Solar Energy Conversion Devices and Plants

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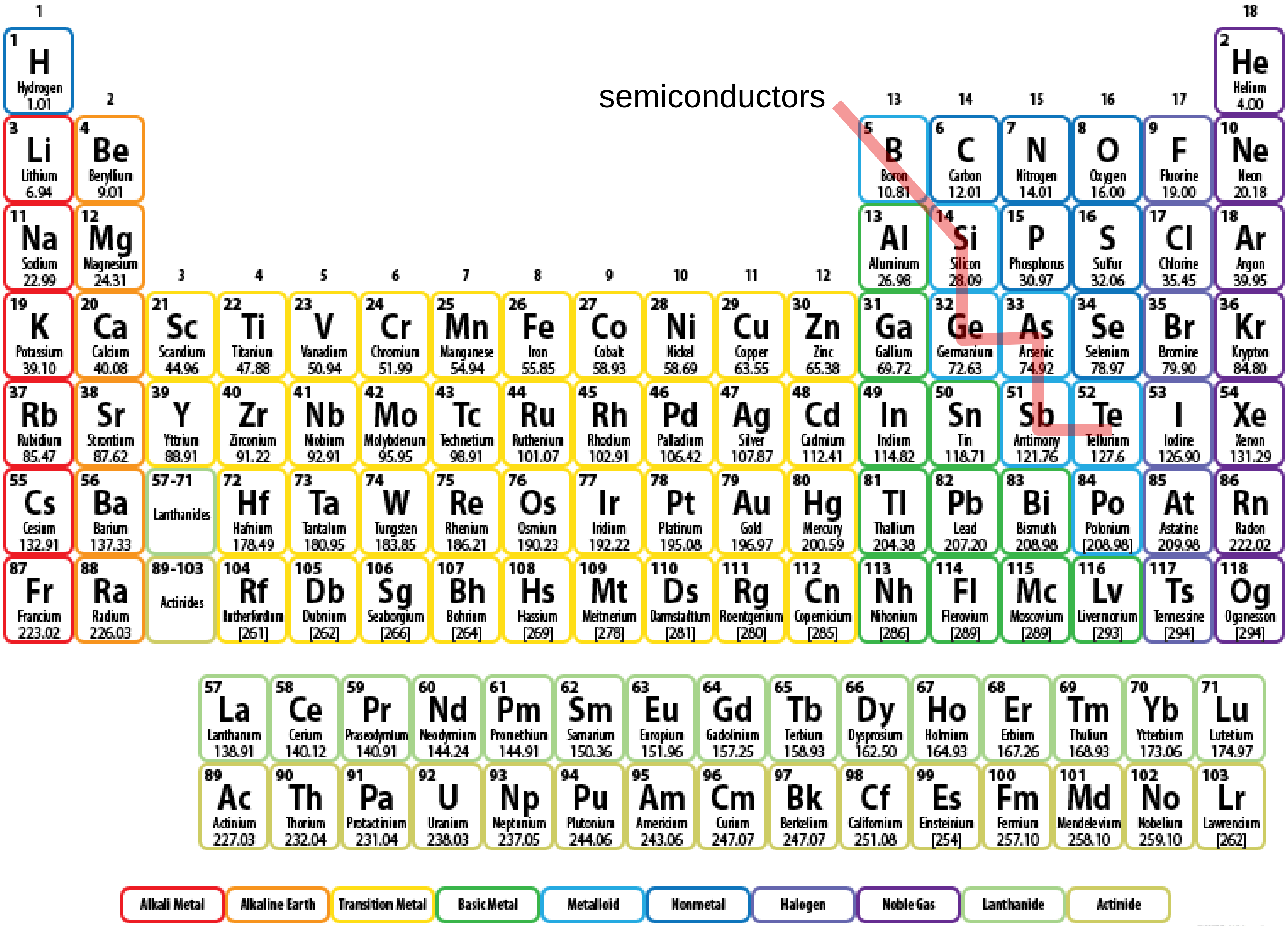
Laboratory of Renewable Energy Science and Engineering

Outline

- Semiconductors:
  - Chemistry
  - Physics
  - Transport

Periodic table of elements



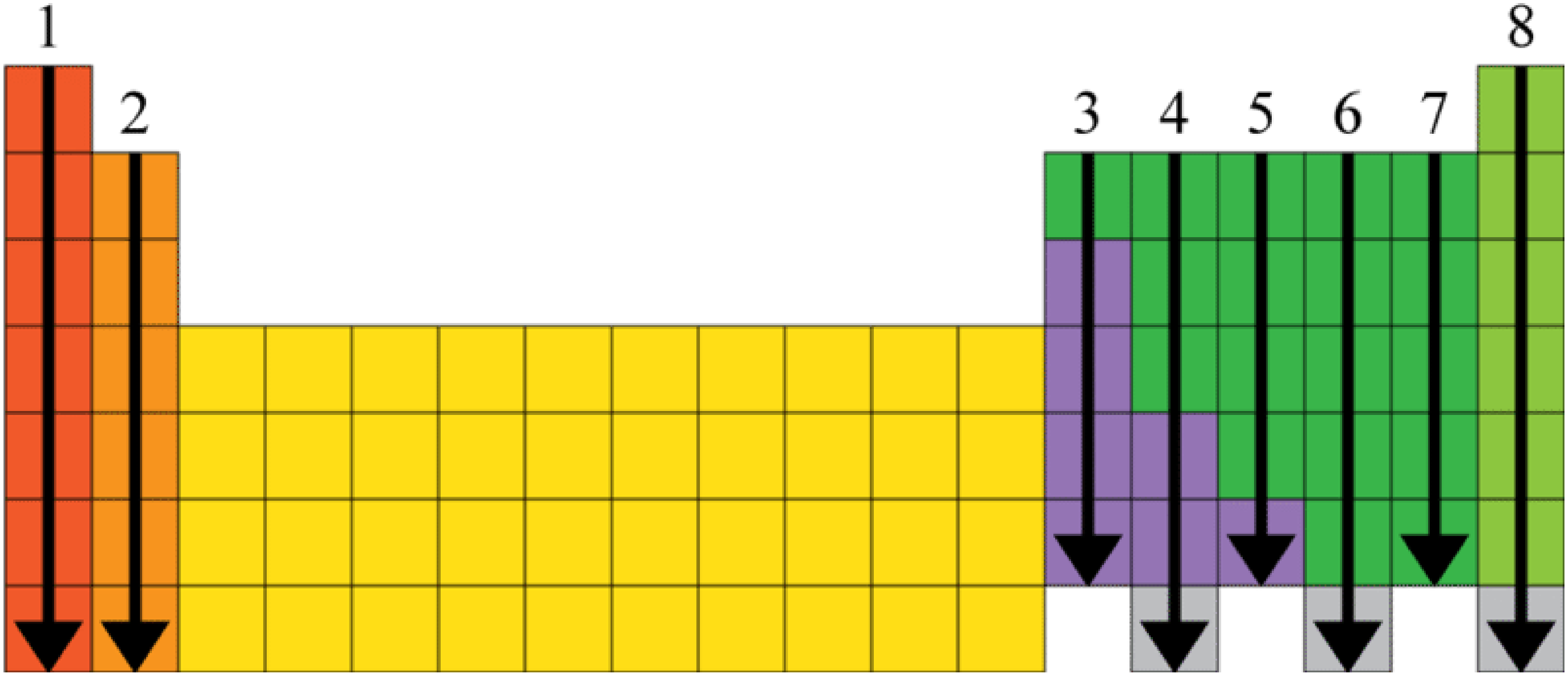
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H Hydrogen 1.01																	2 He Helium 4.00
3 Li Lithium 6.94	4 Be Beryllium 9.01											5 B Boron 10.81	6 C Carbon 12.01	7 N Nitrogen 14.01	8 O Oxygen 16.00	9 F Fluorine 19.00	10 Ne Neon 20.18
11 Na Sodium 22.99	12 Mg Magnesium 24.31											13 Al Aluminum 26.98	14 Si Silicon 28.09	15 P Phosphorus 30.97	16 S Sulfur 32.06	17 Cl Chlorine 35.45	18 Ar Argon 39.95
19 K Potassium 39.10	20 Ca Calcium 40.08	21 Sc Scandium 44.96	22 Ti Titanium 47.88	23 V Vanadium 50.94	24 Cr Chromium 51.99	25 Mn Manganese 54.94	26 Fe Iron 55.85	27 Co Cobalt 58.93	28 Ni Nickel 58.69	29 Cu Copper 63.55	30 Zn Zinc 65.38	31 Ga Gallium 69.72	32 Ge Germanium 72.63	33 As Arsenic 74.92	34 Se Selenium 78.97	35 Br Bromine 79.90	36 Kr Krypton 84.80
37 Rb Rubidium 85.47	38 Sr Strontium 87.62	39 Y Yttrium 88.91	40 Zr Zirconium 91.22	41 Nb Niobium 92.91	42 Mo Molybdenum 95.95	43 Tc Technetium 98.91	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.91	46 Pd Palladium 106.42	47 Ag Silver 107.87	48 Cd Cadmium 112.41	49 In Indium 114.82	50 Sn Tin 118.71	51 Sb Antimony 121.76	52 Te Tellurium 127.6	53 I Iodine 126.90	54 Xe Xenon 131.29
55 Cs Cesium 132.91	56 Ba Barium 137.33	57-71 Lanthanides	72 Hf Hafnium 178.49	73 Ta Tantalum 180.95	74 W Tungsten 183.85	75 Re Rhenium 186.21	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.97	80 Hg Mercury 200.59	81 Tl Thallium 204.38	82 Pb Lead 207.20	83 Bi Bismuth 208.98	84 Po Polonium [208.98]	85 At Astatine 209.98	86 Rn Radon 222.02
87 Fr Francium 223.02	88 Ra Radium 226.03	89-103 Actinides	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [278]	110 Ds Darmstadtium [281]	111 Rg Roentgenium [280]	112 Cn Copernicium [285]	113 Nh Nihonium [286]	114 Fl Flerovium [289]	115 Mc Moscovium [289]	116 Lv Livermorium [293]	117 Ts Tennessine [294]	118 Og Oganesson [294]

