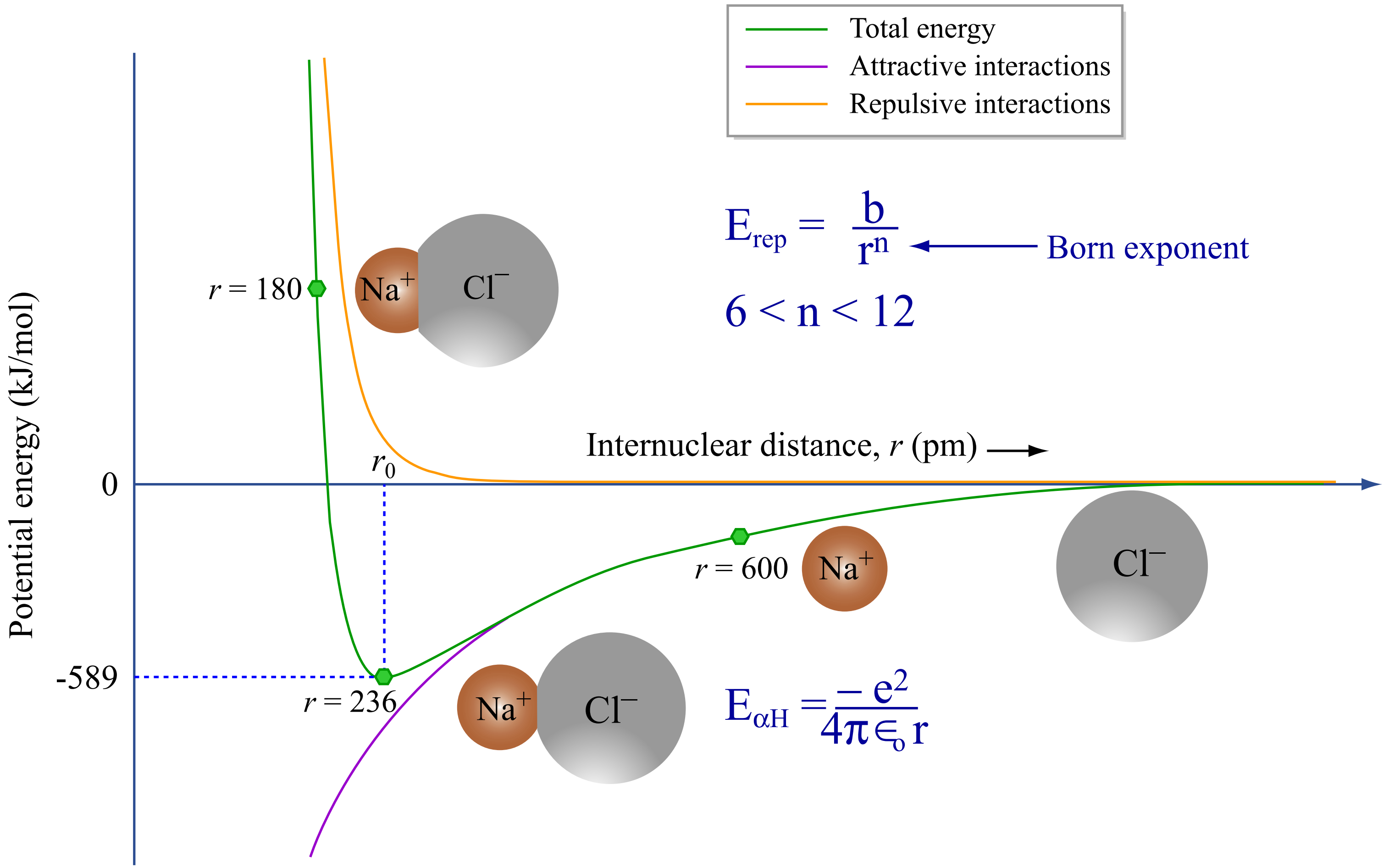
Welcome to 3.091

Lecture 9

September 28, 2009

Drawing Lewis Structures



$$E_{rep} = \frac{b}{r^n}$$

$$6 < n < 12$$

$$E_{\alpha H} = \frac{-e^2}{4\pi\epsilon_o r}$$

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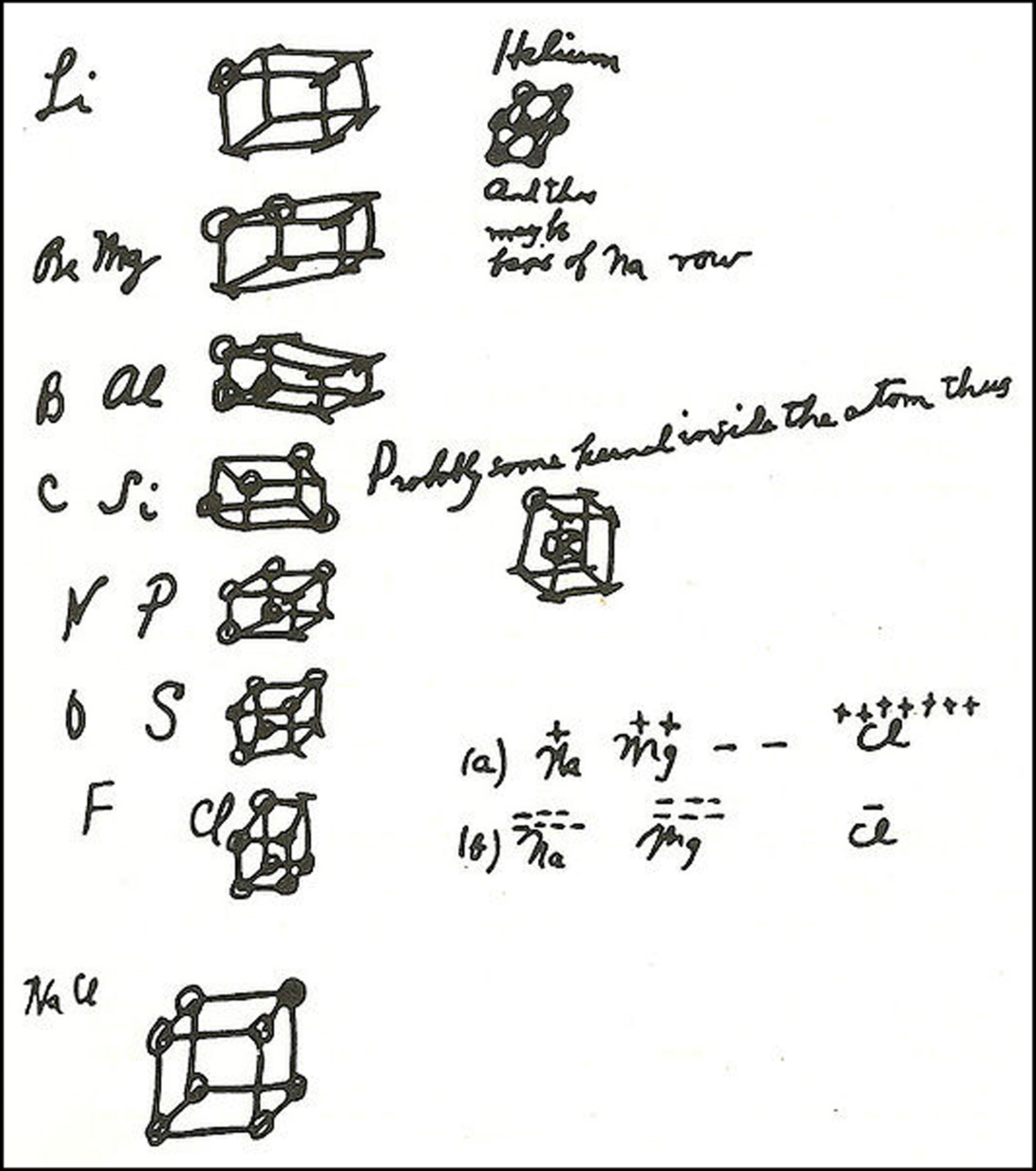

