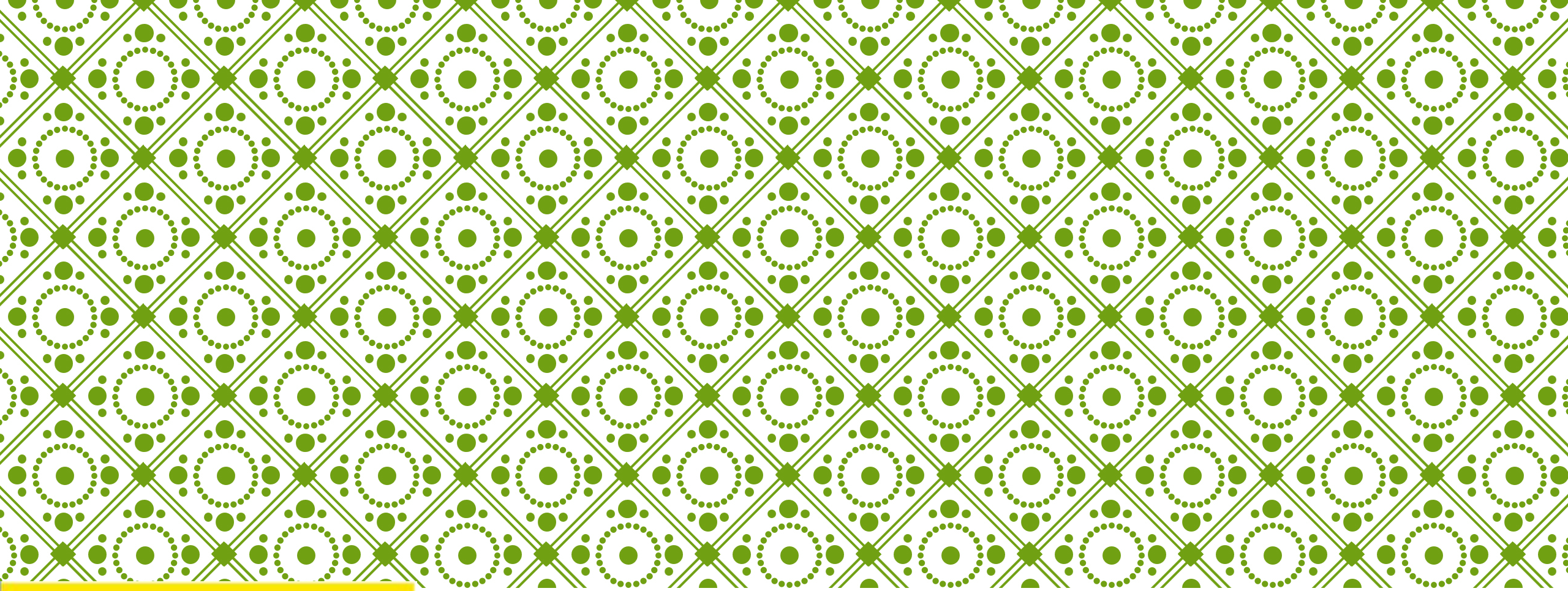


UNSW SYDNEY | Australia's Global University

CHEM1011 LECTURE 10

Dr Shannan Maisey

QUANTUM NUMBERS RECAP

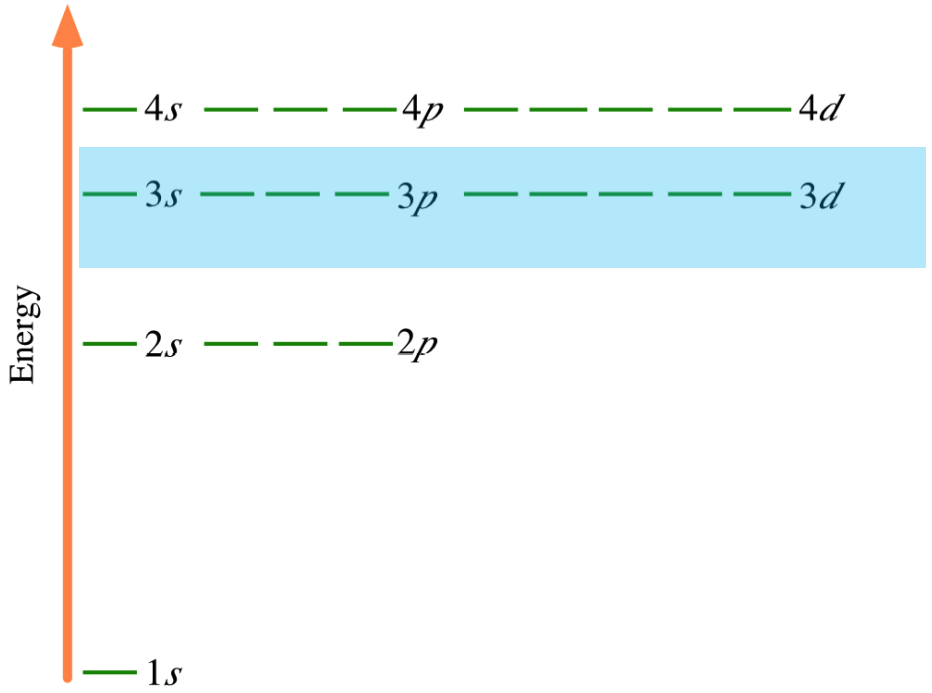
- **Electrons** behave like particles but also like **waves.**
- Electrons in atoms behave in a wave-like manner that **cannot be described using classical mechanics.**
- **Quantum mechanics can describe the energy and probability of locating an electron** in an atom by finding solutions to the Schrödinger equation (these **solutions are atomic orbitals,** regions where electron density is high).
- There are four variables (**quantum numbers**) used to describe the electron in an orbital: n, ℓ, m_ℓ ,and m_s

Useful resource:
https://chem.libretexts.org/Core/Physical_and_Theoretical_Chemistry/Quantum_Mechanics/09._The_Hydrogen_Atom/Atomic_Theory/Electrons_in_Atoms/Atomic_Spectra

HYDROGEN VS. LARGER ATOMS

Hydrogen's orbitals are **degenerate** i.e. the orbitals from the same energy level have the **same energy** – they depend only on *n*, the principal quantum number.

E.g. For *n*=3 the 3*s*, 3*p* and 3*d* orbitals all have the same energy:



All the same energy

LARGER ATOMS

What makes larger atoms different to hydrogen?

They have more protons!

