Chapter 2

Crystal Binding
(晶体的结合)

Objectives

- To understand the **5 fundamental types of crystal binding;**
- To learn the regularity of crystal binding.

Outline

- **Chapter 2.1** Basics of Crystal Binding (晶体结合的基本性质)
- **Chapter 2.2** The 5 Types of Crystal Binding (晶体结合的5种类型)
  - Ionic Binding (离子型结合)
  - Covalent Binding (共价型结合)
  - Metallic Binding (金属型结合)
  - van der Waals Binding (范德瓦耳斯型结合)
  - Hydrogen Binding (氢键型结合)
- **Chapter 2.3** Regularity of Crystal Binding (晶体结合的规律性)

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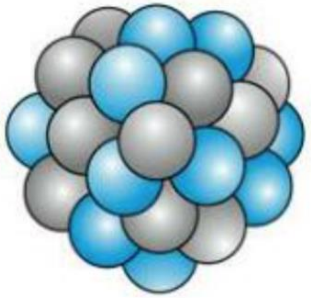
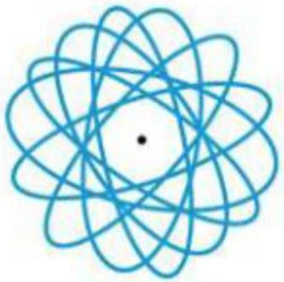
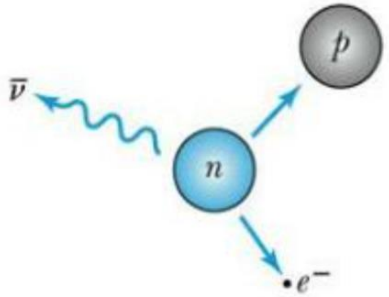
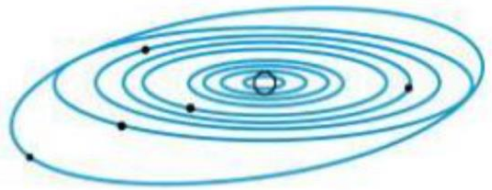
Chapter 2.1: Basics of Crystal Binding (晶体结合的基本性质)

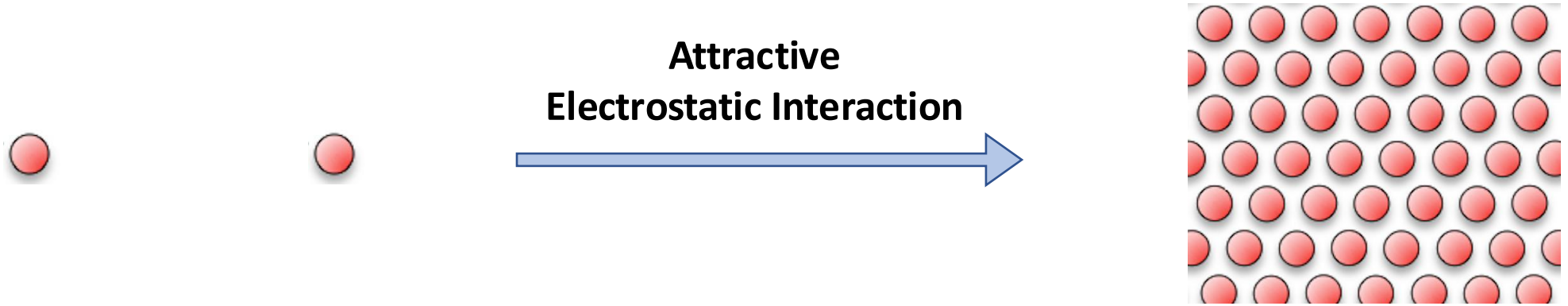
- **What holds a crystal together?**
  - **Four fundamental interactions (forces)** in the universe:

Strong	**Electromagnetic**	**Weak**	**Gravitation**
Gluons	Photon	W and Z bosons	Graviton?
Atomic nuclei Fission and fusion Quark structure of proton and neutron	Atoms and molecules Chemical reactions Light waves Electronics	Neutron decay Beta radioactivity Muon and tau decay Neutrino interactions	Solar system Galaxies Curved spacetime Black holes
			
Relative Strength: 10^{38}	**10^{36}**	**10^{25}**	**1**
Range (in m): 10^{-15}	**∞**	**10^{-18}**	**∞**

Chapter 2.1: Basics of Crystal Binding (晶体结合的基本性质)

➢ What holds a crystal together?

❖ The **attractive electrostatic interaction** (静电吸引相互作用) between the negative charges of **electrons** and the positive charges of **nuclei** is entirely responsible for the cohesion of solids.



Free Particles
Sum of Energies **High**

Hold together to Form a Crystal
Total Energy **Low**

Chapter 2.1: Basics of Crystal Binding (晶体结合的基本性质)

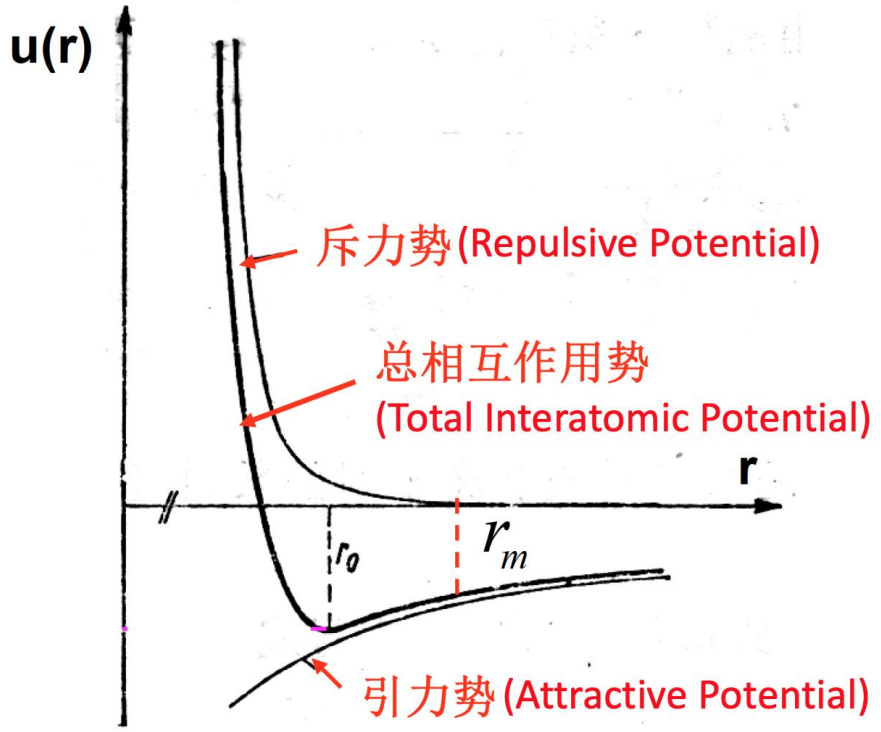
➢ Interatomic Interactions (原子间相互作用)

❖ In general, there are **2** types of interatomic interactions:

1) repulsion (斥力)

2) attraction (引力)

❖ Both repulsion and attraction are dependent of **interatomic distance *r***.