And thus might be basis of Na row

Probably some kernel inside the atom thus

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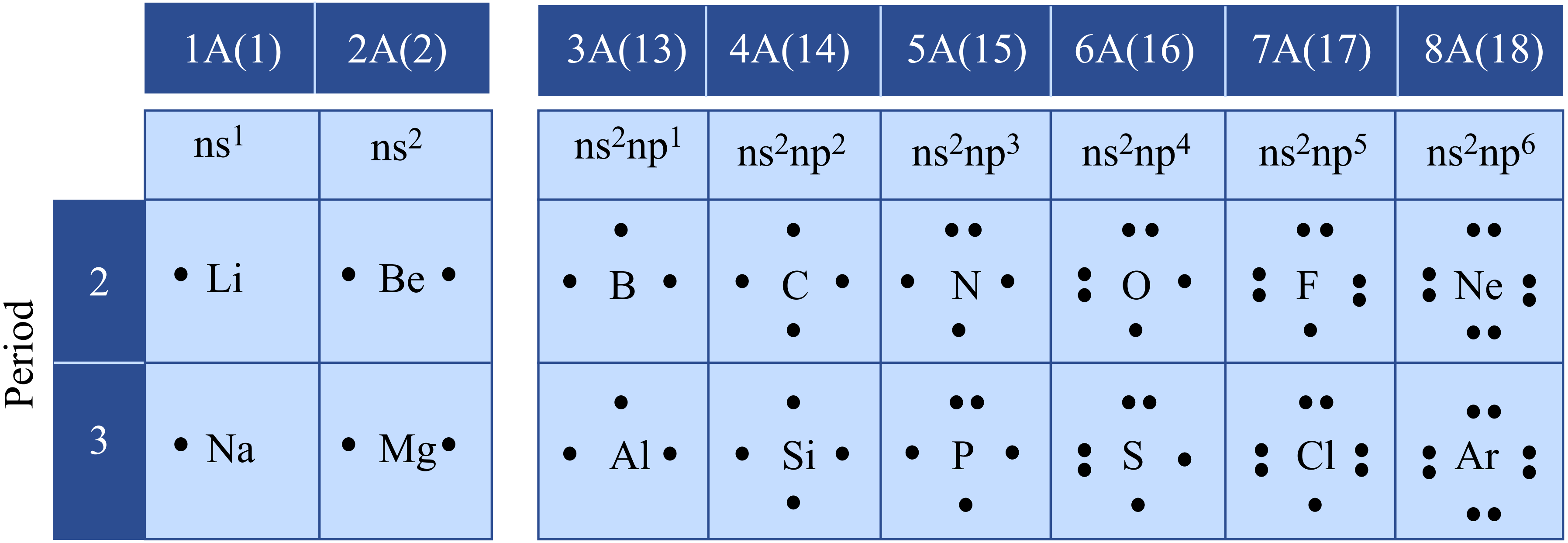
Lewis Notation: Electron - Symbols (1916)



		1A(1)	2A(2)	3A(13)	4A(14)	5A(15)	6A(16)	7A(17)	8A(18)
		ns^1	ns^2	ns^{2}np^1	ns^{2}np^2	ns^{2}np^3	ns^{2}np^4	ns^{2}np^5	ns^{2}np^6
Period	2	• Li	• Be •	• • B •	• • C • •	•• • N • •	•• : O • •	•• : F : •	•• : Ne : ••
	3	• Na	• Mg•	• • Al •	• • Si • •	•• • P • •	•• : S • •	•• : Cl : •	•• : Ar : ••

— *Element symbol* ≡ *Nucleus & inner e$\bar{s}$*

— *Dots* ≡ *Valence e$\bar{s}$*

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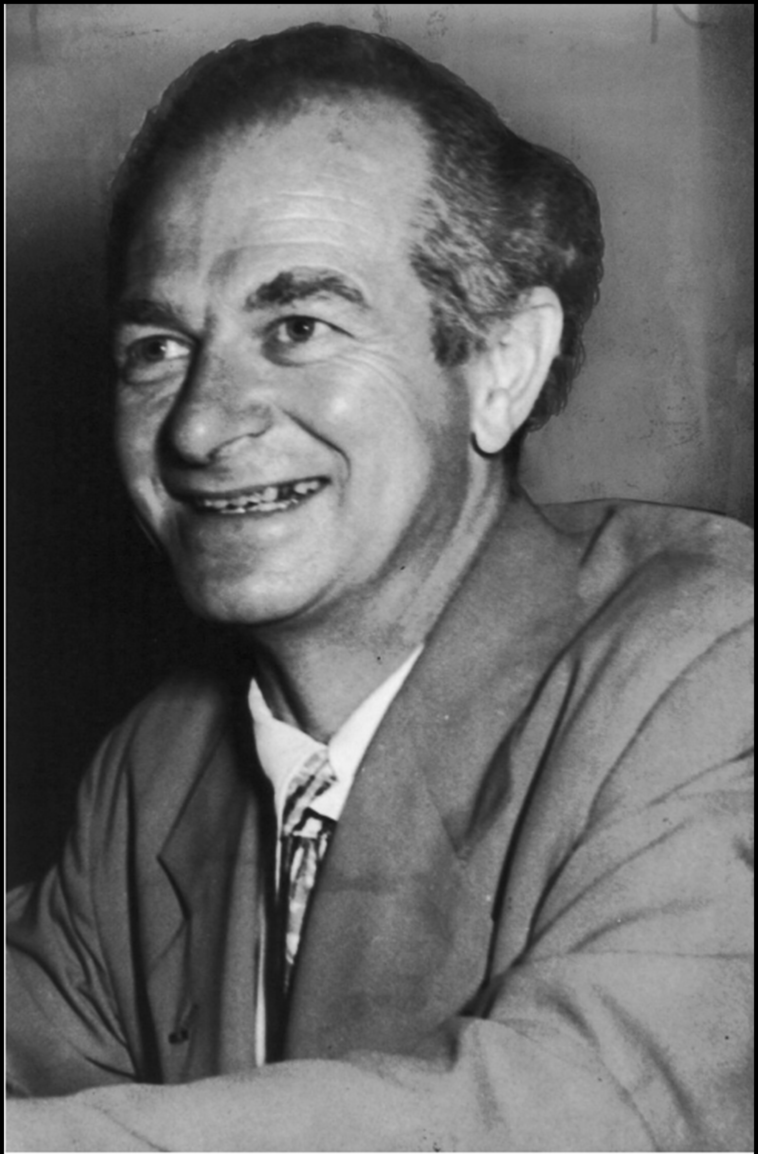
Drawing Lewis Structures