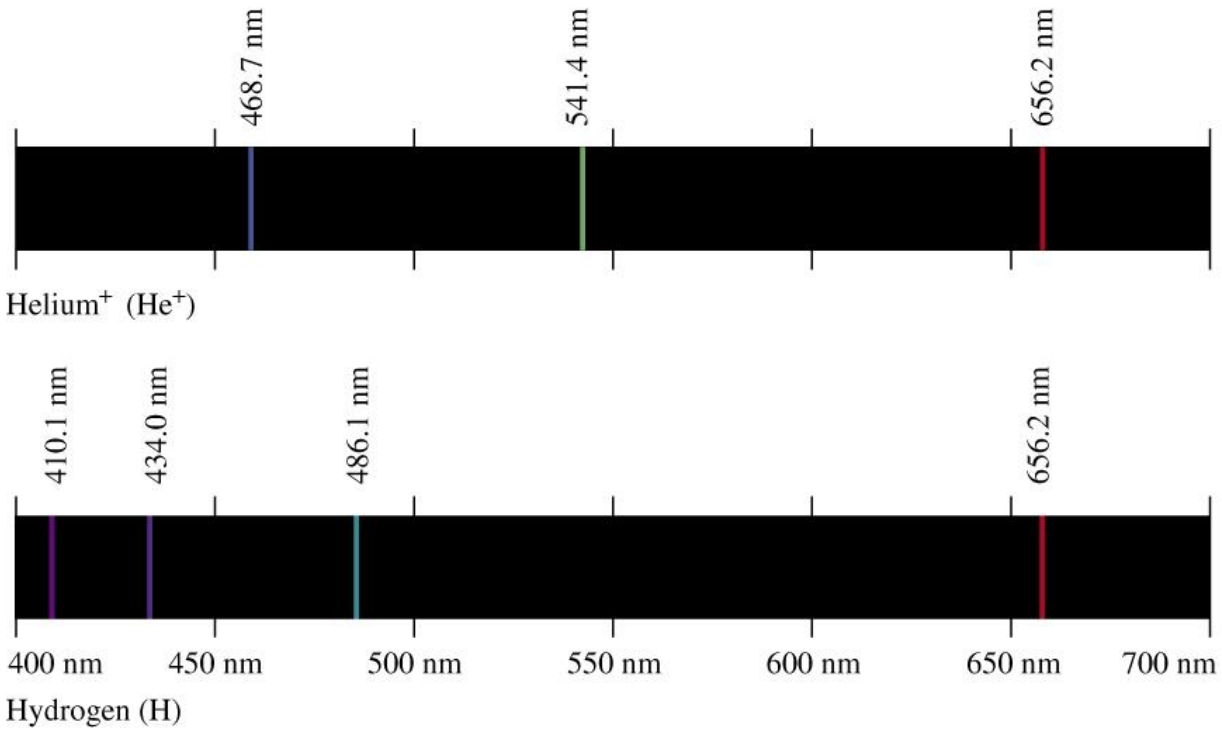
LARGER ATOMS

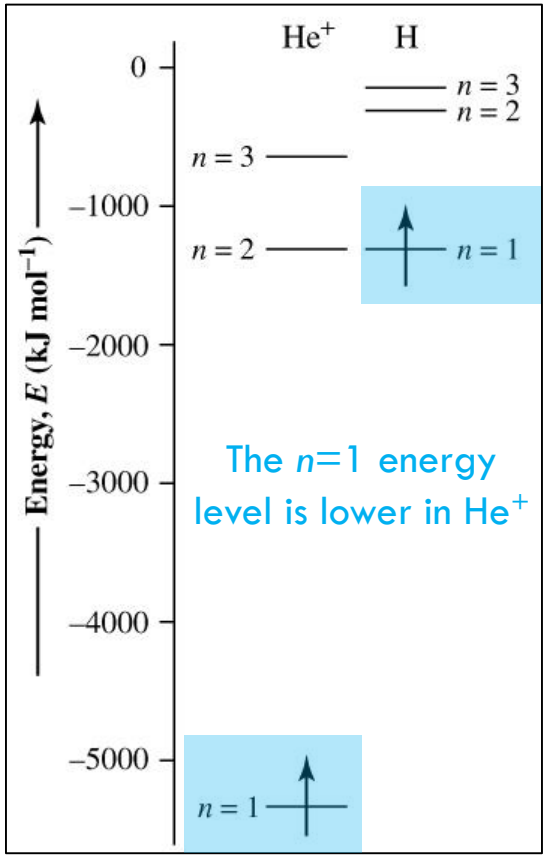
With larger atoms the **nucleus becomes more positive** (more protons) – as a result the electrons experience a greater Coulombic attraction and are pulled *closer* to the nucleus.

As a result the orbitals are *contracted* (compared to hydrogen's energy levels).

The contraction of energy levels will have an effect on the spectra

LARGER ATOMS





The n=1 energy level is lower in He^+

MULTI-ELECTRON ATOMS

For a single-electron system like hydrogen (or He^+ etc) the Schrödinger equation can be solved *exactly*.

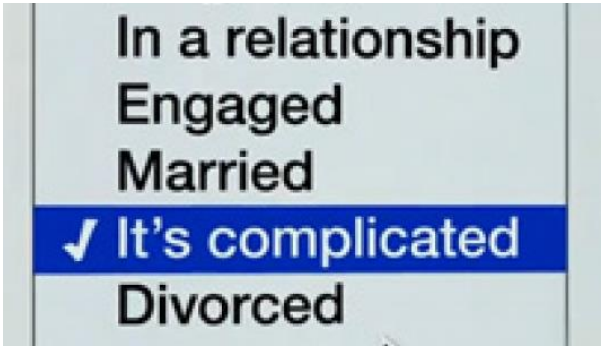
However for systems with more than 1 electron it gets complicated. Why?

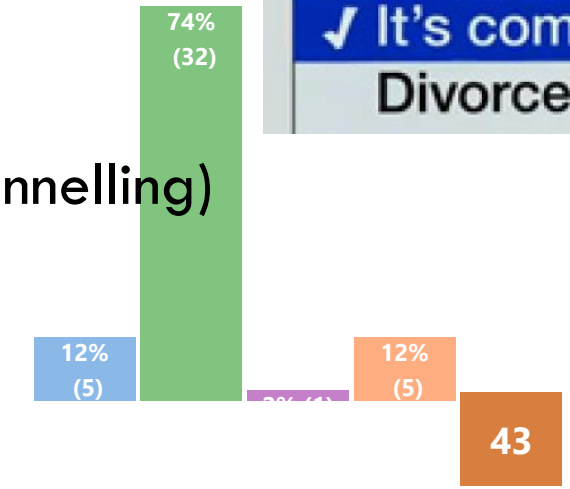
A Electrons cannot be identified from each other

B Electrons repel each other

C Electrons fight each other

D Electrons swap places with each other (quantum tunnelling)





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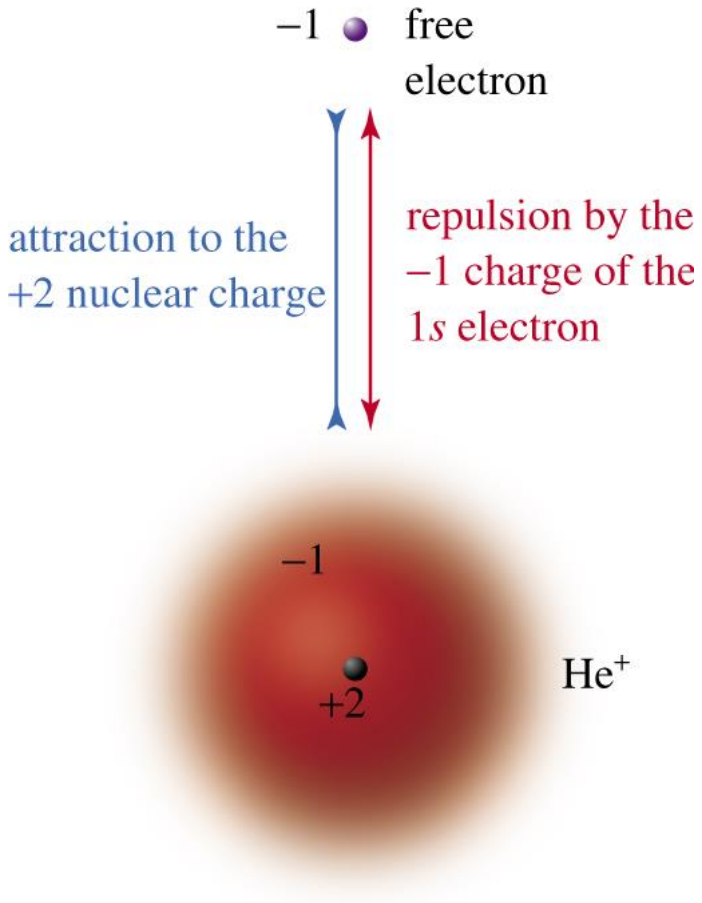
MULTI-ELECTRON ATOMS

For a single-electron system like hydrogen (or He^+ etc) the Schrödinger equation can be solved *exactly*.

However for systems with more than 1 electron it gets complicated – the **electrons repel each other** (the 'many-body problem'). As such calculations require approximations and are more time-consuming (computationally expensive).

One useful approximation is that the orbitals will resemble those of hydrogen.



SHIELDING

Electrons closer to the nucleus "feel" the full strength of the Coulombic attraction to the nucleus. However those further away (higher energy levels) "feel" a **reduced nuclear charge due to the repulsion of electrons closer to the nucleus (shielding)**. The charge on the nucleus has been shielded by the inner electrons.

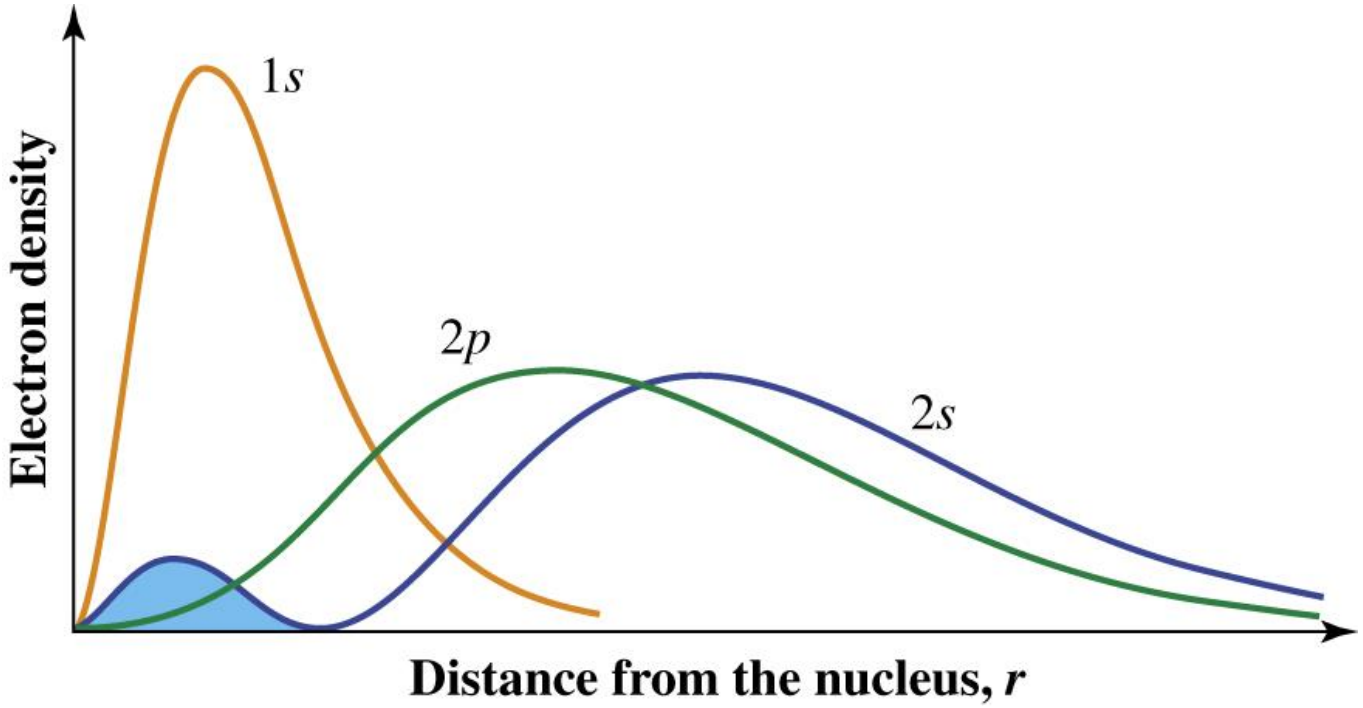
Shielding has a different effect on different orbitals – think about their shape:

