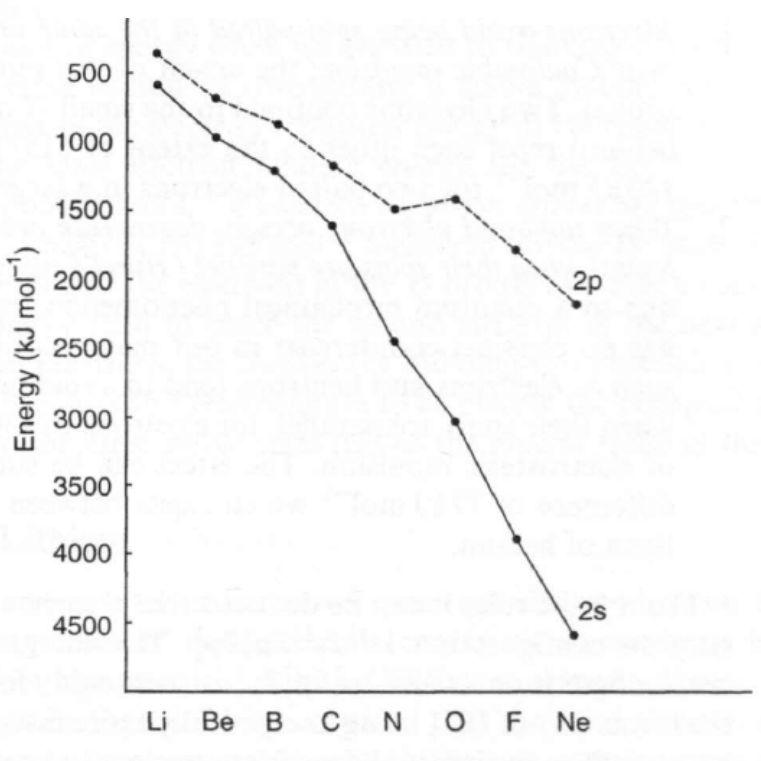


A plot of energy trends of the 2s and 2p orbitals across the first period

- The energy difference between the 2s and 2p orbitals for a given atom gives the magnitude of the 2s ***penetration effect***.
- The 2s orbital becomes more tightly bound to the nucleus as we move from Li to Ne, decreasing in size and ***shielding*** the 2p orbitals from the nuclear charge.



