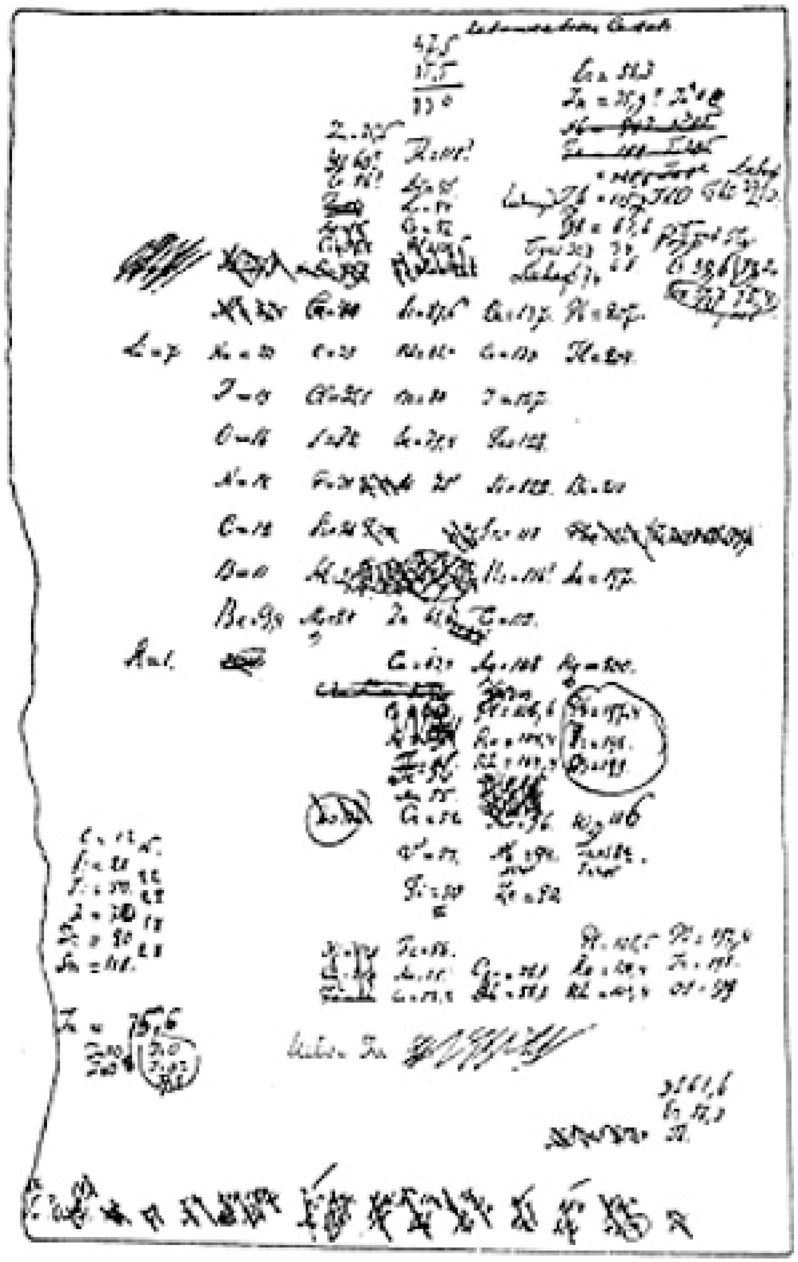
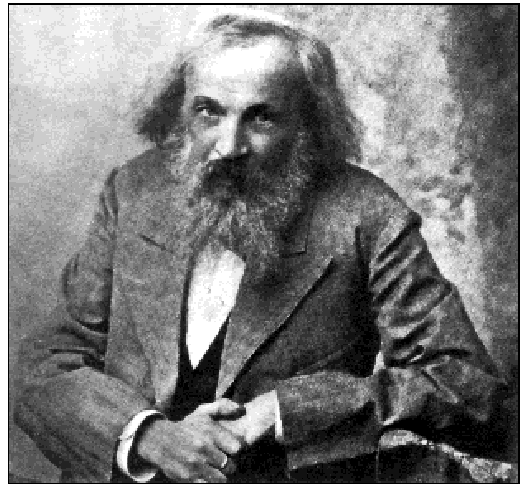
Chemisty before quantum theory (1869)





Mendeleev categorizes elements by similar chemical bondings, physical properties etc. and orders elements by *atomic weight*. *(wrong)*

i.e. all based on **macroscopic** properties.

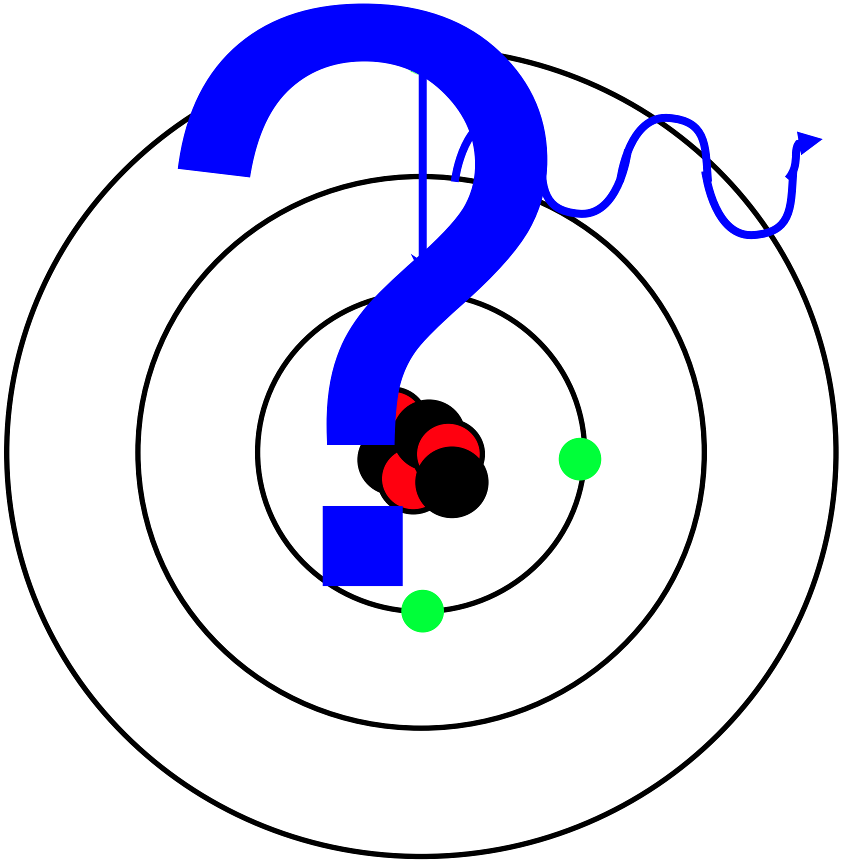
Many missing elements, and the types of bonds (“properties”) get increasingly hard to describe for heavy elements.

However, there are two “holes” in the table that are discovered:

* germanium
* gallium

But no underlying theory (yet) as to why this pattern exists.....

The other problem with Bohr's atom



The shells of the Bohr model were *postulated* to account for the quantized spectrum

De Broglie's waves explained the origin of quantization

But in elements with many electrons why do the electrons go to higher energy orbits instead of all occupying the lowest energy orbit?

