

# Periodic Table of Elements

① N-electron atom: classification of states

Ⓐ  $L \Leftrightarrow |\vec{L}| = \left| \sum_{i=1}^N \vec{l}_i \right|$  total orbital angular momentum

$L = 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad \dots$

(capital letters)

$S \quad P \quad D \quad F \quad G \quad \dots$

z-projections  $-L, -L+1, \dots, 0, \dots, L : 2L+1$  values

Ⓑ  $S \Leftrightarrow |\vec{S}| = \left| \sum_{i=1}^N \vec{s}_i \right|$  total spin

z-projections  $-S, -S+1, \dots, S : 2S+1$  values

Given  $L$  and  $S$ :  $(2L+1) \cdot (2S+1)$  states

Degeneracy is partly lifted when relativistic effects (spin-orbit interaction, ...) are taken into account  $\Rightarrow$  fine structure formed

Good (exact!):  $J = |\vec{J}| = |\vec{L} + \vec{S}|$

Degeneracy in  $J_z$  (in the absence of magnetic field  $\vec{B}$ )

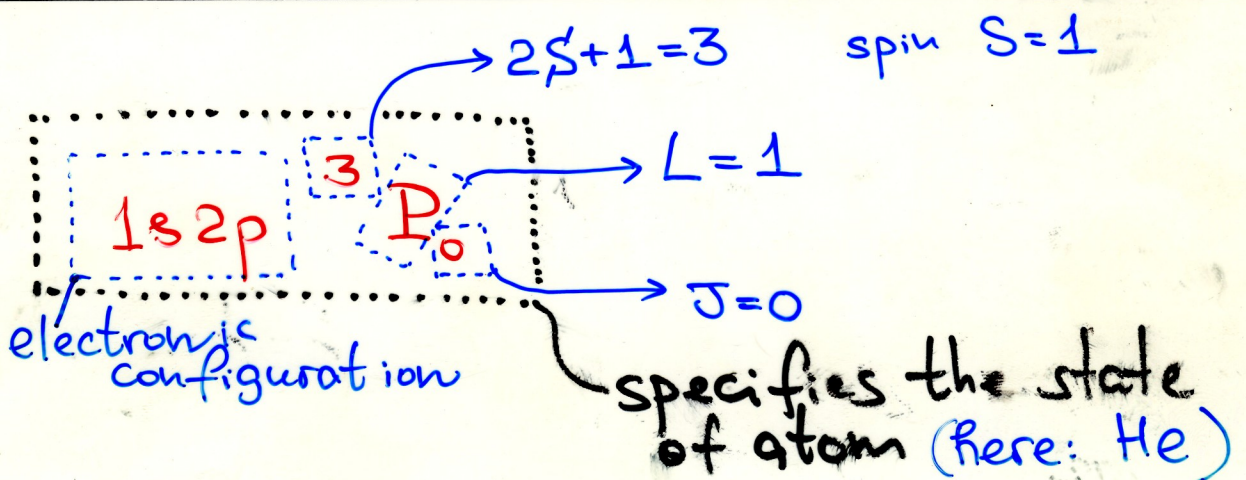


When self-consistent mean-field (Hartree-Fock) approximation used:

each electron moves in an effective field of the nucleus + all other electrons

$U_{\text{eff}}(\vec{r})$  depends on states of spherical symmetry: state of each electron can be labeled by  $l$

Hydrogen	N-electron atom
<ol style="list-style-type: none"> <li><math>l=0, 1, \dots, n-1</math> <math>n \geq l+1</math></li> <li>degeneracy in <math>l</math></li> <li>energy increases with <math>n</math> (<math>E_n = -\frac{R_y}{n^2}</math>)</li> </ol>	<ol style="list-style-type: none"> <li>convention <math>n \geq l+1</math></li> <li>degeneracy in <math>l</math> lifted</li> <li>e.g. <math>E_{4d} &gt; E_{5s}</math></li> </ol>