s orbitals

p orbitals

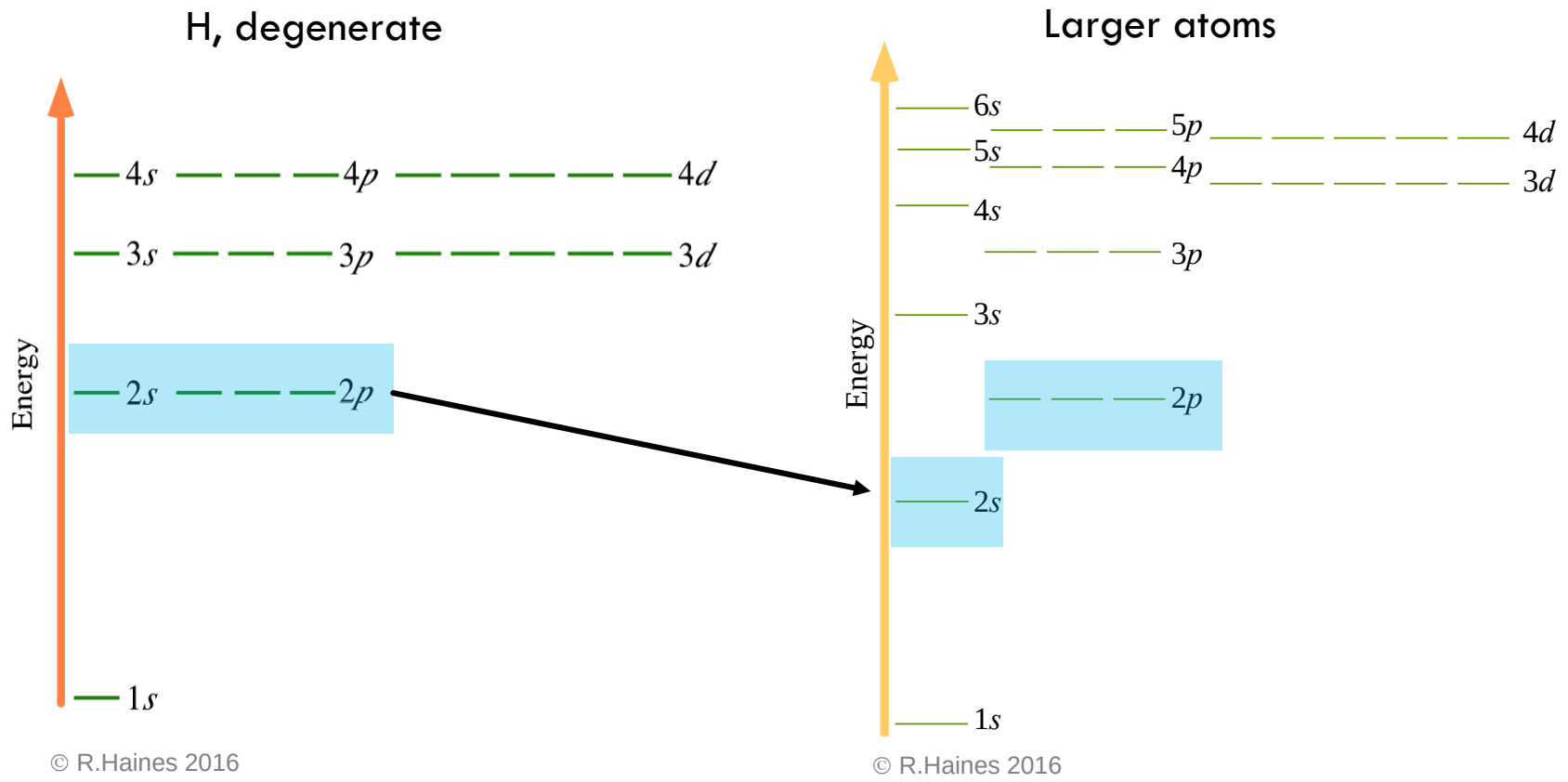
ORBITAL SHAPE AND ENERGY

Compare the *s* and *p* orbitals from the *n*=2 energy level (i.e. 2*s* and 2*p*). Due to greater electron density of the 2*s* closer to the nucleus *(shaded in blue)* this orbital will be lower in energy than the 2*p*. The 2*s* orbital has greater 'penetration' to the nucleus than the 2*p* orbital.



ORBITAL ENERGIES FOR MANY-ELECTRON ATOMS

For this reason the energies of orbitals within an energy level will no longer be degenerate for larger atoms. In general energy in $s < p < d < f$.



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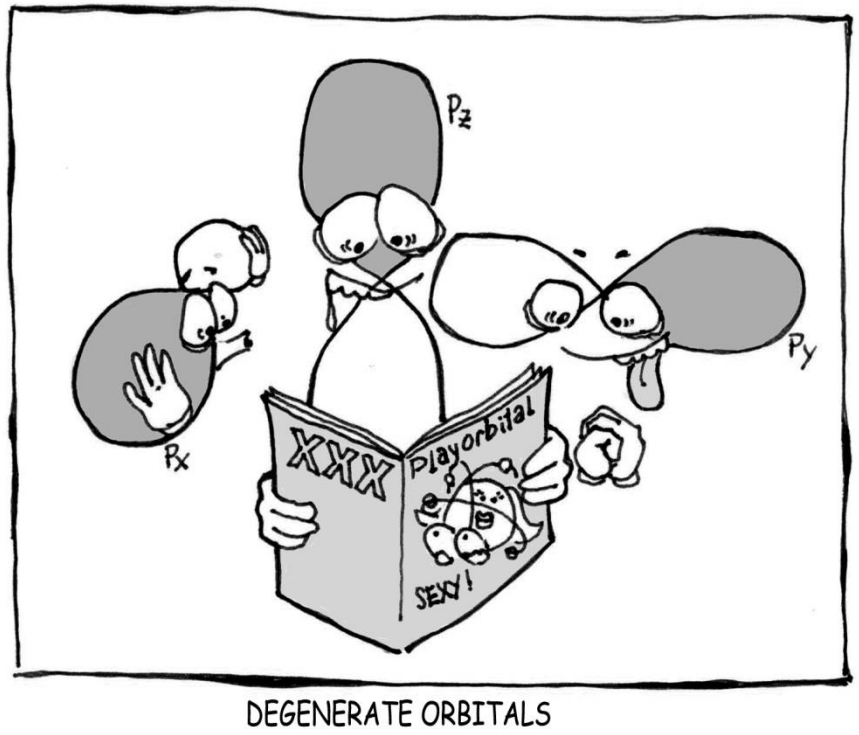
DEGENERATE ORBITALS?

