Particles, atoms, and crystals 3

Many-electron atoms

Modern physics for engineers

David Miller

Many-electron atoms

All atoms other than hydrogen
have some larger integer number
Z, the "atomic number"
of protons in the nucleus
and hence of positive charges
and also Z electrons

Electrons progressively fill the "orbitals"
in order of increasing energy
the "Aufbau" principle

An “average” potential

Many-electron atoms

- Many-electron atoms are complicated because
  - the electrons all interact with one another through their Coulomb repulsion
- A useful approach is to presume that
  - each electron sees an average potential energy
    - from all the other electrons
      - together with the potential from the nucleus

Many-electron atoms

- That average potential is usually determined iteratively
  - which can be a complex process
- Setting the details aside
  - we can still approximately
    - understand how many-electron atoms behave

Central potentials

Central potentials

As a reasonable first approximation

- we can presume that the distribution of charge density from all the other electrons
  - is approximately spherically symmetric
    - at least in the core levels of the atom
      - giving a so-called "central potential"

Central potentials

As a result

- even in more complicated atoms
  - we can continue to use the spherical harmonics
    - as the first approximation to the angular form of the orbitals
      - and use the "hydrogen atom" labels for them
        - e.g., s, p, d, f, etc.

Radial functions

Radial functions

- For many-electron atoms, the radial functions
  - are different from the hydrogen ones
- One electron now sees both the charge on the nucleus
  - and the charge from the other electrons in the atom

Radial functions

But we still expect a set of radial functions

- indexed by some quantum number n
  - with behaviors that are broadly similar to those of the hydrogen atom radial functions
    - for example, in the number of "zeros"
      - and in the relation between the allowed values of l and m and the quantum number n

Particles, atoms, and crystals 3

Filling "shells" in atoms

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Filling of “shells”

For a large Z

- first, we would expect two electrons (of opposite spin)
  - to be very tightly bound in 1s-like states
    - because of the very strong attraction to the Z positive charges of the nucleus

Filling of “shells”

For the next electrons we might add

- those first two electrons partially “screen” or cancel the positive charge on the nucleus
  - so the next 2s-like and 2p-like orbitals will be less tightly bound

Orbitals with larger l

The 2p orbitals

- are slightly farther from the nucleus than the 2s orbitals
  - so the nucleus' positive charge is more screened
    - so they are less tightly bound than the 2s orbitals

This behavior is general for orbitals of progressively larger l

- so now orbitals of different l
  - do not have the same energy any more

Shells and filling rules

If we neglected the different energies for different l

- we would expect "shells" of a given n to fill up
  - 2 1s electrons in the first $n = 1$ shell
  - 8 in the second
    - 2 2s electrons and 6 2p electrons
  - 18 in the third
    - 2 3s electrons, 6 3p electrons, 10 3d electrons
- and so on

Shells and filling rules

Because of the different energies for different l

the states do no quite fill up in this order

One simple rule that is mostly but not perfectly followed:

states are filled up starting from smaller values of $n + l$ and

proceeding to larger values of $n + l$

with the states of lower n being filled first for each particular value of the sum $n + l$