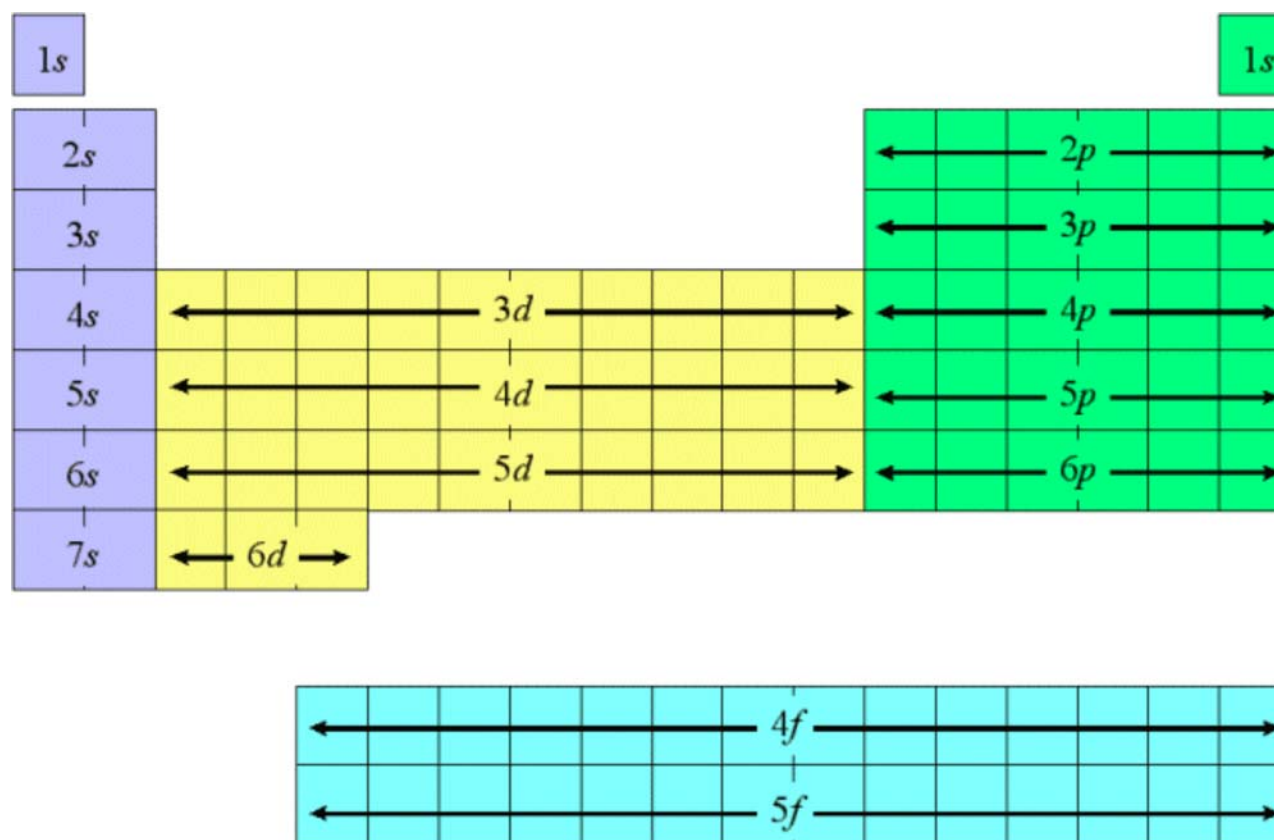


## Electronic Structure of Atoms

Electron configurations and the periodic table

### Electron Configurations and the Periodic Table

The periodic table is structured so that elements with the same type of valence electron configuration are arranged in columns.



- The left-most columns include the alkali metals and the alkaline earth metals. *In these elements the valence s orbitals are being filled*
- On the right hand side, the right-most block of six elements are those in which *the valence p orbitals are being filled*

*These two groups comprise the main-group elements*



Electronic configuration: distribution of electrons over states with different  $n, l$

Fix  $nl \Rightarrow 2(2l+1)$  different states  
 Spin  $\pm 1/2$       orbital degeneracy  $l_z = -l, \dots, 0, \dots, l$

Closed shell  $nl$  :  $2(2l+1)$  electrons there

Hund's Rule :

Fix electronic configuration  $\xRightarrow{2}$  which  $L$  &  $S$  give minimal energy  $^2$

- Maximize total spin  $S$
- (then) • Maximize total  $L$  (for then predetermined  $S$ )

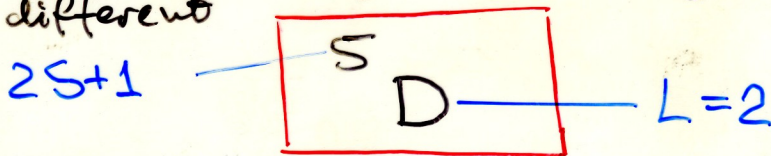
[then electrons maximally avoid each other]

