Modern Atomic Theory - Applications

<u>Reading</u>:	Ch 7, sections 4- 6 Ch 8, sections 2- 5	<u>Homework</u>:	Chapter 7: 59†, 61†, 63†, Chapter 8: 43*, 45*,47*, 49, 65

* = 'important' homework question. † = question from previous 'theory' packet

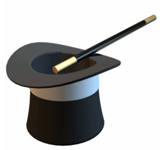
Overview: The RESULTS from the Schrödinger Equation (the ***unique*** set n, l, m_l and m_s *quantum numbers* an electron in an atom possesses) allow for a variety of important determinations

<u>Quantum number interdependency</u>: 'allowed' quantum numbers for electrons in atoms.

The range of each 'allowed' set of quantum numbers for any electron is interdependent. There respective ranges are determined by the following key relationships:

n = 1, 2, 3…. The principle quantum number ('shell' or 'layer')
l = 0 → (n-1) 'Shape' quantum number (0 = 's', 1 = 'p', 2 = 'd')
m_l = 0 → ± l '# of Directions' quantum number
m_s = -½ or +½ 'Type' of electron quantum number (↑, +½ or ↓, -½)

<u>Example</u>: Which of the following represents an impossible combination of *n* and *l*?



Recall the shorthand 'code' for assigning quantum numbers to specific orbitals (electron addresses):

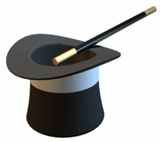
1s (n = 1, l = 0), **2p** (n = 2, l = 1), **2s** (n = ___ , l = ___) ***OR***

Recall that '*more space = more shapes*' i.e.:

'EZ'

n = 1, s *only*	n = 2, s, p *only*	n = 3, s, p, d *only*

<u>a</u>. 1p <u>b</u>. 4s <u>c</u>. 2d

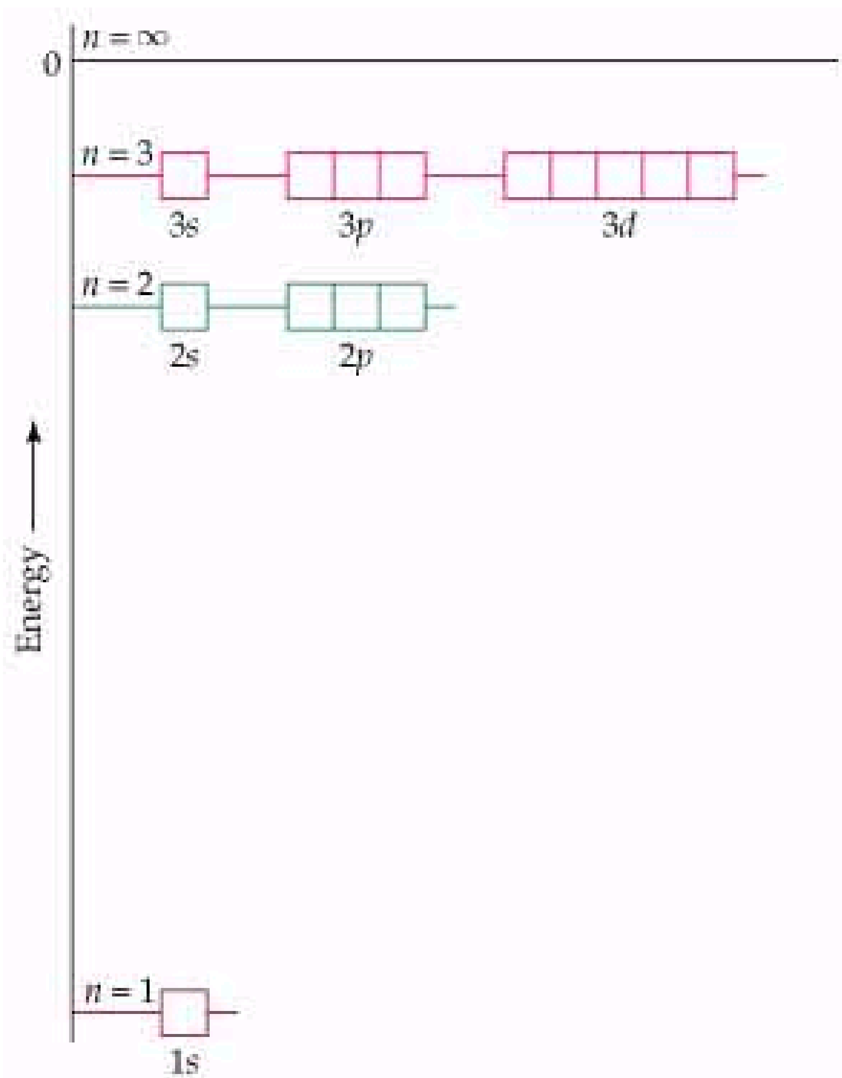


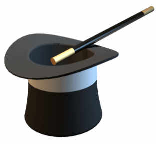
As we will discover, quantum number interdependency describes the location and energy of electrons within atomic orbitals *and* underpins the design of the periodic table

Quantum Mechanical Map of the Atom – Energy Level Diagrams

Background: An orbital 'map' of the atom (energy level diagram) can be constructed using quantum numbers.