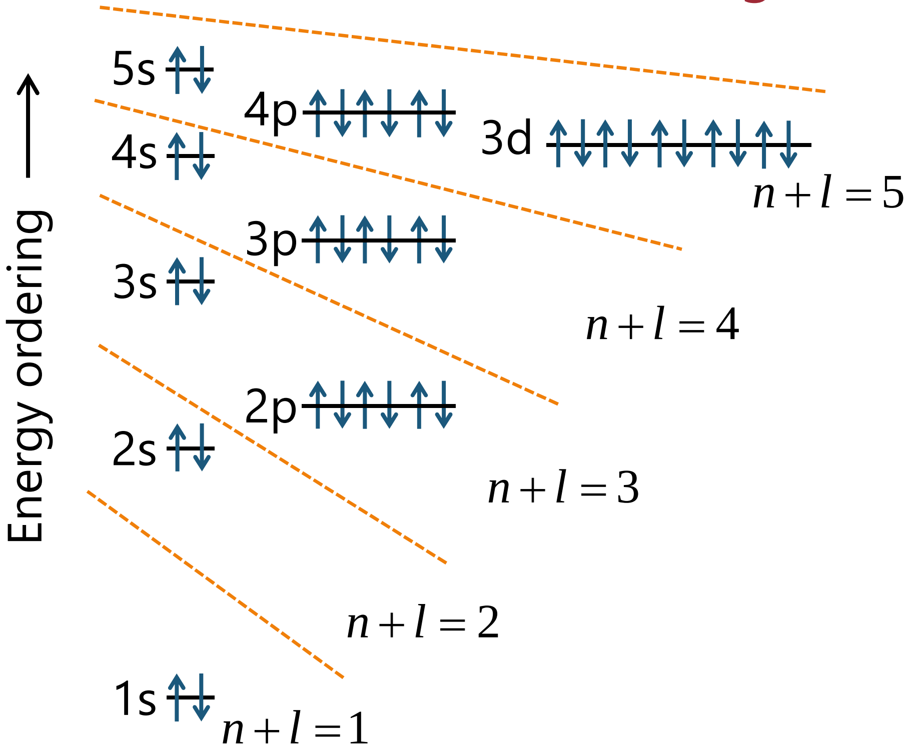
This is Madelung's rule

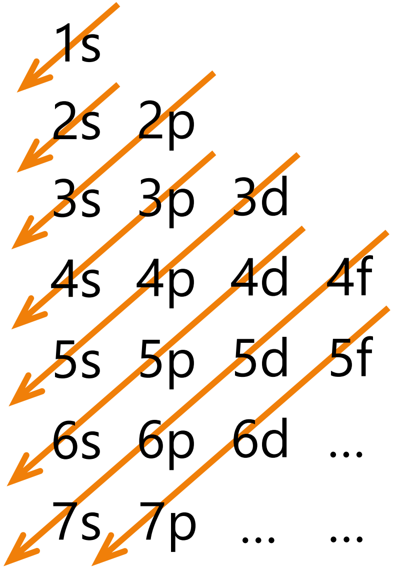
Madelung’s rule

Madelung's rule

Fill states from smaller $n + l$ to larger $n + l$

And within that, filling states from smaller n to larger n





Madelung's rule

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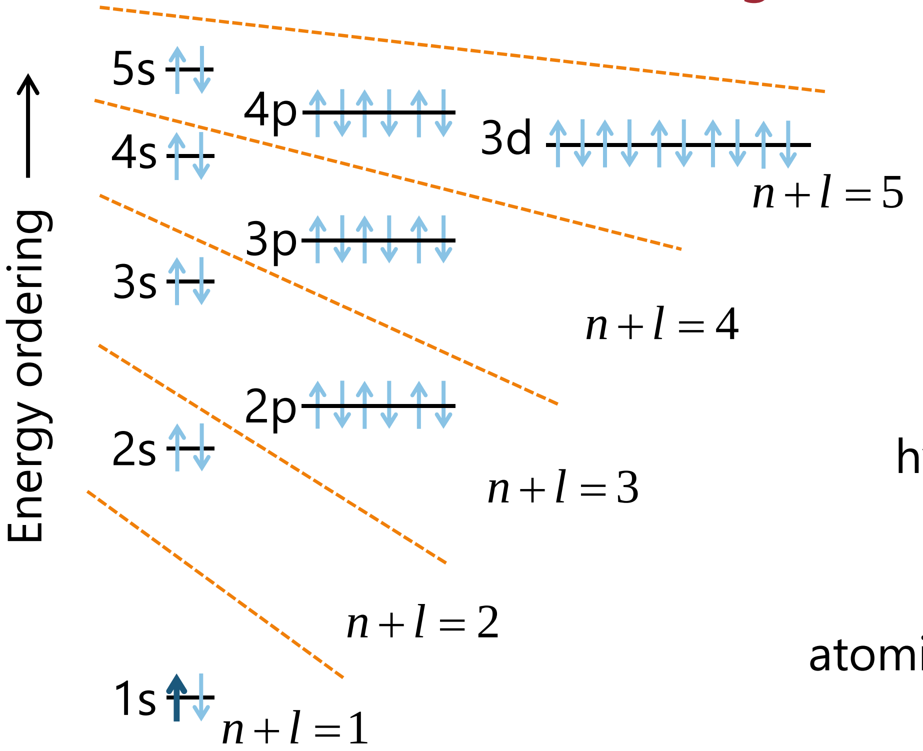
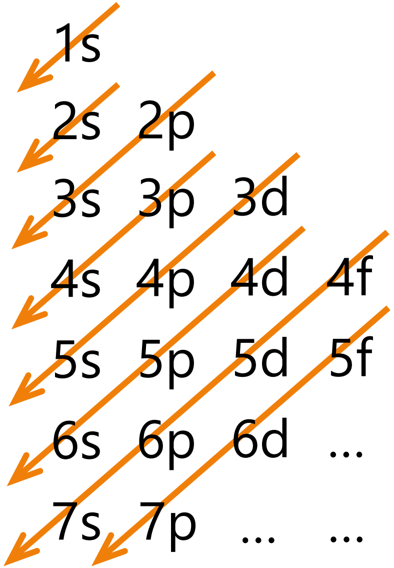
And within that, filling states from smaller n to larger n