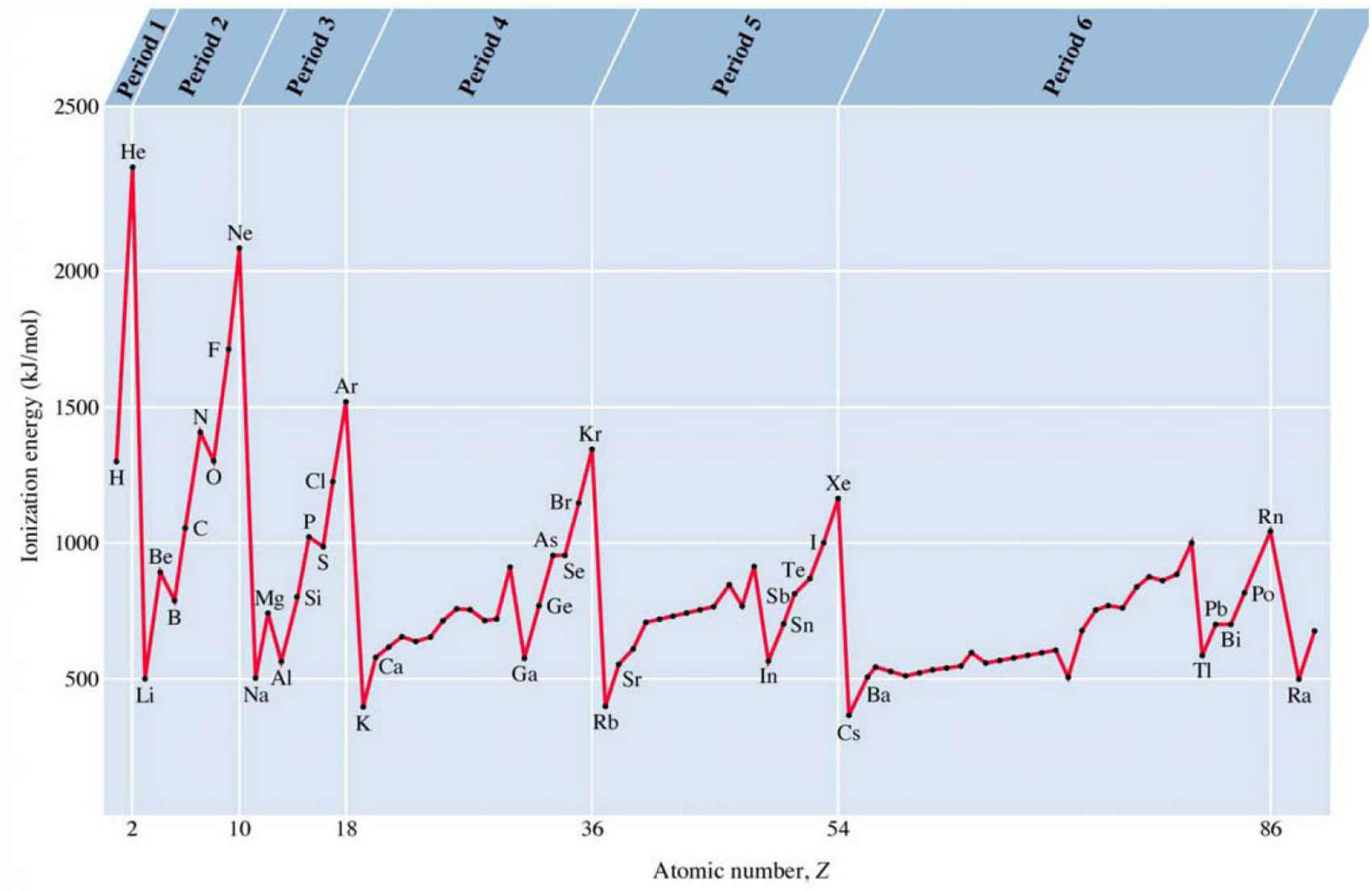
The variation in first ionization energies across the first period