The solution:

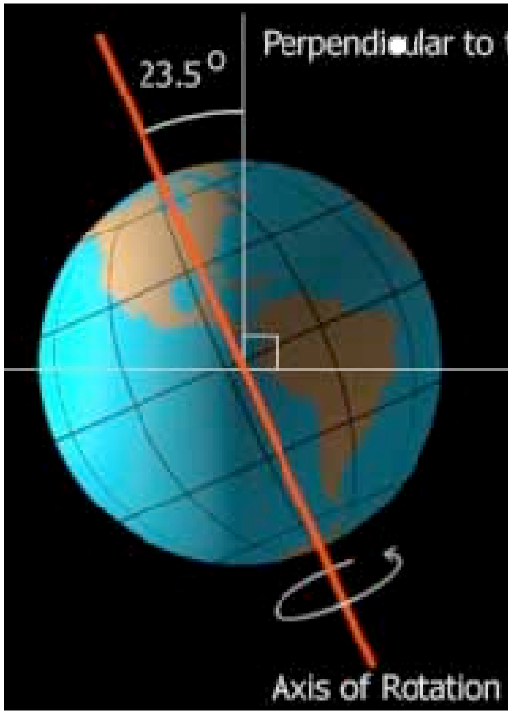
- electrons have one more quantum number: spin

- ***Pauli exclusion principle***

No two "fermions" can be in the *same state*.
(i.e. at least one of the "quantum numbers" must be different)

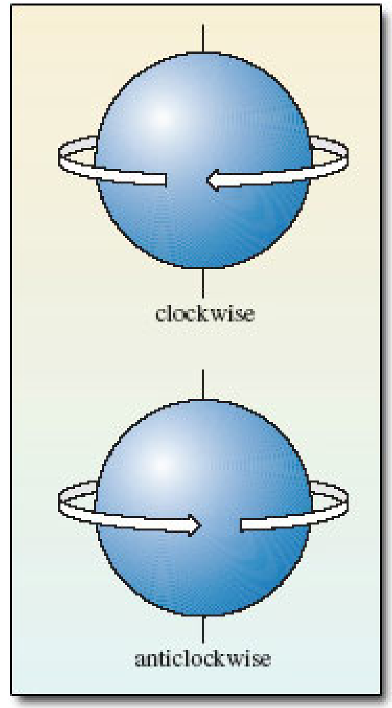
A new spin on particles

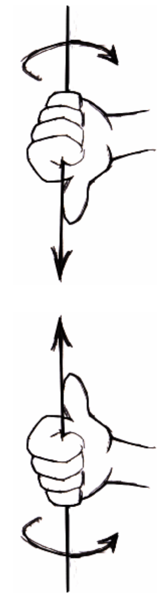
What are “fermions”? To answer this we need an additional quantum number **spin**



“spin down”

“spin up”





Earth “spins” on its axis as it goes around the sun.

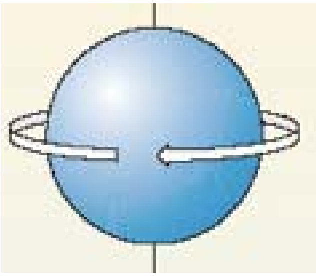
Other particles (electrons, protons, neutrons,...) also spin around their own axes.

Unlike large objects, the spin is quantized (can only take particular values).
For electrons, protons and neutrons only two options called “spin up” and “spin down”

Bosons v. Fermions

Orbitals: $2\ell + 1$ possible orientations (m values)

Spin s: $2s + 1$ possible orientations (m values)



Electrons have two orientations $\Rightarrow$ "spin $\frac{1}{2}$"

Fermions are particles with an *even* number of possible orientations ($s = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$)

Bosons are particles with an *odd* number of possible orientations ($s = 0, 1, 2, \ldots$)

Bosons "want" to be in the same state.

(critical for lasers!)

Fermions *cannot* to be in the same state.

This is the Pauli principle!

(critical for atomic structure!)

Fermion	Boson	
Electrons	Photon	Familiar particles
Neutron		
Proton		
He-3	He-4	Atoms
⋮	⋮	
Quarks	Gluons	Other elementary particles
Neutrino	W/Z bosons	

Quantum chemistry

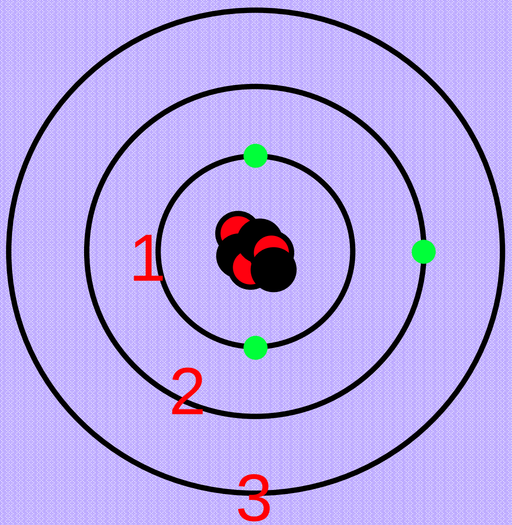
Start by looking at the different possible states

n	l	m	spin
1	0	0	Up
1	0	0	Down
2	0	0	Up
2	0	0	Down
2	1	-1	Up
2	1	-1	Down
2	1	0	Up
2	1	0	Down
2	1	1	Up
2	1	1	Down
3	0	0	Up
etc	etc	etc	etc

Two electrons to fill n=1 "shell"

Eight electrons to fill n=2 "shell"

Lowest energy for Lithium



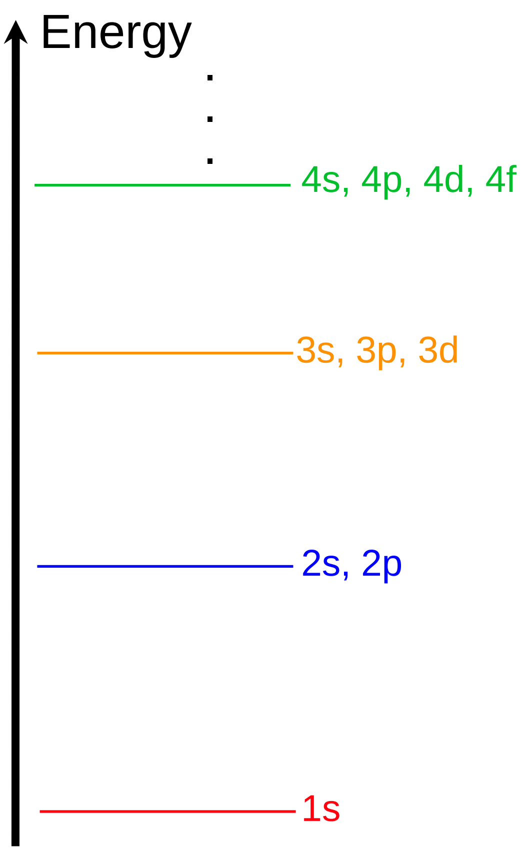
(Bohr + Pauli)

Electron in n=2 shell cannot fall into the n=1 shell as all the states are already taken!