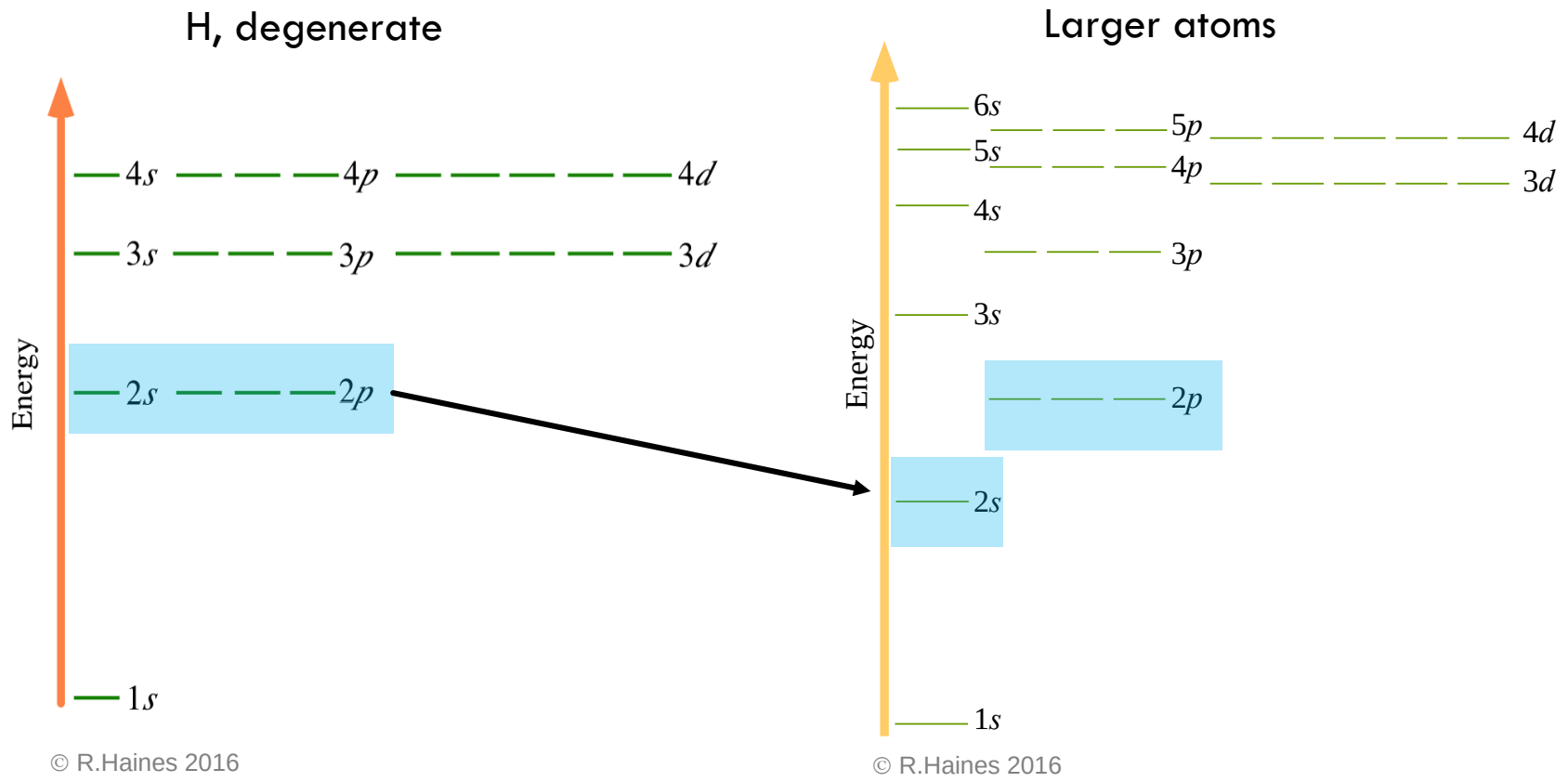


DEGENERATE ORBITALS

In quantum chemistry….
Degenerate means ‘of equal energy’
So degenerate orbitals are not antisocial layabouts, there are simply a group of orbitals with the same energy

ORBITAL ENERGIES FOR MANY-ELECTRON ATOMS

For this reason the energies of orbitals within an energy level will no longer be degenerate for larger atoms. In general energy in $s < p < d < f$.



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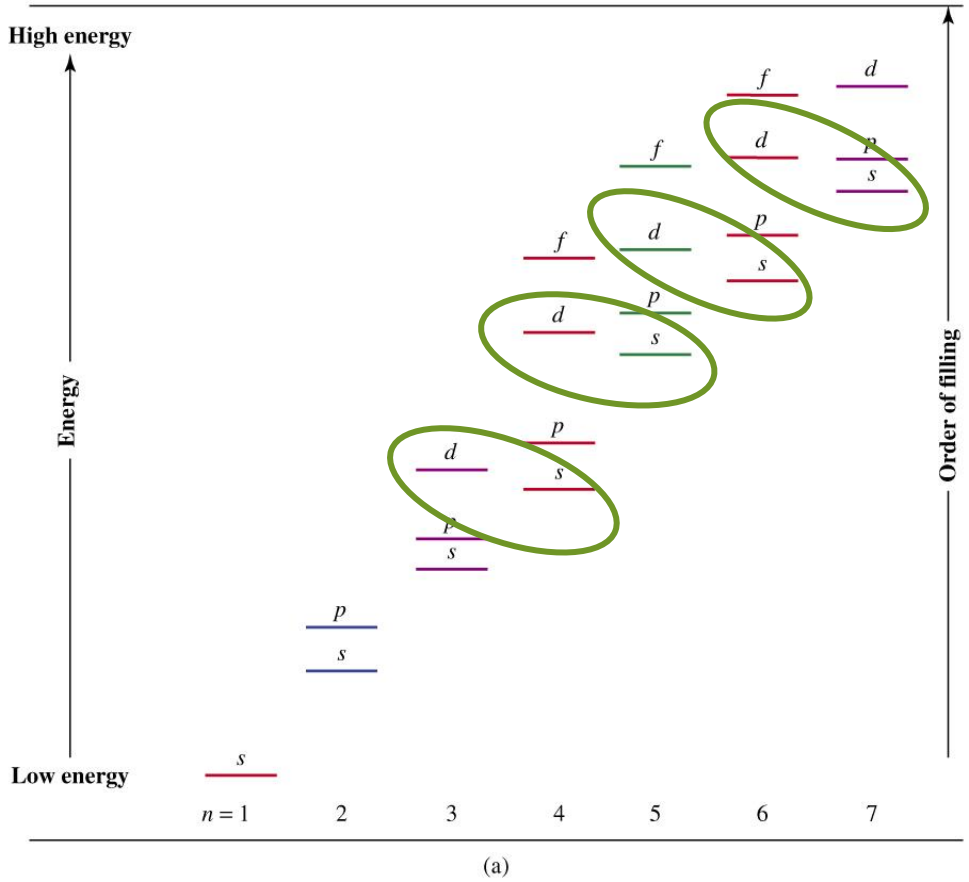
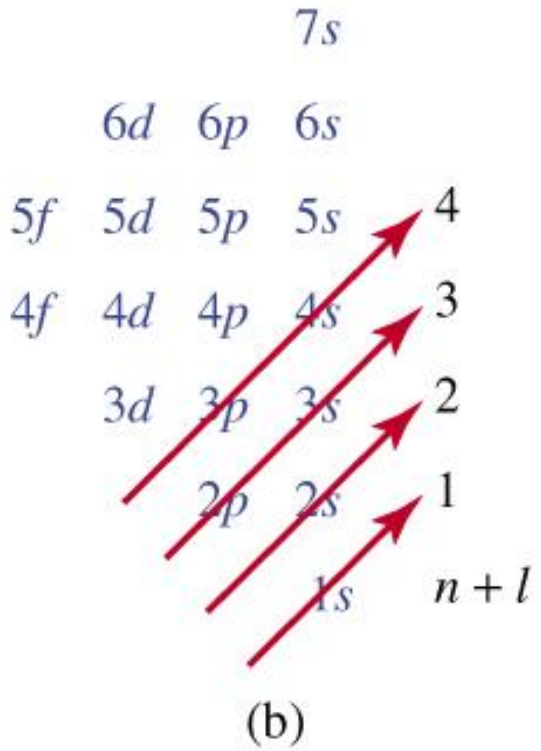
AUFBAU ('BUILDING UP') PRINCIPLE

When assigning electrons to orbitals they will **fill in the order from lowest energy first** (*Aufbau* principle).



How do we remember the order?