• Need to consider only open shells

Example: 4 d-electrons

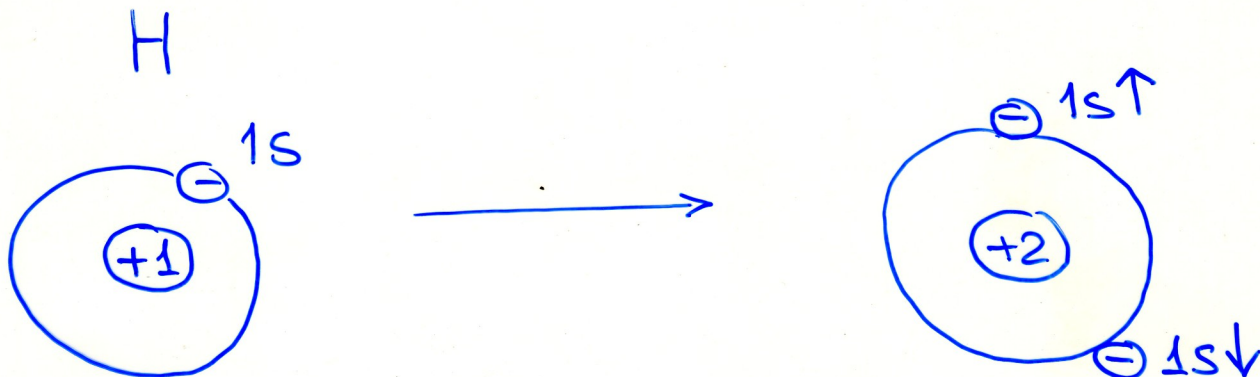
• d:  $l=2$        $l_z = 0, \pm 1, \pm 2 \Rightarrow$  spins can be  $\uparrow\uparrow\uparrow\uparrow : S=2$

$l_z$  must be different :  $+2, +1, 0, -1$        $l_z = 2$        $L=2$

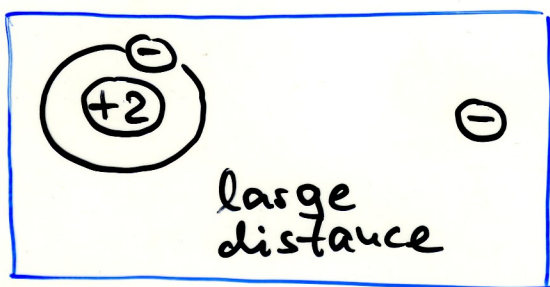




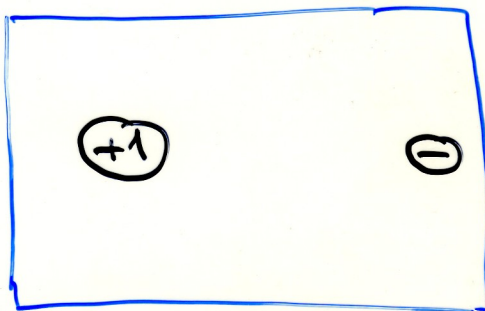
# Ionization energy vs atomic number $Z$



adding  $\ominus$  to  $\text{He}^+$ :

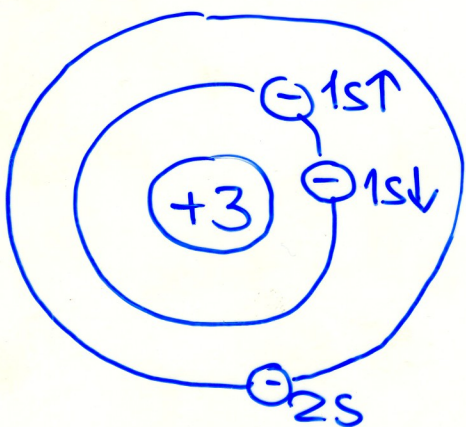


similar to



But at small distances  $\ominus$  feels  $(+2)$   
not  $(+1)$

$\Rightarrow$  binding in He is stronger than in H



Li

Competing effects:

- ① levels deepen for  $(+3)$
- ② need to jump to 2s

loose binding for Li



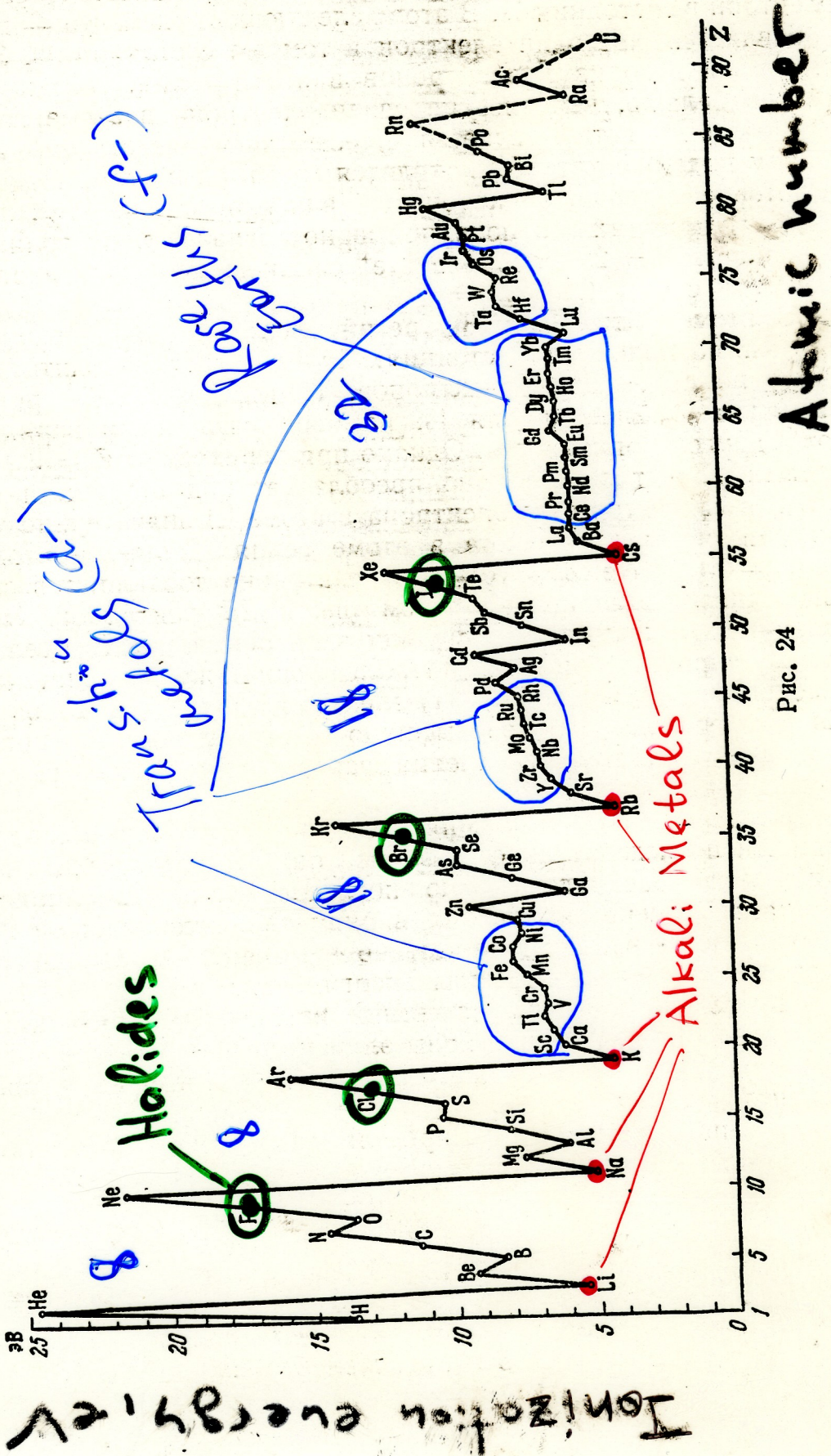


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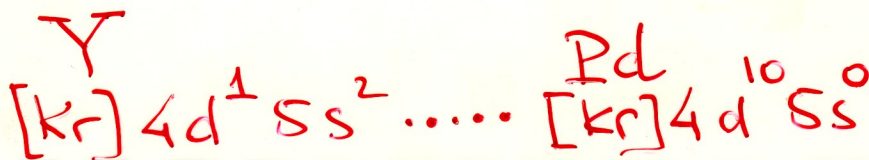
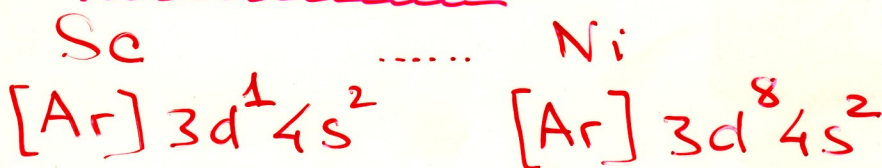