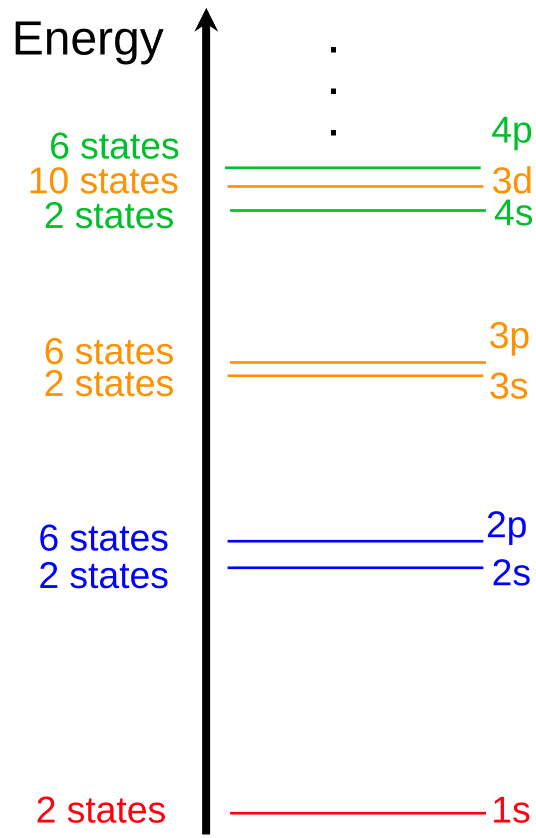
The energy level structure

For hydrogen, only the “n” quantum number was needed to get the energy

In heavier elements, electron-electron interactions make energy depend on **n** and **l**.