hydrogen

$1s^1$

atomic number 1



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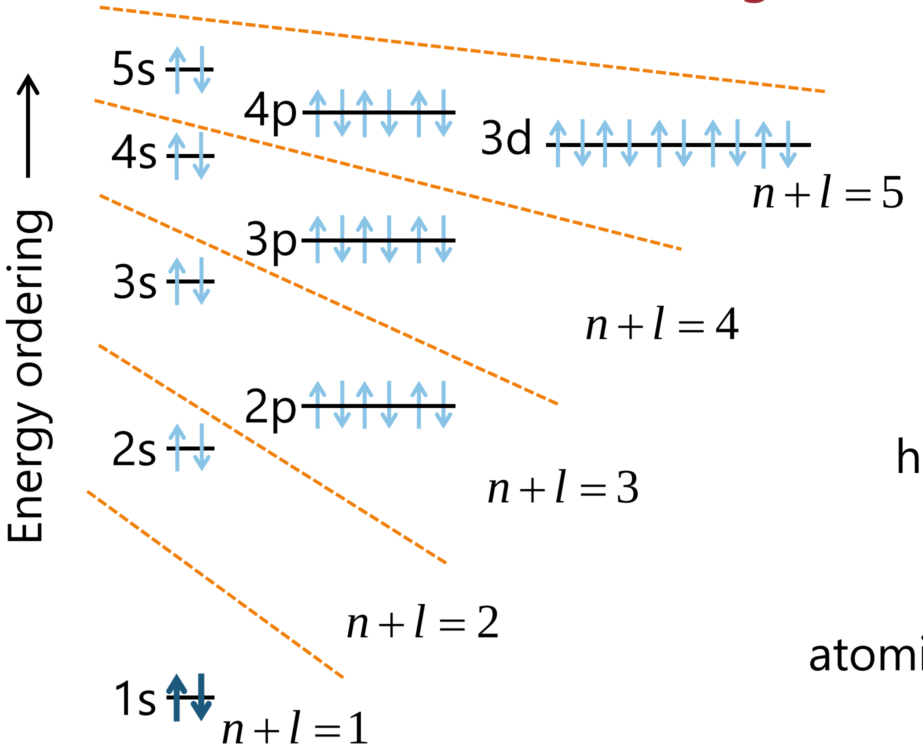
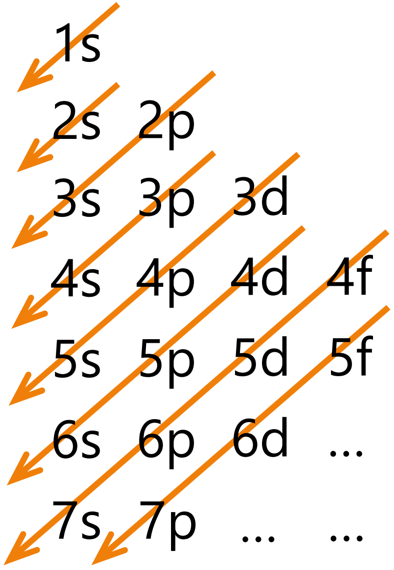


helium

$1s^2$

atomic number 2



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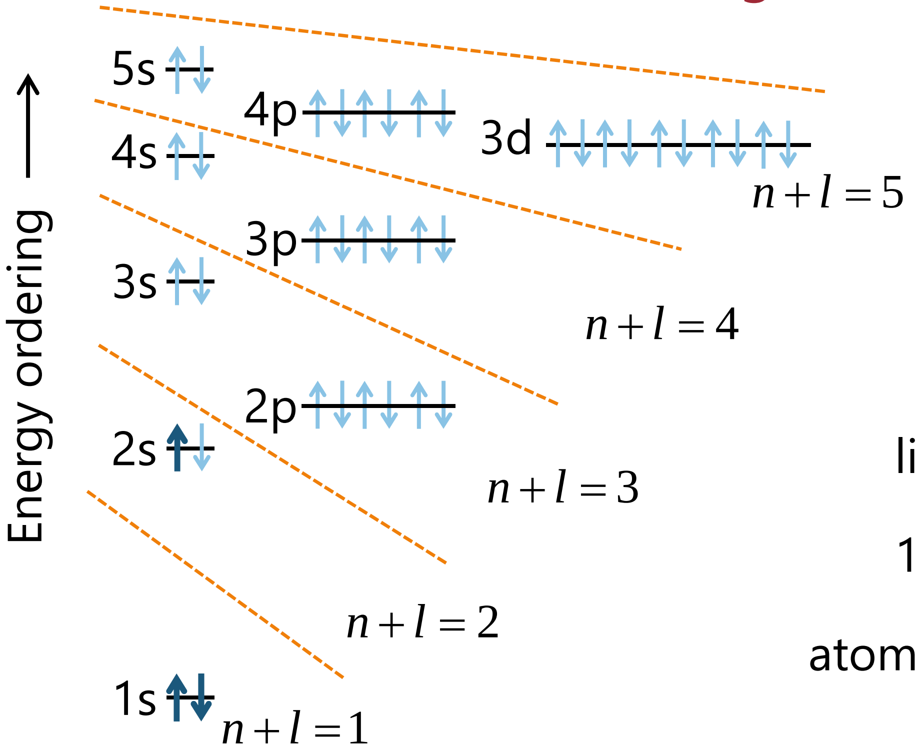
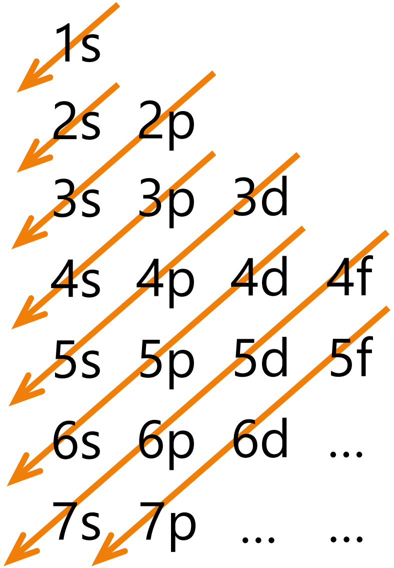