1. center the element with lowest AVEE
2. count all valence electrons
3. draw a single bond from each surrounding atom to the central atom; subtract 2 valence e^-s for each bond
4. distribute remaining e^-s in pairs until each atom has 8 e^-s in total; place NB pairs on peripheral atoms starting with highest AVEE



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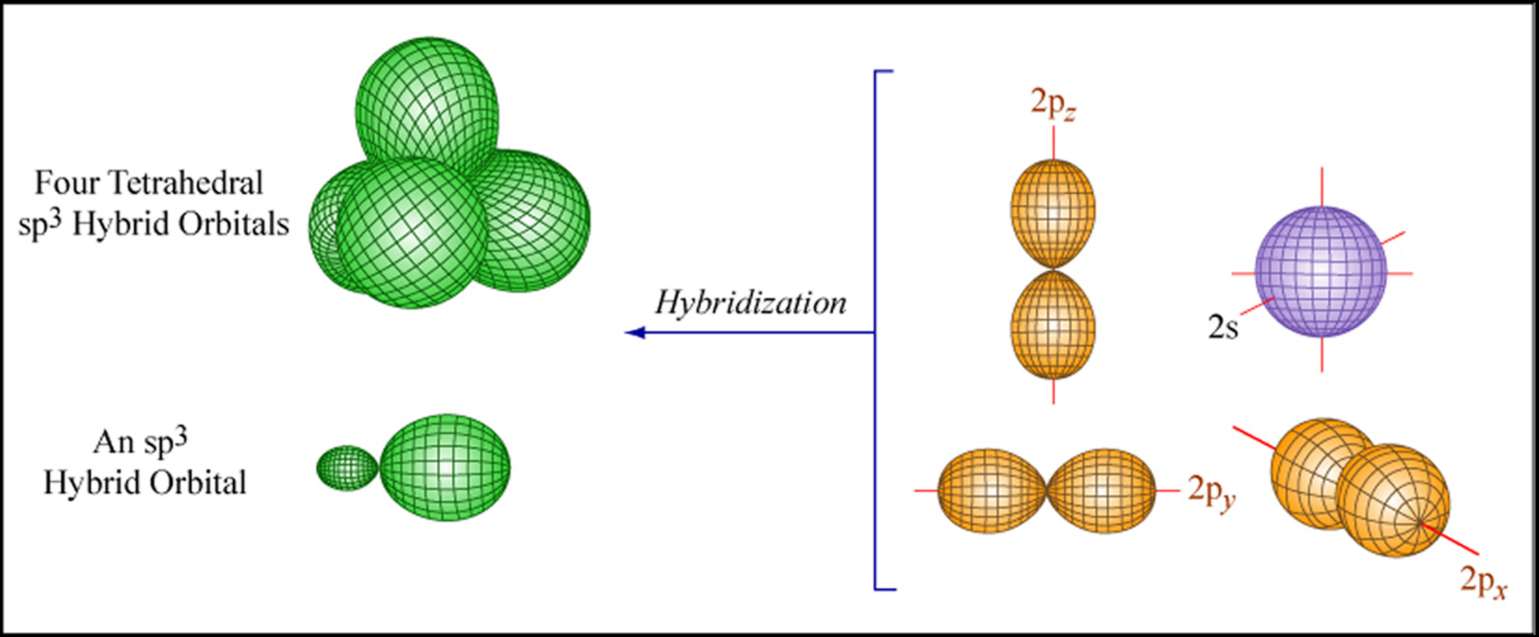

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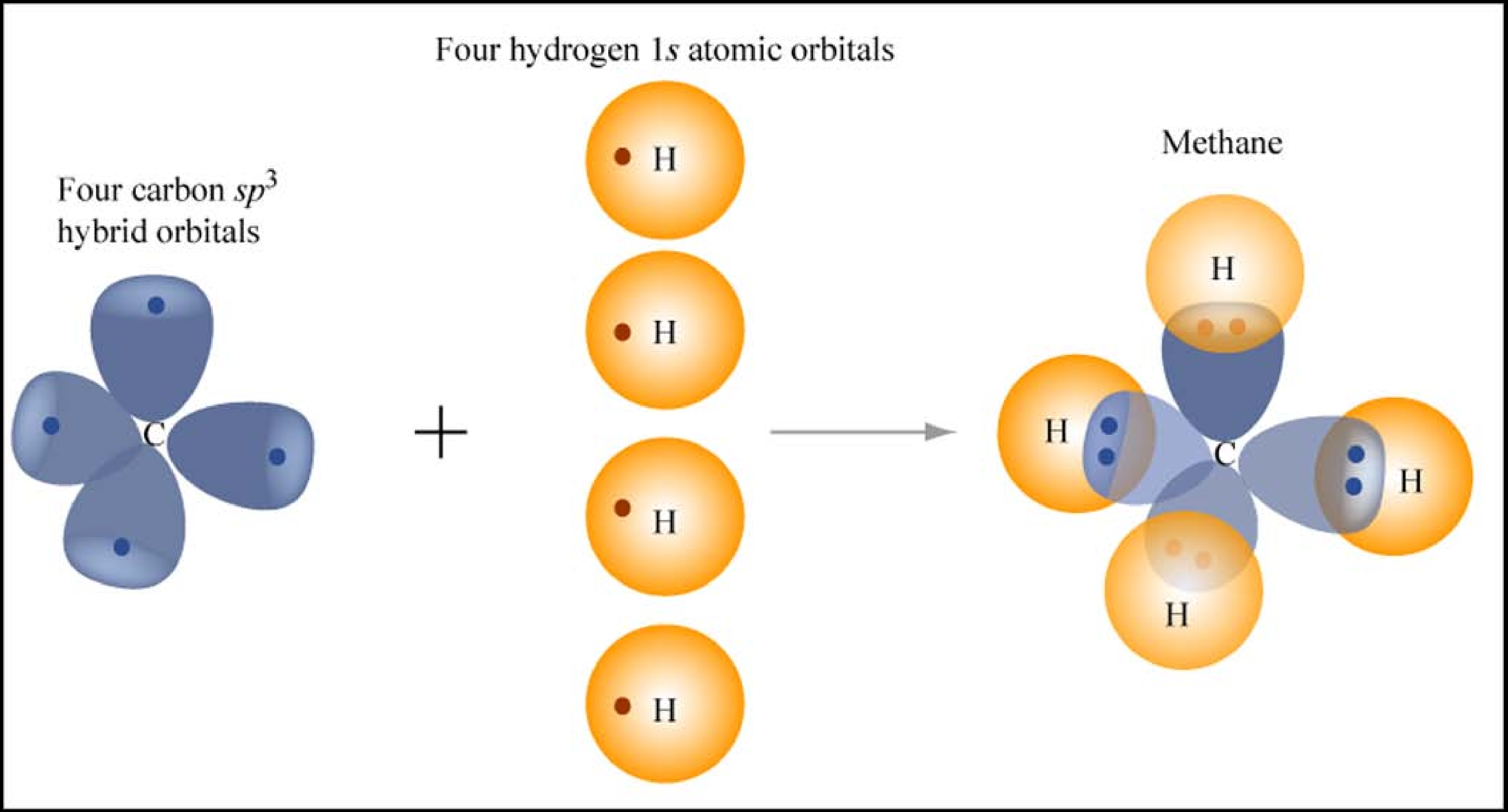