Hydrogen

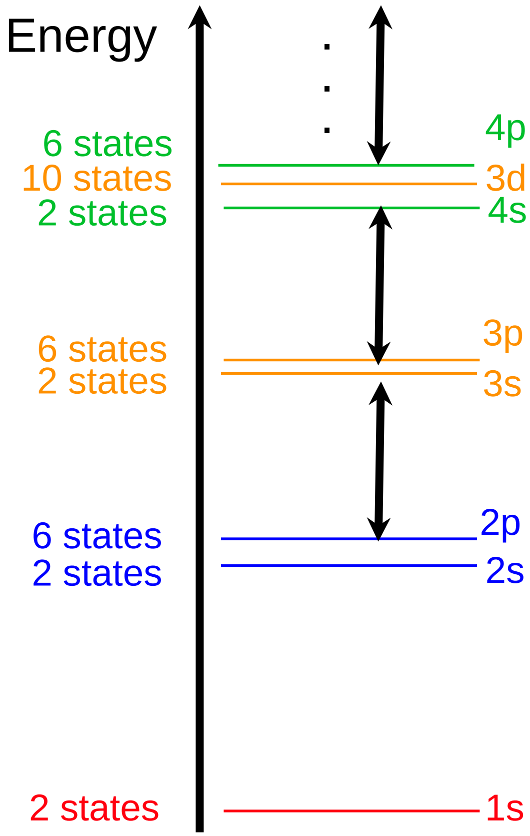


Note the 4th shell will start filling before the 3rd shell is full

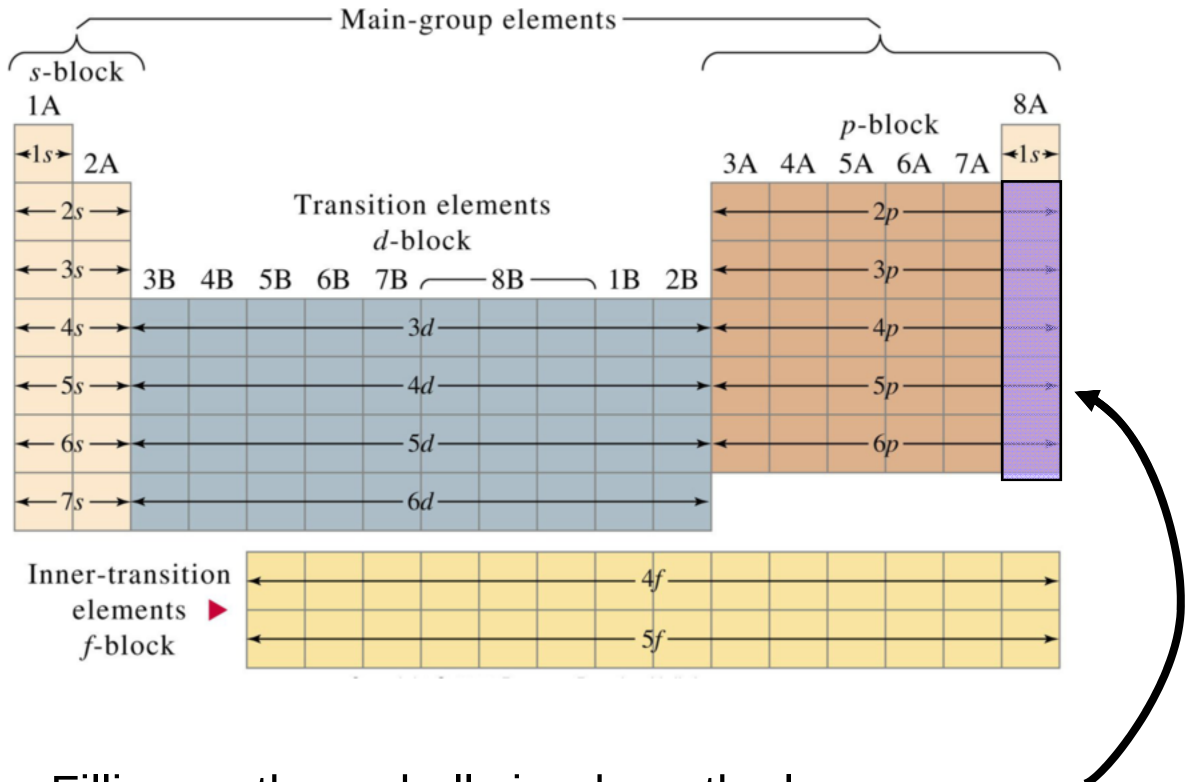
Typical multi-electron atoms

m and spin still ~ “degenerate”, so not shown on this diagram

The inert elements



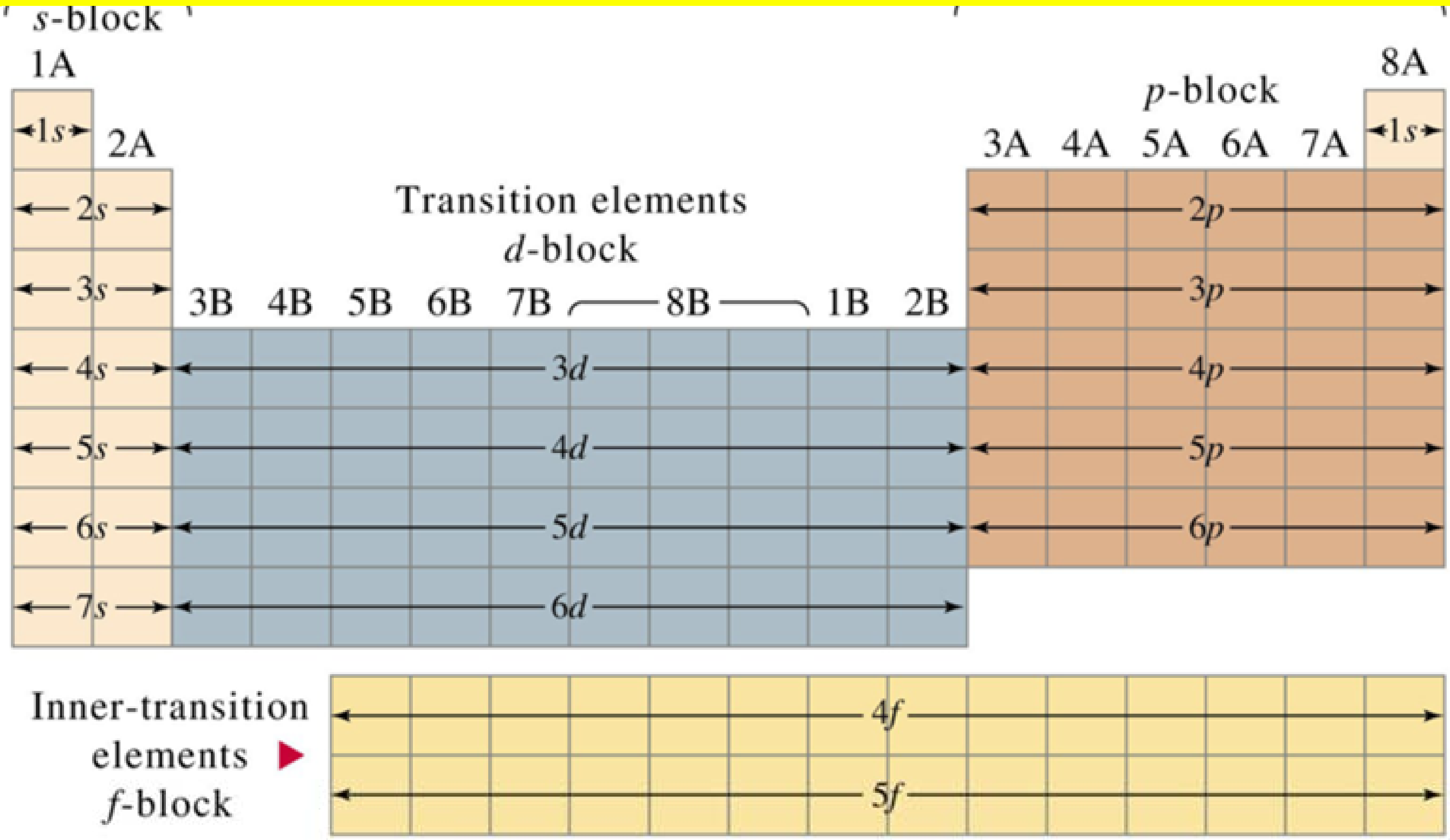
Typical multi-electron atoms



Filling up the p shells is where the large gaps occur -- these are the inert elements!

Test yourself:
How many protons does the second (i.e. not Helium) inert ("noble") gas have? You only need the diagram on the left.

Chemistry = Schroedinger energy levels + Pauli principle!

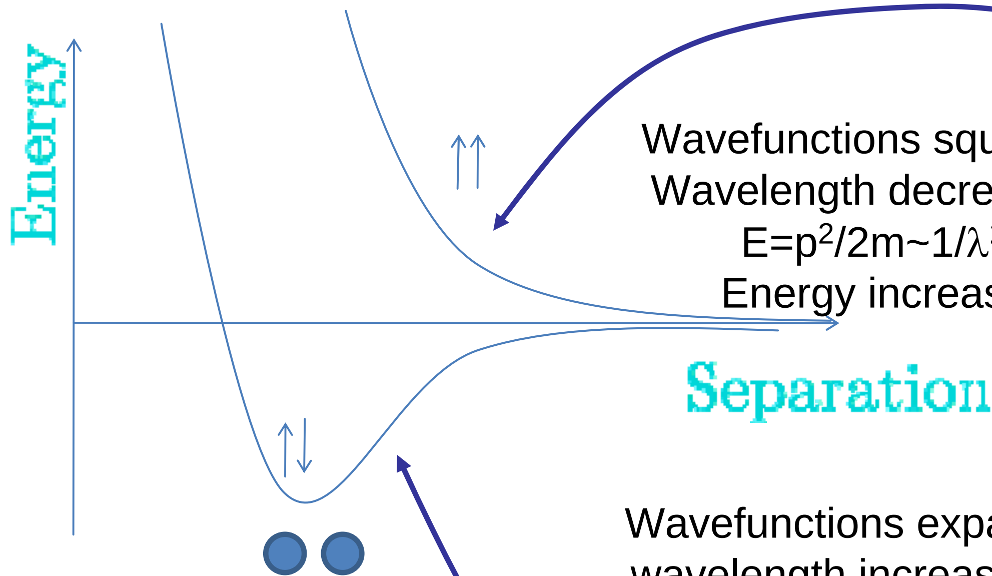


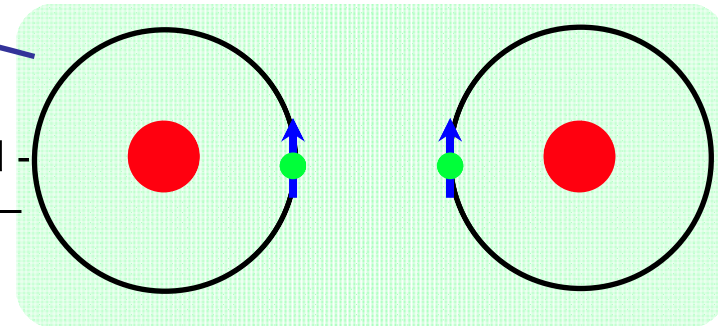
- Only the outer levels of the electrons useful for bonding
- Structure of table mimics the electron shell structure

(Note that elements are characterized by *atomic number*,
not *atomic weight* first proposed by Mendeleev)

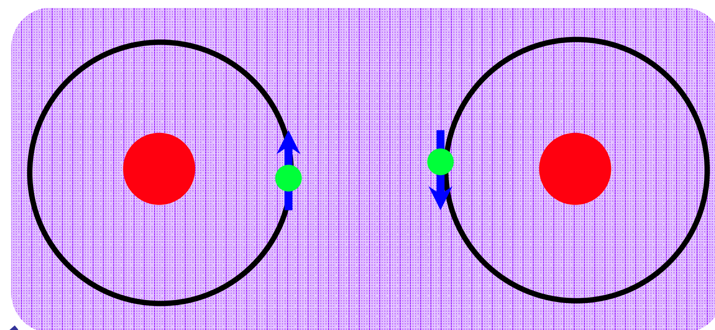
Covalent bonding

Hydrogen-Hydrogen bonding





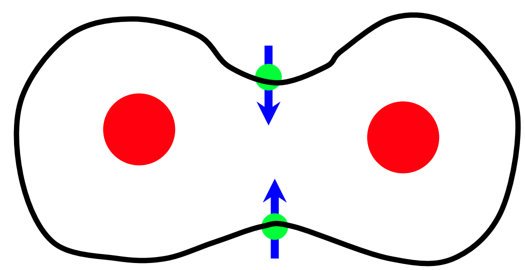
Wavefunctions squished -
Wavelength decreases –
$E=p^2/2m\sim 1/\lambda^2$ –
Energy increases



Wavefunctions expand -
wavelength increases –
$E=p^2/2m\sim 1/\lambda^2$ –
Energy lowered

No H3 molecule.