57 La Lanthanum 138.91	58 Ce Cerium 140.12	59 Pr Praseodymium 140.91	60 Nd Neodymium 144.24	61 Pm Promethium 144.91	62 Sm Samarium 150.36	63 Eu Europium 151.96	64 Gd Gadolinium 157.25	65 Tb Terbium 158.93	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93	68 Er Erbium 167.26	69 Tm Thulium 168.93	70 Yb Ytterbium 173.06	71 Lu Lutetium 174.97
89 Ac Actinium 227.03	90 Th Thorium 232.04	91 Pa Protactinium 231.04	92 U Uranium 238.03	93 Np Neptunium 237.05	94 Pu Plutonium 244.06	95 Am Americium 243.06	96 Cm Curium 247.07	97 Bk Berkelium 247.07	98 Cf Californium 251.08	99 Es Einsteinium [254]	100 Fm Fermium 257.10	101 Md Mendelevium 258.10	102 No Nobelium 259.10	103 Lr Lawrencium [262]

Alkali Metal | Alkaline Earth | Transition Metal | Basic Metal | Metalloid | Nonmetal | Halogen | Noble Gas | Lanthanide | Actinide

Periodic table

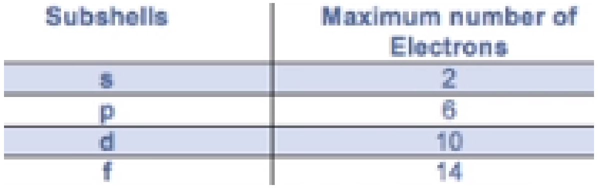
- Number of valence electrons (maximum of 8)



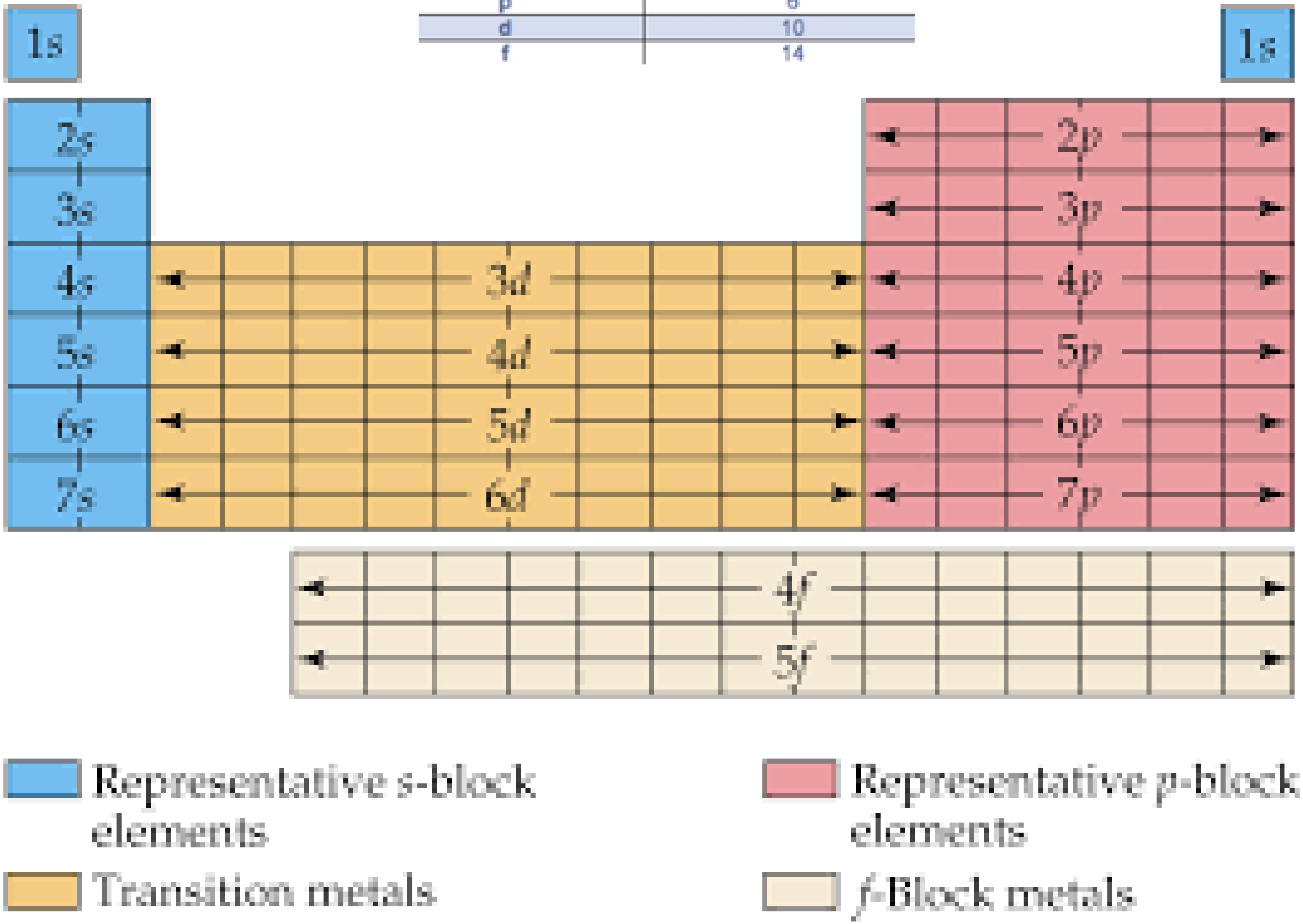
- Lewis dot structure (example period 2):

Periodic table

- Number of «shells»



Subshells	Maximum number of Electrons
s	2
p	6
d	10
f	14



Periodic table

- Number of «shells»