Chapter 2.1: Basics of Crystal Binding (晶体结合的基本性质)

➢ Interatomic Interactions (原子间相互作用)

❖ Total interatomic potential:

$$u(r) = -\frac{a}{r^m} + \frac{b}{r^n} \qquad a, b, m, n > 0$$

Attractive Potential **Repulsive Potential**

Chapter 2.1: Basics of Crystal Binding (晶体结合的基本性质)

➢ Interatomic Interactions (原子间相互作用)

❖ To bind two atoms together, it requires:

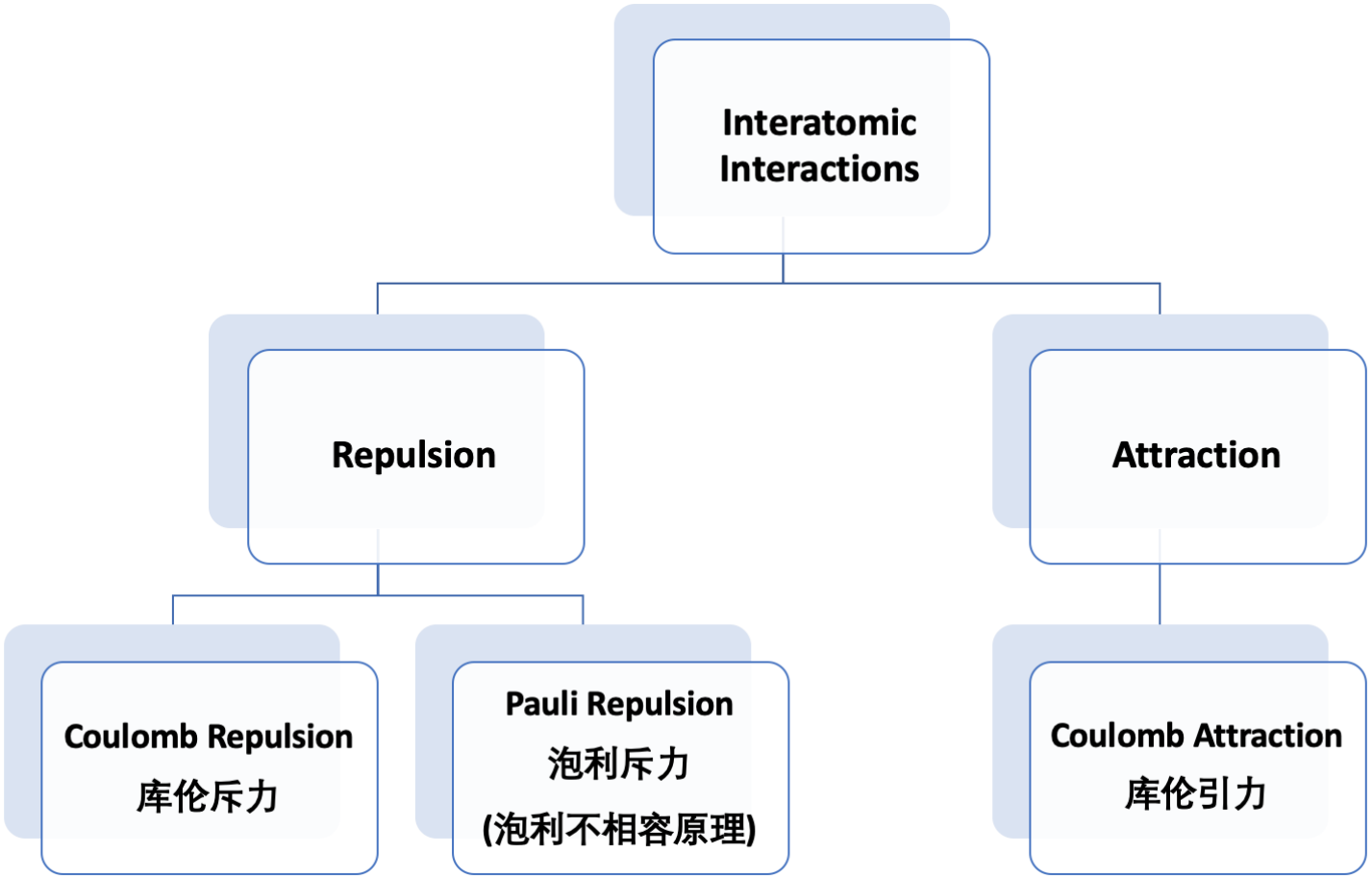
$$f(r) = -\left.\frac{\partial u(r)}{\partial r}\right|_{r_0} = 0$$

$$\left.\frac{\partial^2 u(r)}{\partial r^2}\right|_{r_0} > 0$$

$$\rightarrow \quad n > m$$

Chapter 2.1: Basics of Crystal Binding (晶体结合的基本性质)

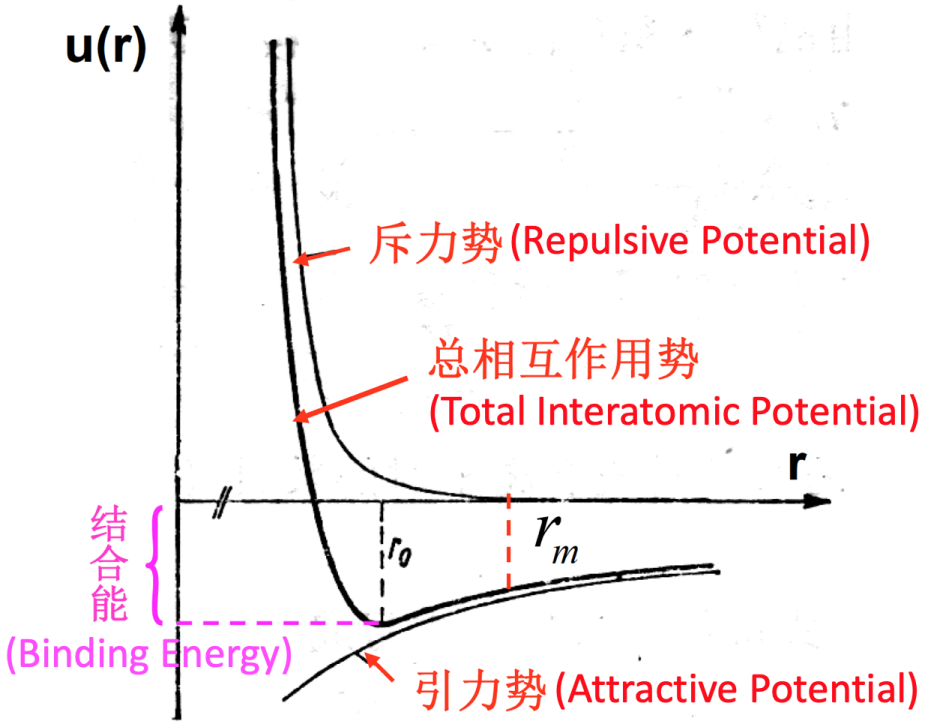
- **Interatomic Interactions (原子间相互作用)**



Chapter 2.1: Basics of Crystal Binding (晶体结合的基本性质)

➢ Binding Energy of Solids (固体的结合能)

❖ Binding energy (结合能), also called cohesive energy (内聚能), is defined as the energy consumed by separating a solid into static neutral free particles that are infinitely far from each other in distance.