Groups of elements are formed:

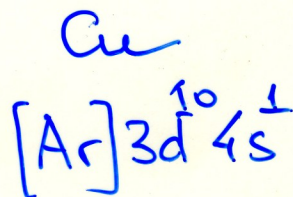
in each group binding (in general) increases with  $Z$

ne	<u>Groups</u>	# of electrons	closed shell elements
1s		2	He
2s 2p		8	Ne
3s 3p		8	Ar
4s 3d 4p		18	Kr
5s 4d 5p		18	Xe
6s 4f 5d 6p		32	Rn
7s 6d 5f ...		not filled in Nature	

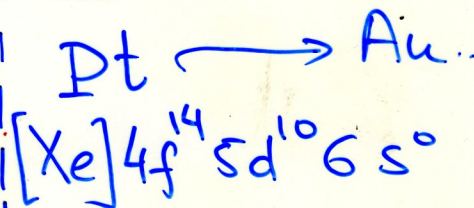
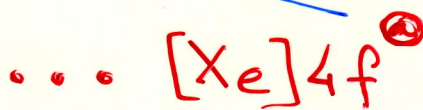
gradual filling of d-levels gives transition metals



Noble Metals



filling of f-orbitals:  
Rare Earths



# Monovalent metals

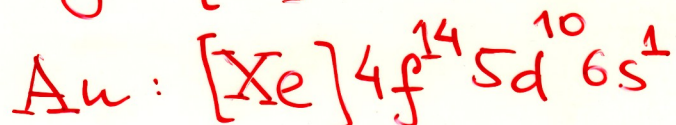
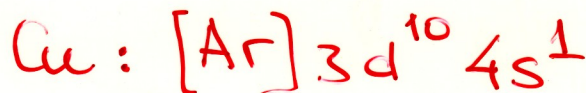
Alkali Metals  
(BCC)



Noble Metals  
(FCC)

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## Metallic Bonding

$K^+$  + 1 collectivized electron  
ion cores

ions embedded in a sea of electrons

$Cu^{11+}$  + 11 electrons  
ion cores per unit cell

metallic + covalent  
Bonding (d-electrons)

	$r_{ion}$ (Å)	$r_{met}$ (Å)	$r_{met}/r_{ion}$
Li	0.60	1.51	2.52
K	1.33	2.26	1.70
Cu	0.96	1.28	1.33
Au	1.37	1.44	1.05

isolated ion                      nearest-n. distance



# Ionic Crystals (insulators)

simplest model: ions  $\equiv$  hard charged  $\pm$  spheres

Pauli exclusion principle

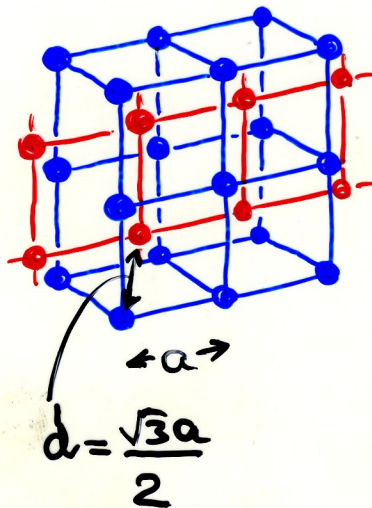
held together by electrostatic forces

① Alkali Halides (I-VII ionic cr.)

	$\text{Li}^+$	$\text{F}^-$	
	$\text{Na}^+$	$\text{Cl}^-$	
cations	$\text{K}^+$	$\text{Br}^-$	anions
	$\text{Rb}^+$	$\text{I}^-$	
	$\text{Cs}^+$		

All Form NaCl structure (FCC with a basis)  
except  $\text{CsCl}$   $\text{CsBr}$   $\text{CsI}$  :

BCC-like:



Simple cubic with a basis

8 nearest neighbors

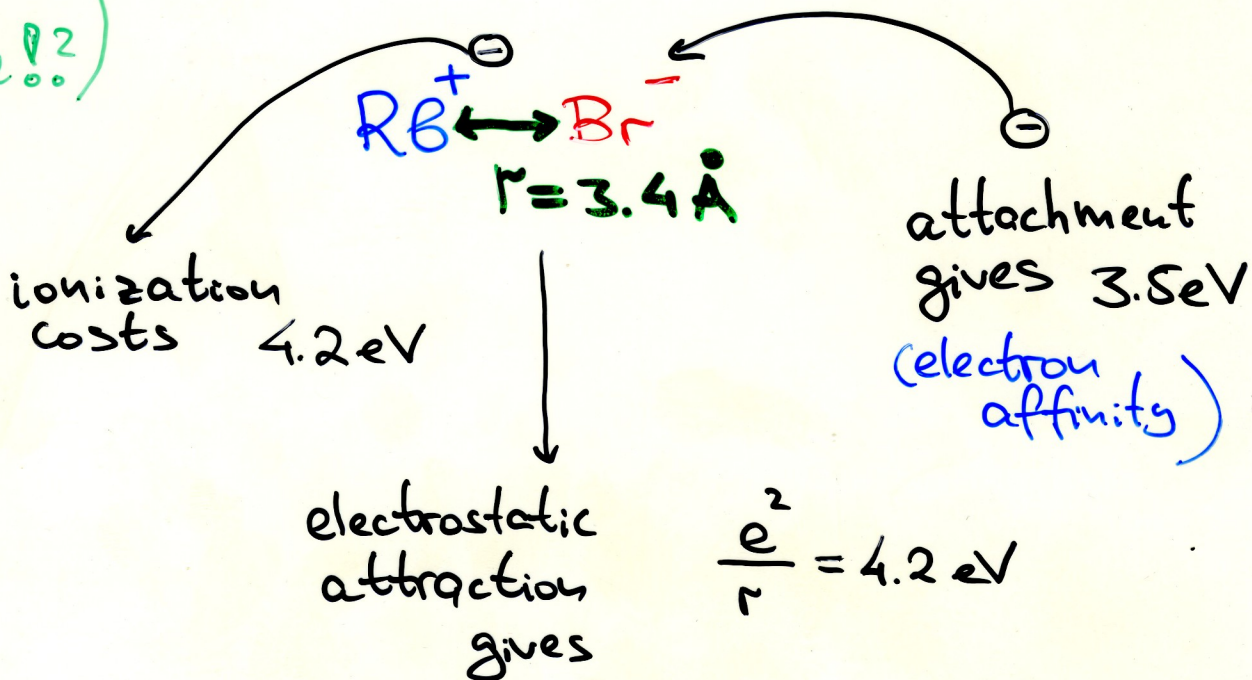
## ② II-VI Ionic Crystals

Be <sup>++</sup>	O <sup>--</sup>	
Mg <sup>++</sup>	S <sup>--</sup>	sulfur
Ca <sup>++</sup>	Se <sup>--</sup>	selenium
Sr <sup>++</sup>	Te <sup>--</sup>	Tellurium
Ba <sup>++</sup>		

All form NaCl structure,  
 except BeS BeSe BeTe: zincblende  
 (tetrahedrally coordinated)  
covalent + ionic bonding  
 BeO MgTe: wurtzite

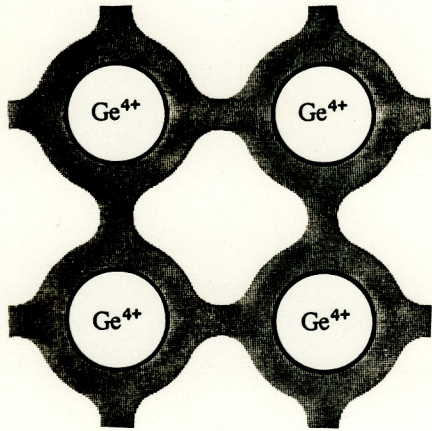
### Simple energy consideration

(just one neighbor considered!)