Subshells	Maximum number of Electrons
s	2
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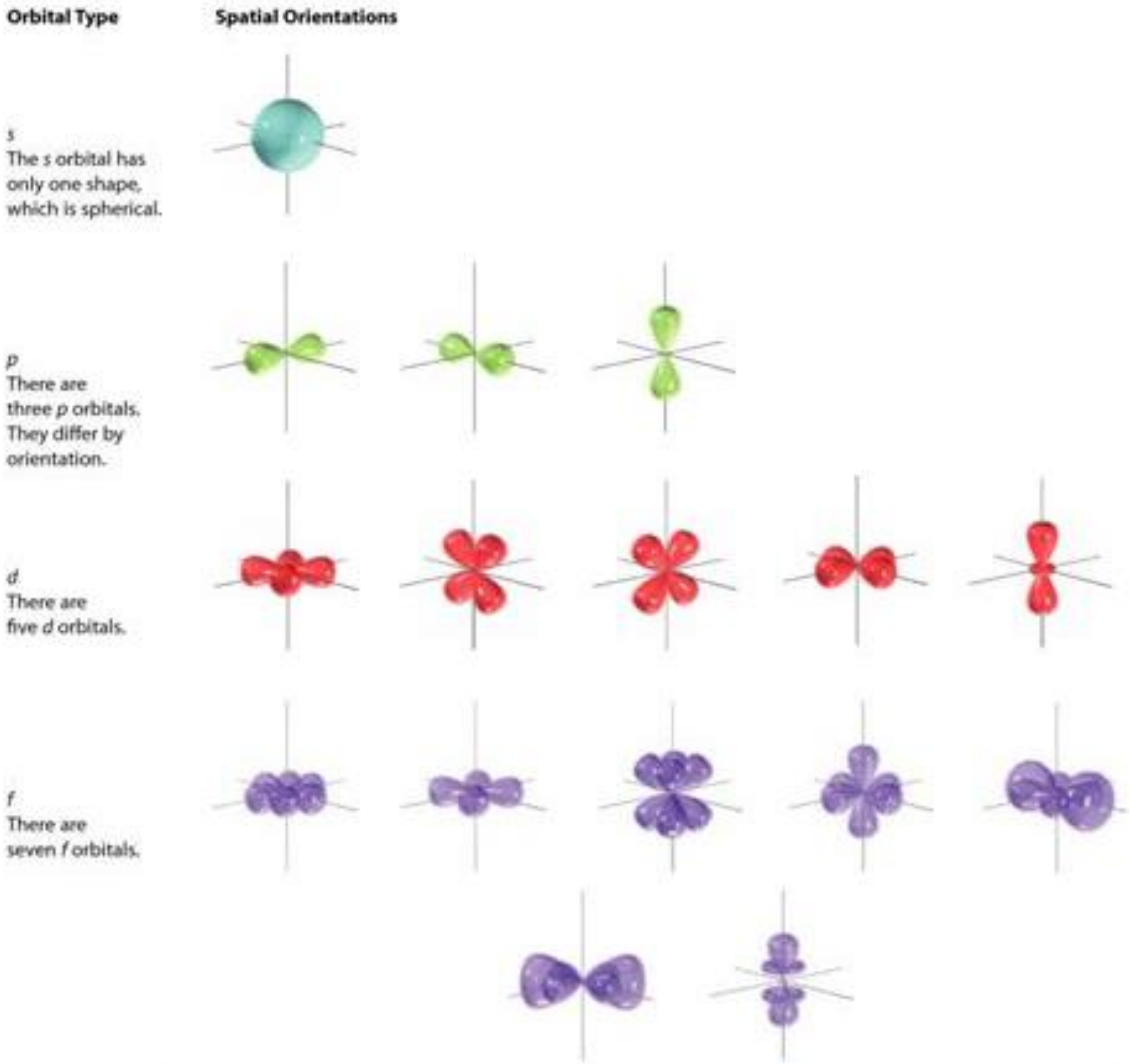

Orbital Type | **Spatial Orientations**

s
The *s* orbital has only one shape, which is spherical.

p
There are three *p* orbitals. They differ by orientation.

d
There are five *d* orbitals.

f
There are seven *f* orbitals.

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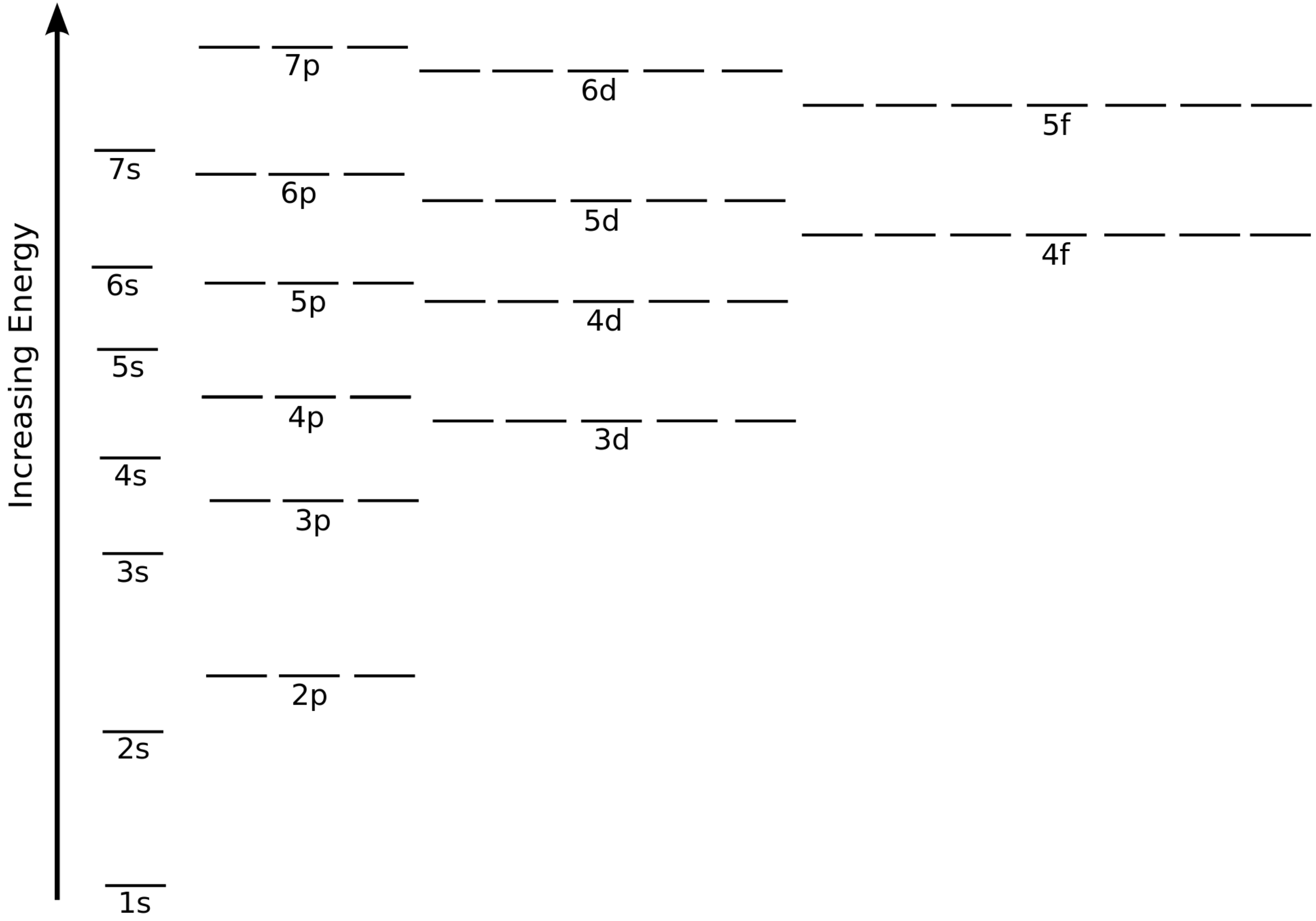
Periodic table

- Energy levels



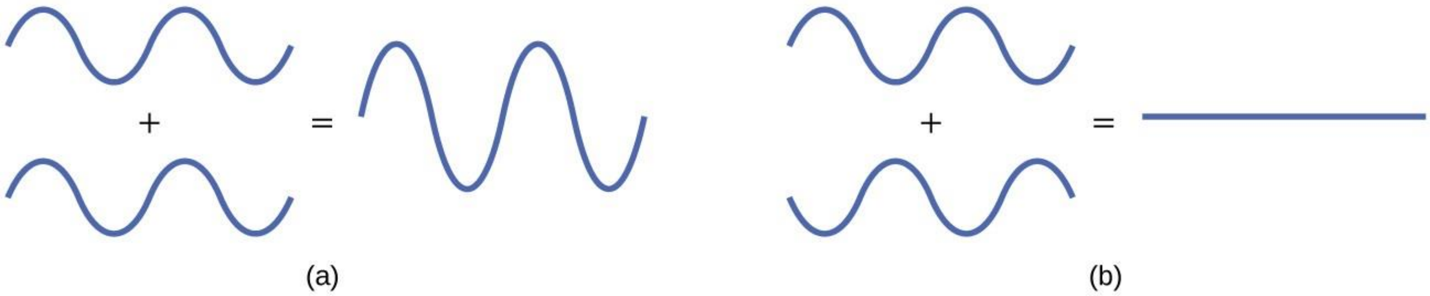
Molecular orbitals

- Molecular orbital (MO) theory uses the combination of atomic orbitals to yield molecular orbitals that are *delocalized* over the entire molecule rather than being localized on its constituent atoms

- MO theory describes the distribution of electrons in molecules in much the same way that the distribution of electrons in atoms is described using atomic orbitals. Using quantum mechanics, the behavior of an electron in a molecule is still described by a wave function, analogous to the behavior in an atom. Just like electrons around isolated atoms, electrons around atoms in molecules are limited to discrete (quantized) energies. The region of space in which a valence electron in a molecule is likely to be found is called a *molecular orbital*.