A plot of energy trends of the 2s and 2p orbitals across the first period

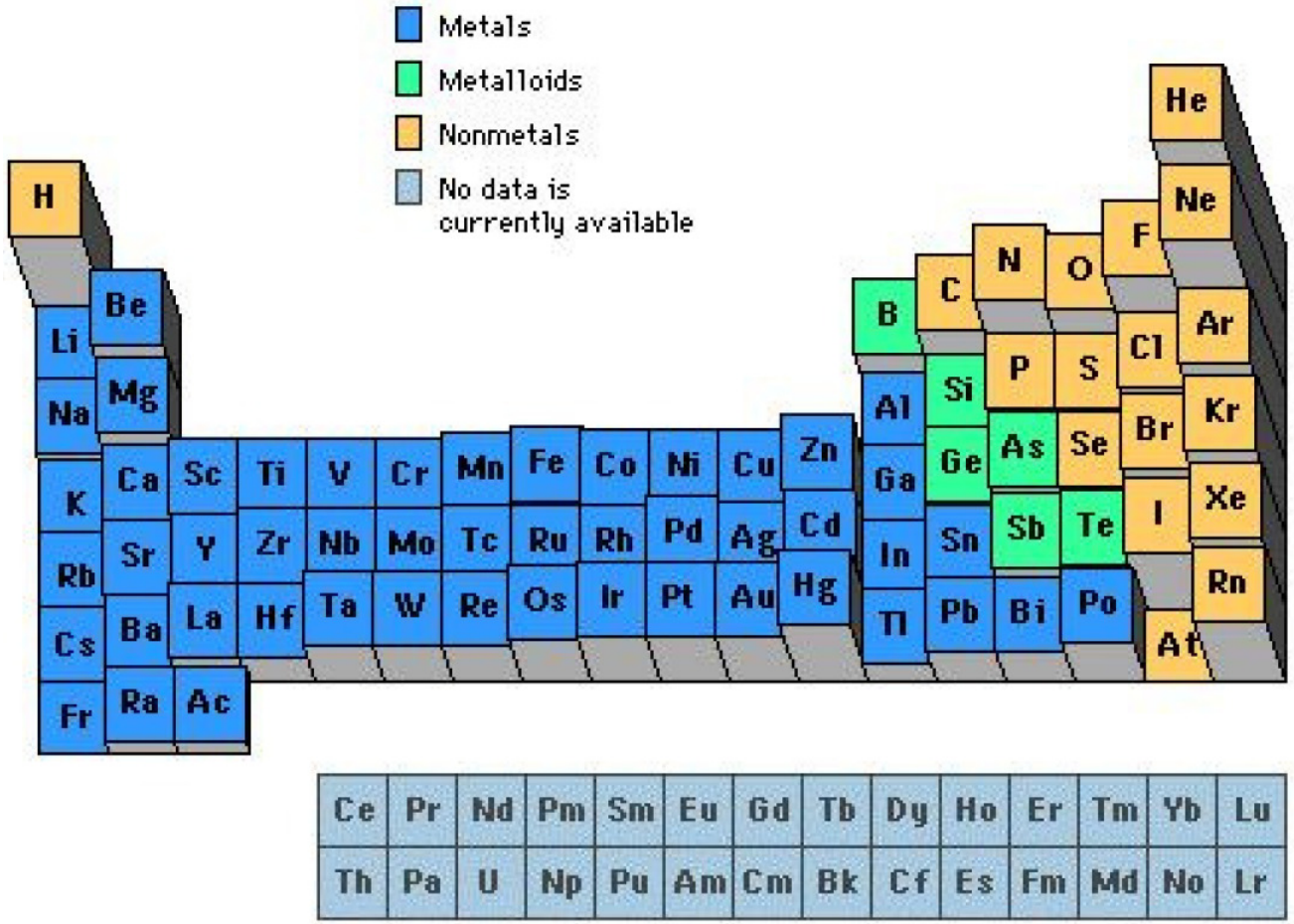
B : $1s^2 2s^2 2p^1$

O :$1s^2 2s^2 2p^4$



- **Ionization energies decrease down a group and increase across a period**

  (metals have higher ionization energies than non-metals)



- **Ionization energies decrease down a group and increase across a period**

  (metals have higher ionization energies than non-metals)

Inert pair effect

"large amount of energy required to remove ns^2 electrons"

Second ionization of lithium > 7000 $kJmol^{-1}$!!

Second Short Period (#3)

- After filling the *n* = 2 shell at Ne, the next element Na begins to fills the *n* = 3 shell. The next seven elements complete the 3s and 3p orbitals in a regular manner following the rules adopted for the *n* = 2 shell:

Na: $1s^2 2s^2 2p^6 3s^{\uparrow}$

Mg: $1s^2 2s^2 2p^6 3s^{\uparrow\downarrow}$

Al: $1s^2 2s^2 2p^6 3s^{\uparrow\downarrow} 3p_x^{\uparrow}$

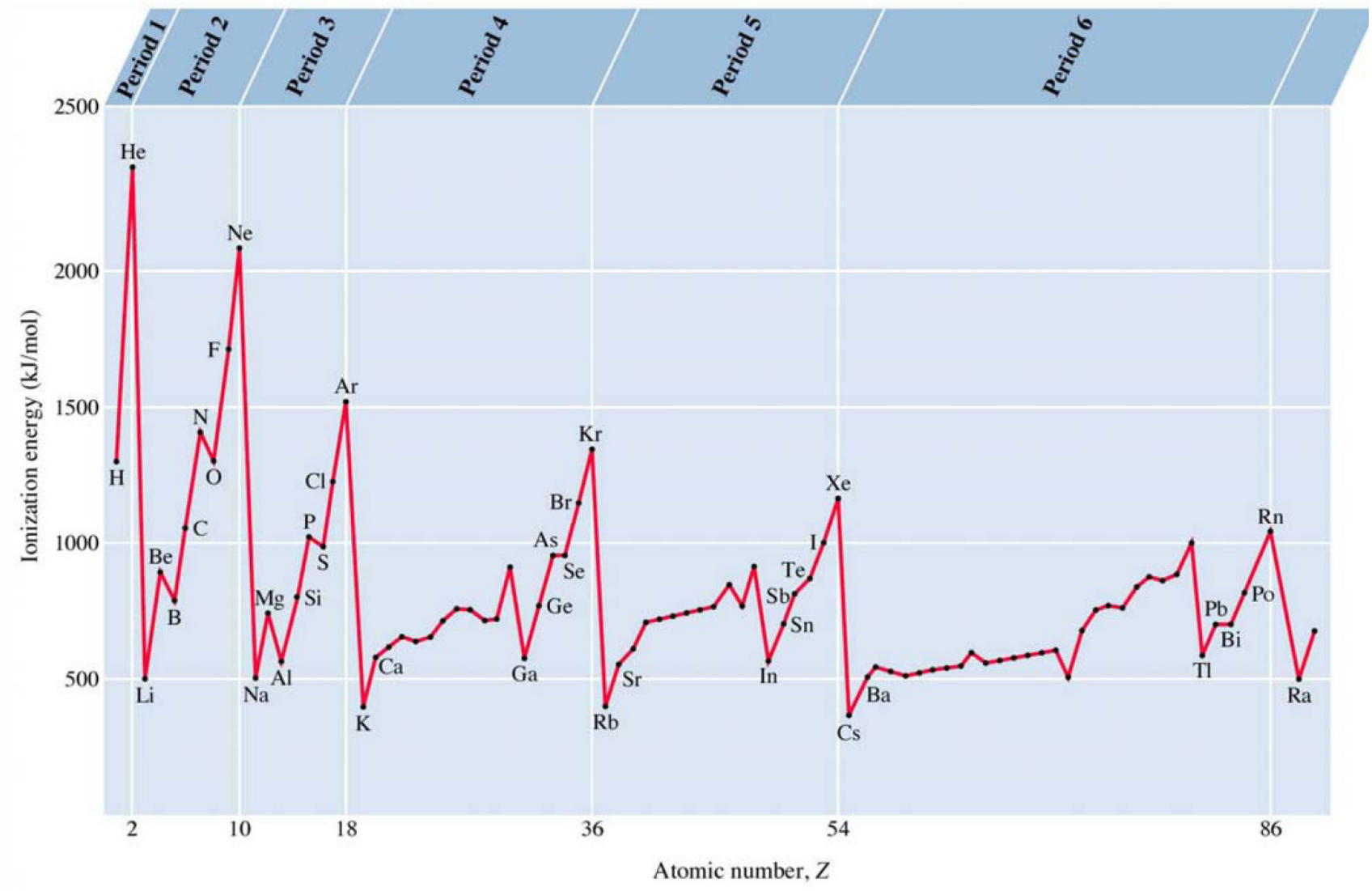
Si: $1s^2 2s^2 2p^6 3s^{\uparrow\downarrow} 3p_x^{\uparrow} p_y^{\uparrow}$

P: $1s^2 2s^2 2p^6 3s^{\uparrow\downarrow} 3p_x^{\uparrow} p_y^{\uparrow} p_z^{\uparrow}$

S: $1s^2 2s^2 2p^6 3s^{\uparrow\downarrow} 3p_x^{\uparrow\downarrow} p_y^{\uparrow} p_z^{\uparrow}$

Cl: $1s^2 2s^2 2p^6 3s^{\uparrow\downarrow} 3p_x^{\uparrow\downarrow} p_y^{\uparrow\downarrow} p_z^{\uparrow}$