Task: Understand the layout and construction of the **energy level diagram** (for orbitals up to n= 3) for **hydrogen**. See next page for details.





Recall what each quantum number represents, and how they are related to one another – this gives the *distance*, *shape* and *direction* of the allowed orbitals for each shell (n value). Include this information in the above energy level diagram.

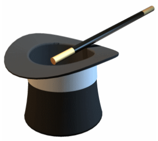
Recall that each orbital (box) can contain up to 2 *e* - we will use this fact later.

Energy Level Diagrams for Many Electron Atoms

And now we move the goal posts! **For many electron atoms (everything *but* H), electron – electron interactions cause the 's' orbital of each shell to contract, i.e. get closer to the nucleus**. This is most pronounced for the 4s, which dips *below* the 3d (!) *when* the 3s and 3p levels are filled (see slide and appendix)

Task: Sketch the Energy Level diagram for a many electron atom. Compare and contrast this diagram with that for H.

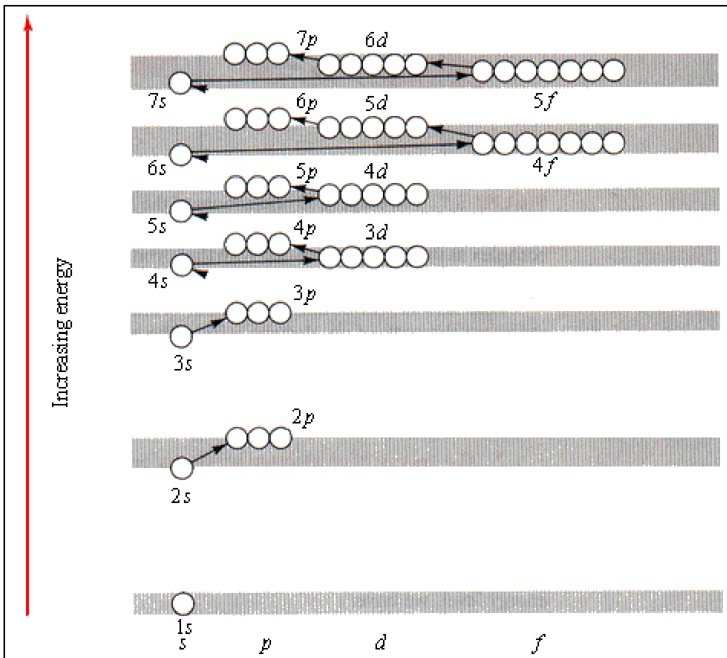
<u>Application 1</u>: Electronic Configurations ('filling the parking lot')



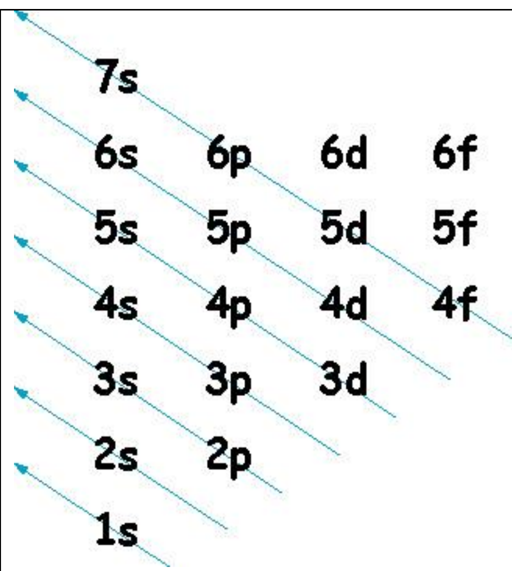
The Energy level diagrams essentially give us a map of the atom's orbitals ('parking lot'). We can now fill these atomic orbitals with electrons ('fill the parking spaces') by applying some simple rules