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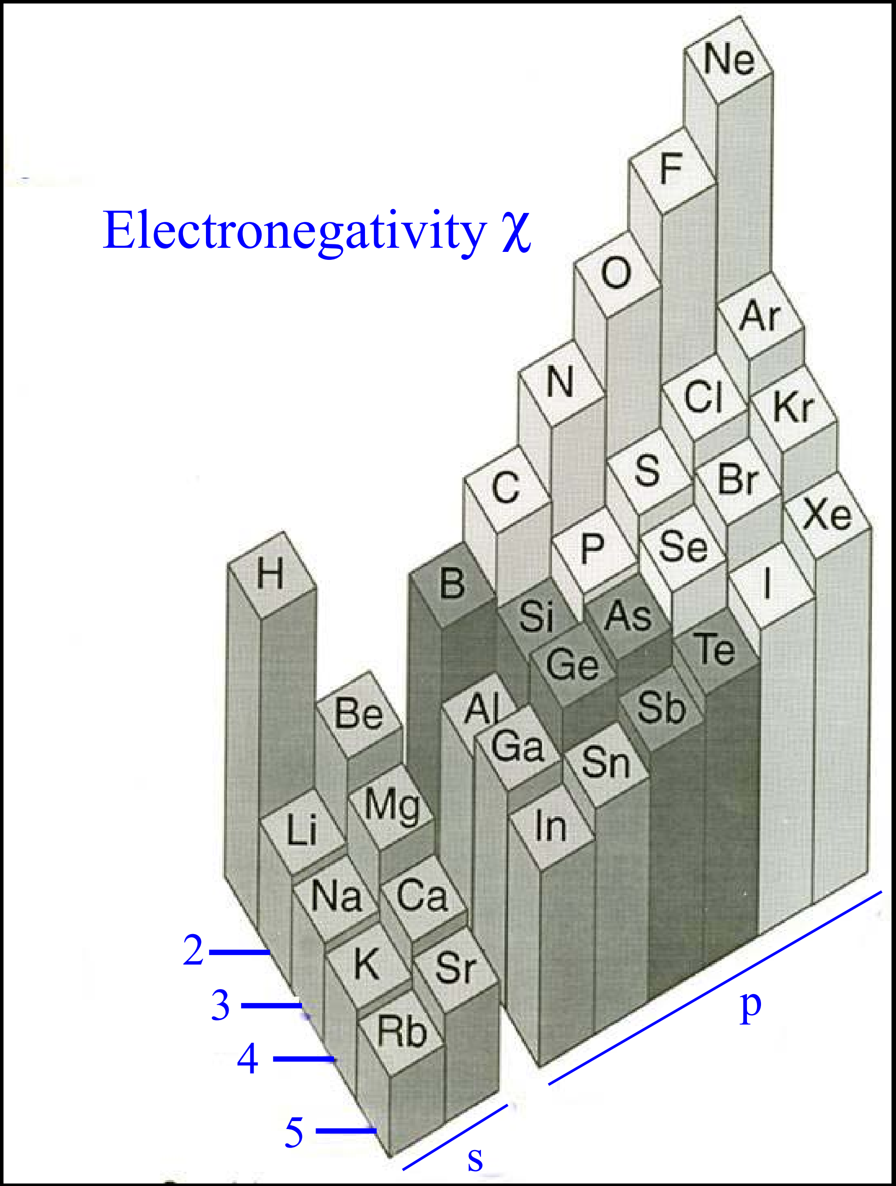

Nonmetals have high χ

Metal have
low χ

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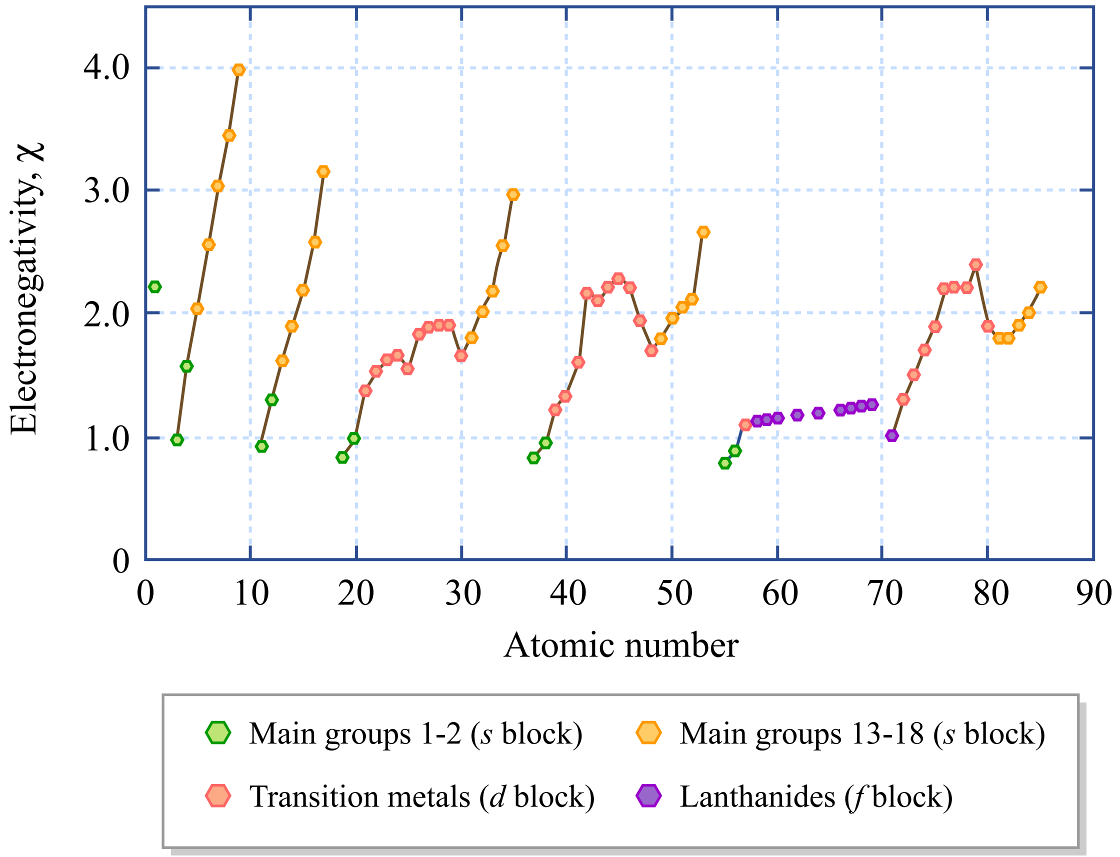