Ar: $1s^2 2s^2 2p^6 3s^{\uparrow\downarrow} 3p_x^{\uparrow\downarrow} p_y^{\uparrow\downarrow} p_z^{\uparrow\downarrow}$



- **Ionization energies decrease down a group and increase across a period**

  (metals have higher ionization energies than non-metals)

First Long Period (#4)

- One might expect potassium (K) to have the electronic configuration

  K: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$ (= [Ar]$3d^1$)

- In fact the electronic configuration **K: [Ar]$4s^1$** is favored.
- ***Internal electron repulsion and the penetration effect serve to reduce the energy of the 4s orbital 255 kJmol^{-1} below that of the 3d orbital***.
- Due to the increased nuclear charge and reduced shielding of nuclear charge the next electron also occupies the 3s orbital giving calcium an electronic configuration **Ca: [Ar]$3s^2$**

(remember Madelung law!)

- It is only at scandium do we start to fill the 3d shell

  Sc:[Ar]$4s^2 3d^1$

- The ground state of Sc hinges on delicate balance of *penetration*, *interelectron repulsions* and poor mutual 3d – 4s *nuclear shielding* which can only be achieved if the 3s orbital is fully occupied.

- **The actual orbitals occupied are always those which result in the lowest energy for the atom as a whole due to penetration and shielding effects (4s < 3d)**

- This lowest energy configuration depends on several factors already discussed thus far:

  - penetration effect

  - nuclear shielding

  - electron repulsion

- On ionization of the first row transition metals the first two electrons come from the 4s orbital, thus their M^{2+} and M^{3+} ions have $[Ar]3d^n$ configurations.
- Following oxidation the relative increase of effective nuclear charge alters the balance of 3d vs 4s orbital energies.

Sc: $[Ar]4s^2 3d^1$ **Sc^+: $[Ar]4s^1 3d^1$** **Sc^{2+}: $[Ar]3d^1$**

Ca: $[Ar]4s^2$ **K: $[Ar]4s^1$**

- After Sc the five d orbitals are filled successively moving across the first row transition metals
- Some unique cases exist:

Cr: $[Ar]3d^5 4s^1$ **Cu: $[Ar]3d^{10} 4s^1$**

not

Cr: $[Ar]4s^2 3d^4$ **Cu: $[Ar]4s^2 3d^9$**

- One electron has passed from the 4s-orbital to a 3d-orbital to generate a half-filled (Cr) or filled (Cu) subshell. ***In this case, the half-filled or completely-filled subshells stabilize the 3d orbital.***
- Thus Cr and Mn are both d^5 metals while Cu and Zn are both d^{10} metals.
- For the second and third row transition metals the increased nuclear charge results in the d and s orbitals becoming even closer in energy, making it tougher to predict ground state configurations.

- On filling the 3d shell at Zn: $[Ar]3d^{10}4s^2$ the next available orbitals are the three degenerate 4p orbitals giving gallium the electronic configuration