Molecular orbitals

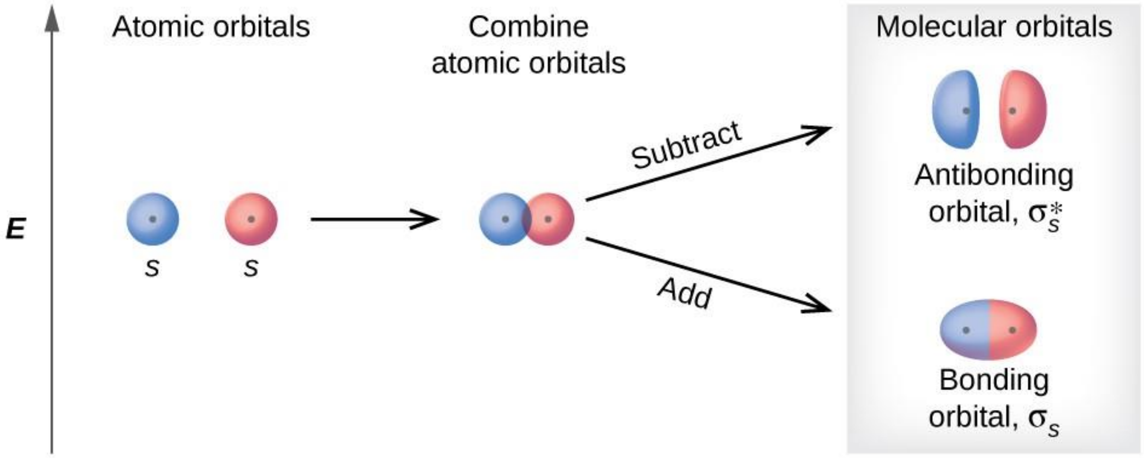
- The mathematical process of combining atomic orbitals to generate molecular orbitals is called the *linear combination of atomic orbitals (LCAO)*
- The wave function describes the wavelike properties of an electron. Molecular orbitals are combinations of atomic orbital wave functions
- Combining waves can lead to constructive interference, in which peaks line up with peaks, or destructive interference, in which peaks line up with troughs



- In orbitals, the waves are three dimensional, and they combine with in-phase waves producing regions with a higher probability of electron density and out-of-phase waves producing nodes, or regions of no electron density

Molecular orbitals

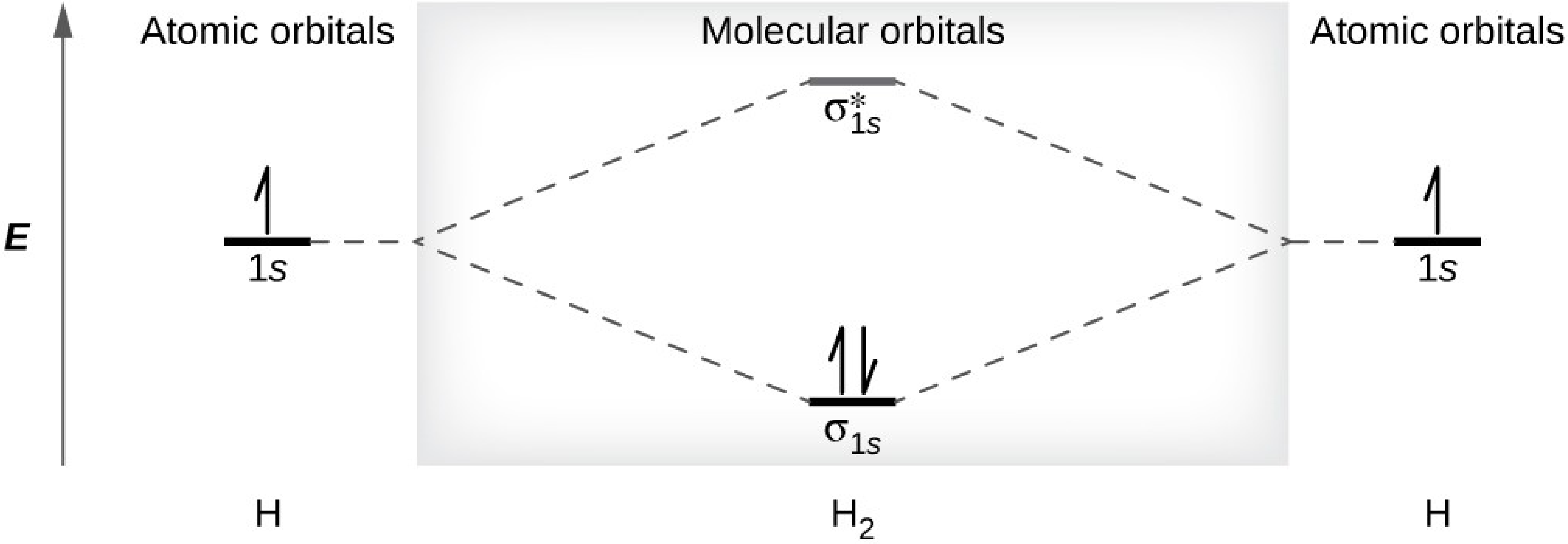
- When atoms combine to molecule, we get molecular orbitals that can be:
  - Lower-energy bonding orbitals (for example σ-orbitals)
  - Higher-energy anti-bonding orbitals (for example σ*-orbitals)



- Atomic vs. molecular orbitals:
  - Atomic s-orbitals become molecular σ-orbitals
  - Atomic p-orbitals become molecular π-orbitals
  - Atomic d-orbitals become molecular δ-orbitals
  - Atomic f-orbitals become molecular γ-orbitals

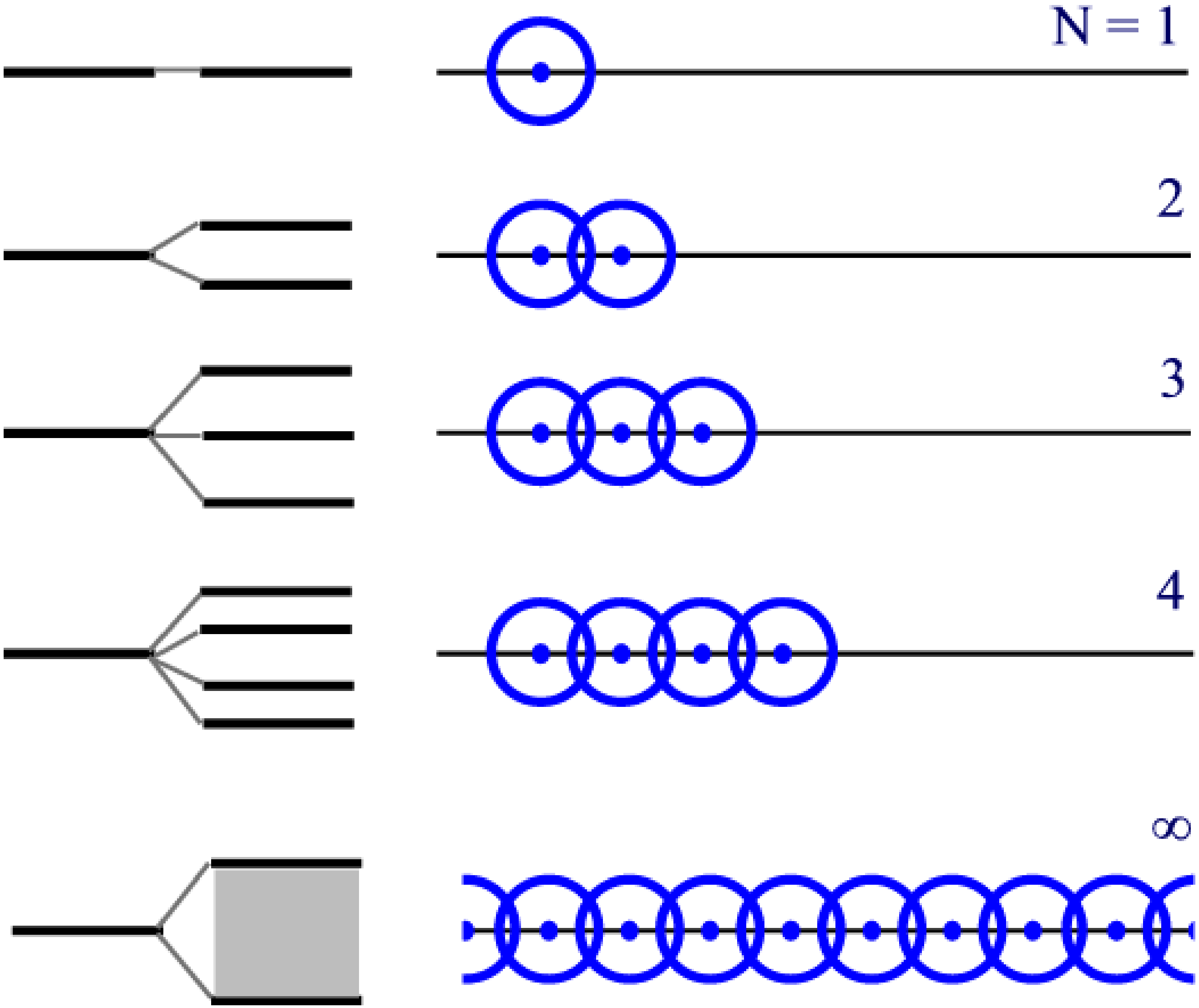
Molecular orbitals

- Example (H_2):