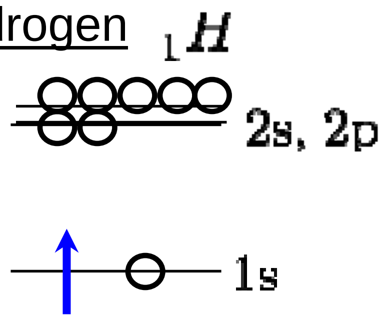
No room for a "third" electron in the *n=1* shell



Spin "up" & "down" share *n=1* level:
Form H_2 with less energy than 2H

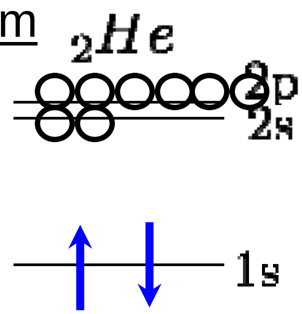
Covalent bonding

Hydrogen

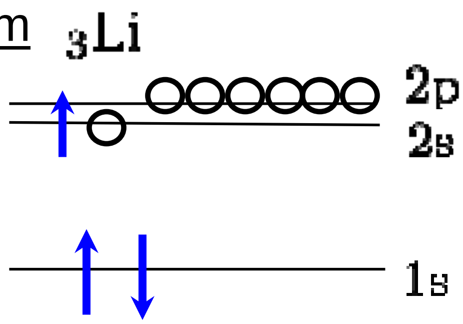


(note: this spin could be “up” or down)

Helium



Lithium



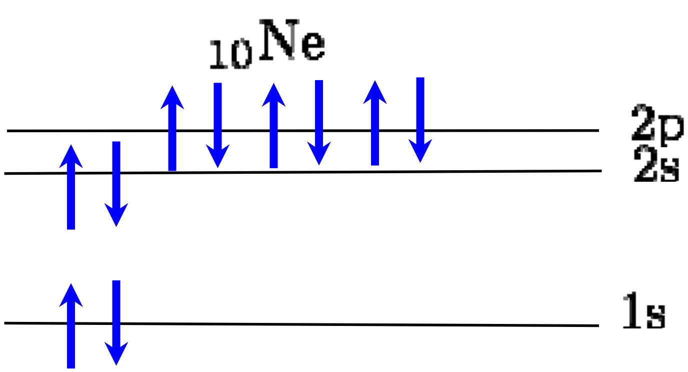
(note: top spin could be “up” or down)

O represent “empty state”

Note: Helium is stable -- it is impossible to add an electron into the 2s state (Pauli).

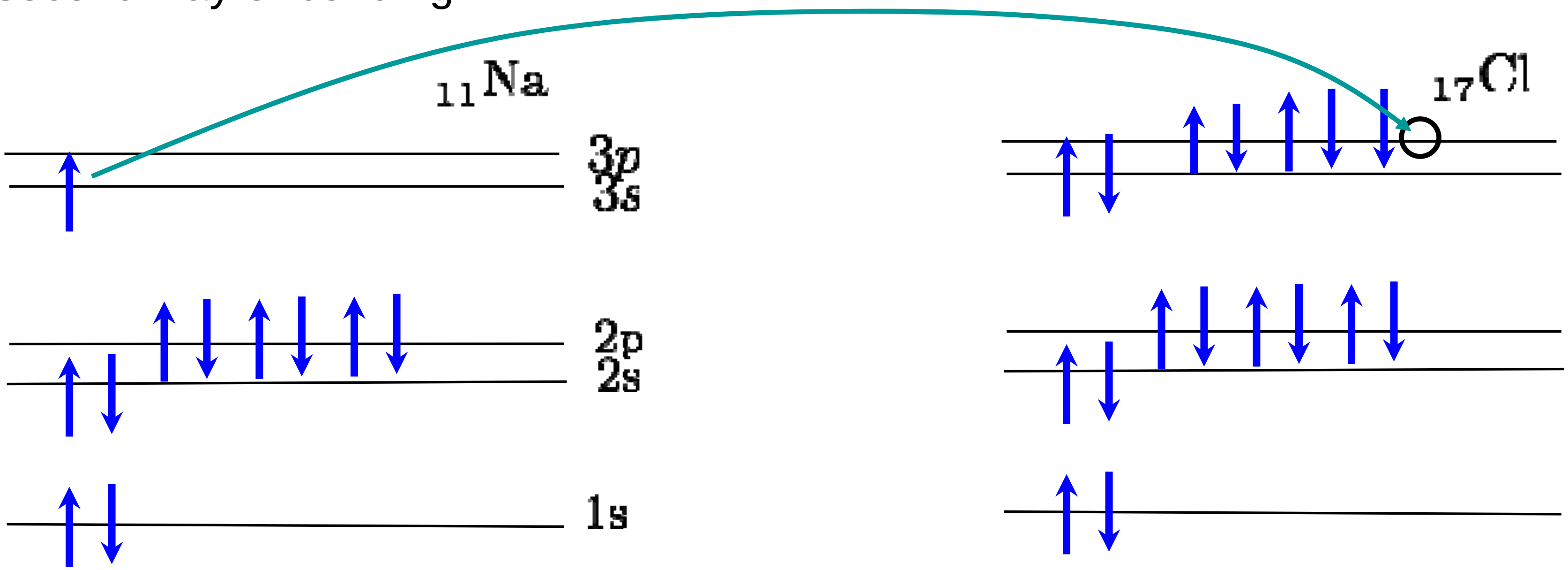
Next stable element fills 2s + 2p
(need 10 electrons => 10 protons
i.e. *Neon*)

Neon



Ionic bonding

A second way of bonding:



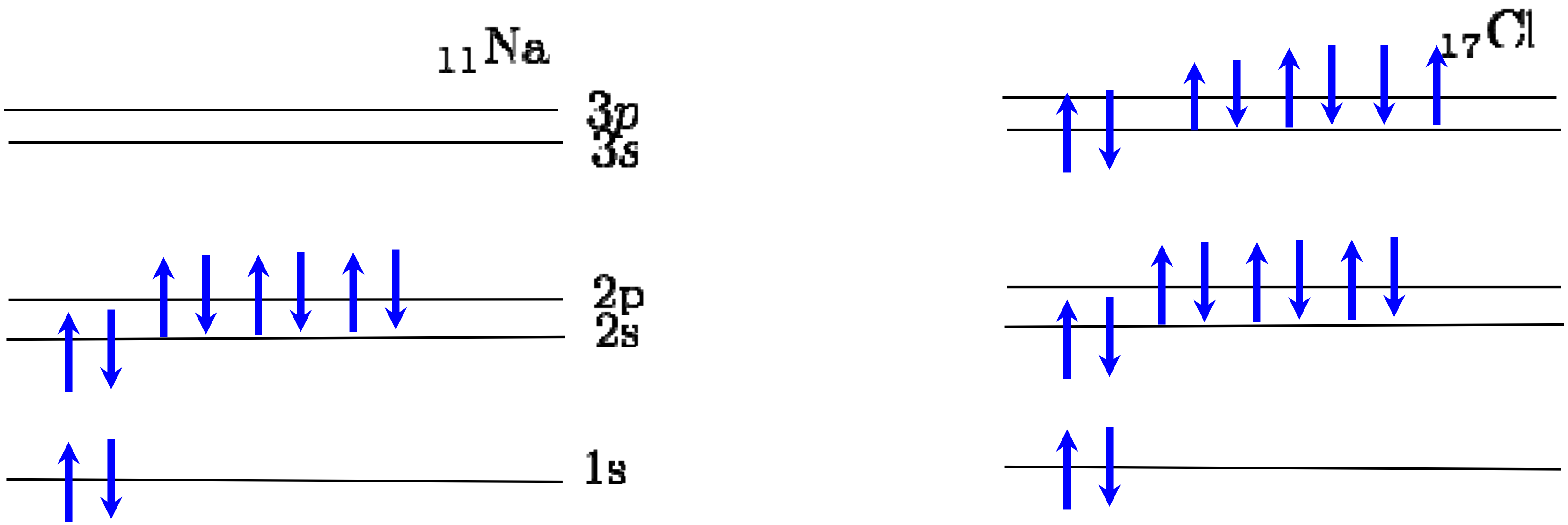
(Recall 3d is with 4s and 4p)