<u>Rules for filling energy level diagrams</u>

1. **Number electrons 'attracted' ≡ Number protons in nucleus**
2. **Electrons fill lowest energy levels first (why?) – this is the *Aufbau principle* ('building up')**
3. **Electrons only pair up 'when they have to' (why?) – this is *Hund's rule***
4. **There can be no more than 2 electrons per orbital (why?) – this is the *Pauli exclusion principle***



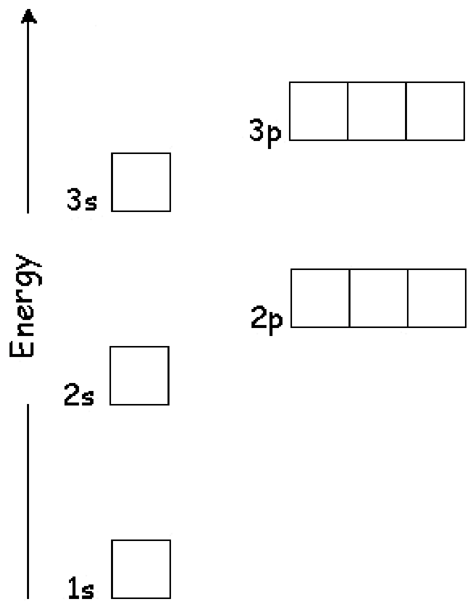
Energy level diagram illustrating the order of filling orbitals



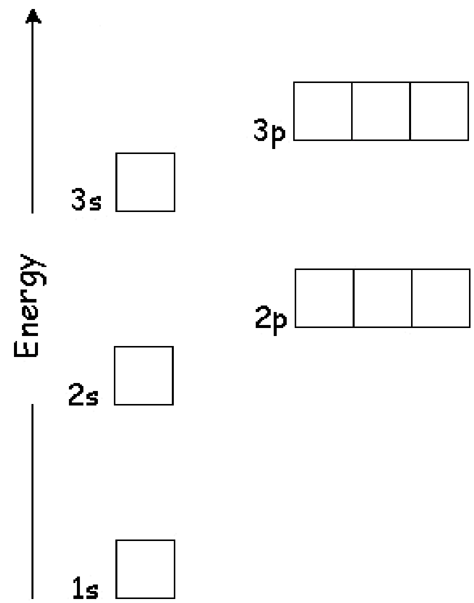
Summary of the order of filling orbitals

Task: Use the blanks provided to sketch energy level diagrams for the specified atoms

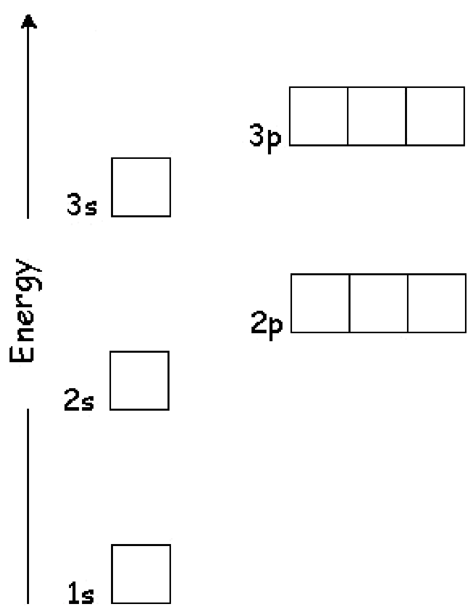
Nitrogen ($_{7}N$)



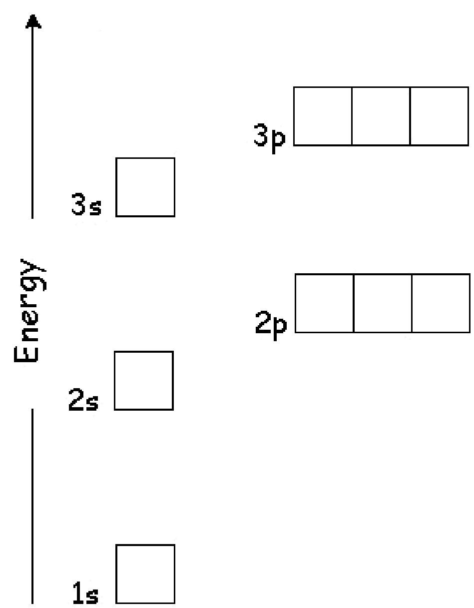
Fluorine ($_{9}F$)



Phosphorous ($_{15}P$)

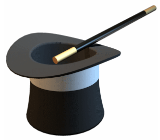


Chlorine ($_{17}Cl$)



Question: Do you notice any similarities to the atoms' respective 'dot' diagrams?