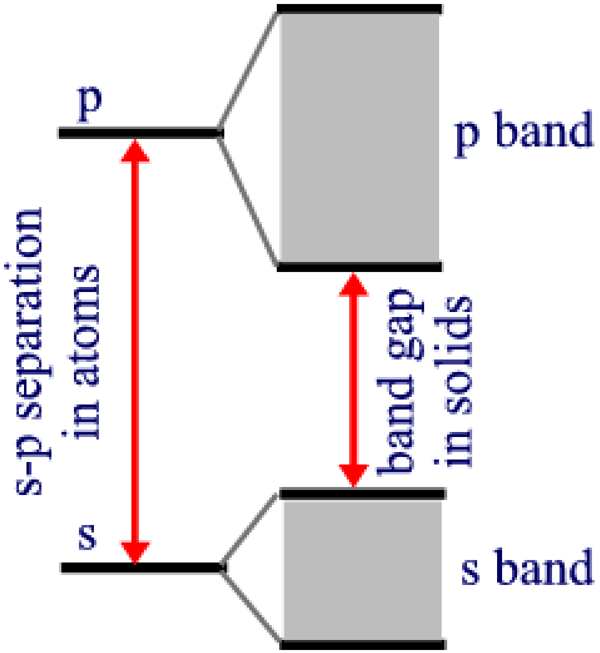
Bands

- Molecular orbitals for a full crystal will become a band:



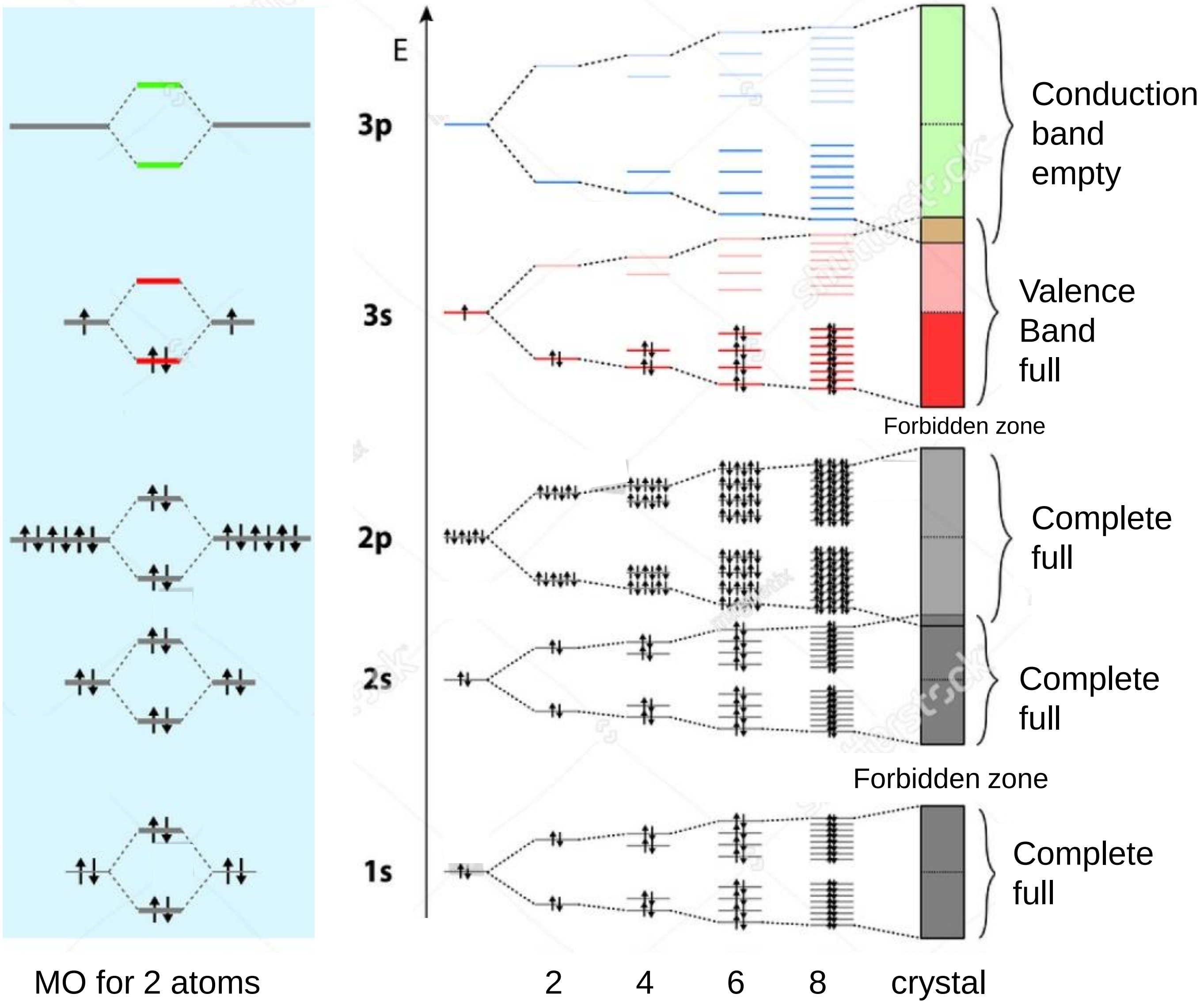
Bands

- If the atoms involved have also p orbitals available then multiple bands are available
- Just as there were energy separations between the s and p orbitals on the atom that varied from atom to atom, there are band gaps that vary from solid to solid, depending on which atoms in the solid
- In each of these bands, we can consider the lowest energy levels to correspond to fully bonding molecular orbitals and the highest levels correspond to fully antibonding MOs.



Bands

- Example Na crystal (bands can overlap, metals):



Bands

- Valence band: Band of electron orbitals, the outermost electron orbital of an atom of any specific material that electrons actually occupy. The valence band energy describes highest occupied energy state of the valence band

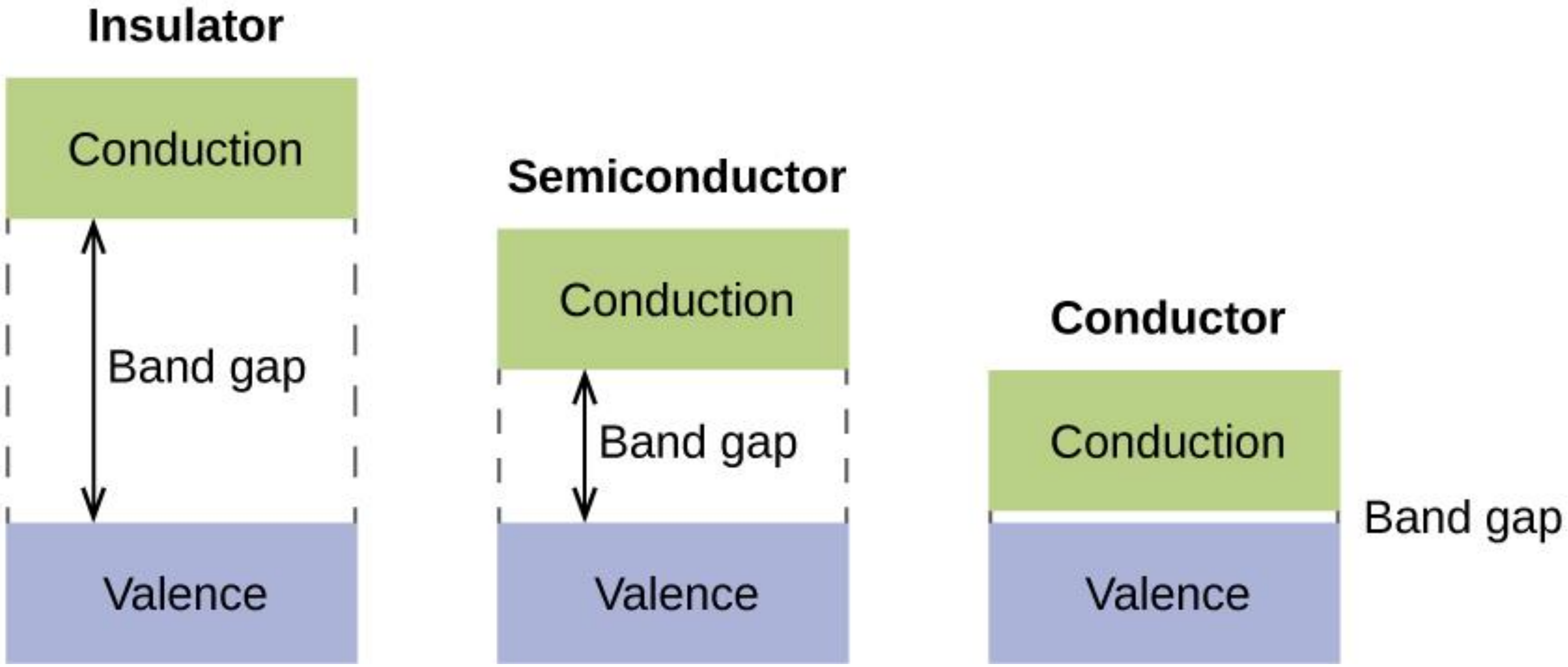
- Conduction band: Band of electron orbitals, at 0K unoccupied. If electrons are in these orbitals (for example by irradiating the material), they have enough energy to move freely in the material. The conduction band energy describes lowest unoccupied state of the conduction band