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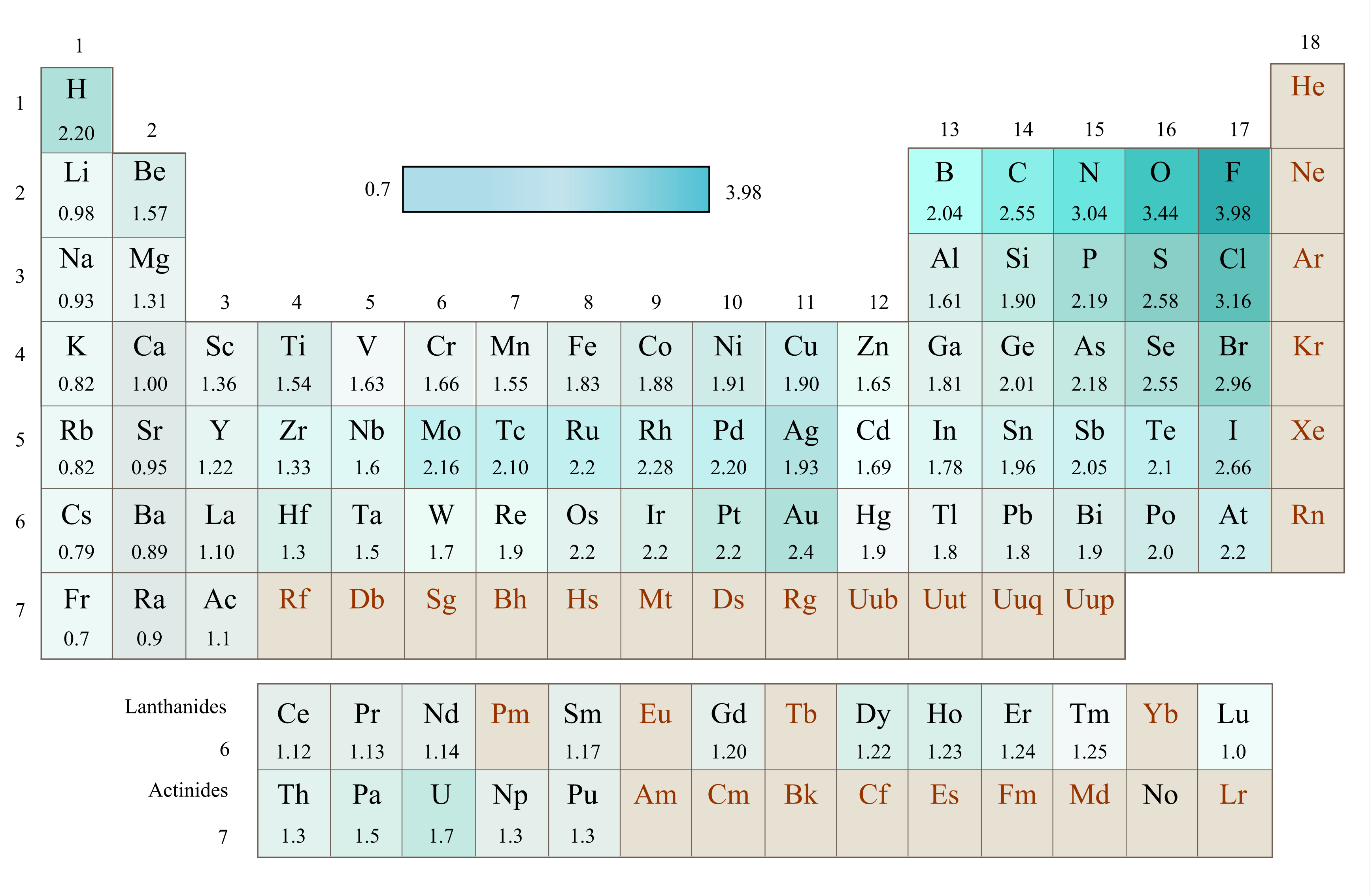

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 2.20																	He
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 2.10	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe
6	Cs 0.79	Ba 0.89	La 1.10	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn
7	Fr 0.7	Ra 0.9	Ac 1.1	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup			

Lanthanides 6	Ce 1.12	Pr 1.13	Nd 1.14	Pm	Sm 1.17	Eu	Gd 1.20	Tb	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb	Lu 1.0
Actinides 7	Th 1.3	Pa 1.5	U 1.7	Np 1.3	Pu 1.3	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

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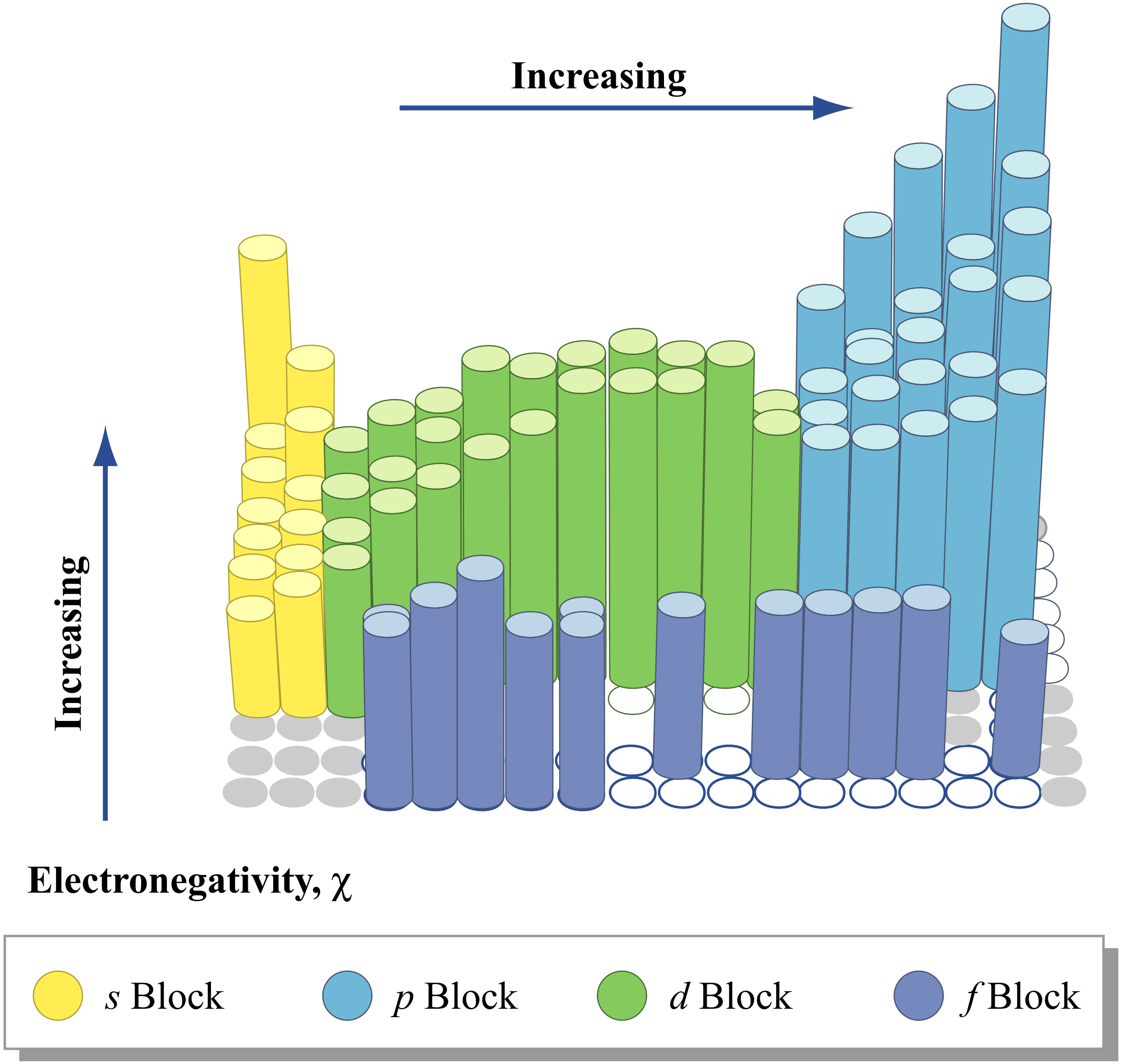