one "extra" electron

one "missing" electron

Ionic bonding

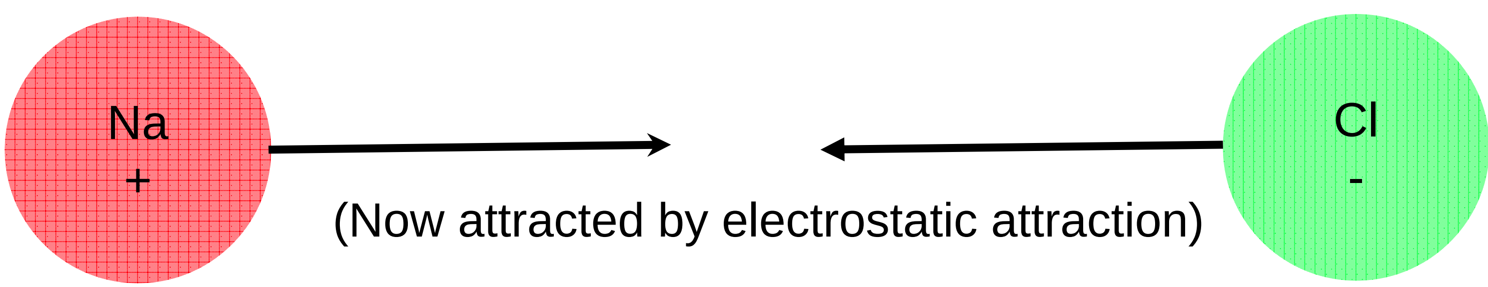
A second way of bonding: electrons transferred to complete the shells



(Recall 3d is with 4s and 4p)

Now stable (but #p > #e)

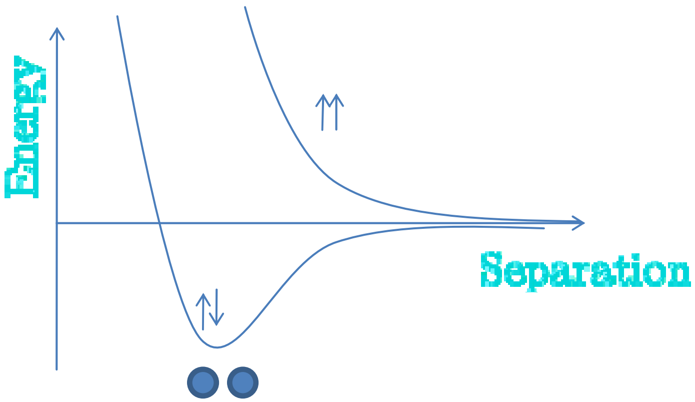
Now stable (but #p < #e)



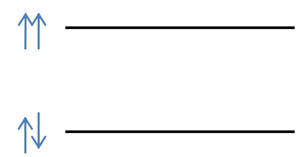
(Now attracted by electrostatic attraction)

Electron bands

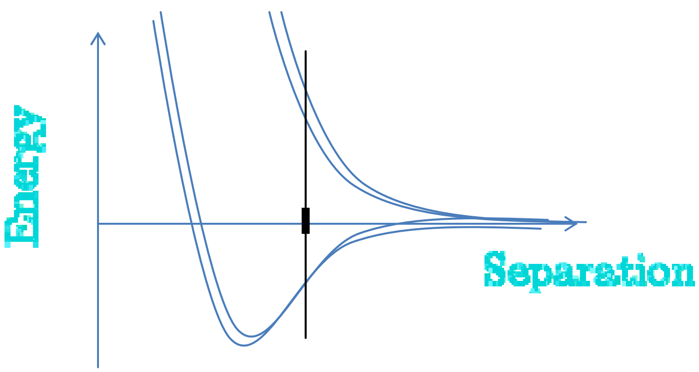
We have seen that the different alignment of spins give rise to different atom-atom potentials:

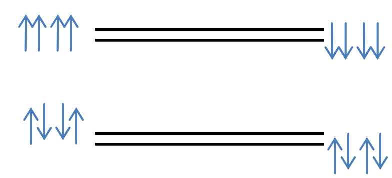


“free” electrons
(cnts. levels)



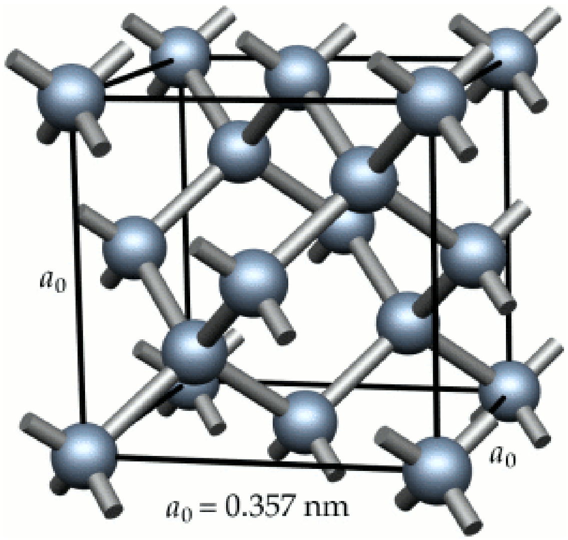
Four atoms similar:





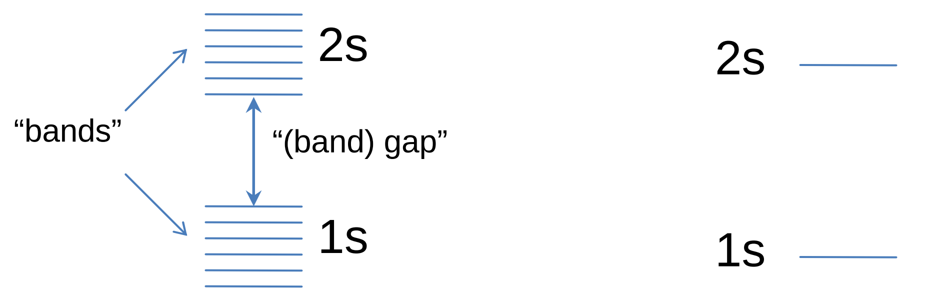
General pattern:
1) More atoms => more levels closely spaced.
2) Levels cluster into “bands” with large gaps between them

Electron bands



This box (*cell*) repeated ~ 10^{23} times!

Leads to many levels close together in a "band"



Many atoms One atom

We get the *band names* from the atomic orbital they split from

Filling orbitals before large gap ⇒ inert element (atom-atom bonding)

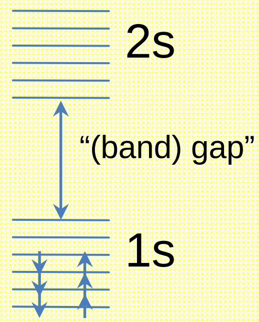
is analogous to:

Filling bands before large gap ⇒ non-conductive element

Why? To conduct electrons have to move freely -- means being able to move around in "unoccupied levels".