- The band gap is the distance between the valence band and the conduction band. It represents the minimum energy that is required to excite an electron up to a state in the conduction band

- HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) are types of molecular orbitals and used in chemistry to describe valence and conduction bands

Bands

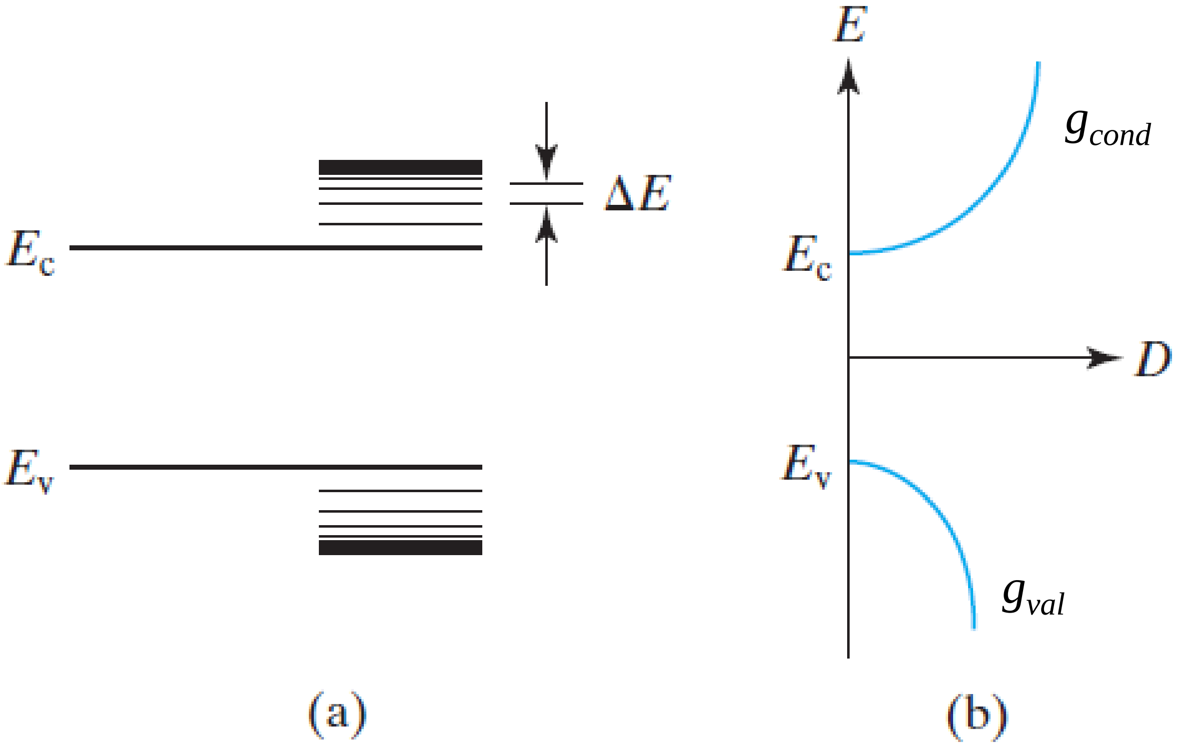
- Valence and conduction bands give idea about the nature of solid:
  - Metals/conductors: Vance band partially filled and/or overlaps with conduction band
  - Semiconductors: Valence band full and band gap between valence and conduction band relatively small
  - Insulators: Valence band full but band gap between valence and conduction band large



Intrinsic semiconductor

- Density of States (DoS):

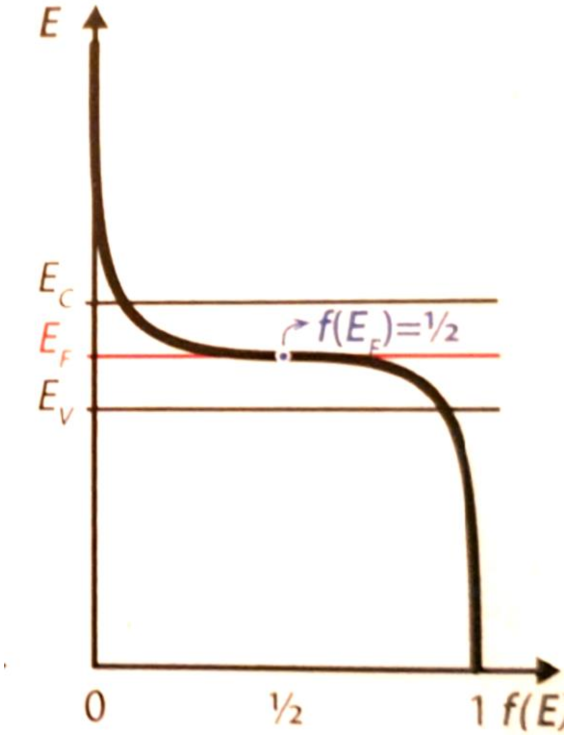
$$g_{cond}(E) = 4\pi\left(\frac{2m_n^*}{h^2}\right)^{3/2}\sqrt{E - E_{cond}} \qquad g_{val}(E) = 4\pi\left(\frac{2m_p^*}{h^2}\right)^{3/2}\sqrt{E_{val} - E}$$

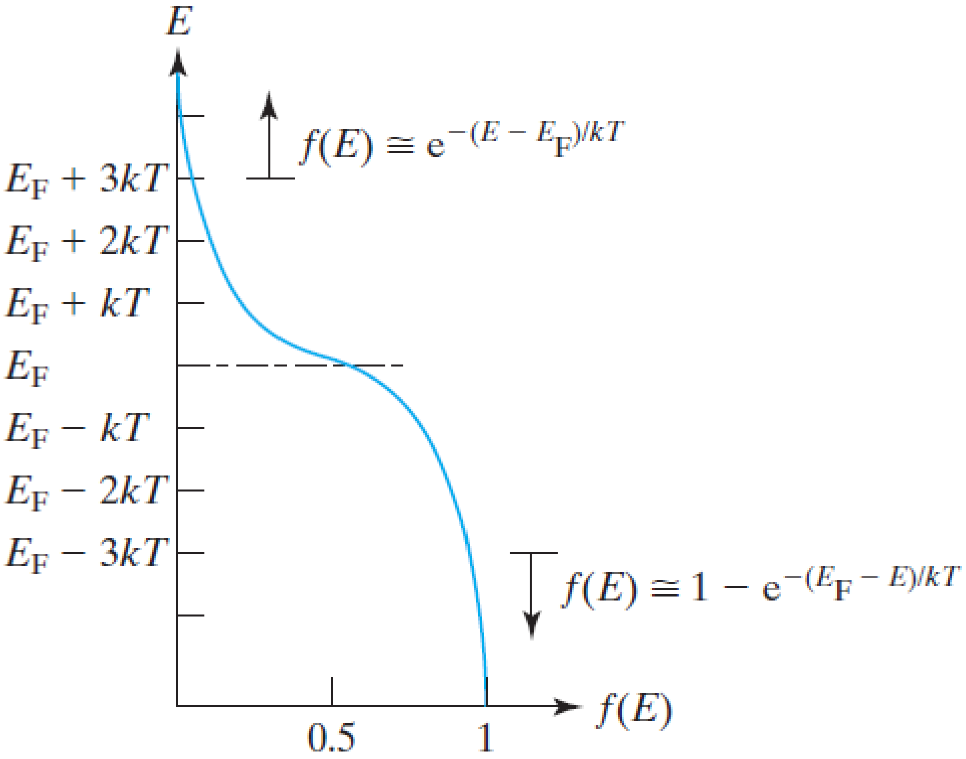


Intrinsic semiconductor

- Fermi-Dirac distribution describes actual distribution of electrons:

$$f(E) = \frac{1}{1 + \exp\left(\frac{E - E_f}{k_B T}\right)}$$





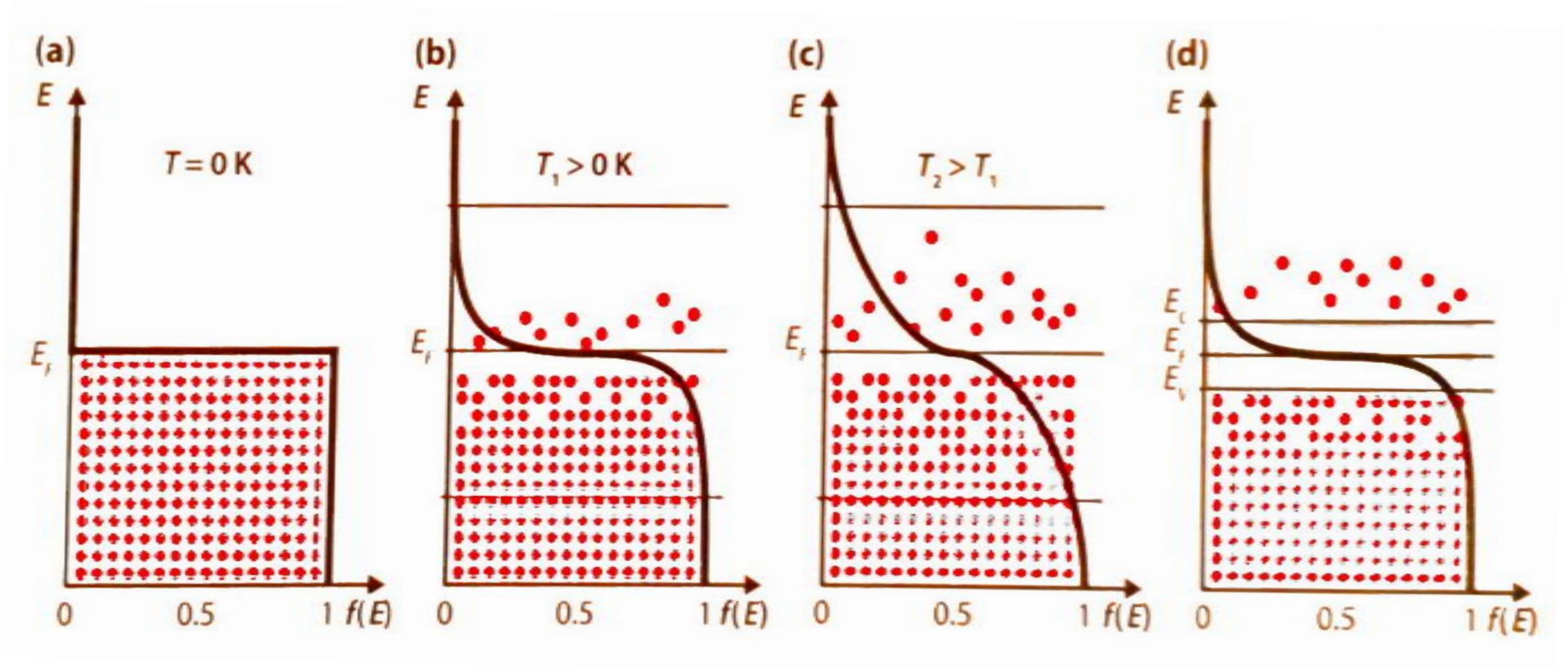
Intrinsic semiconductor

- Fermi energy level, E_f:
  - The Fermi level of a solid-state body is the thermodynamic work required to add one electron to the body
  - Average energy of an electron in the material
  - Fermi level is a hypothetical energy level of an electron, such that at thermodynamic equilibrium this energy level would have a 50% probability of being occupied at any given time
  - The Fermi level does not necessarily correspond to an actual energy level (in an insulator the Fermi level lies in the band gap), nor does it require the existence of a band structure.
  - The Fermi level is a precisely defined thermodynamic quantity, and differences in Fermi level can be measured simply with a voltmeter.

Intrinsic semiconductor

- Temperature-dependence of Fermi-Dirac distribution:

$$f(E) = \frac{1}{1 + \exp\left(\dfrac{E - E_f}{k_B T}\right)}$$

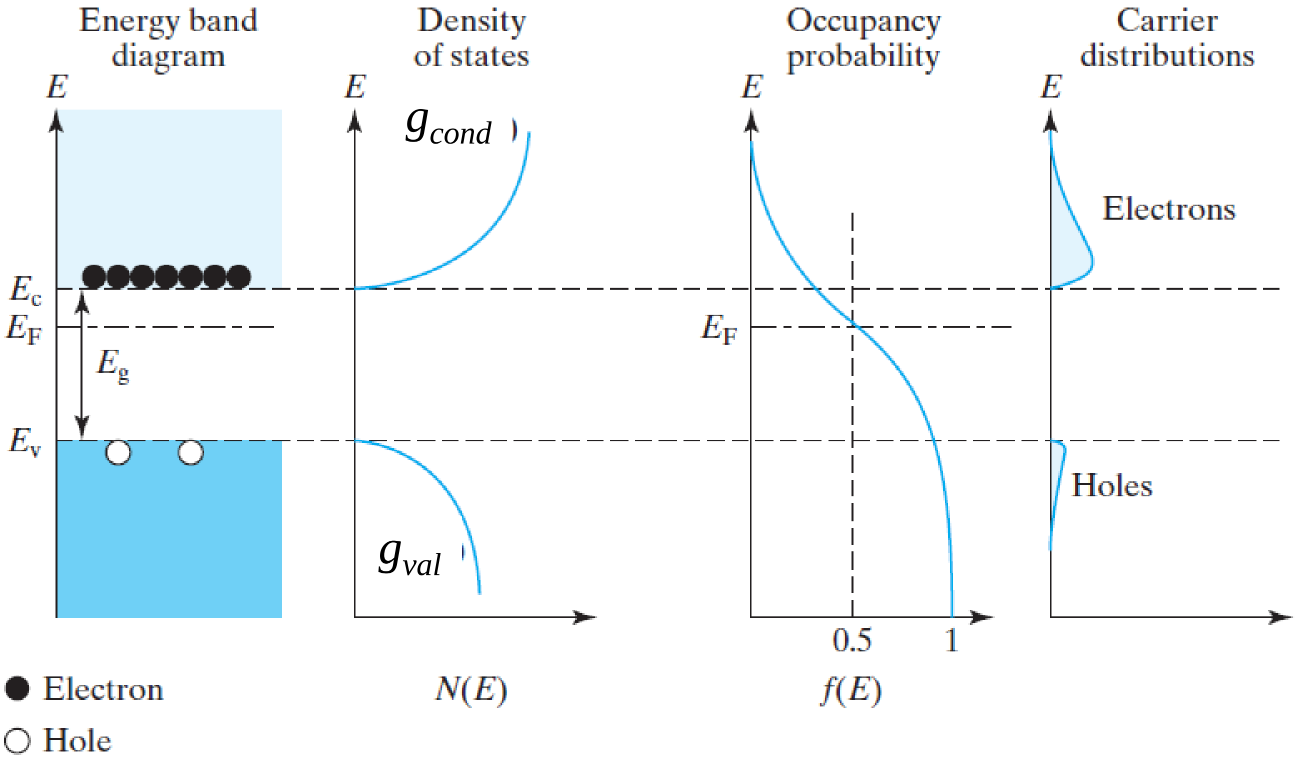


Intrinsic semiconductor

- Electron and hole densities (carrier distribution):

$$n(E) = g_{cond}(E)\,f(E)$$

$$p(E) = g_{val}(E)\left[1 - f(E)\right]$$



Intrinsic semiconductor

- Total concentration of electron and holes in conduction and valence band, respectively:

$$n = \int_{E_{cond}}^{E_{top}} n(E)dE = \ldots = N_c \exp\left(\frac{E_f - E_{cond}}{k_B T}\right)$$