Electronegativity, χ

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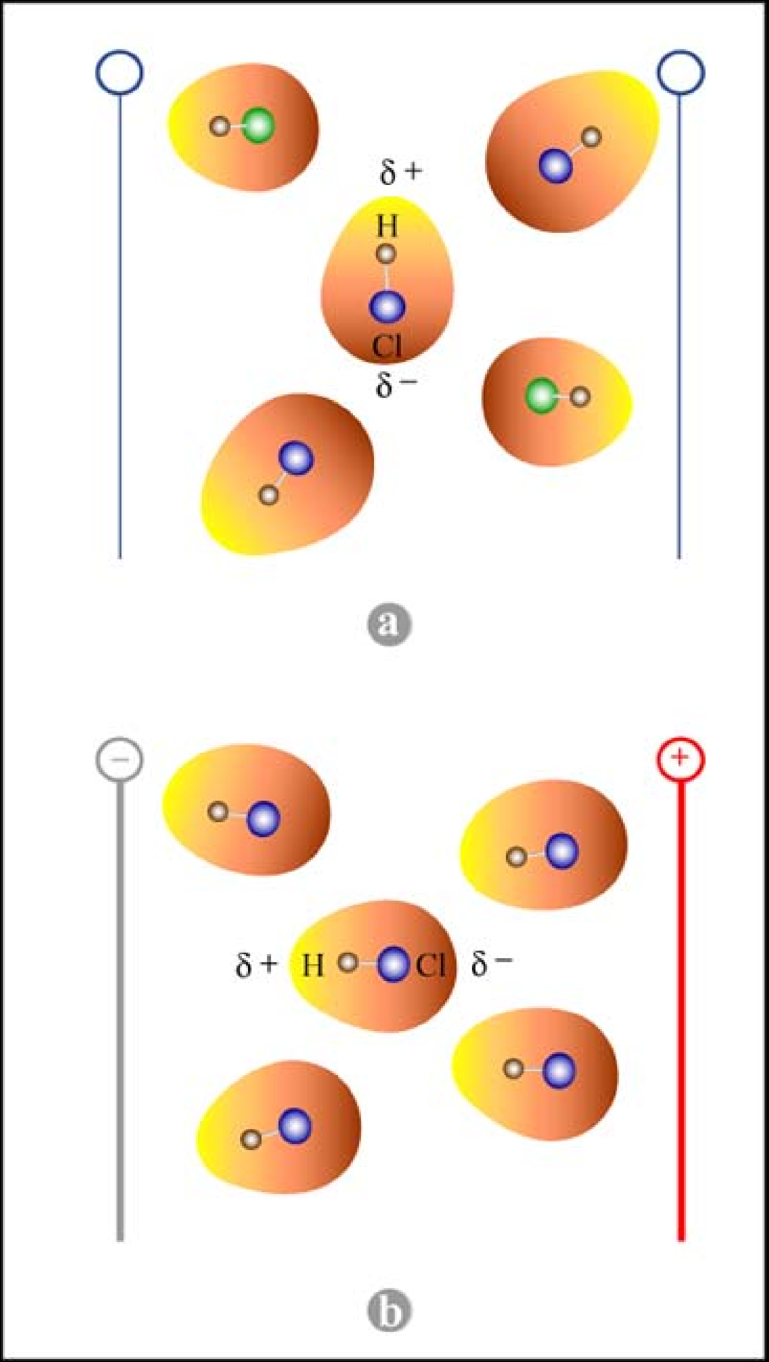

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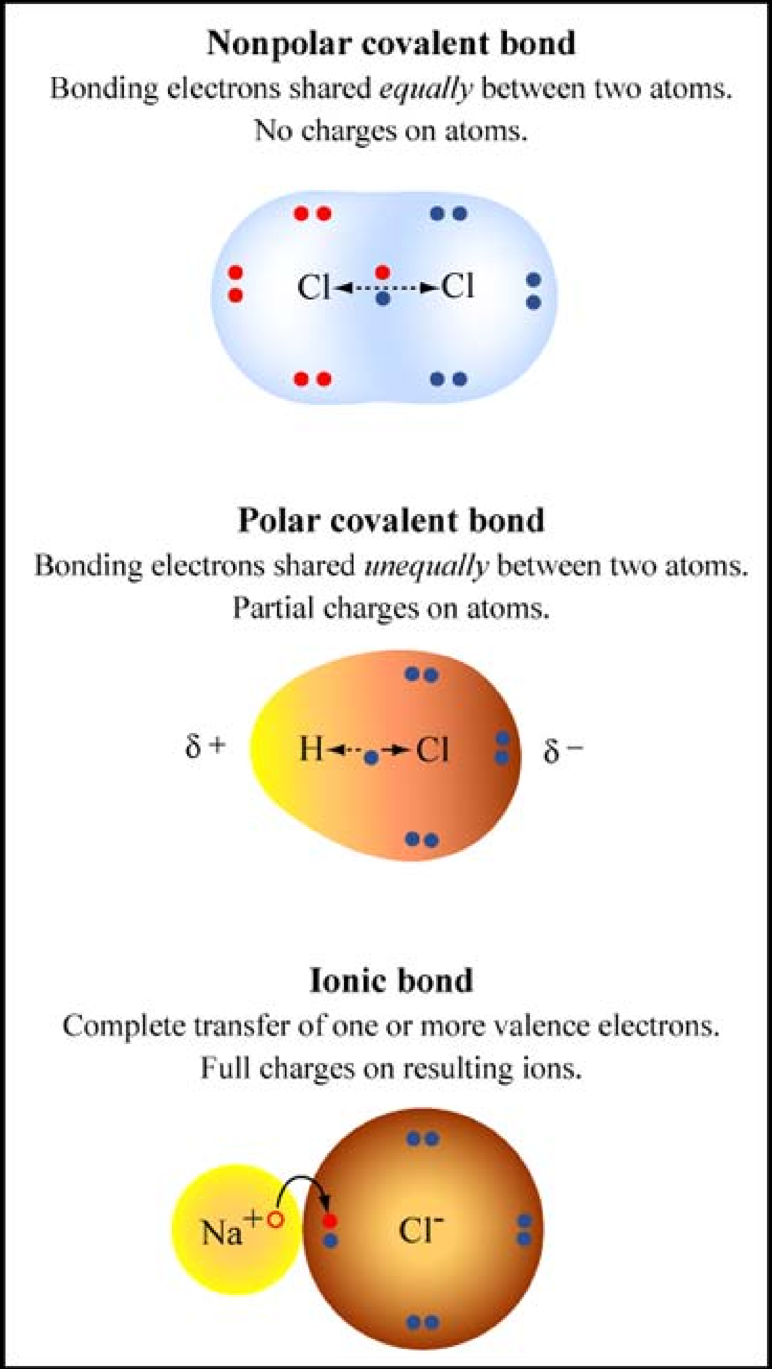