lithium

$1s^2 2s^1$

atomic number 3



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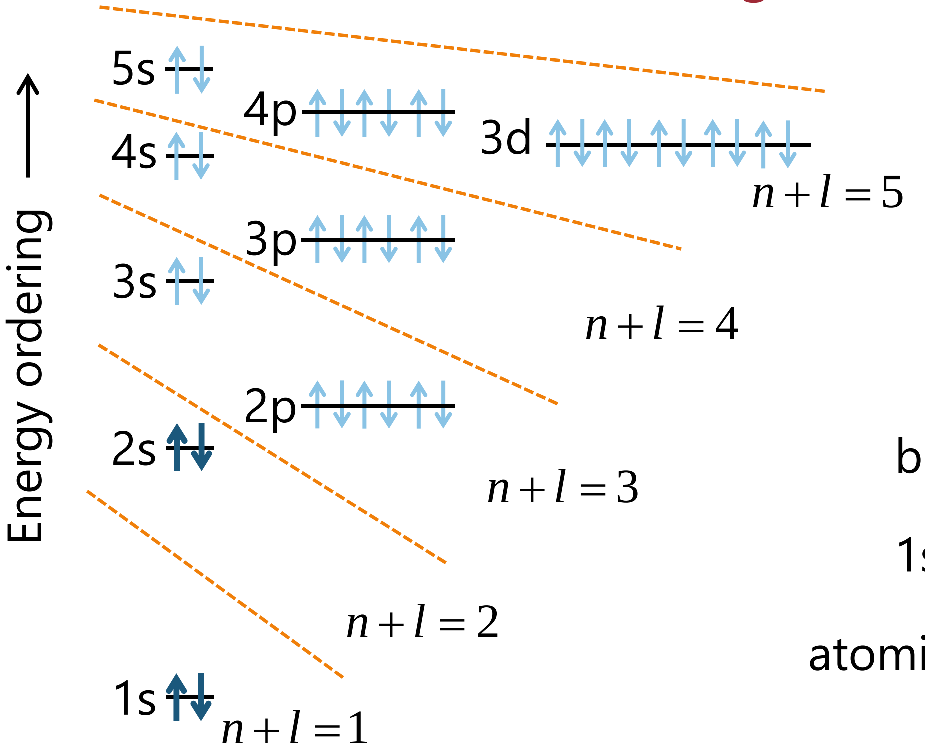
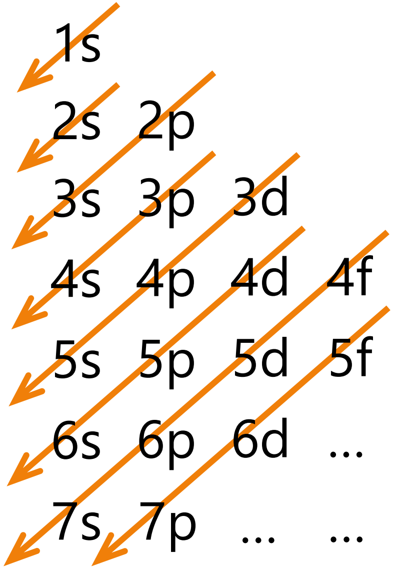