Orbital capacities are as follows:

s set: 2 electrons

p set: 6 electrons

d set: 10 electrons

f set: 14 electrons

AUFBAU PRINCIPLE AND ORDER OF ORBITAL FILLING

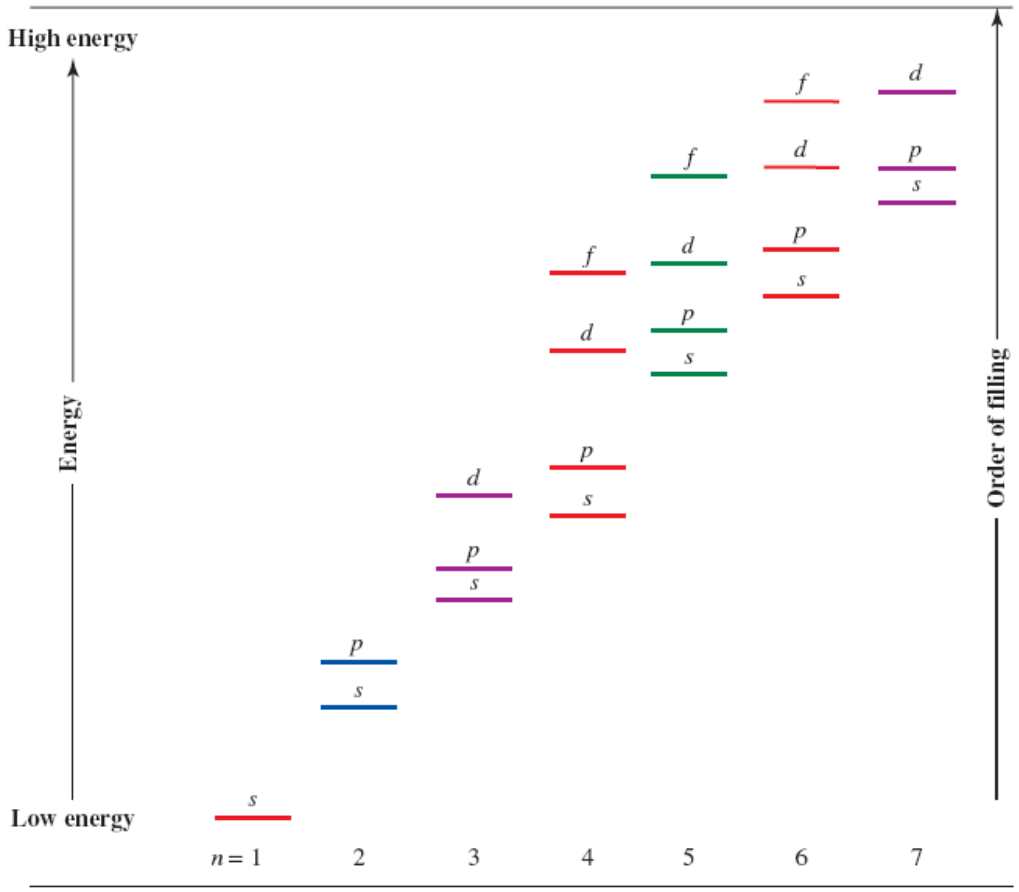
1. Each electron in an atom occupies the most stable available orbital.
2. No two electrons can have identical quantum numbers.
3. Orbital capacities are as follows:

s set: 2 electrons

p set: 6 electrons

d set: 10 electrons

f set: 14 electrons

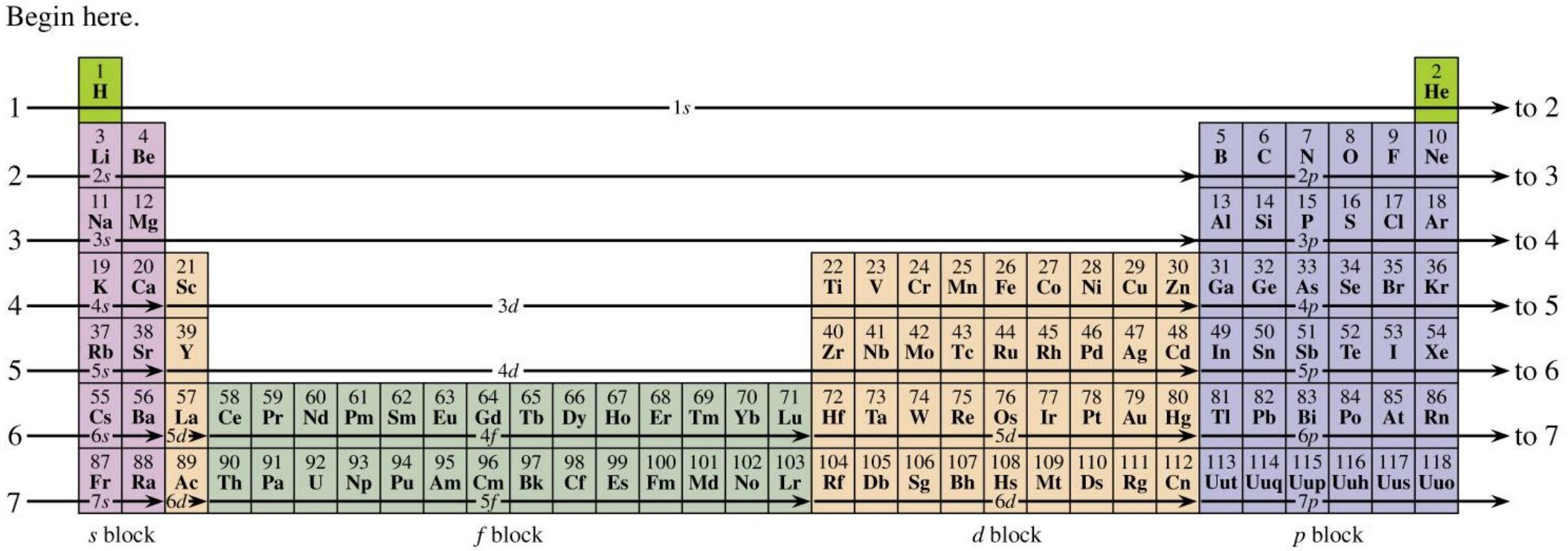


LEARNING OUTCOMES SO FAR

- ❑ List the allowed values of the quantum numbers for orbitals in hydrogen–like atoms.
- ❑ Sketch the shapes of *s*, *p*, and *d* orbitals.
- ❑ Write ground–state electron configurations for all main group elements and first–row transition metals and ions of these elements using 'arrows in boxes' and '1*s*1' notation.
- ❑ Identify isoelectronic species and predict relative sizes of these species.
- ❑ Predict the magnetic properties of isolated atoms and ions.

AUFBAU PRINCIPLE

Use the periodic table to help you. This shows the shells and orbital filling order.



ELECTRON CONFIGURATION

A particular arrangement of electrons in the orbitals of an atom is known as a **configuration.** The configuration with the lowest energy is called the _____ground state_____.

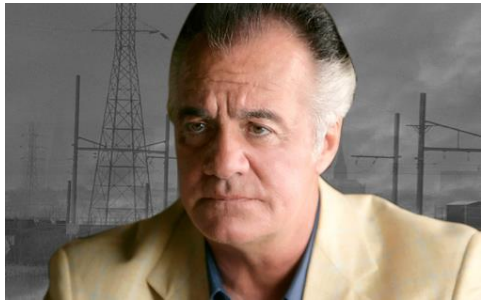
Rules:

1. Each electron must have a unique set of quantum numbers. So, **up to two electrons can occupy a single orbital**. This is a consequence of the **Pauli exclusion principle.**
2. Electrons will occupy all orbitals of the same energy before pairing up (filling) the same orbital. This is **Hund's rule.**

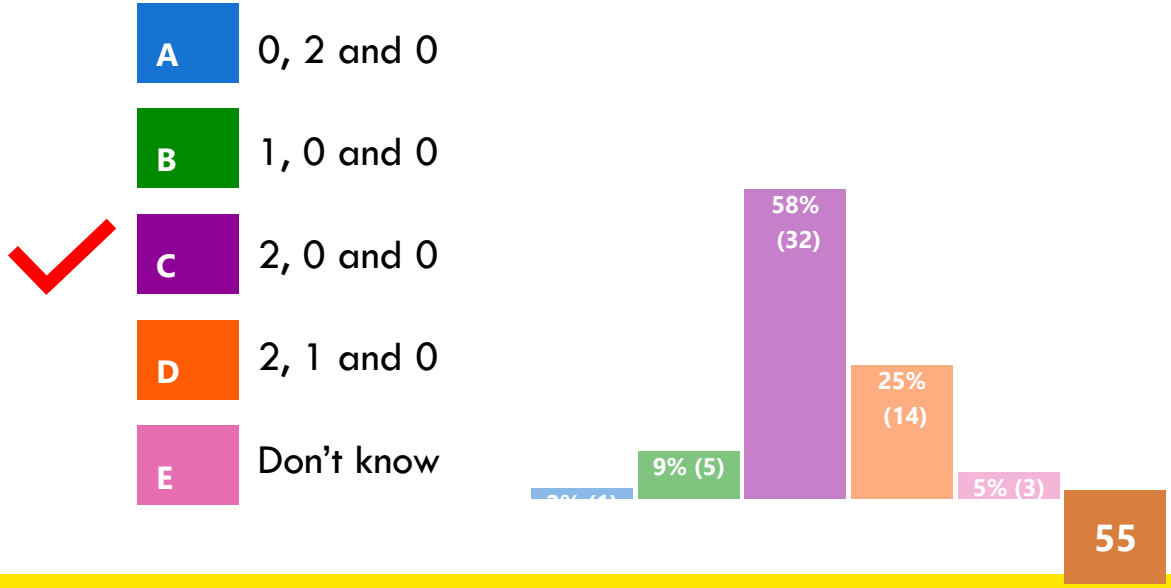
PAULI EXCLUSION PRINCIPLE

Each electron in atom is unique – despite being indistinguishable – therefore **each electron must have its own set of quantum numbers**. Any electrons in the same orbital with have the same n, ℓ, and m_ℓ quantum number (e.g. 2*s* orbital is $n =$ ___, $\ell =$ ___, and $m_\ell =$ ___).