Nonpolar covalent bond

Bonding electrons shared *equally* between two atoms.
No charges on atoms.

Polar covalent bond

Bonding electrons shared *unequally* between two atoms.
Partial charges on atoms.

Ionic bond

Complete transfer of one or more valence electrons.
Full charges on resulting ions.

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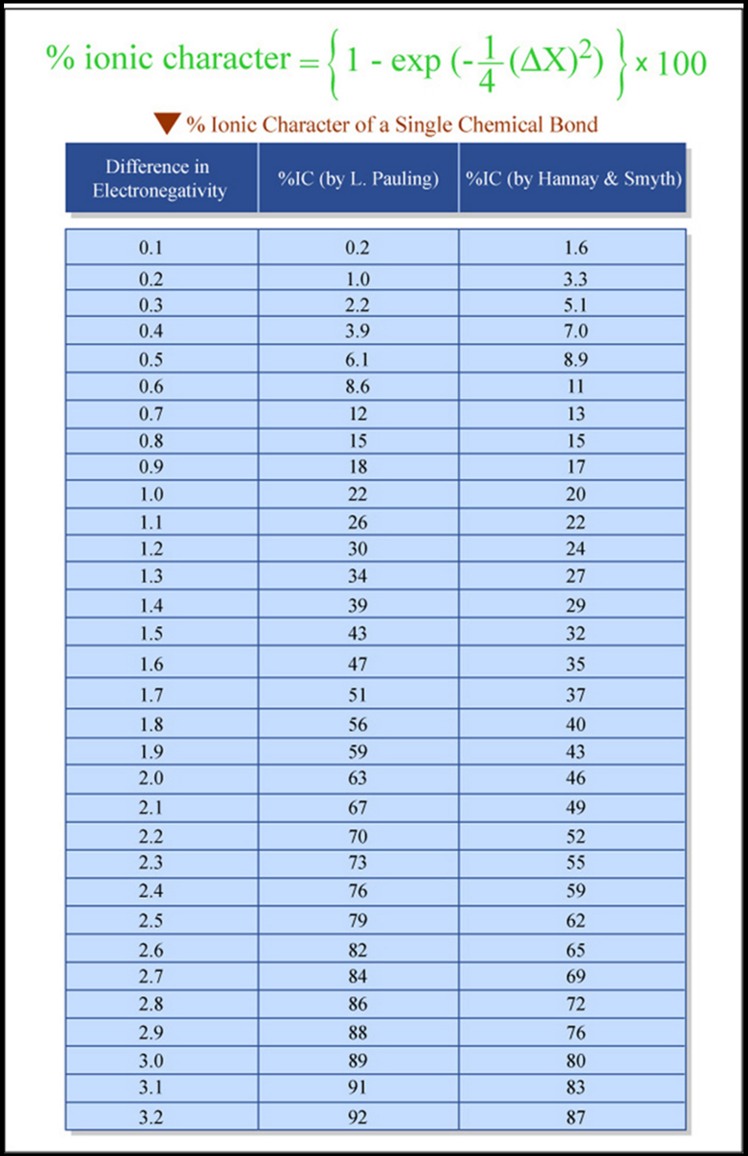

$$\%\ \text{ionic character} = \left\{1 - \exp\left(-\frac{1}{4}(\Delta X)^2\right)\right\} \times 100$$

▼ % Ionic Character of a Single Chemical Bond

Difference in Electronegativity	%IC (by L. Pauling)	%IC (by Hannay & Smyth)
0.1	0.2	1.6
0.2	1.0	3.3
0.3	2.2	5.1
0.4	3.9	7.0
0.5	6.1	8.9
0.6	8.6	11
0.7	12	13
0.8	15	15
0.9	18	17
1.0	22	20
1.1	26	22
1.2	30	24
1.3	34	27
1.4	39	29
1.5	43	32
1.6	47	35
1.7	51	37
1.8	56	40
1.9	59	43
2.0	63	46
2.1	67	49
2.2	70	52
2.3	73	55
2.4	76	59
2.5	79	62
2.6	82	65
2.7	84	69
2.8	86	72
2.9	88	76
3.0	89	80
3.1	91	83
3.2	92	87

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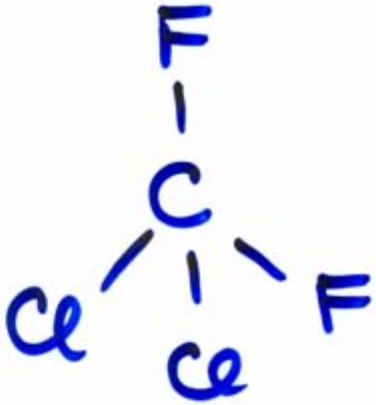
Thomas “sp^3” Midgley

Freon 12: designer molecule, tailored chemical

- early refrigerants were toxic or flammable, e.g., ammonia, methyl chloride, sulfur dioxide
- in late 1920s Midgley discovered CCl_2F_2 with properties of a refrigerant ***and*** propellant: **perfect!**



dichlorodifluoromethane

chlorofluorocarbon

CFC

- but in the upper atmosphere, u.v. light breaks the C – Cl bond, and atomic Cl attacks ozone

$$Cl + O_3 \Rightarrow ClO + O_2$$

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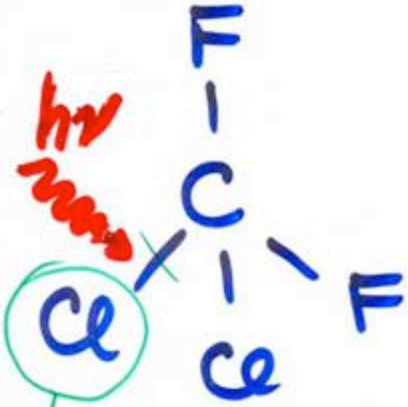