Chapter 2.1: Basics of Crystal Binding (晶体结合的基本性质)

➢ Binding Energy of Solids (固体的结合能)

❖ In practice, the binding energy $\boldsymbol{E_b}$ of a solid can be calculated by the difference between the sum of energies $\boldsymbol{E_N}$ of N constituent free particles and the total energy $\boldsymbol{U_0}$ of the solid:

$$\boldsymbol{E_b = E_N - U_0}$$

If we set $\boldsymbol{E_N = 0}$, it is obtained that $\boldsymbol{E_b = -U_0}$.

Chapter 2.1: Basics of Crystal Binding (晶体结合的基本性质)

➢ Binding Energy of Solids (固体的结合能)

❖ In general, the contributions to the total energy $\boldsymbol{U_0}$ of a solid include:

1. **The interatomic interaction energy (原子间相互作用能) at $\boldsymbol{T = 0\ \mathrm{K}}$;**
2. The lattice vibration energy (晶格振动能) at finite temperature ($T \neq 0\ \mathrm{K}$);
3. The zero-point energy (零点能) at $T = 0\ \mathrm{K}$;
4. The energy as a result of defects (缺陷能);
5. ……

Chapter 2.1: Basics of Crystal Binding (晶体结合的基本性质)

➢ Fundamental Types of Crystal Binding (晶体结合的基本类型)

Crystal Binding

Ionic Binding **离子型结合**	By electrostatic attraction between **oppositely charged ions**.
Covalent Binding **共价型结合**	By **shared electron pairs** between atoms.
Metallic Binding **金属型结合**	By electrostatic attraction between **conduction electrons** and positively charged **metal ions**.
van der Waals Binding **范德瓦尔斯型结合**	By interaction between polar and non-polar atoms or molecules.
Hydrogen Binding **氢键型结合**	By electrostatic attraction between a **hydrogen** and **another adjacent atom**.

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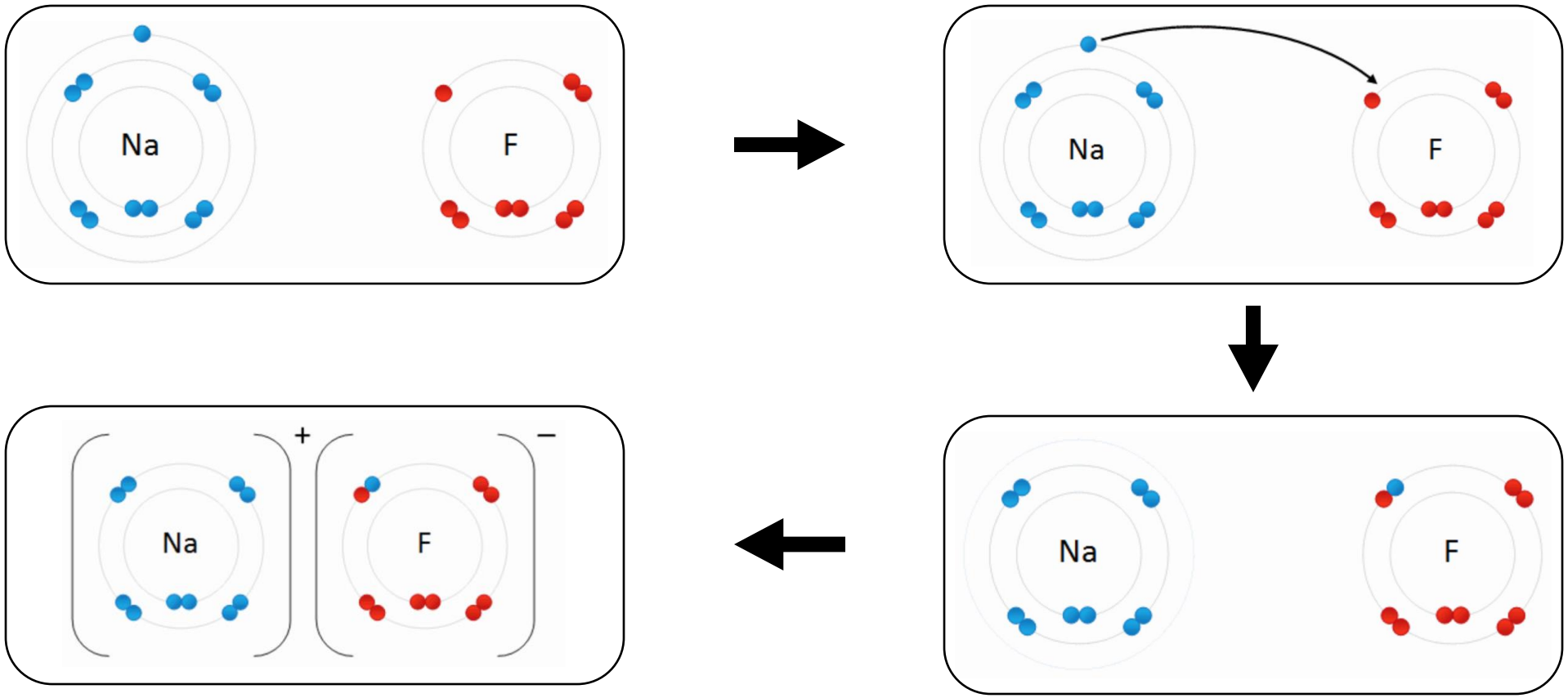
Chapter 2.2.1: Ionic Binding (离子型结合)

➢ Ionic Bond (离子键)

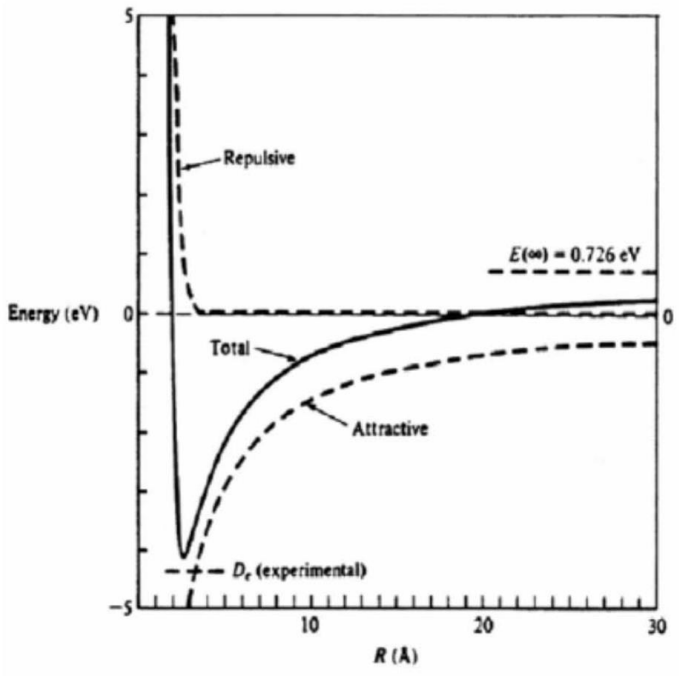
❖ An example of how an ionic bond is formed between the atoms of Na and F:

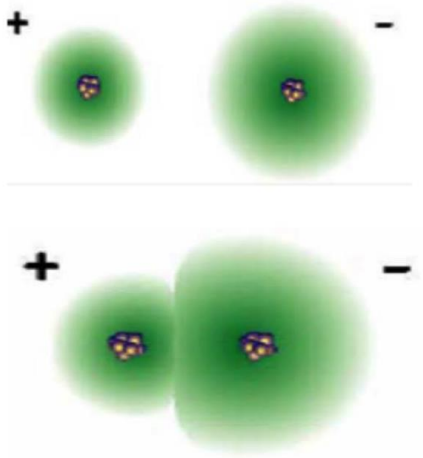


Chapter 2.2.1: Ionic Binding (离子型结合)

➢ Ionic Bond (离子键)

❖ Ionic bond is the result of **electrostatic (Coulomb) attraction** between ions of opposite charges that are viewed as **charged spheres**.





$$E_{att} = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 R}$$

Energy of Attraction
(**Coulomb Attraction**)

$$E_{rep} = \frac{C}{R^n}$$

$(n = 10\sim12)$

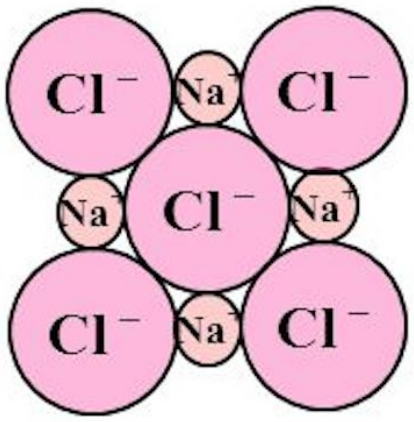
Energy of Repulsion
(**Pauli Repulsion**)

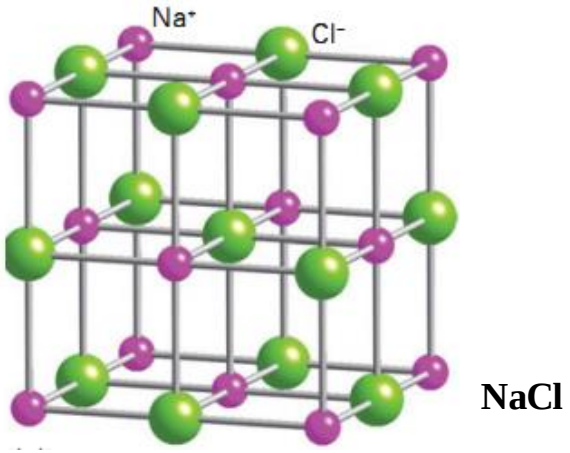
z_1 and z_2 are the electrical charges of the ions in unit of elementary charge e.
ε_0 is the dielectric permittivity of vacuum. R is the distance between the nuclei.

Chapter 2.2.1: Ionic Binding (离子型结合)

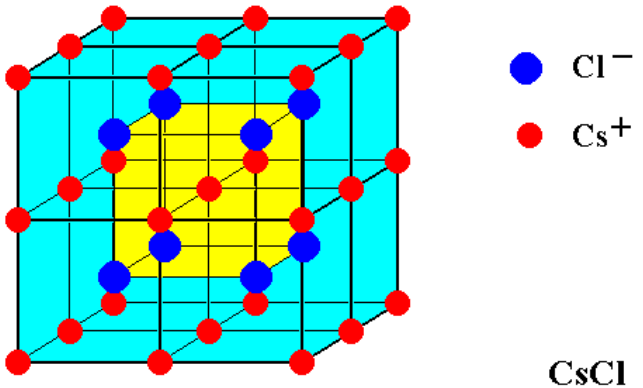
➢ Ionic Crystals (离子晶体)

- ❖ **Ionic crystals** are formed as a result of **ionic binding (bond)** in the crystals.
- ❖ Typical ionic crystals are compounds consisting of alkali metals (碱金属) and halogen elements (卤族元素), such as **NaCl, CsCl, NaF, ZnS**…





NaCl



CsCl

Chapter 2.2.1: Ionic Binding (离子型结合)

➢ Binding Energy of Ionic Crystals

❖ The interaction potential between any two ions:

$$u(r_{ij}) = \pm\frac{z_1 z_2 e^2}{4\pi\varepsilon_0 r_{ij}} + \frac{b}{r_{ij}^n}$$

❖ The total interaction potential **(binding energy)** of an ionic crystal with $\boldsymbol{N}$ ions:

$$U = \frac{N}{2}\sum_{j(\neq i)}^{N} u(r_{ij}) = \frac{N}{2}\sum_{j(\neq i)}^{N}\left(\pm\frac{z_1 z_2 e^2}{4\pi\varepsilon_0 r_{ij}} + \frac{b}{r_{ij}^n}\right)$$

Chapter 2.2.1: Ionic Binding (离子型结合)

➢ Binding Energy of Ionic Crystals

set $r_{ij} = m_j r$ (r: distance between two nearest-neighbor ions)

$$U = \frac{N}{2}\left(-\frac{z_1 z_2 e^2}{4\pi\varepsilon_0 r}M + \frac{B}{r^n}\right)$$

$$M = \sum_{j(\neq i)}^{N}\left(\pm\frac{1}{m_j}\right) \qquad B = \sum_{j(\neq i)}^{N}\frac{b}{m_j^n}$$

❖ In real ionic crystals, the typical binding energy of an ionic bond is about **6.5 ~16.0 eV.**

Chapter 2.2.1: Ionic Binding (离子型结合)

➢ Madelung Constant (马德隆常数)

❖ Madelung constant is a dimensionless constant used in determining the **electrostatic potential of a single ion** in an ionic crystal by approximating the ions by point charges.

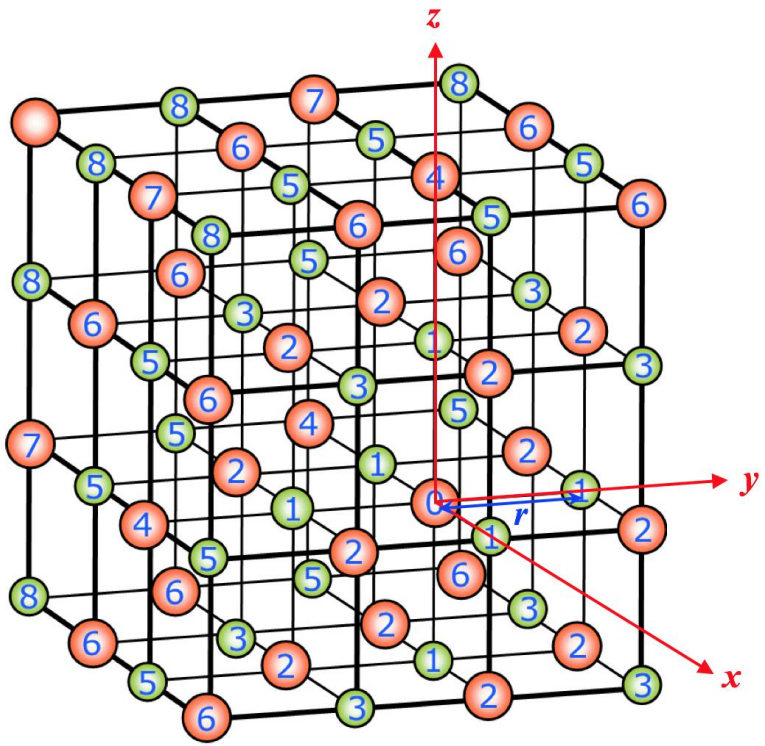
$$M = \sum_{j(\neq i)}^{N} \left(\pm \frac{1}{m_j} \right)$$