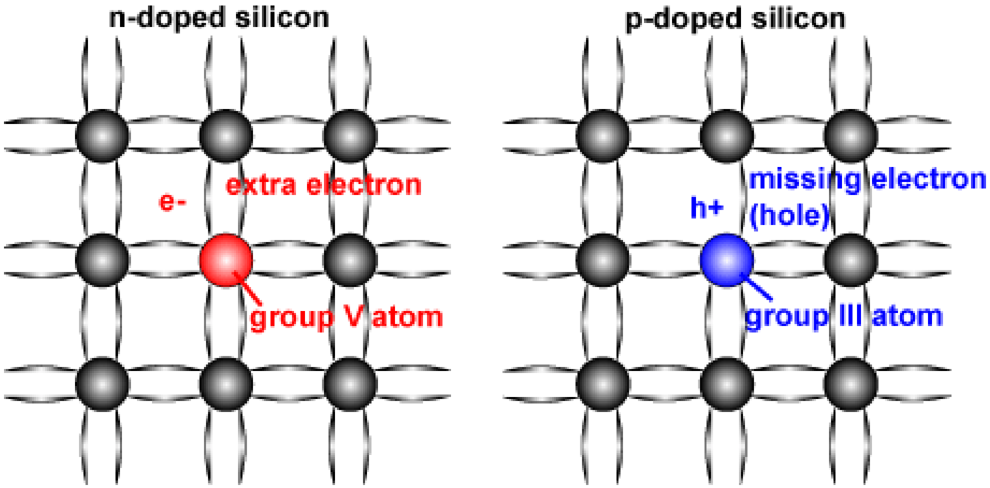
$$p = \int_{E_{bottom}}^{E_{val}} p(E)dE = \ldots = N_v \exp\left(\frac{E_{val} - E_f}{k_B T}\right)$$

$$n \cdot p = n_{\mathrm{int}}^2$$

- Intrinsic carrier density: $n = p = n_{\mathrm{int}}$
- Intrinsic density of Si in the range of 10^{10} /cm^3 for Si

Doping of semiconductors

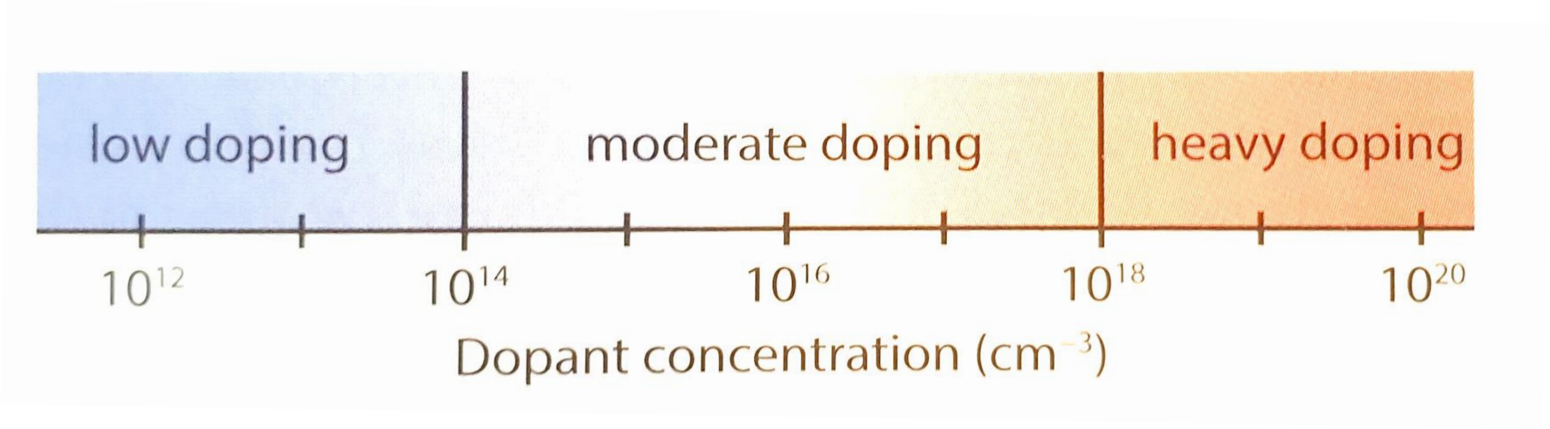
- Additionally, doping can be used to increase charge carriers:
  - n-doped: material with more valence electrons than base material (electrons are majority carrier), the “impurity” atoms (enhancing concentration of e^-) are called donors and their concentration is N_D
  - p-doped: materials with less valence electrons than base material (holes are majority carrier), the “impurity” atoms (enhancing concentration of h^+) are called acceptors and their concentration is N_A



Doping of semiconductors

- Note (for the example Si): substituting Si atoms with one type of impurity atoms (P or Br) increased the concentration of one type of mobile charge carriers (e^- or h^+) but charge neutrality of material is maintained

- Typical doping concentrations for c-Si:



Doping of semiconductors

- Local charge density:

$$\rho = q\left(p + N_D^+ - n - N_A^-\right)$$

  - With density of ionized donor and acceptor atoms (N_D^+, N_A^-)
  - Elementary charge (q)

- In equilibrium, semiconductor is charge-neutral everywhere:

$$\left(p + N_D^+ - n - N_A^-\right) = 0 = \left(p + N_D - n - N_A\right)$$

- For n-doped: $p + N_D - n = 0$ $\quad p = \dfrac{n_{\text{int}}^2}{n} \approx \dfrac{n_{\text{int}}^2}{N_D} << n$

- For p-doped: $p - n - N_A = 0$ $\quad n = \dfrac{n_{\text{int}}^2}{p} \approx \dfrac{n_{\text{int}}^2}{N_A} << p$

Doping of semiconductors

- Fermi-level for:
  - For n-doped:

$$E_{cond} - E_f = k_B T \ln\left(\frac{N_c}{N_D}\right)$$

  - For p-doped:

$$E_f - E_{val} = k_B T \ln\left(\frac{N_v}{N_A}\right)$$

Transport in semiconductors

- Free charge carriers randomly moving, but no net movement
- Net movement only if «driver»:
  - Diffuse in the material according to the concentration gradient

$$J_{x,n} = qD_n \frac{dn}{dx} \qquad J_{x,p} = -qD_p \frac{dp}{dx}$$

  - Drift in the material according to an electric field

$$J_{x,n} = qn\mu_n E_x \qquad J_{x,p} = qp\mu_p E_x$$

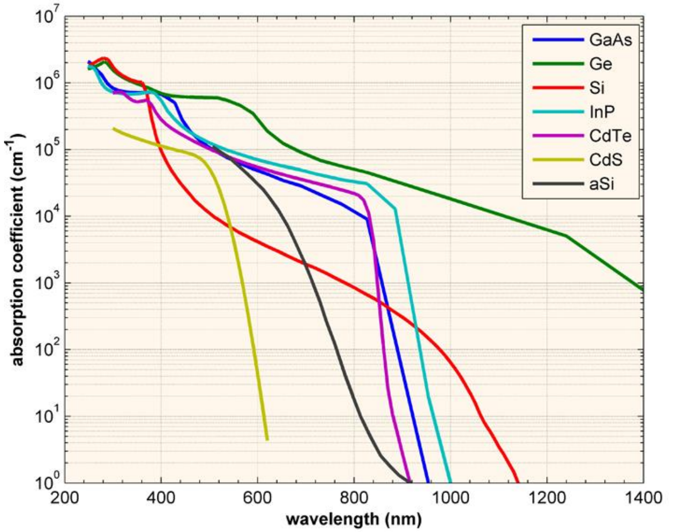
  - Continuity equation: $\frac{dn}{dt} = \frac{1}{q}\frac{dJ_n}{dx} + G - R \qquad \frac{dp}{dt} = -\frac{1}{q}\frac{dJ_p}{dx} + G - R$

  - Plus Poisson eq. for electric field

$$\nabla \cdot \left(\varepsilon \nabla V\right) = -q\left(p - n + N_D^+ - N_A^-\right)$$

Absorption in semiconductor

- Semiconductor under irradiation:
  - Electron-hole pairs are generated by solar irradiation, if the energy is larger than the band gap energy they are absorbed



  - Absorption depth is inversely proportional to absorption coefficient, according to Beer’s law:

$$I = I_0 \exp(-\alpha l) \qquad\qquad I \overset{l=1/\alpha}{=} I_0 \exp(-1) \rightarrow 0.36 \cdot I_0$$

  - Generation rate (electron-hole-pairs): $\left|\frac{dI}{dl}\right| = \alpha N_0 \exp(-\alpha l)$

Photonflux [#/m^2/s] = *I*/*E*

Interfaces at semiconductor

- Semiconductor interfaces:

  - Metal-semiconductor junctions:
    - Schottky junction
    - Ohmic contact

  - Semiconductor-semiconductor junction:
    - pn junction

  - Semiconductor-liquid electrolyte junction