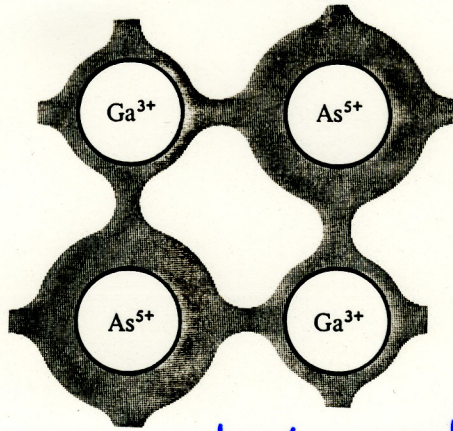




# Distribution of electron density

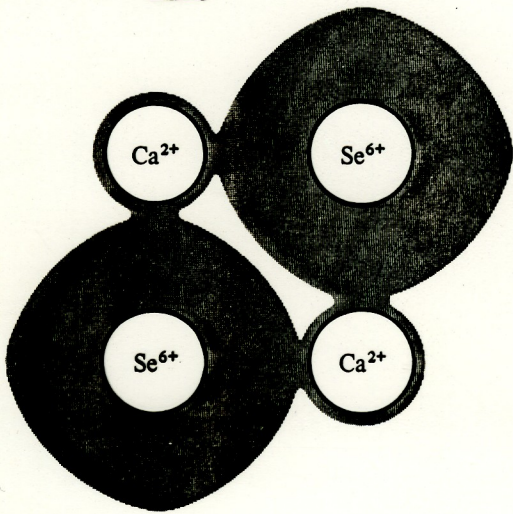


(a) Perfectly Covalent  
IV



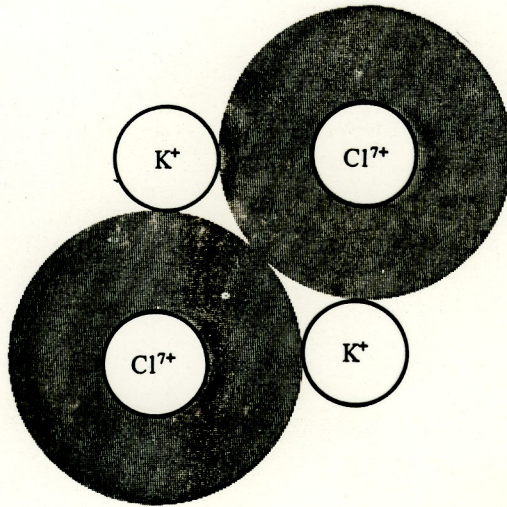
Covalent + weakly ionic

III-V  
(A<sub>3</sub>B<sub>5</sub>)



(c) Ionic + weakly covalent

II-VI  
(A<sub>2</sub>B<sub>6</sub>)



(d) Perfectly Ionic

I-VII

$\left\{ \begin{array}{l} \text{IV-N} \\ \text{III-V} \end{array} \right.$  tetrahedrally coordinated covalent bonds (diamond)  
 $\left\{ \begin{array}{l} \text{IV-N} \\ \text{III-V} \end{array} \right.$  zincblende structure  
semiconductors



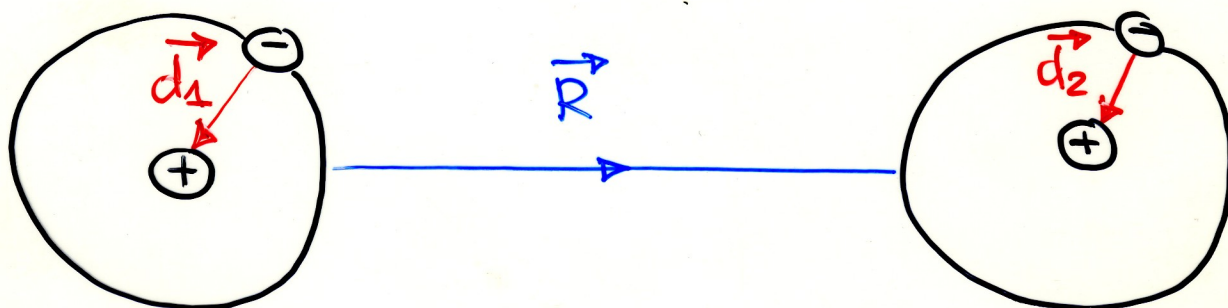
# Molecular Crystals (insulators)

Noble gases Ne Ar Kr Xe

(He crystallizes under pressure; quantum crystal zero-point fluctuations)  $\text{light} \leftrightarrow \frac{\hbar^2}{ma^2}$

Solid  $O_2$   $N_2$

Binding due to van der Waals forces



Atoms in the ground (S) state (spherical symmetry)  $\Rightarrow \langle \vec{d}_1 \rangle = 0$   
 $\langle \vec{d}_2 \rangle = 0$

