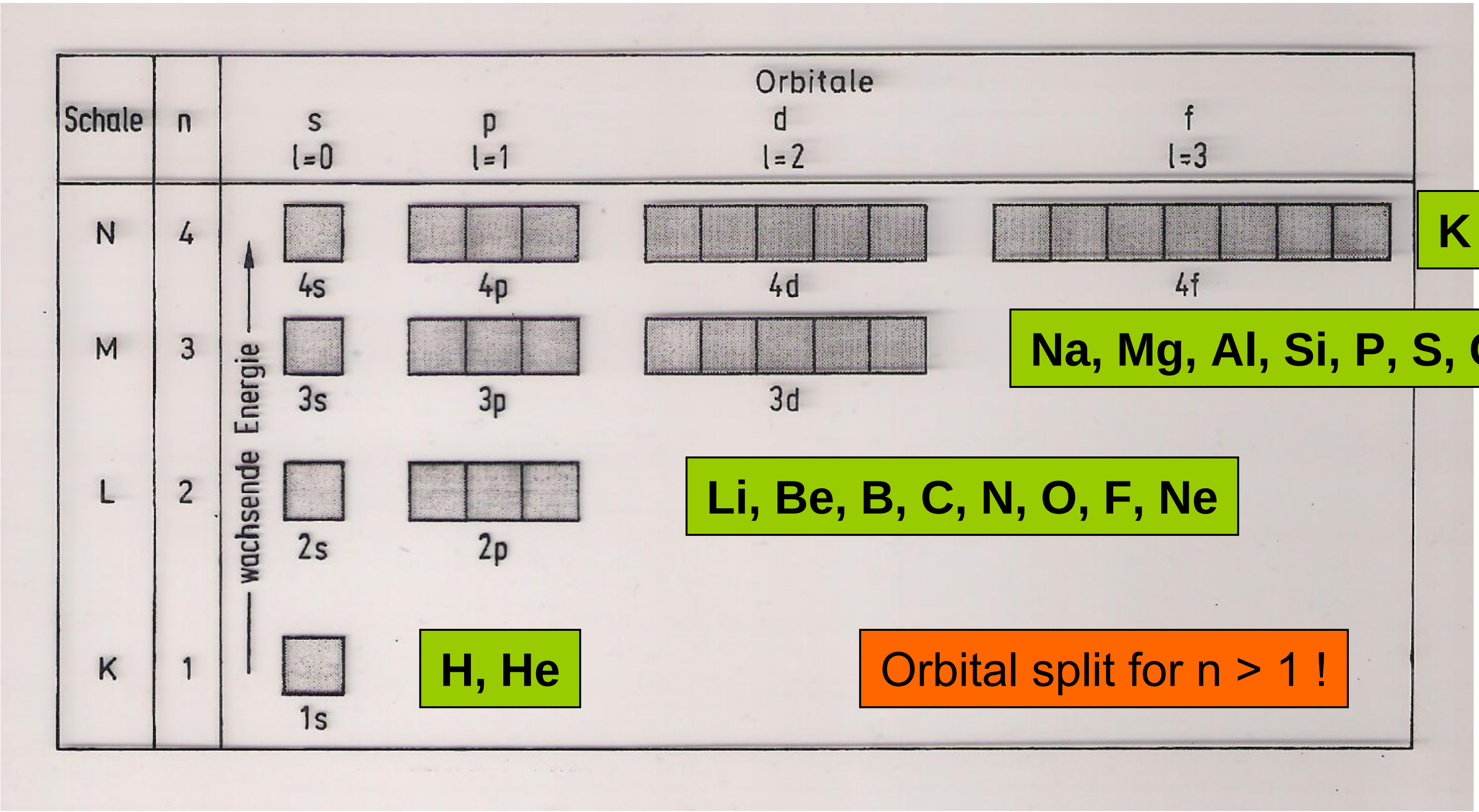
Molecular structure and bonding

To understand the formation and structure of molecular compounds, first one has to learn, recognize, use, count, take into account:

- the periodic table with groups and periods,
- the number of electrons and valence electrons (i.e. count electrons), (2 (K), 8 (L) = 2 + 6, 18 (M) = 2 + 6 + 10, 32 (N) = 2 + 6 + 10 + 14, etc.),
- the electronic structure (ground state, exited state),
- the need of 2 electrons for a bond,
- atomic orbitals and quantum states (with quantum numbers n, m, l, s),
- the energy levels of the different shells, subshells, orbitals,
- the maximum number of shells, subshells, orbitals, and electrons,
- the numbers and/or maximum numbers of bonds, an atom likes to or can build or have,
- the **Lewis** concept/structure.