<u>Orbital ‘box’ diagrams and electronic configurations</u>



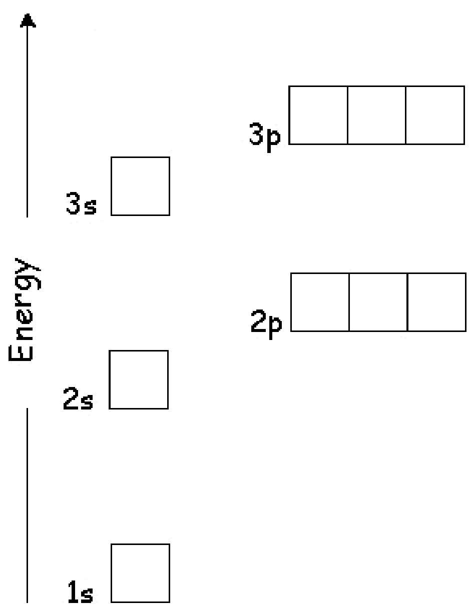
Once the order of filling orbitals is known (from energy level diagrams), this information can be presented in abbreviated form.

Orbital ‘box’ diagrams **and electronic** ***configurations*** **achieve this goal**

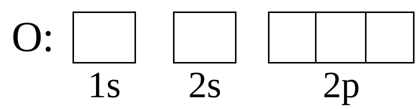
An ***orbital box diagram*** **is simply a ‘linear version’ of the atom’s respective** ***energy level diagram*****.**

<u>Example</u>: Energy level and Orbital box diagrams for Oxygen

<u>Energy Level Diagram</u>



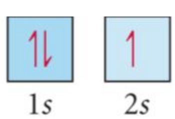
<u>‘Box’ Diagram</u>



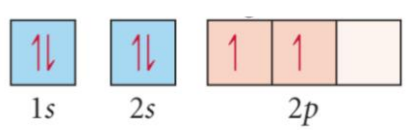
<u>Notes</u>:

<u>More Examples:</u>

Li:



C:



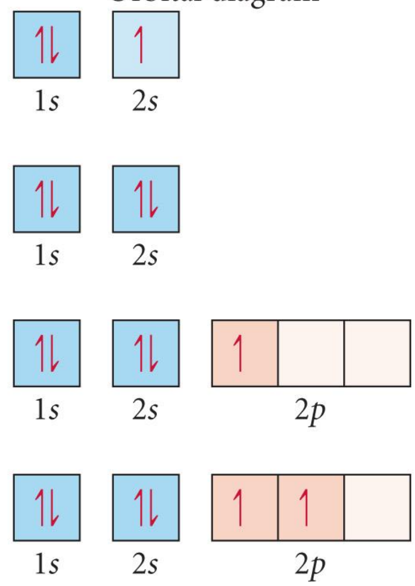
An *electronic configuration* is a 'shorthand' version of the atom's respective *orbital box diagram*.

The number of electrons in each orbital or set of degenerate orbitals is represented by *superscripts* (these are not mathematical 'powers')

Examples

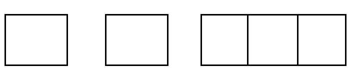
Symbol	Number of electrons	Electron configuration
Li	3	$1s^2 2s^1$
Be	4	$1s^2 2s^2$
B	5	$1s^2 2s^2 2p^1$
C	6	$1s^2 2s^2 2p^2$

Orbital diagram



Task: Draw an *Orbital box diagram* and write an *electronic configuration* for Nitrogen

Orbital 'Box' Diagram

N: 

1s 2s 2p

Electronic Configuration

N: 1s 2s 2p

Notes:

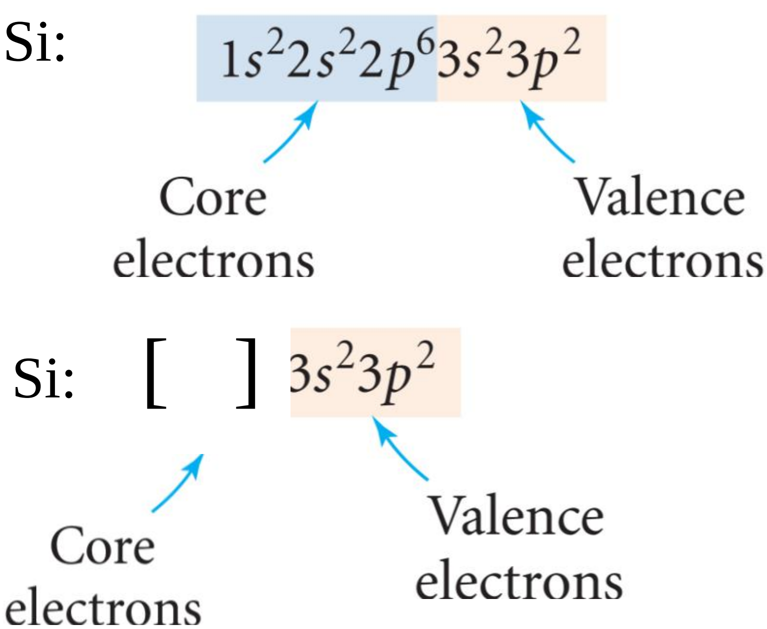
Condensed Electron Configurations

An atom's *core* electrons have, by definition, an inert gas or complete shell configuration.

The respective *inert gas electron configuration* of an atom's core electrons can be substituted for the corresponding *inert gas atomic symbol* in a condensed electronic configuration

Where: [He] = $1s^2$, [Ne] = $1s^2\ 2s^2\ 2p^6$, [Ar] = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

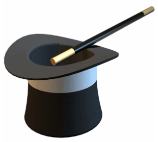
Worked Example: Silicon



Worked Examples:

Atom	Electron Configuration	Condensed Electron Configuration
Li	Li: $1s^2\ 2s^1$	Li: [He] $2s^1$
Mg		
K		

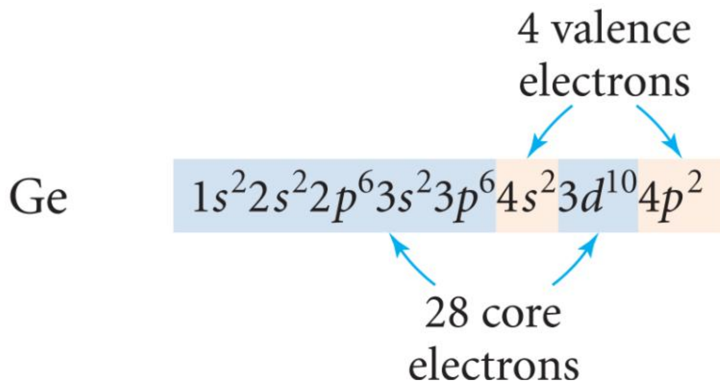
Details: Transition and other ‘heavy’ element and/or ion electronic configurations

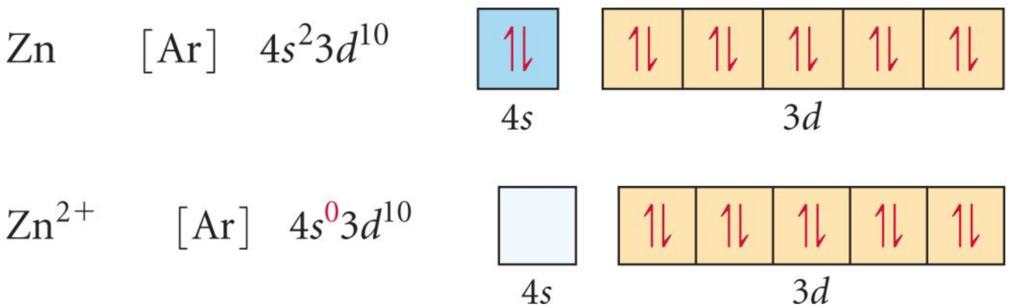


The ‘d’ orbitals of any ‘post calcium’ element or ion, by definition, belong to the ‘core’ – WHY?

Answer:

Examples:





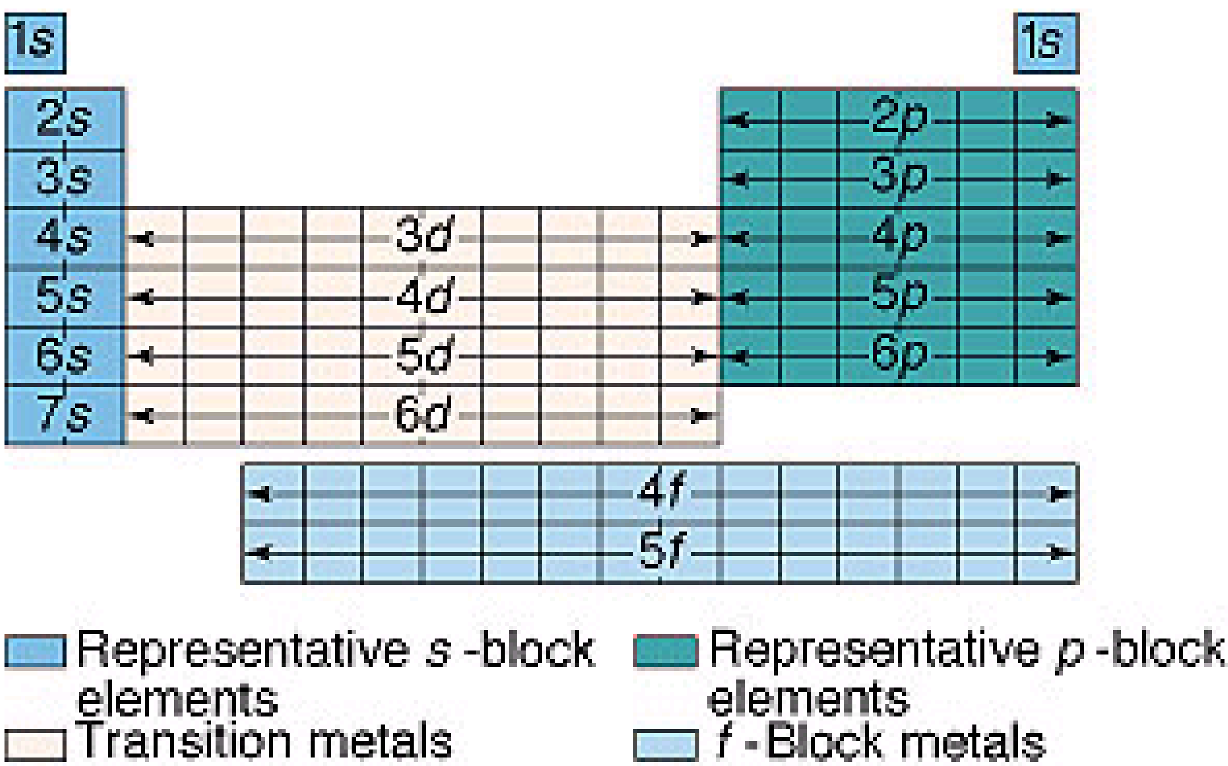
Task: Write a condensed electronic configuration for Bromine. How many valence electrons does this element have?

<u>Application 2</u>: Construction of the Periodic Table

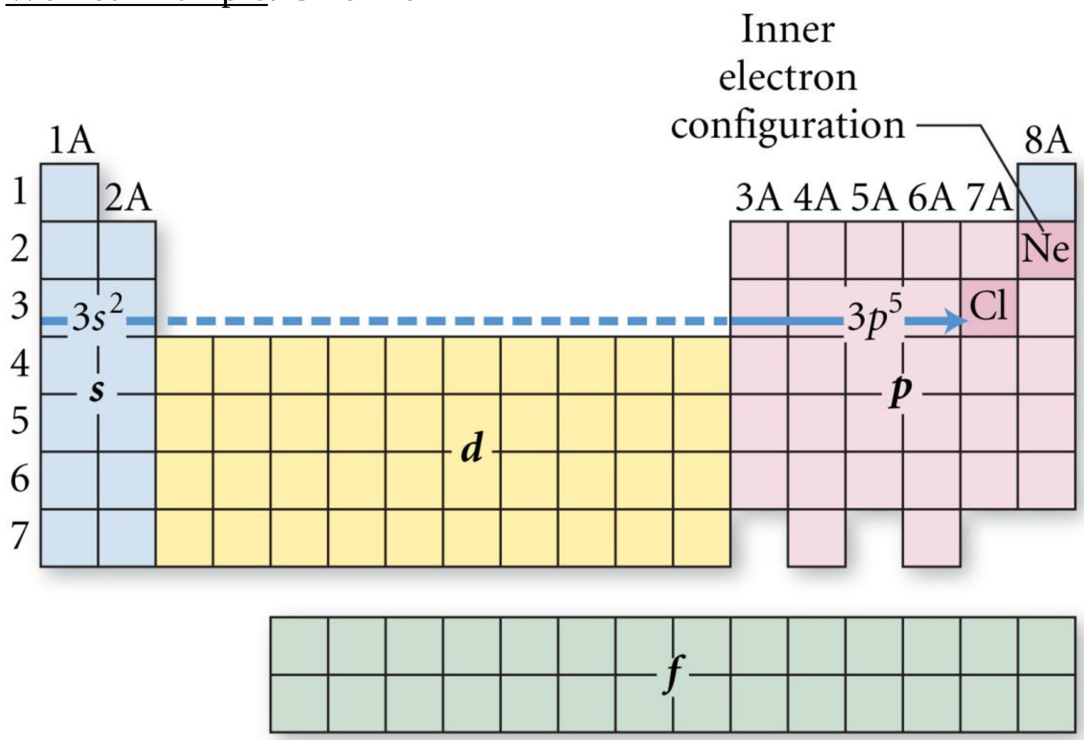
The relationship between the arrangement of an atom's total number of electrons and it's position in the periodic table is well understood in terms of the empirical 'battleship' analogy (column 2 = 2 valence *e*, row 3 = 3rd shell etc.)