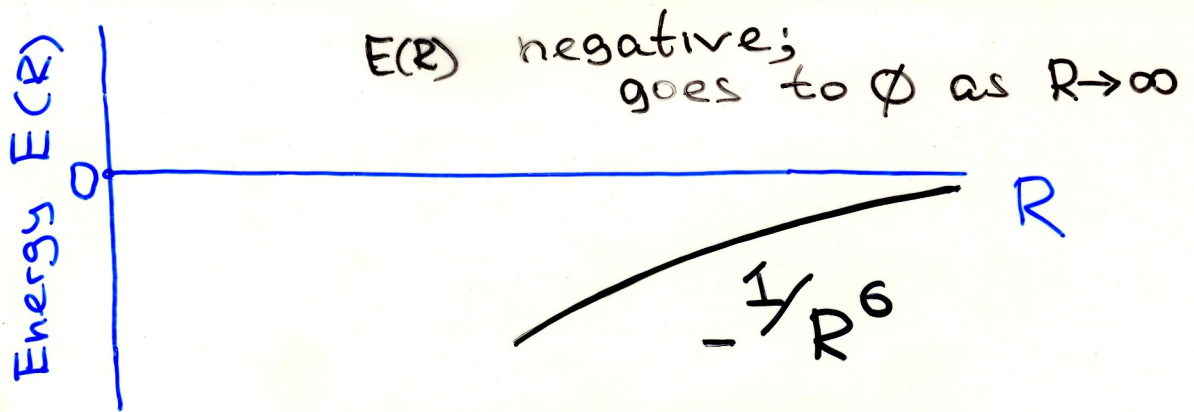
$$\hat{U} = \frac{\vec{d}_1 \cdot \vec{d}_2 - 3(\vec{d}_1 \cdot \hat{n})(\vec{d}_2 \cdot \hat{n})}{R^3}$$

$$E^{(0)} = \langle \hat{U} \rangle = 0 \quad \text{zero order PT} \quad (R \gg a_B)$$

$$E^{(1)} = \sum_n' \frac{|\langle n | \hat{U} | 0 \rangle|^2}{E_0 - E_n} = E(R) < 0$$

$E_0 < E_n$   
ground state!





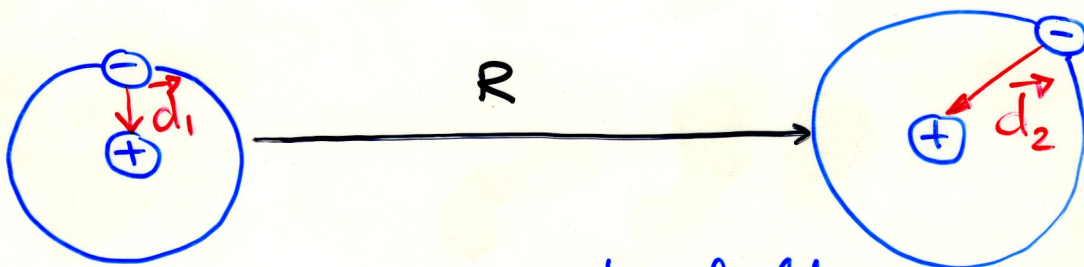
Induced attraction  
between neutral atoms

Attraction force  $\vec{F} = \frac{\partial E}{\partial \vec{R}} \sim \frac{1}{R^7}$

Physical origin: though  $\langle \vec{d}_1 \rangle = \langle \vec{d}_2 \rangle = 0$

dipoles induce correlations with each other  $\Rightarrow \langle \vec{d}_1 \cdot \vec{d}_2 \rangle \neq 0$

More transparently:



electric field  
 $|\vec{E}| \sim \frac{d_1}{R^3}$

induced dipole:  
 $d_2 = \alpha E \sim \alpha \frac{d_1}{R^3}$

energy  
 $\frac{d_1 \cdot d_2}{R^3} \sim \frac{\alpha d_1^2}{R^6}$

$\langle d_1^2 \rangle \neq 0$

$\alpha$ : polarizability

# Hydrogen-Bonded Crystals (insulators)

- ion core  $\equiv$  proton, no size ( $10^{-13}$  cm)

- H ionization potential is unusually high

H: 13.6 eV

Li: 5.39 eV

Na: 5.14 eV

K: 4.34 eV

- the closed shell contains just 2 electrons (He)

does not behave as alkali atom when forms ion crystals

can form only one covalent bond when sharing an electron

$H^+$  can sit anywhere on a surface of any negative ion  $A^-$