dichlorodifluoromethane

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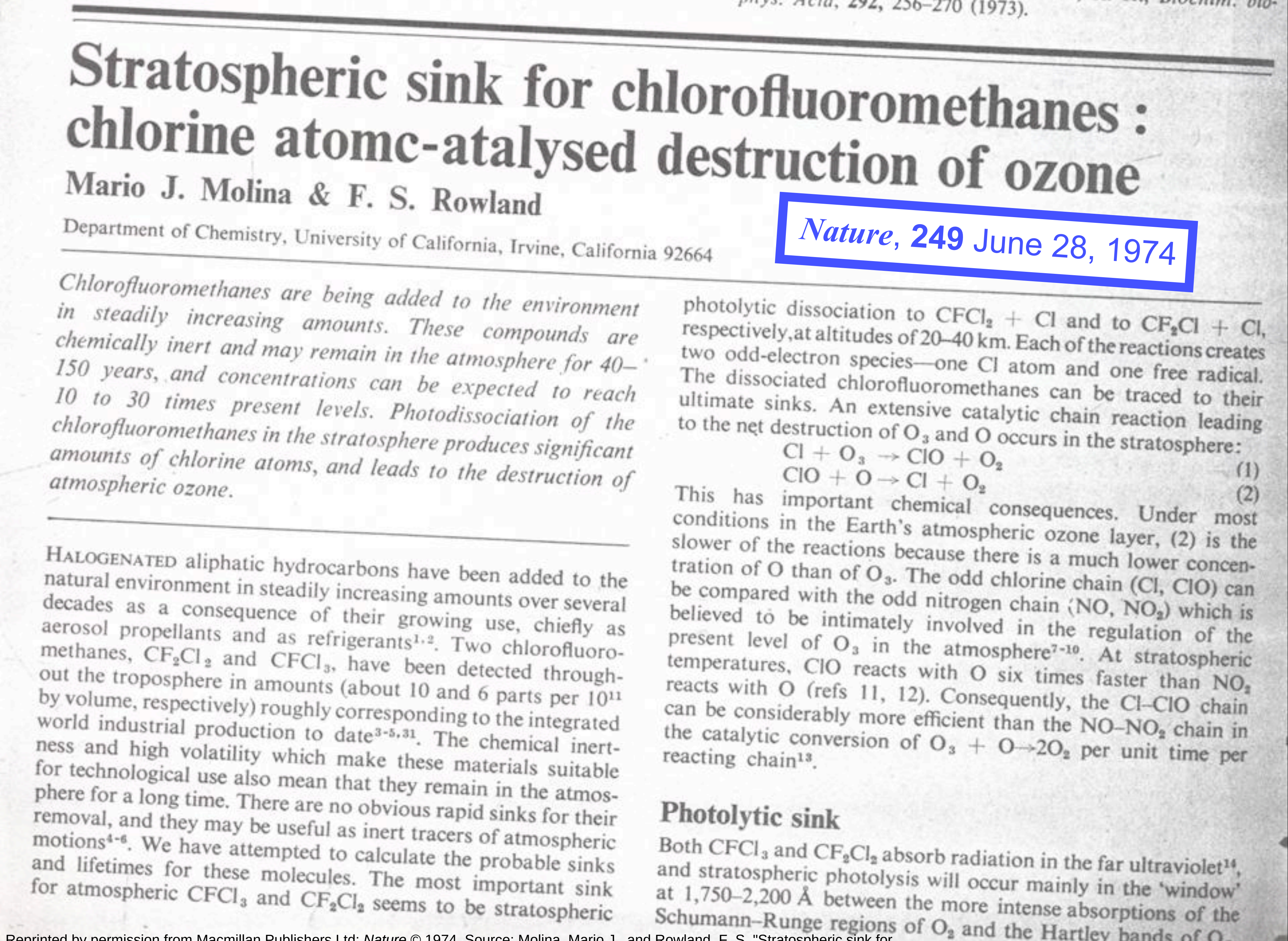
$$Cl + O_3 \Rightarrow ClO + O_2$$

CFCs ⇒ ozone depletion

Figure removed due to copyright restrictions.
Chandler, David L. "MIT scientist shares Nobel for identifying ozone damage." *The Boston Globe*, October 12, 1995.



phys. Acta, 292, 256–270 (1973).

Stratospheric sink for chlorofluoromethanes: chlorine atomc-atalysed destruction of ozone

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Department of Chemistry, University of California, Irvine, California 92664

Chlorofluoromethanes are being added to the environment in steadily increasing amounts. These compounds are chemically inert and may remain in the atmosphere for 40–150 years, and concentrations can be expected to reach 10 to 30 times present levels. Photodissociation of the chlorofluoromethanes in the stratosphere produces significant amounts of chlorine atoms, and leads to the destruction of atmospheric ozone.

HALOGENATED aliphatic hydrocarbons have been added to the natural environment in steadily increasing amounts over several decades as a consequence of their growing use, chiefly as aerosol propellants and as refrigerants[1,2]. Two chlorofluoromethanes, CF_2Cl_2 and $CFCl_3$, have been detected throughout the troposphere in amounts (about 10 and 6 parts per 10^{11} by volume, respectively) roughly corresponding to the integrated world industrial production to date[3-5,31]. The chemical inertness and high volatility which make these materials suitable for technological use also mean that they remain in the atmosphere for a long time. There are no obvious rapid sinks for their removal, and they may be useful as inert tracers of atmospheric motions[4-6]. We have attempted to calculate the probable sinks and lifetimes for these molecules. The most important sink for atmospheric $CFCl_3$ and CF_2Cl_2 seems to be stratospheric photolytic dissociation to $CFCl_2 + Cl$ and to $CF_2Cl + Cl$, respectively, at altitudes of 20–40 km. Each of the reactions creates two odd-electron species—one Cl atom and one free radical. The dissociated chlorofluoromethanes can be traced to their ultimate sinks. An extensive catalytic chain reaction leading to the net destruction of O_3 and O occurs in the stratosphere:

$$Cl + O_3 \rightarrow ClO + O_2 \tag{1}$$

$$ClO + O \rightarrow Cl + O_2 \tag{2}$$

This has important chemical consequences. Under most conditions in the Earth's atmospheric ozone layer, (2) is the slower of the reactions because there is a much lower concentration of O than of O_3. The odd chlorine chain (Cl, ClO) can be compared with the odd nitrogen chain (NO, NO_2) which is believed to be intimately involved in the regulation of the present level of O_3 in the atmosphere[7-10]. At stratospheric temperatures, ClO reacts with O six times faster than NO_2 reacts with O (refs 11, 12). Consequently, the Cl–ClO chain can be considerably more efficient than the NO–NO_2 chain in the catalytic conversion of $O_3 + O \rightarrow 2O_2$ per unit time per reacting chain[13].

Photolytic sink

Both $CFCl_3$ and CF_2Cl_2 absorb radiation in the far ultraviolet[14], and stratospheric photolysis will occur mainly in the 'window' at 1,750–2,200 Å between the more intense absorptions of the Schumann–Runge regions of O_2 and the Hartley bands of O_3.

Nature, **249** June 28, 1974

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3.091SC Introduction to Solid State Chemistry
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