beryllium

$1s^2 2s^2$

atomic number 4



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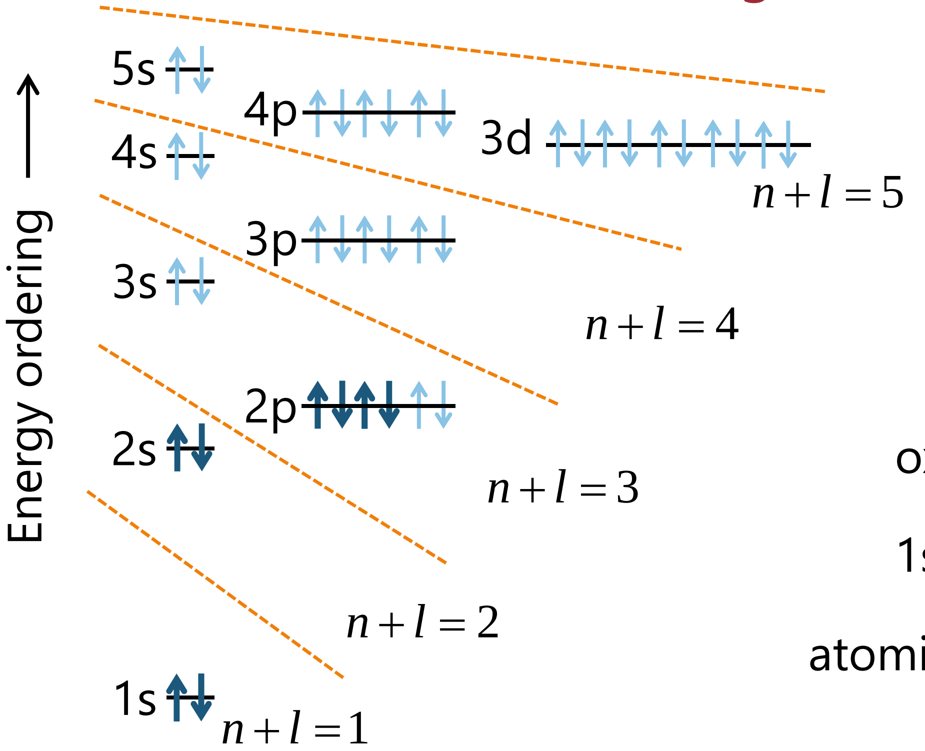
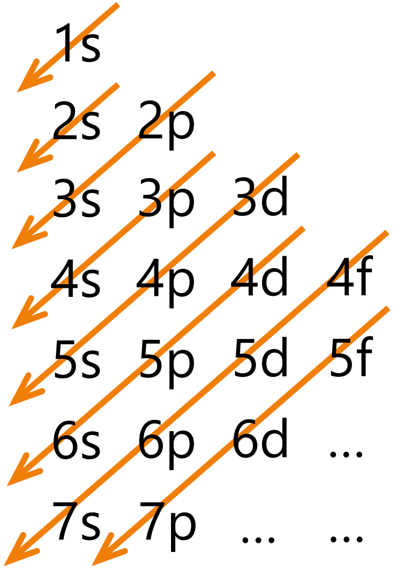


oxygen

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

atomic number 8



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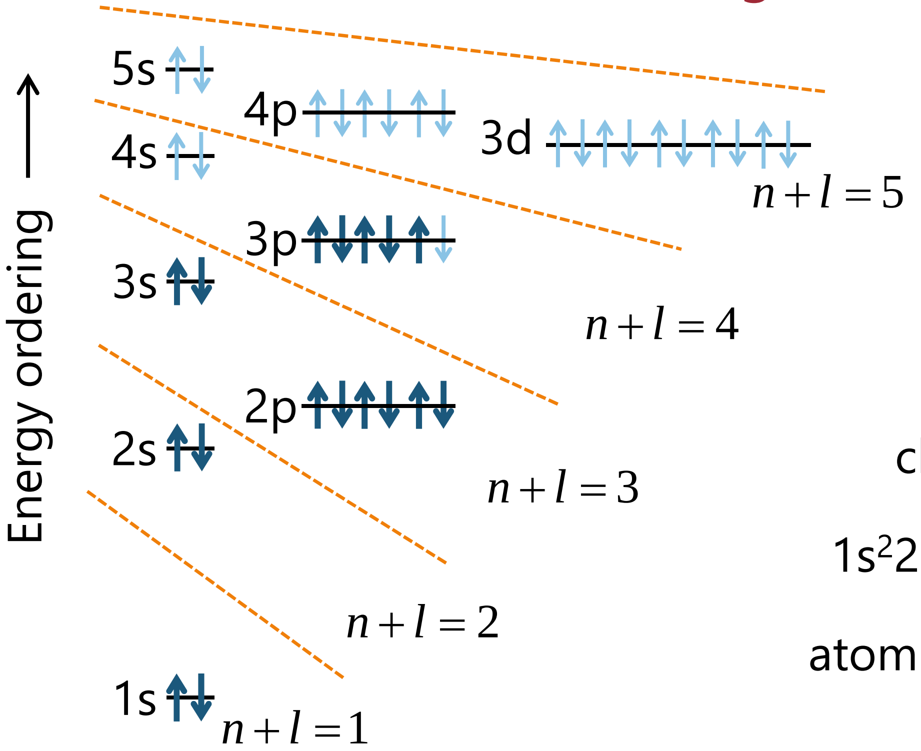
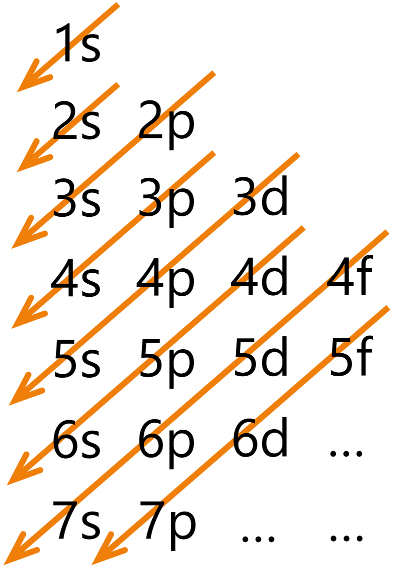