Since there are two possible values allowed for the magnetic spin quantum number there is a **maximum of two electrons in an orbital**. They will have different sets of quantum numbers if one is spin up ($m_s = +½$) and the other spin down ($m_s = -½$).



Wolfgang Pauli
Nobel Prize for Physics in 1945



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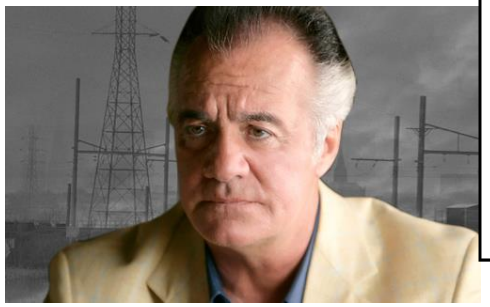
PAULI EXCLUSION PRINCIPLE

Each electron is unique – despite being indistinguishable – therefore **each electron must have its own set of quantum numbers.** Any electrons in the same orbital with have the same n, ℓ, and m_ℓ quantum numbe

Since there are ... number there is a **maximum of t** ... antum numbers if one is spin up (



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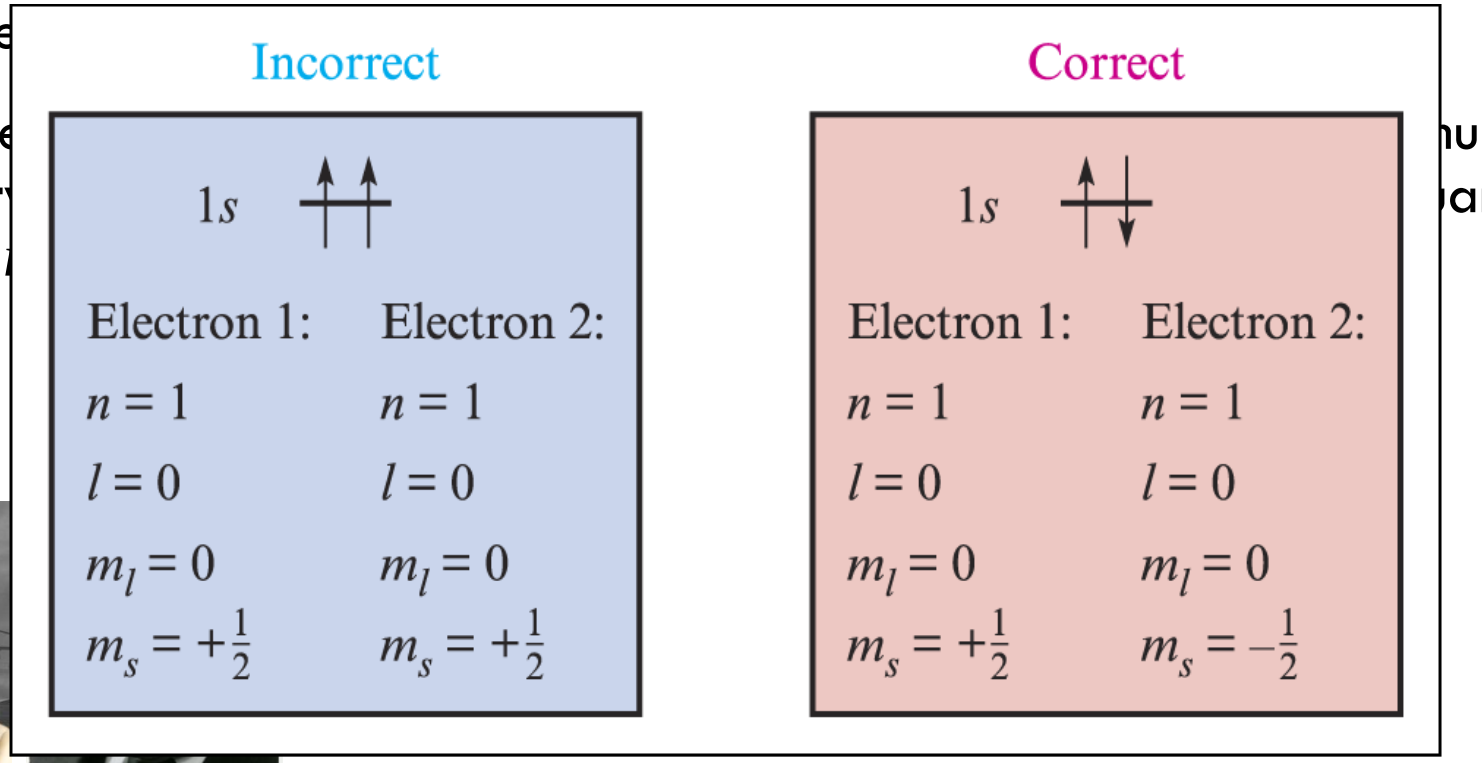


Housecroft and Constable, *Chemistry*, 4th Edition © Pearson Education Limited 2010

HUND'S RULE

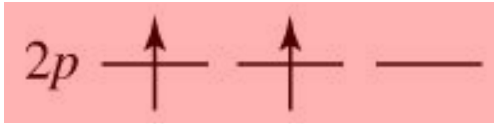
Since electrons repel each other they will **occupy another orbital with the same energy before pairing up in the same orbital** with another electron. Electrons will maintain the same spin quantum number in each orbital (i.e. have parallel spins).

Electrons are antisocial!

Incorrect

Incorrect

Correct

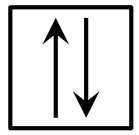


ELECTRON CONFIGURATION NOTATION

There are two notations commonly used to write electron configurations:

1. **Arrow in boxes**

Arrows are electrons with the direction indicating the spin. The box represents an orbital.



2. **Written**

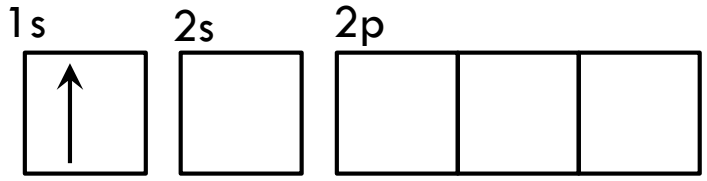
Orbitals are written in filling order as one ‘word’, with electrons in superscript.

$1s^2$

GROUND STATE ELECTRON CONFIGURATIONS

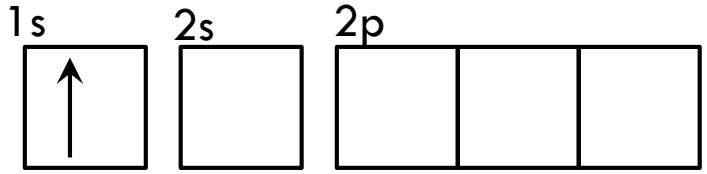
$1s^1$

Hydrogen: Z= 1



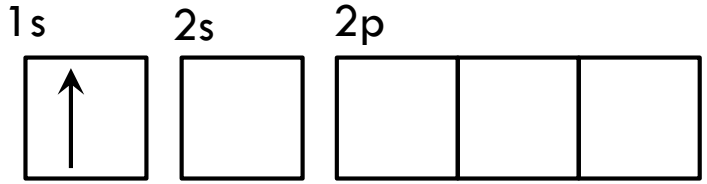
$1s^2$

Helium: Z=2



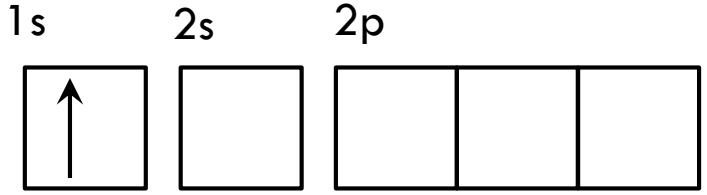
$1s^2$ _____

Lithium: Z= 3



$1s^2$ _____

Beryllium: Z= 4



$1s^2$ _____

Boron: Z= 5

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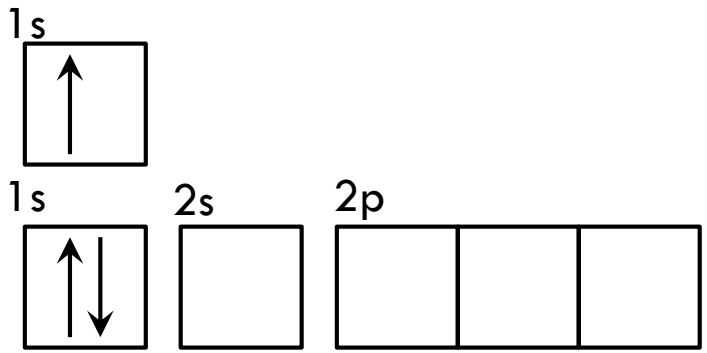
GROUND STATE ELECTRON CONFIGURATIONS



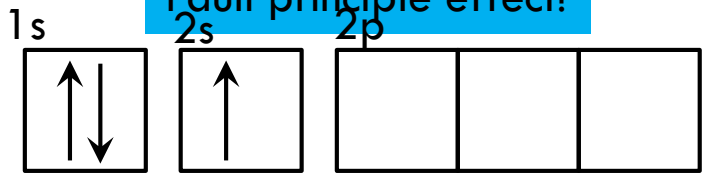
$1s^1$

Hydrogen: Z=1

$1s^2$

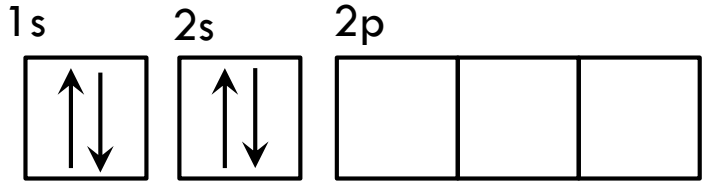
Helium: Z= 2

Pauli principle effect!