We can now build an analogous (*non-empirical*) model of the periodic table using quantum mechanical results in place of 'dot' diagrams

***'Read across'* the period table while applying the filling of orbitals rules to obtain the electronic configuration of *any* element. This methodology is illustrated in the following version of the periodic table** (see slide / appendix)



Worked Example: Chlorine



Electronic configuration of Chlorine

Cl: *or* Cl:

Determine the following atoms' electronic configurations of the by 'reading across' the periodic table

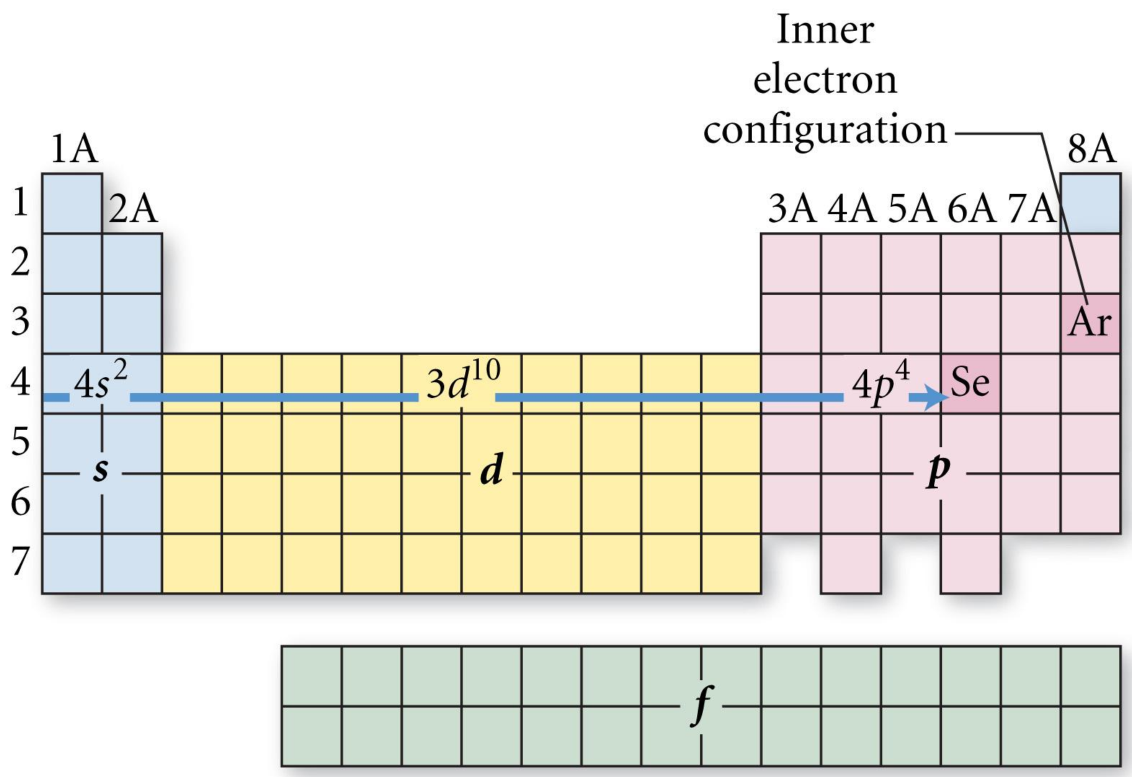
Li: *or* Li:

Al: *or* Al:

Se: *or* Se:
(see next page for hint)

Xe: *or* Xe:

Review: 'reading across' to find the electronic configuration of Se



Note: The periodic table has a total of 7 rows. This means that the largest known atoms have a maximum of 7 shells. For the largest fully complete shells, l has a range of $0 \rightarrow 4$. The 'new' types of orbital now allowed (when l = 4) are *f* orbitals – filling these orbitals creates the Lanthanide (4*f*) and Actinide (5*f*) series, between the 's' and 'd' blocks, in rows 6 and 7 respectively. Similar to the 3d elements (which appear in row 4), the 'f' block elements also appear in lower rows (e.g. 4*f* in row 6) due to the contraction of lower lying orbitals – this effect is called the *lanthanide contraction.*

Review: Why are the '*s*', '*p*', '*d*' and '*f*' element blocks so named?