chlorine

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

atomic number 17



Madelung’s rule

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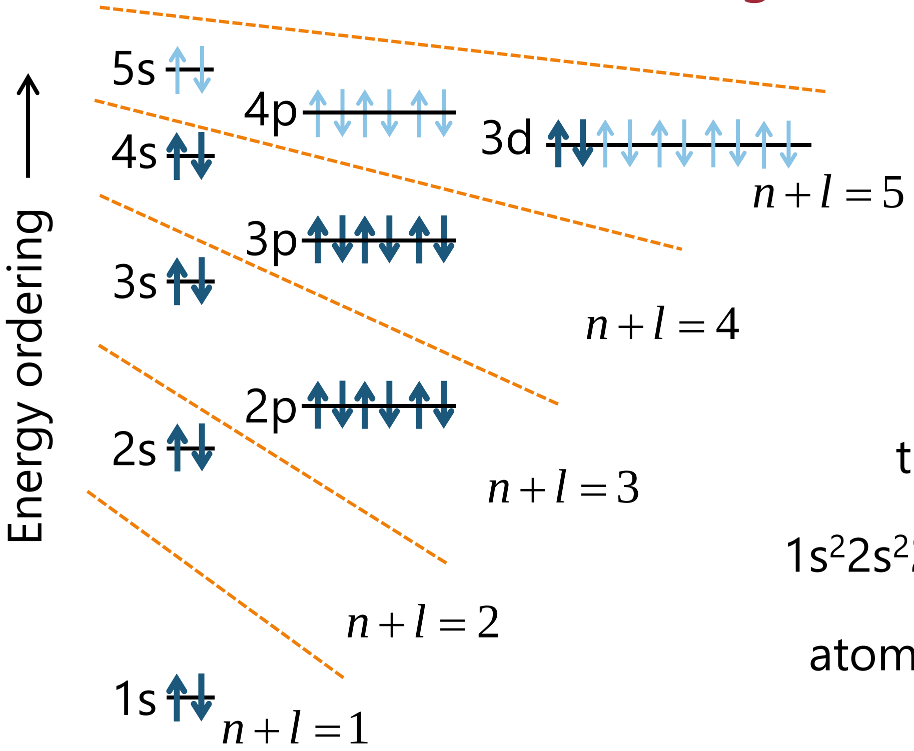
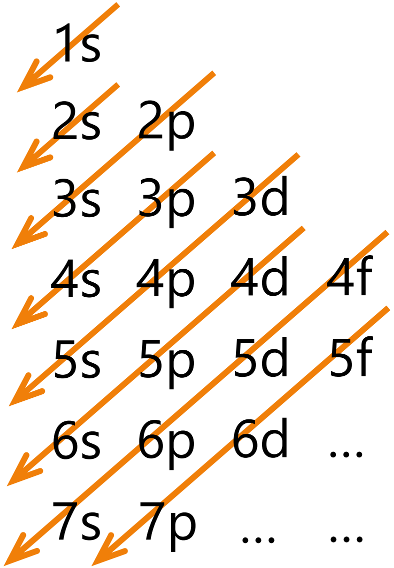
And within that, filling states from smaller n to larger n



titanium

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$

atomic number 22



"Noble gas" shorthand for atomic configurations

To save some writing

and because the "filled" inner shells of higher numbered atoms have the same configurations

we can use the atomic configurations of the noble gasses as a shorthand notation

$$[\mathrm{He}] \equiv 1s^2$$
$$[\mathrm{Ne}] \equiv 1s^2 2s^2 2p^6 \equiv [\mathrm{He}]\ 2s^2 2p^6$$
$$[\mathrm{Ar}] \equiv 1s^2 2s^2 2p^6 3s^2 3p^6 \equiv [\mathrm{Ne}]\ 3s^2 3p^6$$
$$[\mathrm{Kr}] \equiv 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 \equiv [\mathrm{Ar}]\ 3d^{10} 4s^2 4p^6$$
$$[\mathrm{Xe}] \equiv 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 \equiv [\mathrm{Kr}]\ 4d^{10} 5s^2 5p^6$$

Order of notation for atomic configurations

The order for the notation does not matter

The configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$ for titanium is in "Madelung's rule" order

The noble gas configurations are in order of increasing n

and then in order of increasing l within each group with the same n

$$[\mathrm{He}] \equiv 1s^2$$

$$[\mathrm{Ne}] \equiv 1s^2 2s^2 2p^6 \equiv [\mathrm{He}]\ 2s^2 2p^6$$

$$[\mathrm{Ar}] \equiv 1s^2 2s^2 2p^6 3s^2 3p^6 \equiv [\mathrm{Ne}]\ 3s^2 3p^6$$

$$[\mathrm{Kr}] \equiv 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 \equiv [\mathrm{Ar}]\ 3d^{10} 4s^2 4p^6$$

$$[\mathrm{Xe}] \equiv 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 \equiv [\mathrm{Kr}]\ 4d^{10} 5s^2 5p^6$$

Multi-electron atoms and chemistry

This approach to multi-electron atoms

- largely explains the electronic configuration of atoms
  - and why it is the electrons in the last or "valence" "shell"
    - that participate in most of the chemical reactions
      - those being the least tightly bound electrons in the atom