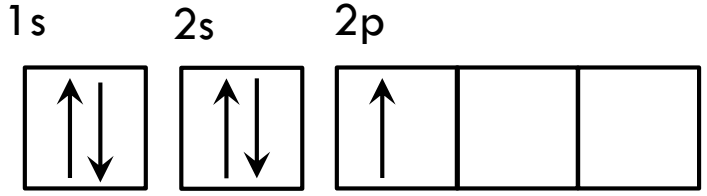
$1s^2 2s^1$

Lithium: Z= 3



$1s^2 2s^2$

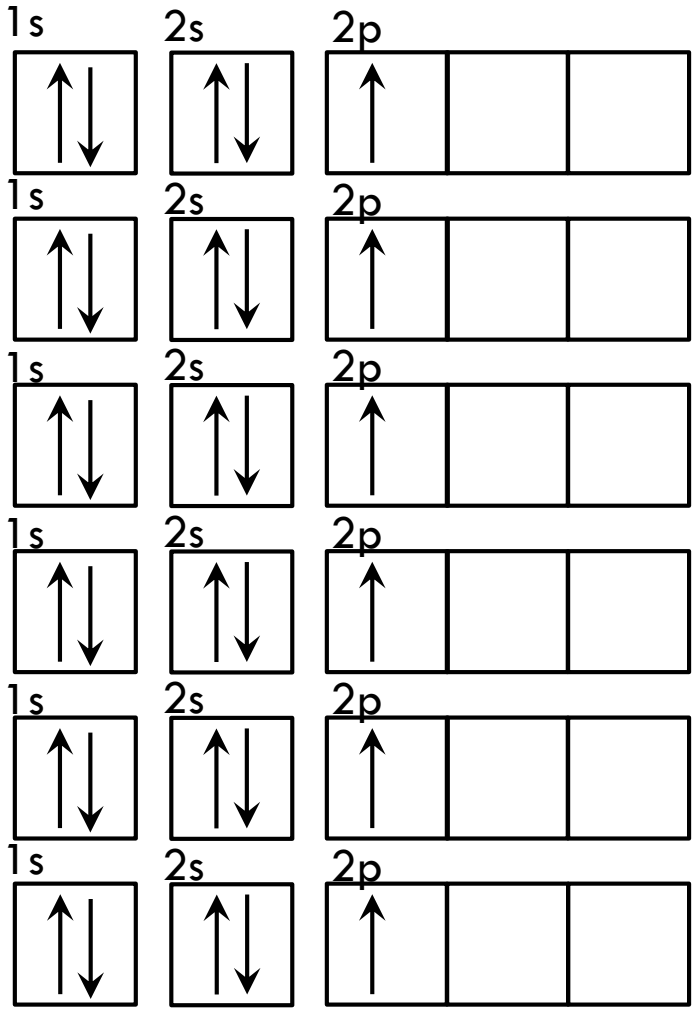
Beryllium: Z= 4



$1s^2 2s^2 2p^1$

Boron: Z= 5

GROUND STATE ELECTRON CONFIGURATIONS



Boron: Z=5

$1s^2 2s^2 2p^1$

$1s^2 2s^2 2p$_____ **Carbon: Z= 6**

$1s^2 2s^2 2p$_____ **Nitrogen: Z= 7**

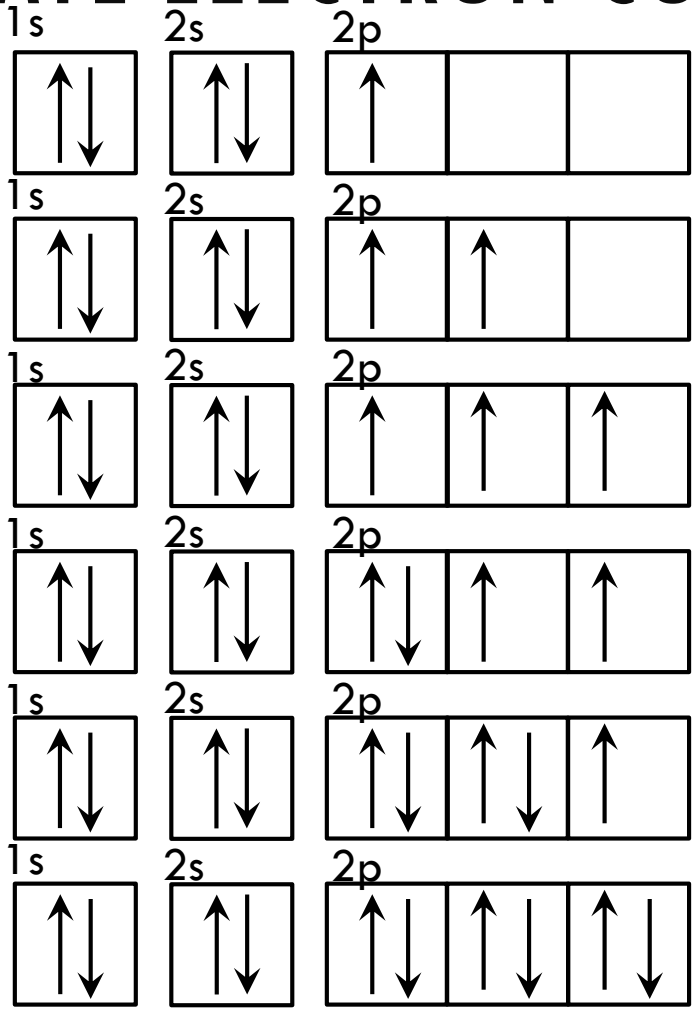
$1s^2 2s^2 2p$_____ **Oxygen: Z= 8**

$1s^2 2s^2 2p$_____ **Fluorine: Z= 9**

$1s^2 2s^2 2p$_____ **Neon: Z= 10**

GROUND STATE ELECTRON CONFIGURATIONS

Hund's rule!



$1s^2 2s^2 2p^1$

Boron: Z=5

$1s^2 2s^2 2p^2$

Carbon: Z= 6

$1s^2 2s^2 2p^3$

Nitrogen: Z= 7

$1s^2 2s^2 2p^4$

Oxygen: Z= 8

$1s^2 2s^2 2p^5$

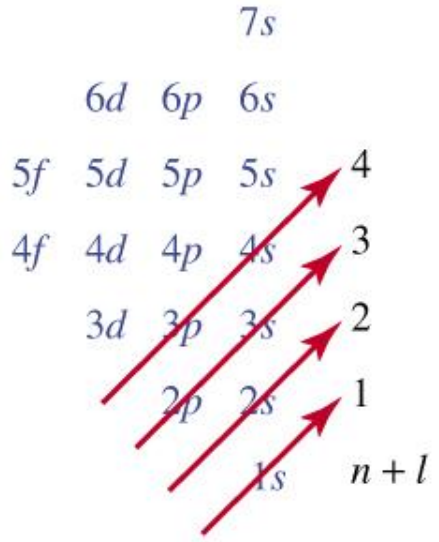
Fluorine: Z= 9

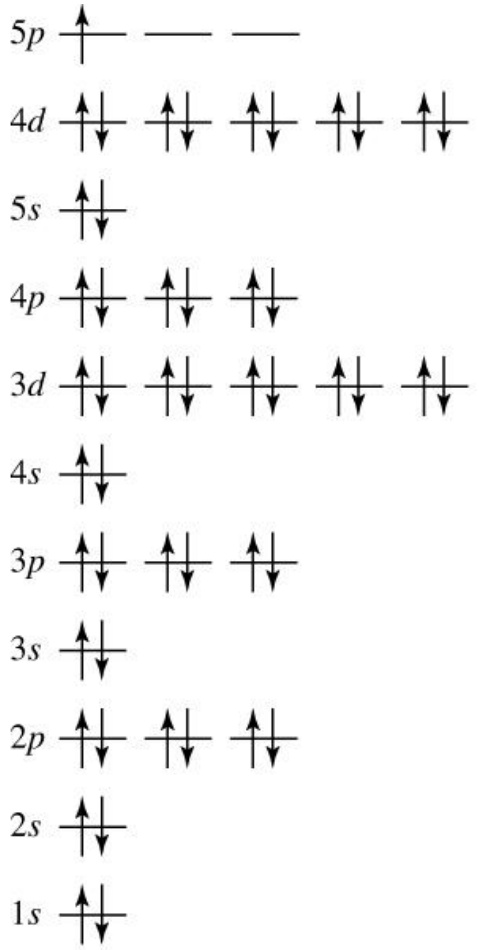
$1s^2 2s^2 2p^6$

Neon: Z= 10

EXAMPLE

What is the electronic configuration of Indium (Z=49)?