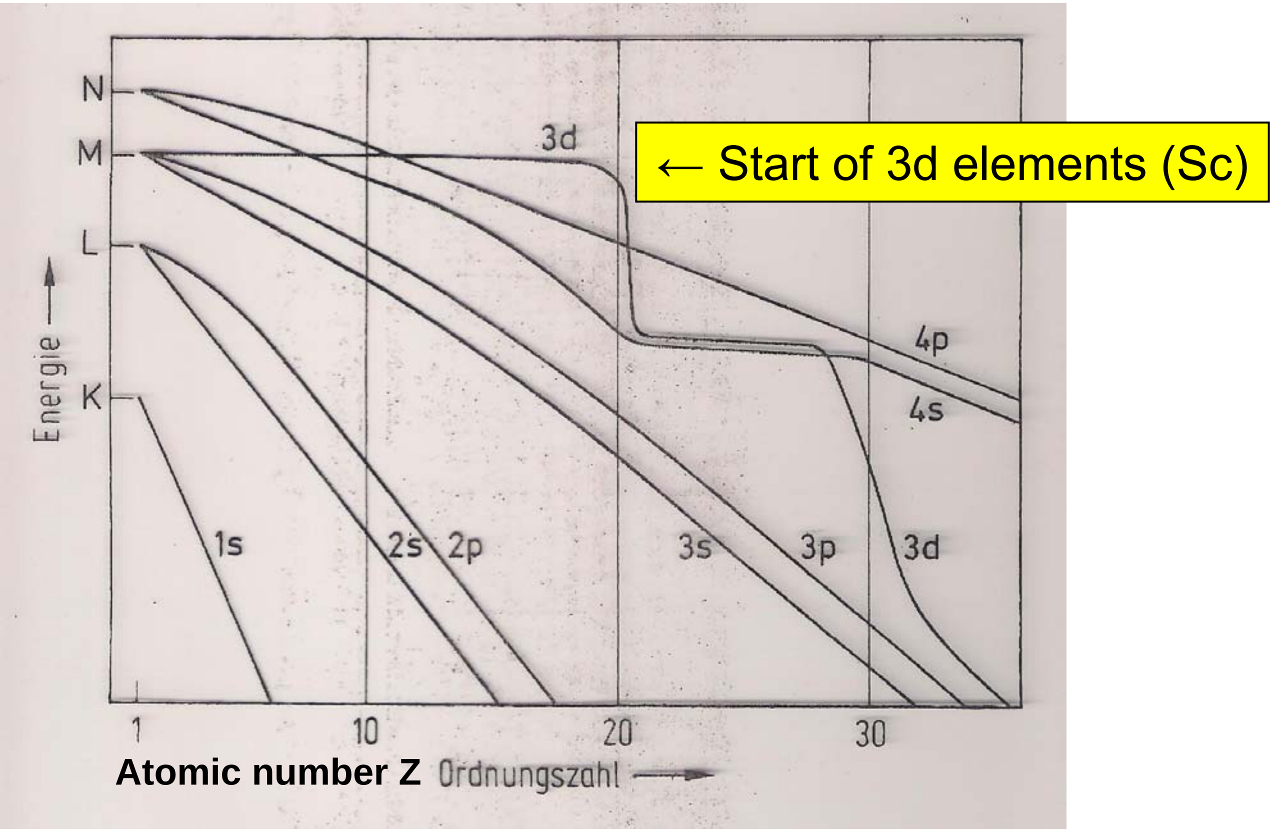
Schematic representation of atomic shells (n) and subshells/orbitals (s, p, d, f). The orbitals (or quantum states) are defined by the quantum numbers n, m, l, s.



Energy increases with increasing n, and is high between the shells (except d and f).

n → size, l → shape, m → orientation, s → spin of e; **Pauli principle** (not all 4 quantum numbers can be equal), **Hund's rule** (spin maximizing).

Energies of the atomic shells K, L, M, N and the subshells/orbitals s, p, d, f



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It is useful to learn also the maximum number of shells (n), subshells/orbitals (s, p, d, f), and electrons an atom can have.

Shell	**n**	**Orbital**	**Nunber of orbitals**	**Number of electrons in orbital**	**shell ($2n^2$)**
K	1	1s	1	2	2
L	2	2s	1	2	8
		2p	3	6	
M	3	3s	1	2	18
		3p	3	6	
		3d	5	10	
N	4	4s	1	2	32
		4p	3	6	
		4d	5	10	
		4f	7	14	

The next step is to find the numbers and/or maximum numbers of bonds, an atom likes to or can have, e.g. in hydrogen compounds of group 4 to 8 elements.

Main group	4	5	6	7	8
2. Periode	C	N	O	F	Ne
3. Periode	Si	P	S	Cl	Ar
Electron * configuration	s [↑↓] p [↑][↑][ ]	s [↑↓] p [↑][↑][↑]	s [↑↓] p [↑↓][↑][↑]	s [↑↓] p [↑↓][↑↓][↑]	s [↑↓] p [↑↓][↑↓][↑↓]
Number of possible bonds	2 /4*	3	2	1	0
Existing H compouns	CH_4 SiH_4	NH_3 PH_3	H_2O H_2S	HF HCl	none
Lewis formula	H H:C:H H	$H:\overline{N}:H$ H	$H:\overline{\underline{O}}:H$	$H:\overline{\underline{F}}\vert$	–

use – instead of :

* Promotion/exitation of an 1s electron of C, Si to 1p needs a lot of energy (460 kJ/mol for C), but is compensated by the formation of 2 additional bonds (CH_4 instead of CH_2).

For promotion to a d level, the energy is to high.