Chapter 2.2.1: Ionic Binding (离子型结合)

➢ Madelung Constant (马德隆常数)

❖ In the case of NaCl:

$$M = \sum_{j(\neq i)}^{N} \frac{(-1)^{(m_{jx}+m_{jy}+m_{jz})}}{\left(m_{jx}^2 + m_{jy}^2 + m_{jz}^2\right)^{1/2}}$$



NaCl Crystal

Chapter 2.2.1: Ionic Binding (离子型结合)

➢ Madelung Constant (马德隆常数)

❖ Madelung constant for some real ionic crystals:

Crystal Structure	M
NaCl	1.747565
CsCl	1.762675
ZnS (Cubic)	1.6381
ZnS (Hexagonal)	1.641
CaF_2	5.039
TiO_2	4.816

Chapter 2.2.1: Ionic Binding (离子型结合)

➢ Characteristics of Ionic Binding (离子型结合的特点)

i. The electronic configurations of ions correspond to closed electronic shells (离子的电子组态都为闭壳层结构);

ii. The charge distributions of ions have approximately spherical symmetry (离子电荷分布近似球对称);

iii. Large binding energy and high melting point (结合能大, 熔点高);

iv. No directionality and saturation of ionic bonds (离子键没有方向性和饱和性).

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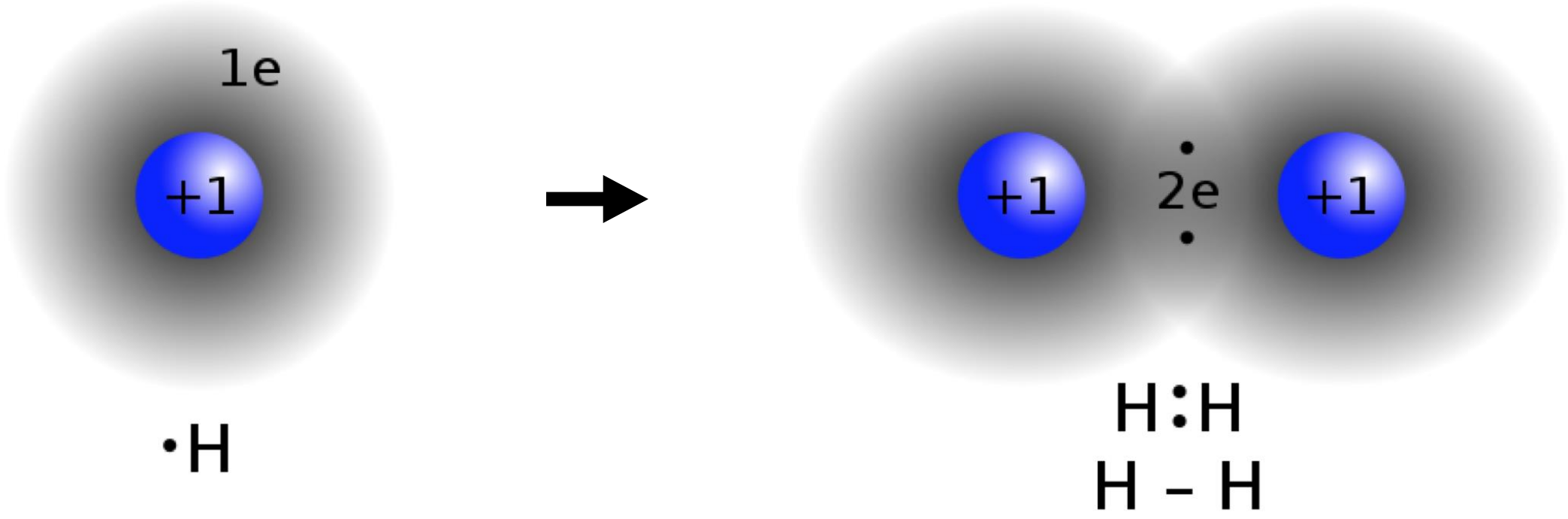
Chapter 2.2.2: Covalent Binding (共价型结合)

➢ Covalent Bond (共价键)

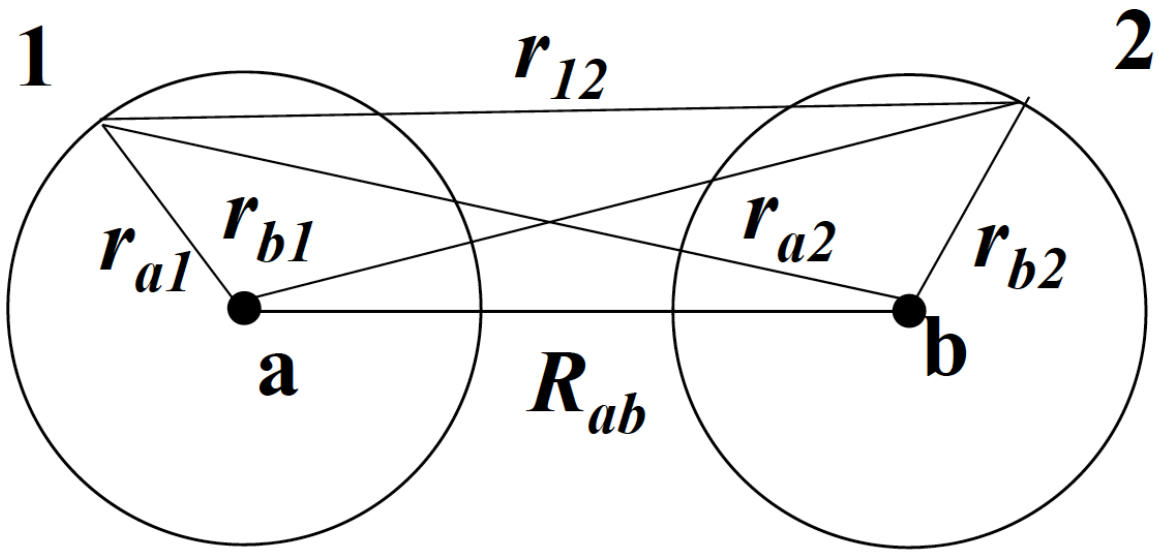
❖ An example of how a covalent bond is formed between two H atoms:



Chapter 2.2.2: Covalent Binding (共价型结合)

➢ Covalent Bond (共价键)

❖ The mechanism of covalent bonding (H_2 as an example):