ELECTRON CONFIGURATION

What ground state atom has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^1$?

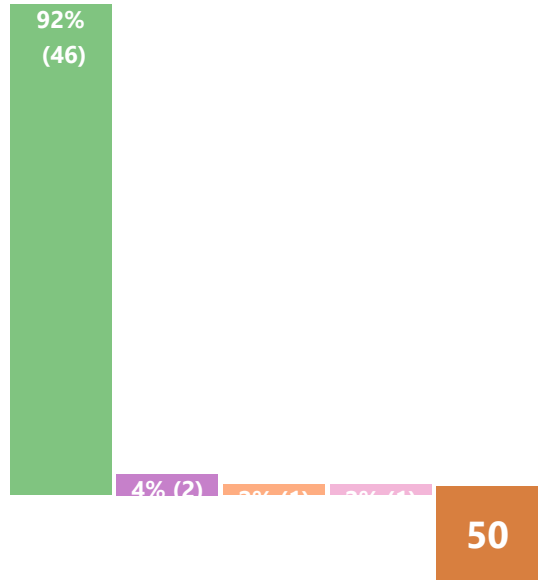
A B

B Al

C Sc

D Ga

E Don't know



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CORE AND VALENCE ELECTRONS

Electrons in filled sublevels (or subshells) matching the configuration of the previous noble gas in the periodic table are called **core electrons.**

The core electrons are sometimes **abbreviated** into the symbol for the preceding noble gas, e.g., boron = **[He]** $2s^2 2p^1$.

Notation	Configuration	Element
[He]	$1s^2$	He (2 electrons)
[Ne]	$[He]2s^2 2p^6$	Ne (10 electrons)
[Ar]	$[Ne]3s^2 3p^6$	Ar (18 electrons)
[Kr]	$[Ar]4s^2 3d^{10} 4p^6$	Kr (36 electrons)
[Xe]	$[Kr]5s^2 4d^{10} 5p^6$	Xe (54 electrons)
[Rn]	$[Xe]6s^2 5d^{10} 4f^{14} 6p^6$	Rn (86 electrons)

Electrons in partially filled shells (those other than the core electrons) are called **valence** electrons. These electrons are the ones doing chemistry most of the time! (They are the ones involved in bonding)

Both the 4s and 3d electrons are regarded as valence electrons of the transition metals although they are formally from different shells (n=3 and 4).

VALENCE ELECTRONS

1 2 3 4 5 6 7

Group number

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

lanthoids and actinoids (*f* block)

6	lanthanoid series *	57 **La** $6s^2 5d^1$	58 **Ce** $6s^2 4f^1 5d^1$	59 **Pr** $6s^2 4f^3$	60 **Nd** $6s^2 4f^4$	61 **Pm** $6s^2 4f^5$	62 **Sm** $6s^2 4f^6$	63 **Eu** $6s^2 4f^7$	64 **Gd** $6s^2 4f^7 5d^1$	65 **Tb** $6s^2 4f^9$	66 **Dy** $6s^2 4f^{10}$	67 **Ho** $6s^2 4f^{11}$	68 **Er** $6s^2 4f^{12}$	69 **Tm** $6s^2 4f^{13}$	70 **Yb** $6s^2 4f^{14}$	71 **Lu** $6s^2 4f^{14} 5d^1$
7	actinoid series **	89 **Ac** $7s^2 6d^1$	90 **Th** $7s^2 6d^2$	91 **Pa** $7s^2 5f^2 6d^1$	92 **U** $7s^2 5f^3 6d^1$	93 **Np** $7s^2 5f^4 6d^1$	94 **Pu** $7s^2 5f^6$	95 **Am** $7s^2 5f^7$	96 **Cm** $7s^2 5f^7 6d^1$	97 **Bk** $7s^2 5f^9$	98 **Cf** $7s^2 5f^{10}$	99 **Es** $7s^2 5f^{11}$	100 **Fm** $7s^2 5f^{12}$	101 **Md** $7s^2 5f^{13}$	102 **No** $7s^2 5f^{14}$	103 **Lr** $7s^2 5f^{14} 6d^1$

UNSW SYDNEY

VALENCE ELECTRONS

How many valence electrons does sulfur have?

S (Z=16)

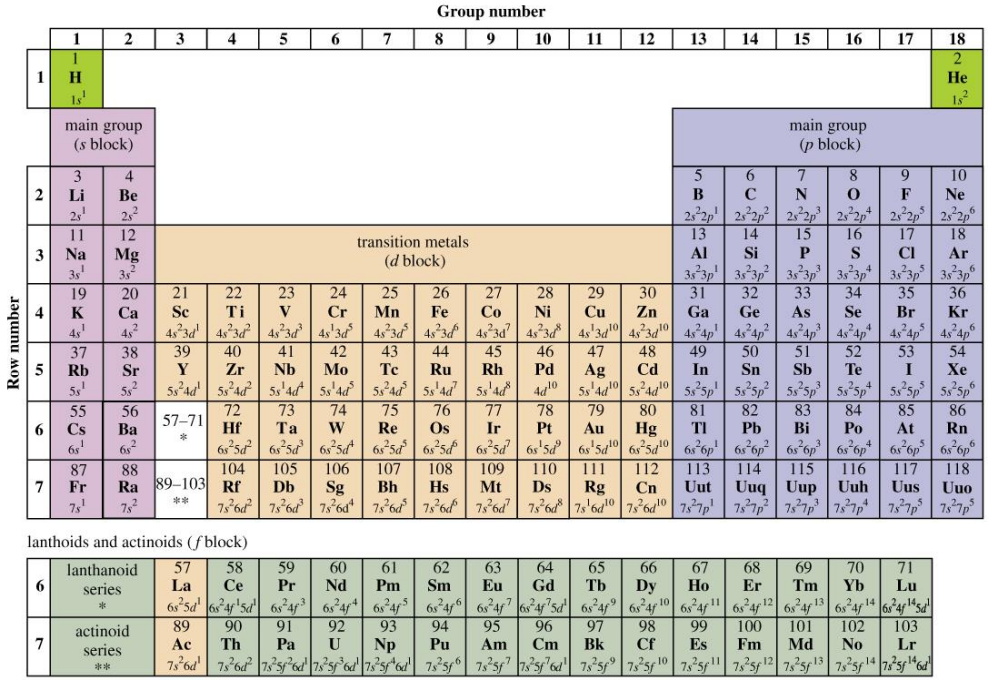
A 2

B 4

C 6

D 16

E Don't know



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UNSW SYDNEY

SHORTHAND NOTATION

What is the ground state configuration, using abbreviated form, of sodium?

Na (Z=11)

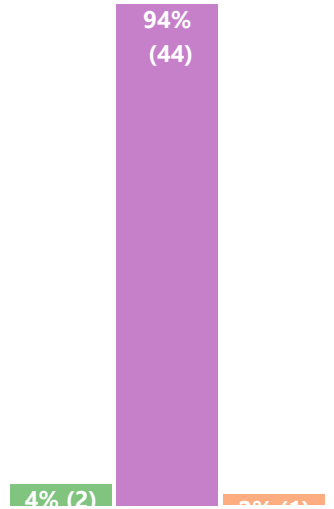
A [Na]

B [Ne]

C $[Ne]3s^1$

D $1s^2 2s^2 2p^6 3s^1$

E Don't know



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SHORTHAND NOTATION

What is the ground state configuration, using abbreviated form, of Cl?

Cl (Z=17)

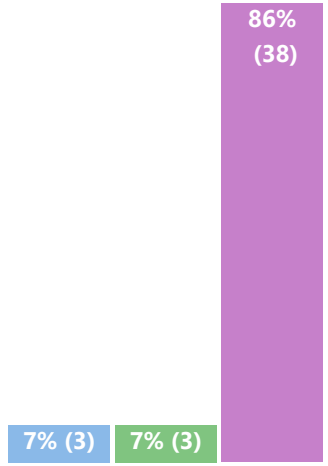
A $[Ar]3p^{-1}$

B $[Ar]3s^2 3p^5$

✓ C $[Ne]3s^2 3p^5$

D $1s^2 2s^2 2p^6 3s^2 3p^5$

E Don't know



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