  Ga: $[Ar]3d^{10}4s^24p^1$

- Continued filling of the 4p orbitals gives the expected configurations

  Ge: $[Ar]3d^{10}4s^24p^2$

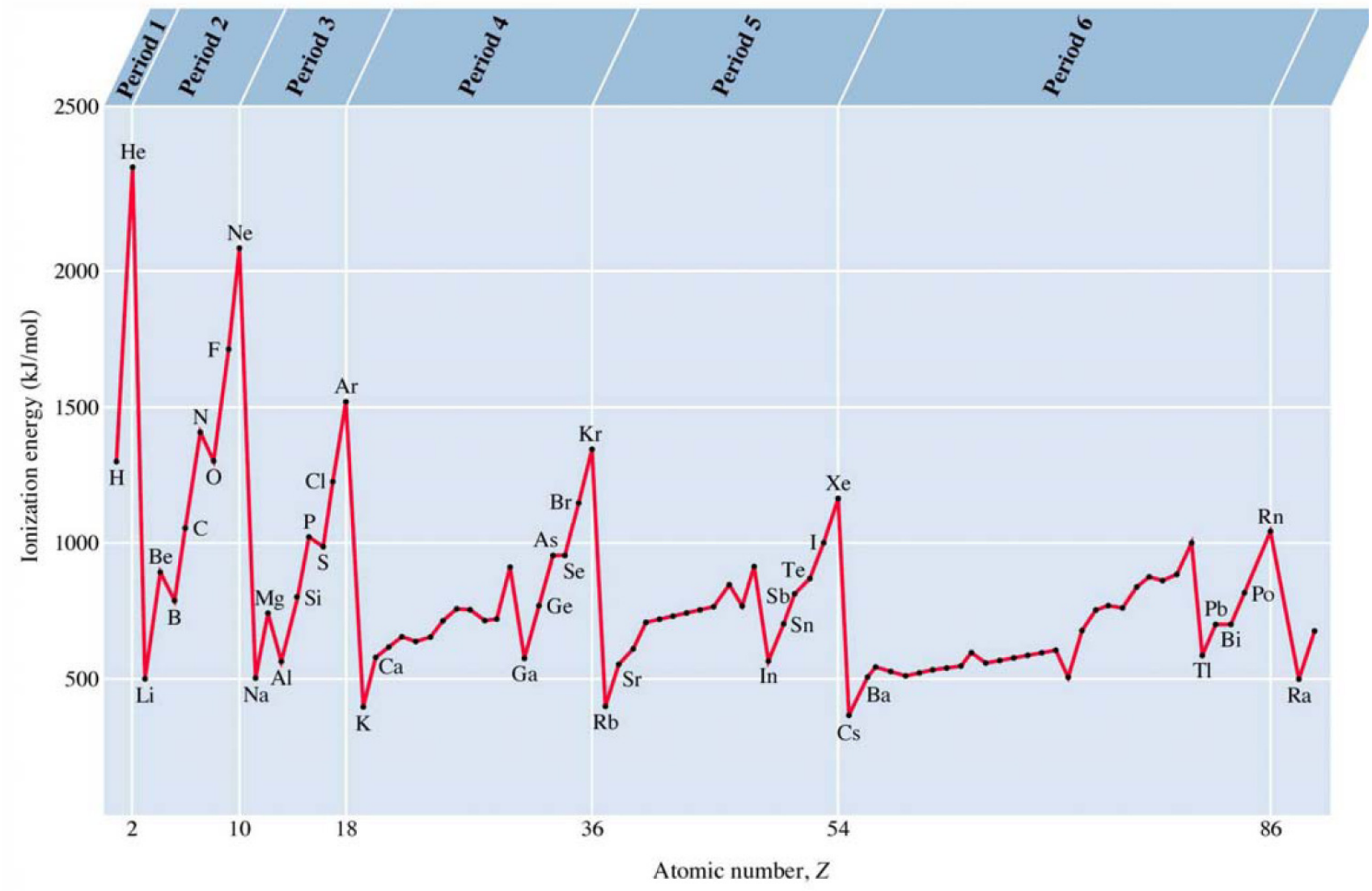
  As: $[Ar]3d^{10}4s^24p^3$

  Se: $[Ar]3d^{10}4s^24p^4$

  Br: $[Ar]3d^{10}4s^24p^5$

  Kr: $[Ar]3d^{10}4s^24p^6$

- The second long period is filled in a similar systematic manner with the 5s orbitals of rubidium (Rb: $[Kr]5s^1$) and strontium (Sr: $[Kr]5s^2$) being filled prior to the 6d orbitals, filled from yttrium (Y: $[Kr]4d^15s^2$) to cadmium (Cd: $[Kr]4d^{10}5s^2$), and the 5p orbitals, filled from indium (In: $[Kr]4d^{10}5s^25p^1$) to xenon (Xe: $[Kr]4d^{10}5s^25p^6$) .



- **Ionization energies decrease down a group and increase across a period**

  (metals have higher ionization energies than non-metals)

QUESTIONS ???