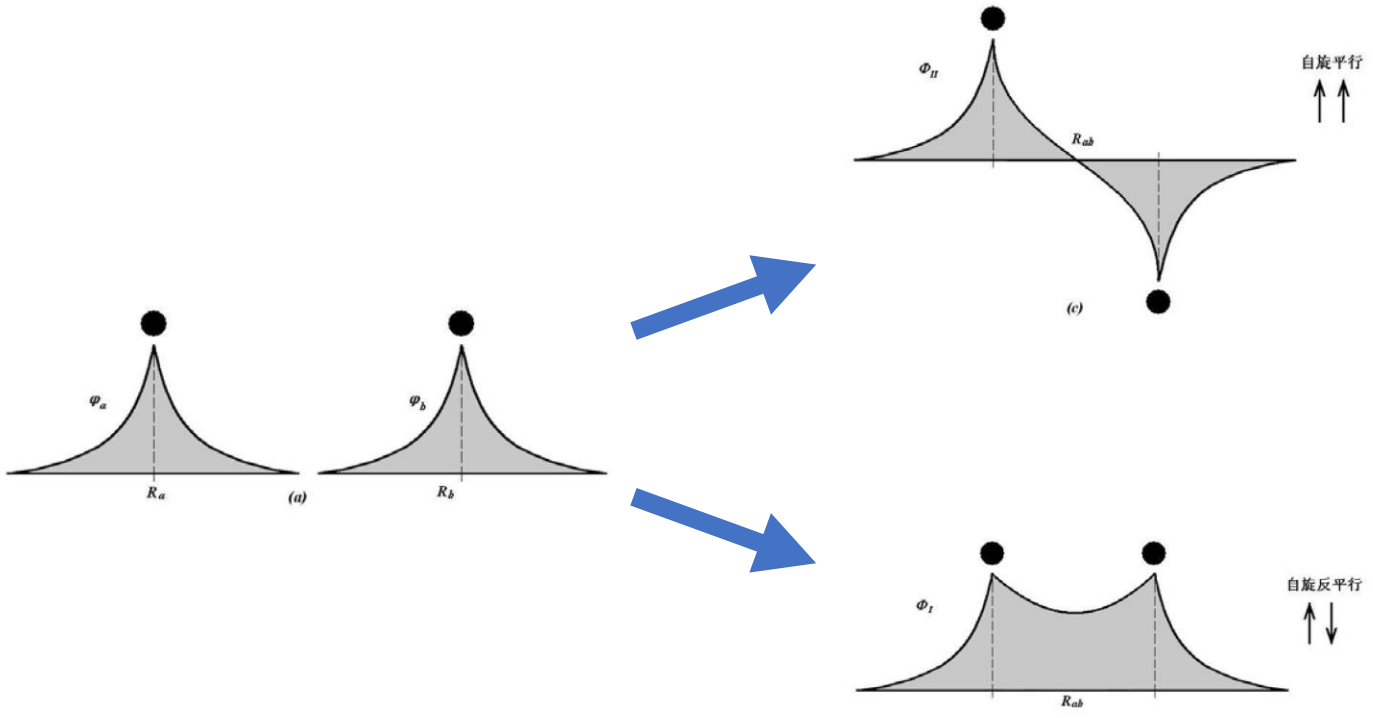


$$\hat{H} = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{r_{a1}} - \frac{e^2}{r_{b2}} - \frac{e^2}{r_{a2}} - \frac{e^2}{r_{b1}} + \frac{e^2}{r_{12}} + \frac{e^2}{R_{ab}}$$

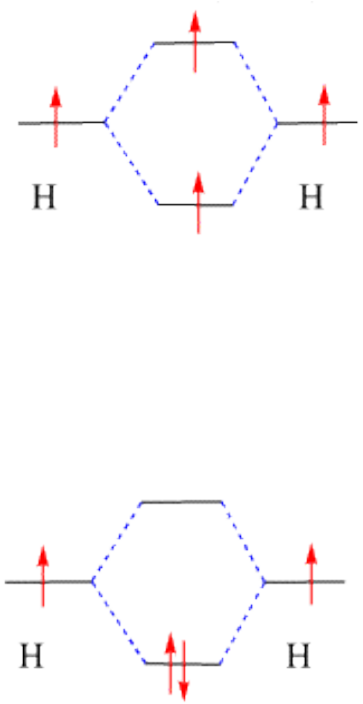
Chapter 2.2.2: Covalent Binding (共价型结合)

➢ Covalent Bond (共价键)

❖ The mechanism of covalent bonding (H_2 as an example):



Wave Functions Overlap



Molecular Levels

$$\Phi_{II} = c_2[\varphi_a^1\varphi_b^2 - \varphi_a^2\varphi_b^1]\chi_S$$

$$E_{II} = K - J$$

High Energy State

$$J < 0$$

$$\Phi_I = c_1[\varphi_a^1\varphi_b^2 + \varphi_a^2\varphi_b^1]\chi_A$$

$$E_I = K + J$$

Low Energy State

Chapter 2.2.2: Covalent Binding (共价型结合)

➢ Covalent Bond (共价键)

❖ The **directionality** of covalent bond (共价键的**方向性**):

a) The "directionality" of covalent bond indicates that the covalent bond can be formed only **along specific directions**.

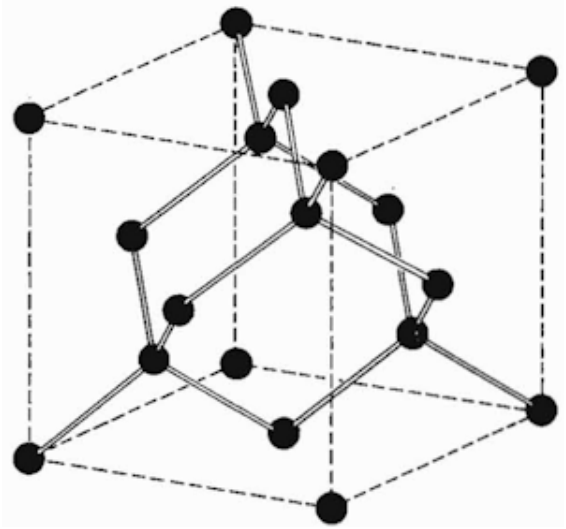
b) The strength of a covalent bond is determined by the overlap between the two atomic orbitals forming the bond, which are **direction dependent**.

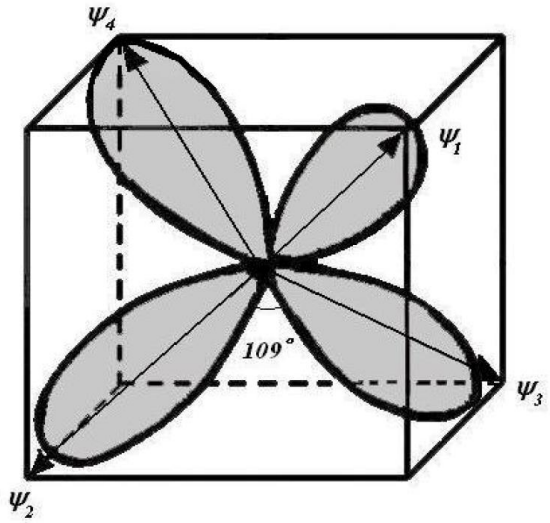
c) A phenomenon underlying the importance of directionality of covalent bond is "**orbital hybridization**" (**轨道杂化**), such as sp^3, sp^2, and sp **hybridization**.