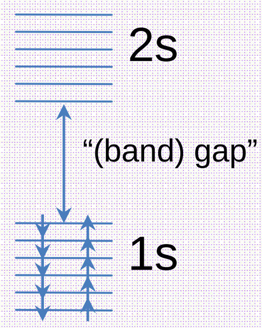
Metals vs. Insulators

Metals



- Electrons *partially* fill a band
- Lots of states that don't require much energy to get into
- => Does not take much energy to move an electron
- Metals conduct electricity

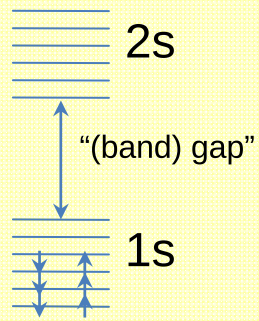
Insulators



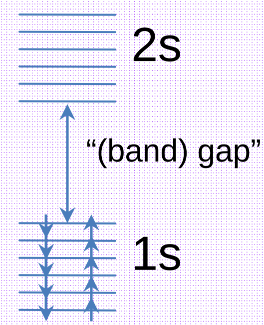
- Electrons *completely* fill a band
- Hard for electrons to move, have to apply a lot of energy to get into unoccupied state.
- Insulators do not conduct electricity

Metals vs. Insulators vs. Semiconductors

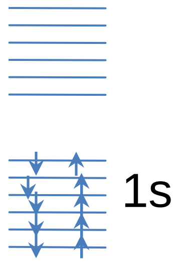
Metals



Insulators



Semiconductors



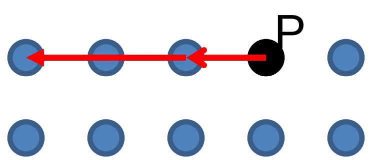
With “doping” semiconductors can be turned into conductors

Micro-electronics

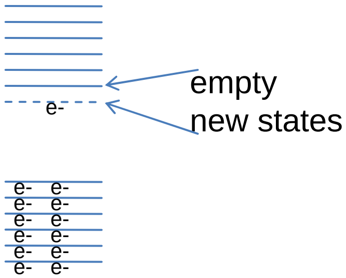
Conducting properties can be tailored by doping

Take Si: Si has 4 electrons on the outermost "shell"=quantum level/orbit
Electrons do not go far from atom

Put P in it: 5=4+1 electrons
P donates extra electron to crystal, can move around freely

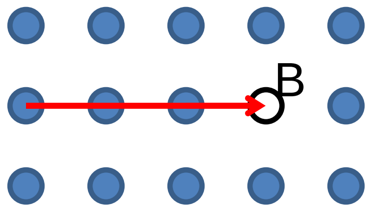


"n-type"

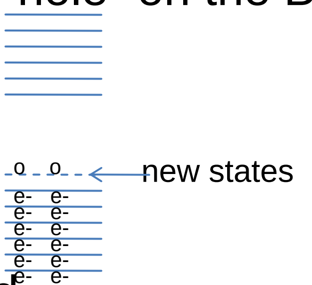


Really small gap
electron moves
around easily

Put in Boron: 3=4-1 electrons. Si electrons can fill the "hole" on the B



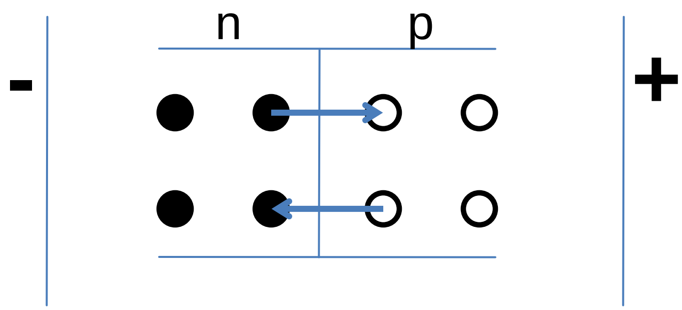
"p-type"



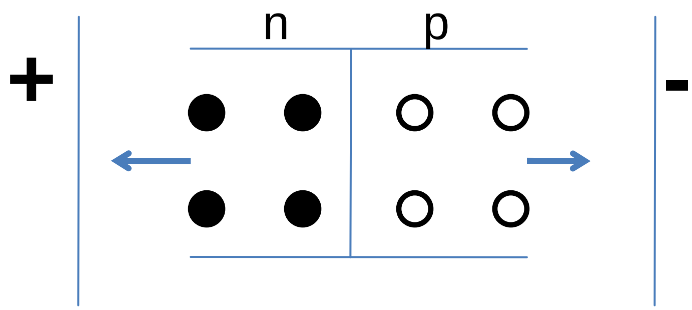
Really small gap,
electrons jump into
hole sequentially

We can say that in fact, that the hole moves around
Hole is absence of electron: "positively charged"

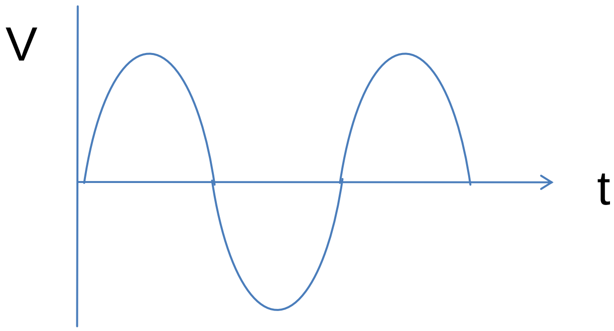
Diodes

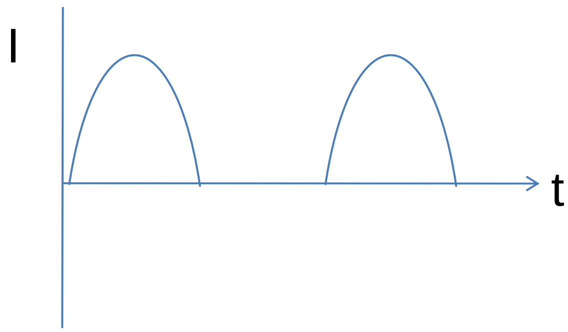


Current through interface



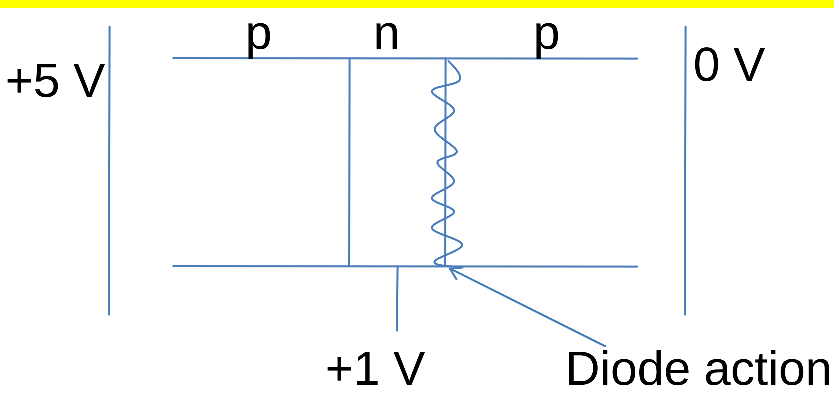
No current through interface





Applying + voltage to n portion switches off current:
Diode rectifies current from AC to DC
(most electrical and computer applications need this)

Transistors



• A third layer controls a diode
• The n layer is so thin that holes can go from left p to right p.
• But, if a + voltage is applied to n layer that closes right n-p diode.
• Result: no current.