Answer:

Wrap Up: Complete *Orbital 'box' diagrams*, *electronic configurations* and *'dot' diagrams* for the following:

Atom	Electronic configuration	Orbital 'box' diagram	'Dot' diagram
H			
F			
P			
Na			
Ne			

Question: What similarities do you notice between the atoms' respective 'dot' and 'box' diagrams?

Exceptions (take home assignment): Break down of the 'dot' models – ground and bound states

Task: Draw an orbital 'box' diagram and sketch a 'dot' diagram illustrating the electronic structure of carbon. Do you notice any inconsistencies?

C: 1s 2s 2p

Carbon: the *isolated* atom's *ground* state

Carbon: the *bonded* atom's *bound* state

Answer:

The 'dot' and Lewis symbols represent the *bonding configurations* of the atoms' electrons (i.e. what they are when the atom is bonded to other atom(s) - they have the max. number of unpaired e)

***Orbital box, electronic configuration* and *energy level diagram* representations show the lowest energy (or ground state) electron arrangement.**

Elements in groups II, III and IV have *different ground* and *bound* electronic configurations

Task: Draw orbital 'box' diagrams illustrating the ground and bound states of Be

Be: 1s 2s 2p
Ground state

Be: 1s 2s 2p
Bound state

Question: Why do elements in groups II, III and IV have different ground and bound electronic configurations?

Answer: 'you have to spend money to make money' – what does this mean in terms of the ground and bound electronic states of atoms?

"Electron Addresses"

The following question was taken from your 3rd practice midterm:

Draw *ground state orbital 'box' diagrams* and write *ground state electronic configurations* for the following atoms and ions:

Carbon atom
Orbital 'box' diagram

Electronic Configuration

Oxide *anion*
Orbital 'box' diagram

Electronic Configuration

Sodium atom
Orbital 'box' diagram

Electronic Configuration

Hydrogen atom
Orbital 'box' diagram

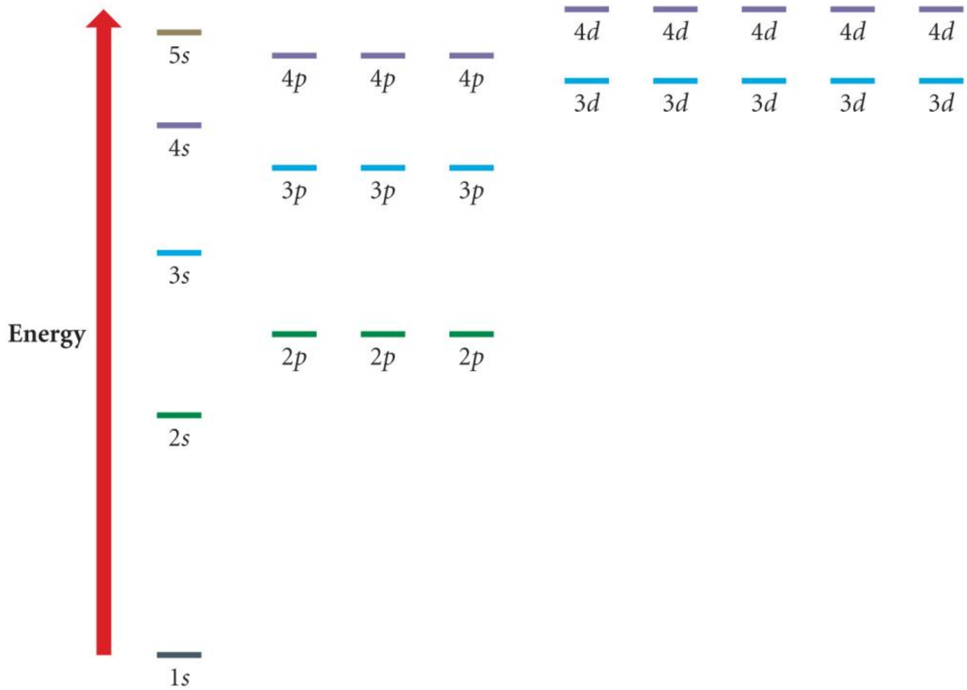
Electronic Configuration

Magnesium *cation*
Orbital 'box' diagram

Electronic Configuration

Appendix

General Energy Ordering of Orbitals for Multielectron Atoms



Orbital Blocks of the Periodic Table