Chapter 2.2.2: Covalent Binding (共价型结合)

➢ Covalent Bond (共价键)

❖ The **directionality** of covalent bond (共价键的**方向性**):





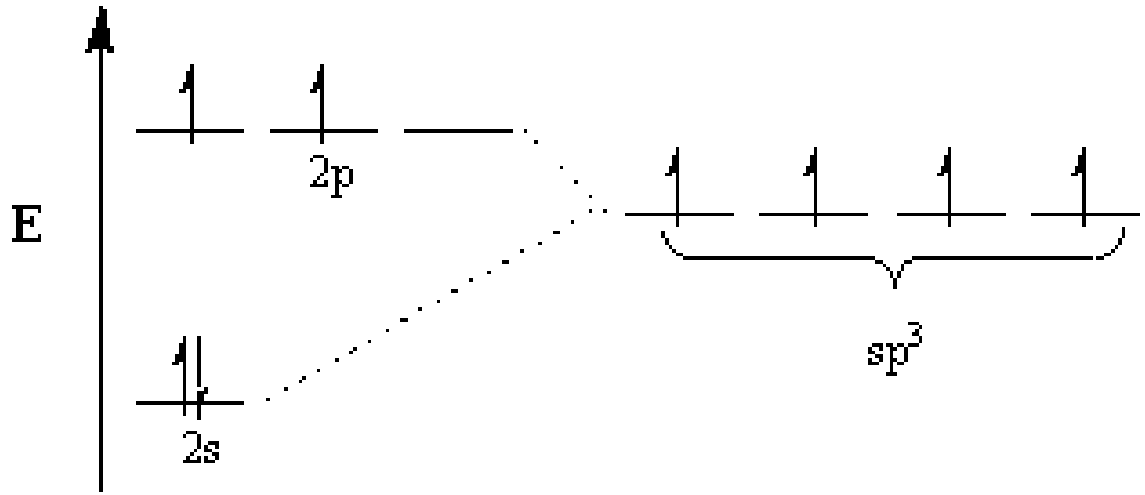
$$
\begin{cases}
\psi_1 = \dfrac{1}{2}(\varphi_{2s} + \varphi_{2p_X} + \varphi_{2p_y} + \varphi_{2p_Z}) & [111] \\
\psi_2 = \dfrac{1}{2}(\varphi_{2s} + \varphi_{2p_X} - \varphi_{2p_y} - \varphi_{2p_Z}) & [1\bar{1}\bar{1}] \\
\psi_3 = \dfrac{1}{2}(\varphi_{2s} - \varphi_{2p_X} + \varphi_{2p_y} - \varphi_{2p_Z}) & [\bar{1}1\bar{1}] \\
\psi_4 = \dfrac{1}{2}(\varphi_{2s} - \varphi_{2p_X} - \varphi_{2p_y} + \varphi_{2p_Z}) & [\bar{1}\bar{1}1]
\end{cases}
$$

Chapter 2.2.2: Covalent Binding (共价型结合)

➢ Covalent Bond (共价键)

❖ The **directionality** of covalent bond (共价键的**方向性**):

e.g., sp^3 hybridization (sp^3杂化):

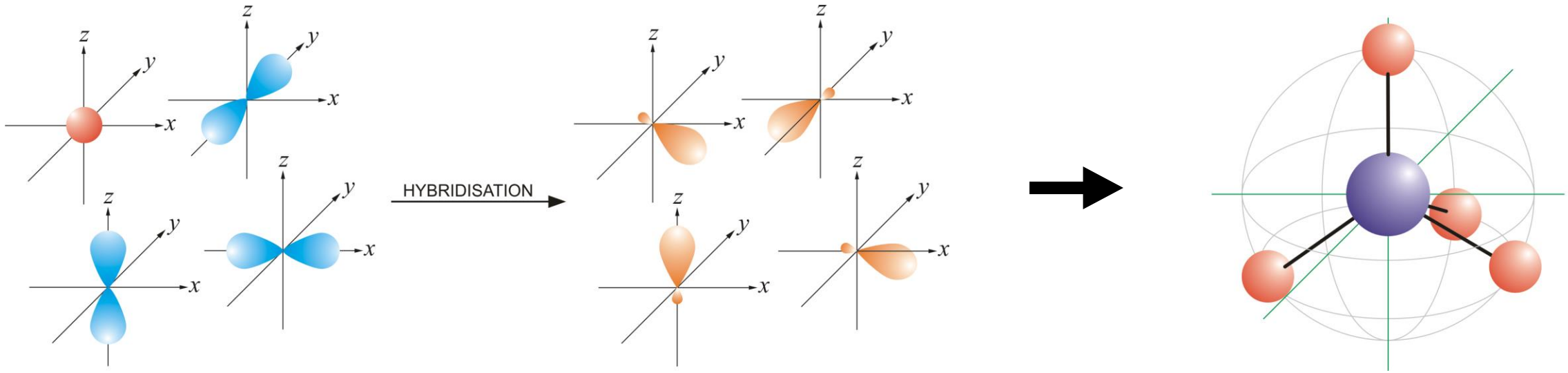


Chapter 2.2.2: Covalent Binding (共价型结合)

➢ Covalent Bond (共价键)

❖ The **directionality** of covalent bond (共价键的**方向性**):

e.g., sp^3 hybridization (sp^3杂化):



Chapter 2.2.2: Covalent Binding (共价型结合)

➢ Covalent Bond (共价键)

❖ The **saturation** of covalent bond (共价键的**饱和性**)

a) There exists a **maximum number of covalent bonds** that an atom can form, which is determined by the number of (unpaired) valence electrons of the atom.

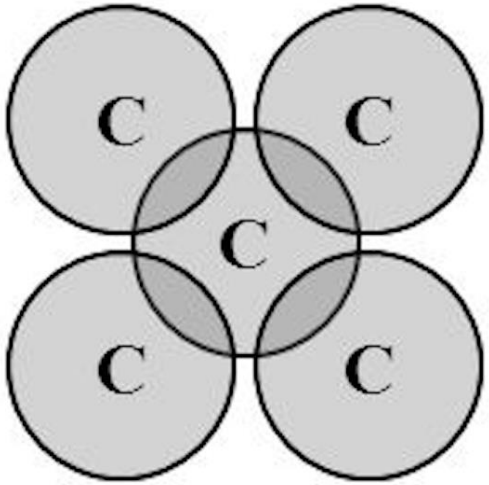
b) Covalent bond can be formed only by **unpaired electrons**.

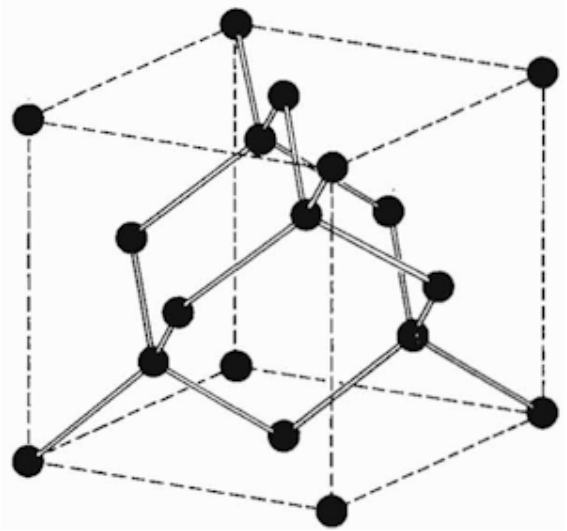
c) Basically, when the valence shell of an atom is no more than half filled, the maximum number of covalent bonds $\boldsymbol{N_{max}}$ is equal to the number of valence electrons $\boldsymbol{N}$, i.e., $\boldsymbol{N_{max} = N}$; when the valence shell is more than half filled, $\boldsymbol{N_{max} < N}$.