Particles, atoms, and crystals 3

Fermions and bosons

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Spin and elementary particles

Spin and elementary particles

- Spin is an intrinsic property of all "elementary" particles
  - Its magnitude is fixed for each type of particle
- Particles divide into two categories
  - fermions
    - which have half-integer spin
  - bosons
    - which have integer spin

Spin and elementary particles

Of the various particles we come across in daily life

- electrons, protons, and neutrons
  - all have spin ½
    - and are fermions
- photons
  - have spin 1
    - and are bosons

Spin and elementary particles

All of the "elementary particles"

- that is, ones that are not apparently made up out of other particles

appear to have either spin ½ or spin 1

- with the exceptions of
  - the Higgs boson
    - which is thought to have spin 0
  - and the graviton
    - which is posited to have spin 2

Compound particles

Compound particles

We can have compound "particles"
- whose spins are sums and/or differences
  - of their constituent particles

Protons and neutrons are not strictly elementary particles
- They are each made of three "quarks"
  - Quarks themselves are fermions

The helium-4 nucleus (the alpha particle)
- is made of 4 spin ½ particles
  - two protons and two neutrons
    - and is a boson

Fermions, bosons and Pauli exclusion

Fermions, bosons and Pauli exclusion

Fermions obey Pauli exclusion

- but bosons do not
  - So, we can have any number of bosons all in the same state

One important consequence

- the laser
  - which can have very large numbers of photons
    - all in the same "mode"
      - i.e., the same light beam

A common misconception

A common misconception

One common misconception is to think that

"electrons interact because they are fermions"

and

"photons do not interact because they are bosons"

A common misconception

In fact

- electrons interact
  - because they are charged
- photons have extremely weak interactions
  - because they are not charged

Helium-4 nuclei

- which are bosons
  - would interact very strongly

A common misconception

- Part of the confusion is that we say that
  - we can have multiple bosons in the same state
- For strongly interacting bosons like helium-4 nuclei
  - that is indeed still true
    - But …

A common misconception

An eigenstate occupied by some large number of helium-4 nuclei

- would not necessarily be the same eigenstate that we would put one helium-4 nucleus in
  - The interaction between the bosons
    - would change the eigenstates of the system

Particles, atoms, and crystals
3

Identical particles

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Identical particles

- We think of classical particles as being
  - "non-identical"
    - One brick is slightly different from another brick
- Quantum mechanical particles of a given type
  - are absolutely identical to one another
    - with no way whatsoever of telling them apart

An analogy for identical particles

This means that the counting of possible states of multiple identical quantum particles

is different from that of classical particles

This kind of perfectly "identical" entities

is actually known to us in our everyday world

An analogy will help!

Identical particles

- Dollar bills are *not* identical
  - They each have different serial numbers
- Dollars in bank accounts
  - are identical
    - It is not meaningful to ask which dollar is in which account
  - This is the sense that quantum mechanical particles of a given kind are identical

Bank account analogy

- Suppose you have
  - an antique jar (*a*) in the kitchen for your spending money
  - and a box (*b*) under the bed for your savings money
- You put your dollar bills
  - each labeled with a unique number
    - into either the antique jar (*a*) or the box (*b*)

a

b

Bank account analogy

This is like the quantum mechanical situation of

non-identical particles (the dollar bills) and

different single-particle states or modes (a or b)

into which they can be put

– the jar or the box

a

b

Bank account analogy

If I have two dollar bills

- then there are four possible situations
  - i.e., states of the entire system
    - of two dollar bills in the antique jar and/or the box