The Transistor ("transfer resistor") is:

1) A switch

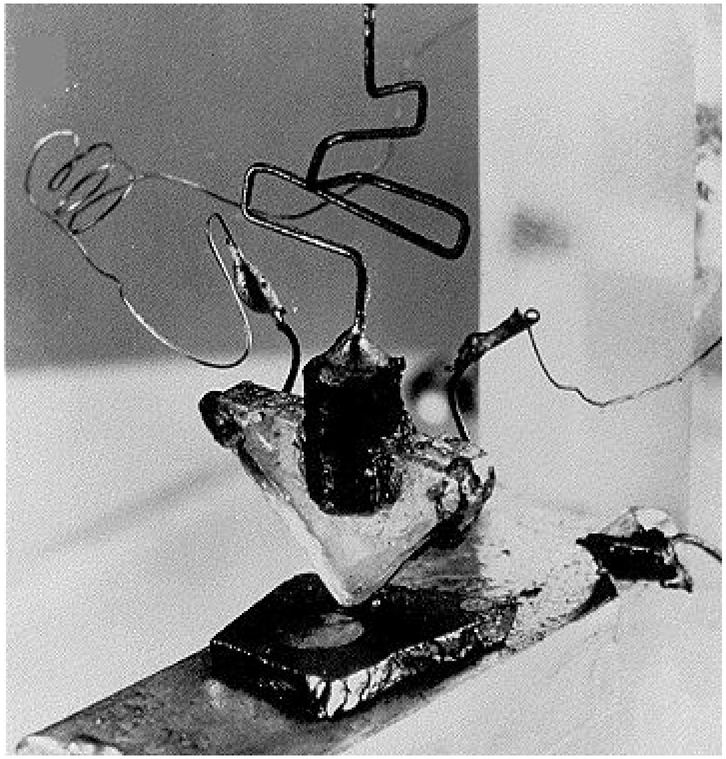
Digital technology: everything is represented in 1's and 0's: open or closed tr.

2) An amplifier

A small current/voltage controls a much larger current. Signal through many elements decays: transistor re-amplifies signal: lot of elements can be put together into vast circuits.

1947 Bardeen, Shockley, and Brattain:
point contact, bigger than quarter. Basic research lead to discovery
1951 Shockley: p-n-p transistor (different layout)
Came to Stanford from East Coast, founded Shockley's Associates
1958 Fairchild: Integrated Circuit (Shockley, Moore, Hoerni, Noyce)
1968 Intel: Microprocessor (Moore, Noyce, Shockley, Grove, and Vadasz)

Transistors

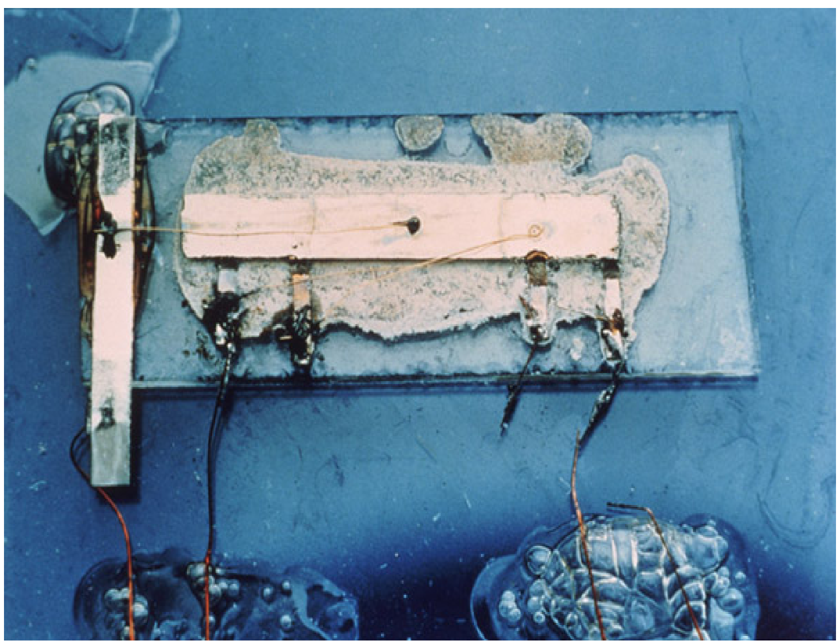


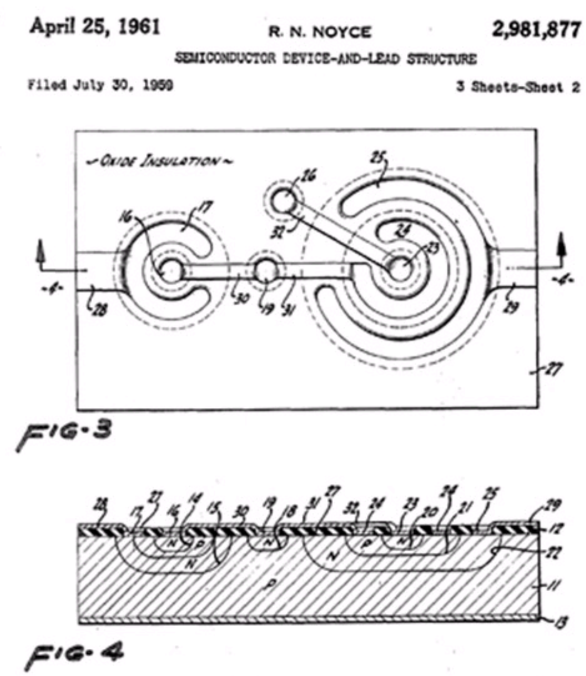
Bardeen, Shockley, Brattain (1947)

Integrated Circuits, Microprocessors

Integrated Circuit

Integrating more than one element
(Texas Inst.) Kilby 1958: resistor + transistor + wires in air
(Fairchild) Noyce 1959-62: 2 transistors + connections
integrated into substrate, no wires in air
Huge litigation, Fairchild won:
Fairchild connection was really “integrated”



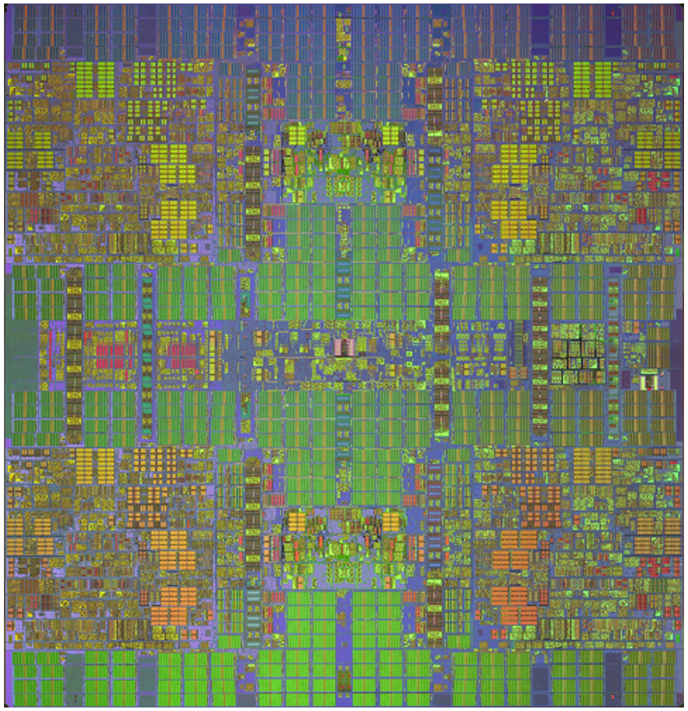


Integrated Circuits, Microprocessors

Microprocessor

Chips were initially for specific purpose
Ted Hoff (Intel): let's make it programmable
so it can perform different functions.

First IC (1971): Intel 4004 - 2300 transistors
Today: Intel Core Duo - 800 million transistors



Summary

- **Periodic table:** chemistry controlled by the # electrons in the outer shell = # of protons in nucleus
- **Chemistry =**
  - **Schrodinger** Energy levels (depend on both **n** and **l**)
  - **Pauli** exclusion principle
- **Chemical bonding**: All molecules want to lower their energy
  - **covalent** (shared electrons)
  - **ionic** (exchanged electrons, electrostatic attraction)
- **Band structure:** Energy level structure of multiple atoms
- **Materials classified according to conduction**
  - **metals**
  - **insulators**
  - **semiconductors**
- **Hole**: An empty state moving around.
- **Diode**: rectifies current
- **Transistor**: switch & amplifier
- **Microelectronics**