Electron configuration and number of bonds for elements of 2. period

Atom or ion	Electron configuration K 1s	L 2s	2p			Number of bonds	Number * of electrons	Examples
Li	↑↓	↑				1	2	LiH
Be*	↑↓	↑	↑			2	4	$BeCl_2$
B*	↑↓	↑	↑	↑		3	6	BF_3
B^-, C*, N^+	↑↓	↑	↑	↑	↑	4	8	BF_4^-, CH_4, NH_4^+
N, O^+	↑↓	↑↓	↑	↑	↑	3	8	NH_3, H_3O^+
O, N^-	↑↓	↑↓	↑↓	↑	↑	2	8	H_2O, NH_2^-
O^-, F	↑↓	↑↓	↑↓	↑↓	↑	1	8	OH^-, HF
O^{2-}, F^-, Ne	↑↓	↑↓	↑↓	↑↓	↑↓	0	–	–

Elements of 2. period can build not more than 4 bonds, because there are only 4 orbitals available → **octett rule**. Consider ground states (Pauli, Hund), exited states.

* Number of electrons in bonds

Electron configuration and number of bonds for elements of 3. period

Atom or ion	Electron configuration									Number of bonds	Number * of electrons	Examples
	3s	3p			3d							
Na	↑									1	2	–
Mg*	↑	↑								2	4	–
Al*	↑	↑	↑							3	6	$AlCl_3$
Si*	↑	↑	↑	↑						4	8	$SiCl_4$
P	↑↓	↑	↑	↑						3	8	PH_3
P*	↑	↑	↑	↑	↑					5	10	PF_5
S	↑↓	↑↓	↑	↑						2	8	H_2S
S*	↑↓	↑	↑	↑	↑					4	10	SF_4
S**, Si^{2-}, P^-	↑	↑	↑	↑	↑	↑				6	12	SF_6, $[SiF_6]^{2-}$
Cl	↑↓	↑↓	↑↓	↑						1	8	HCl
Cl*	↑↓	↑↓	↑	↑	↑					3	10	ClF_3
Cl**	↑↓	↑	↑	↑	↑	↑				5	12	$HClO_3$
Cl***	↑	↑	↑	↑	↑	↑	↑			7	14	$HClO_4$
S^{2-}, Cl^-, Ar	↑↓	↑↓	↑↓	↑↓						0	–	–

For n > 2 one can have more than 4 bonds, because there are empty low-level d orbitals avaiable. For elements of 3. period, the maximum number of bonds is 7.

* Number of electrons in bonds

Highest number of bonds is equivalent to the main group number.

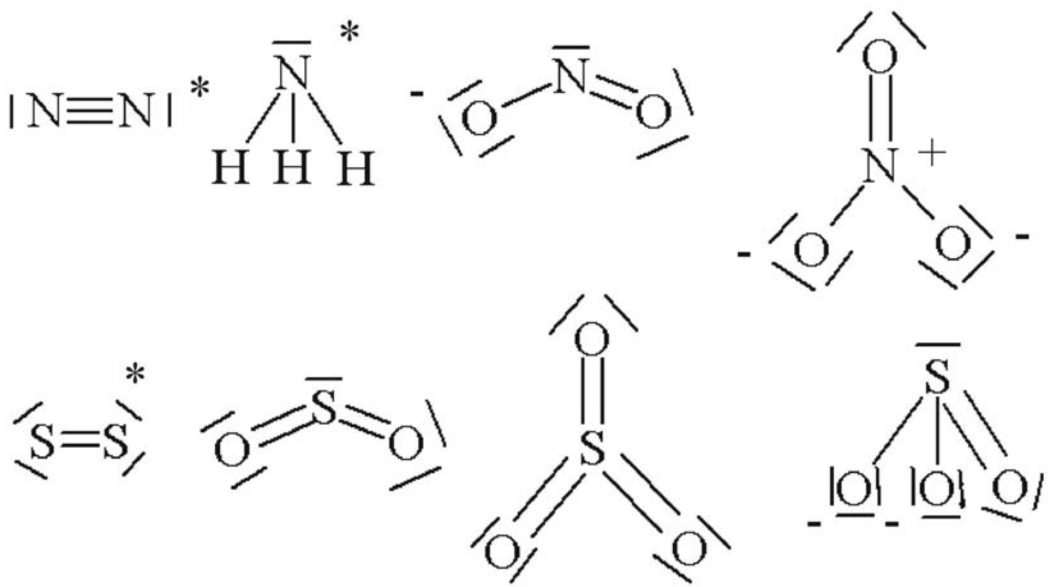
Element	Group	Number of bonds
P	5	3, 5
S	6	2, 4, 6
Cl	7	1, 3, 5, 7

Some examples:

SiF62-, PF5, SF6 do exist

CF62-, NF5, OF6 do not exist

Examples: Lewis structure of N_2, NH_3, NO_2^-, NO_3^-, S_2, SO_2, SO_3, SO_3^{2}. Those which are not necessarily resonance structures/hybrids are marked with an asterisk. $\rightarrow$ Octett rule, hypervalence, formal charges



- are used instead of **:**

* No other resonance structure