a

b

Bank account analogy

bill 1 in the box and bill 2 in the box

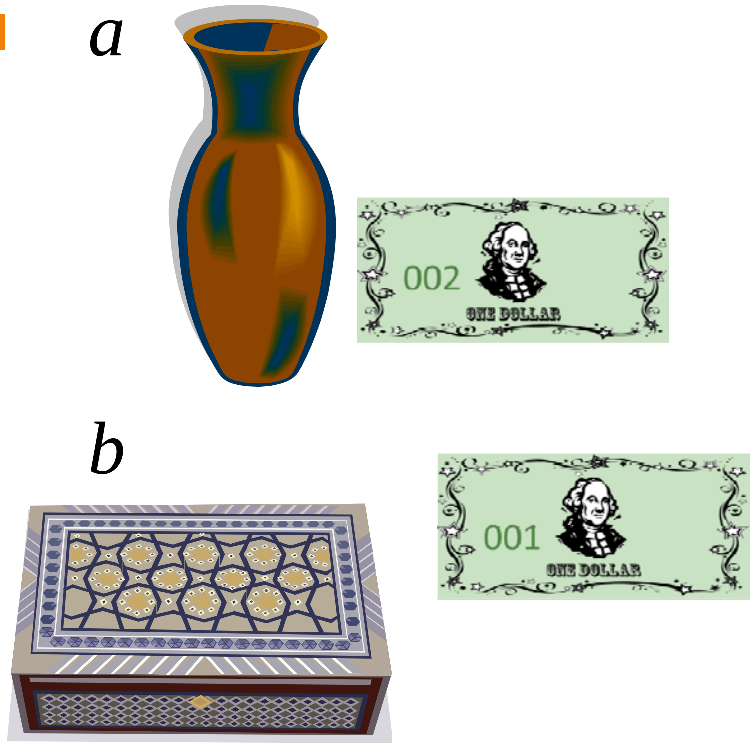
a

b

Bank account analogy

bill 1 in the box and bill 2 in the box

bill 1 in the box and bill 2 in the antique jar



Bank account analogy

bill 1 in the box and bill 2 in the box

bill 1 in the box and bill 2 in the antique jar

bill 1 in the antique jar and bill 2 in the box

a

b

Bank account analogy

bill 1 in the box and bill 2 in the box

bill 1 in the box and bill 2 in the antique jar

bill 1 in the antique jar and bill 2 in the box

bill 1 in the antique jar and bill 2 in the antique jar

a

b

Bank account analogy

bill 1 in the box and bill 2 in the box

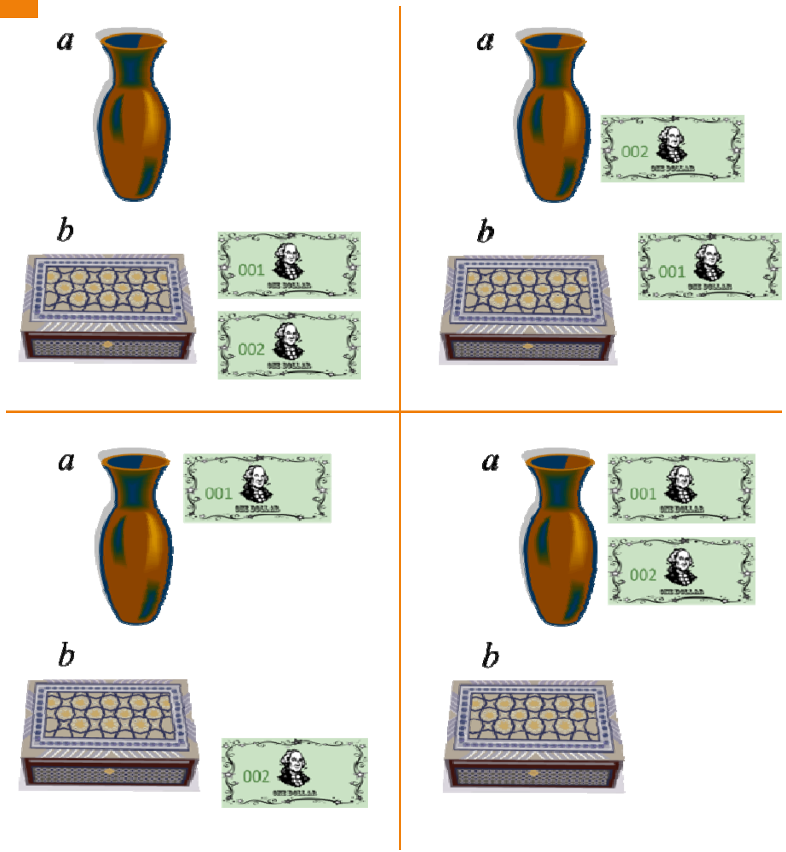
bill 1 in the box and bill 2 in the antique jar

bill 1 in the antique jar and bill 2 in the box

bill 1 in the antique jar and bill 2 in the antique jar

making four states altogether

This reproduces the counting for non-identical particles



Bank account analogy

Consider next that you have two bank accounts

- a checking account (a), and a savings account (b)

You may still have the same amount of money

- $2

You may know how much money you have in each account

- but the dollars are themselves identical in the accounts

So now there are only three possible states

- Two dollars in savings
- One dollar in savings and one in checking
- Two dollars in checking

Bank account analogy

Note that, in these three possible states

- Two dollars in savings
- One dollar in savings and one in checking
- Two dollars in checking

there are

- 2 states with both dollars in the same account
  - but only one in which they are in different accounts

This bank account argument above gives the counting for boson states

Bank account analogy

Consider now that you have two bank accounts

- a checking account (a) and a savings account (b)

but you are living in the Protectorate of Pauliana

- where you may have no more than one dollar in each bank account

Then for your two dollars

- there is only one possible state
  - one dollar in savings
  - one dollar in checking

This gives the counting for fermion states

Counting states with two “bank accounts”

For the case of identical fermions

- there is only one possible state for our two dollars
  - with each dollar being in a different bank account

For identical bosons

- there are three possible states for our two dollars
  - in two of which both are in the same bank account
  - and in one of which they are in different bank accounts

For non-identical (classical) particles

- there are four possible states for our dollar bills
  - in two of which both are in the same bank account
  - and in two of which they are in different bank accounts

Identical particles

This "identicality" of quantum mechanical particles

- changes the way that they distribute themselves among available states
  - when we think about thermal distributions
    - which has major consequences for devices of many kinds