Chapter 2.2.2: Covalent Binding (共价型结合)

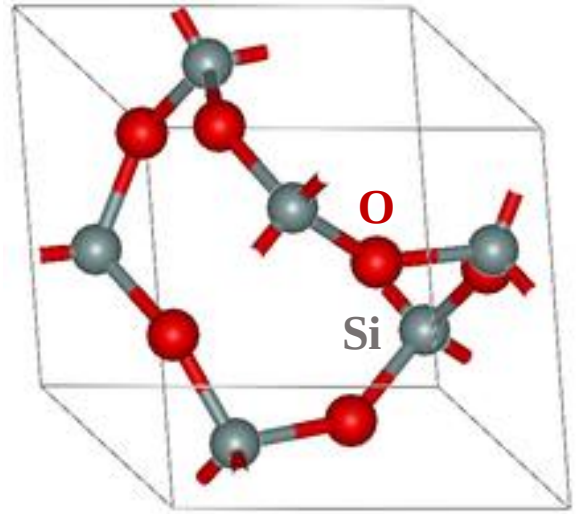
➢ Covalent Crystals (共价晶体)

- ❖ Covalent crystals are formed as a result of covalent binding (bond) in the crystals.
- ❖ Typical covalent crystals include C (diamond), Si, Ge, SiO_2, GaAs…





C (Si, Ge)



SiO_2

Chapter 2.2.2: Covalent Binding (共价型结合)

➢ Binding Energy of Covalent Crystals

- ❖ The binding energies of covalent crystals are too complicated to calculate analytically.
- ❖ They are usually evaluated by means of **quantum chemistry methods**, such as density functional theory (DFT).

共价晶体结合能的计算结果与实验的比较

		晶格常数	结合能	体积弹性模量
C	计算值	3.603Å	7.58 eV/原子	4.33×10^{11} Pa
	实验值	3.567Å	7.37 eV/原子	4.43×10^{11} Pa
	%误差	1%	3%	−2%
Si	计算值	5.451Å	4.67 eV/原子	0.98×10^{11} Pa
	实验值	5.429Å	4.63 eV/原子	0.99×10^{11} Pa
	%误差	0.4%	1%	−1%
Ge	计算值	5.655Å	4.02 eV/原子	0.73×10^{11} Pa
	实验值	5.652Å	3.85 eV/原子	0.77×10^{11} Pa
	%误差	0.2%	4%	−5%

*摘自朱建国等《固体物理学》, p50

Chapter 2.2.2: Covalent Binding (共价型结合)

➢ Characteristics of Covalent Binding (共价型结合的特点)

I. The most important characteristics of covalent binding is the "**directionality**" and "**saturation**" of covalent bonds (共价键的**方向性**和**饱和性**)!

II. The crystal structures are significantly impacted by the "directionality" of covalent bonds (共价键的方向性对晶体结构有重要影响).

III. Covalent binding could have components of ionic binding due to the presence of "polar covalent bonds" ("极性共价键"的存在使得共价型结合也会含有离子型结合的成分).

Outline

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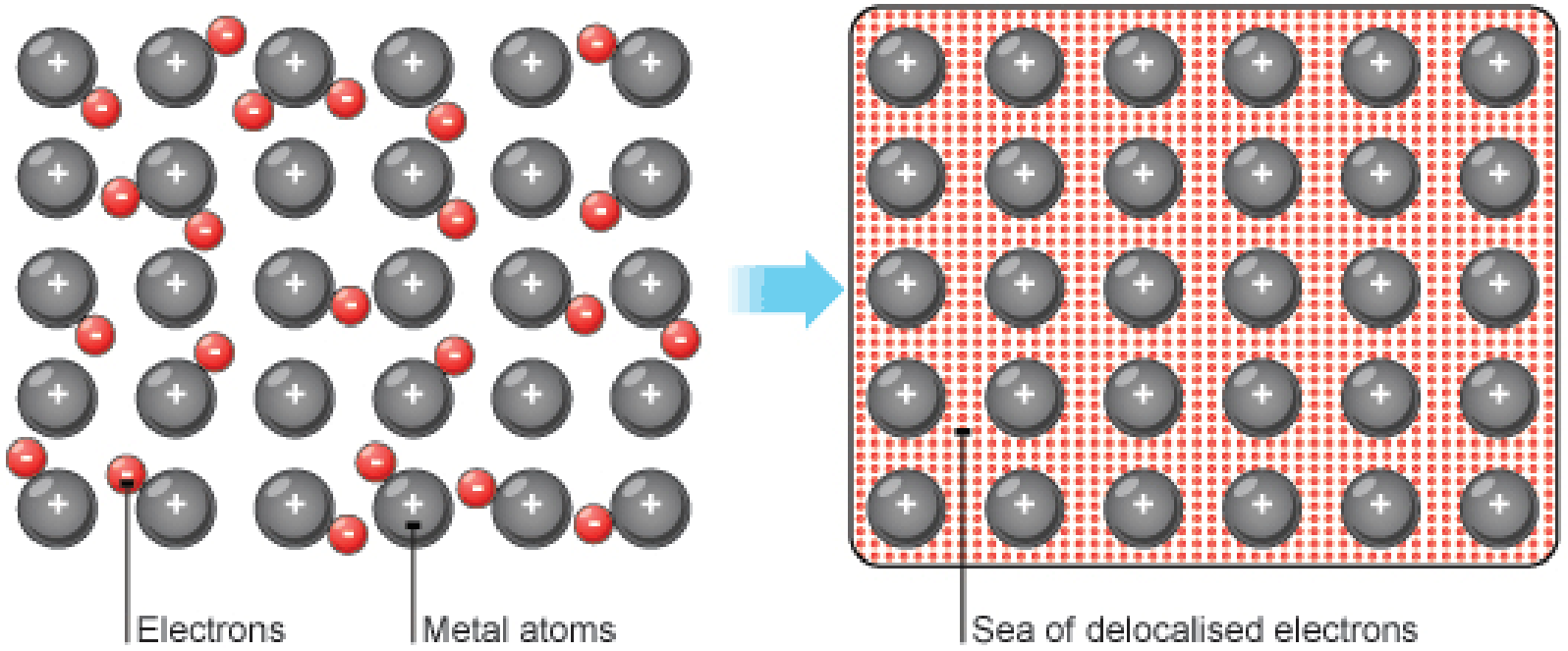
  - Covalent Binding (共价型结合)
  - Metallic Binding (金属型结合)
  - van der Waals Binding (范德瓦耳斯型结合)
  - Hydrogen Binding (氢键型结合)
- **Chapter 2.3** Regularity of Crystal Binding (晶体结合的规律性)

Chapter 2.2.3: Metallic Binding (金属型结合)

➢ Metallic Bond (金属键)

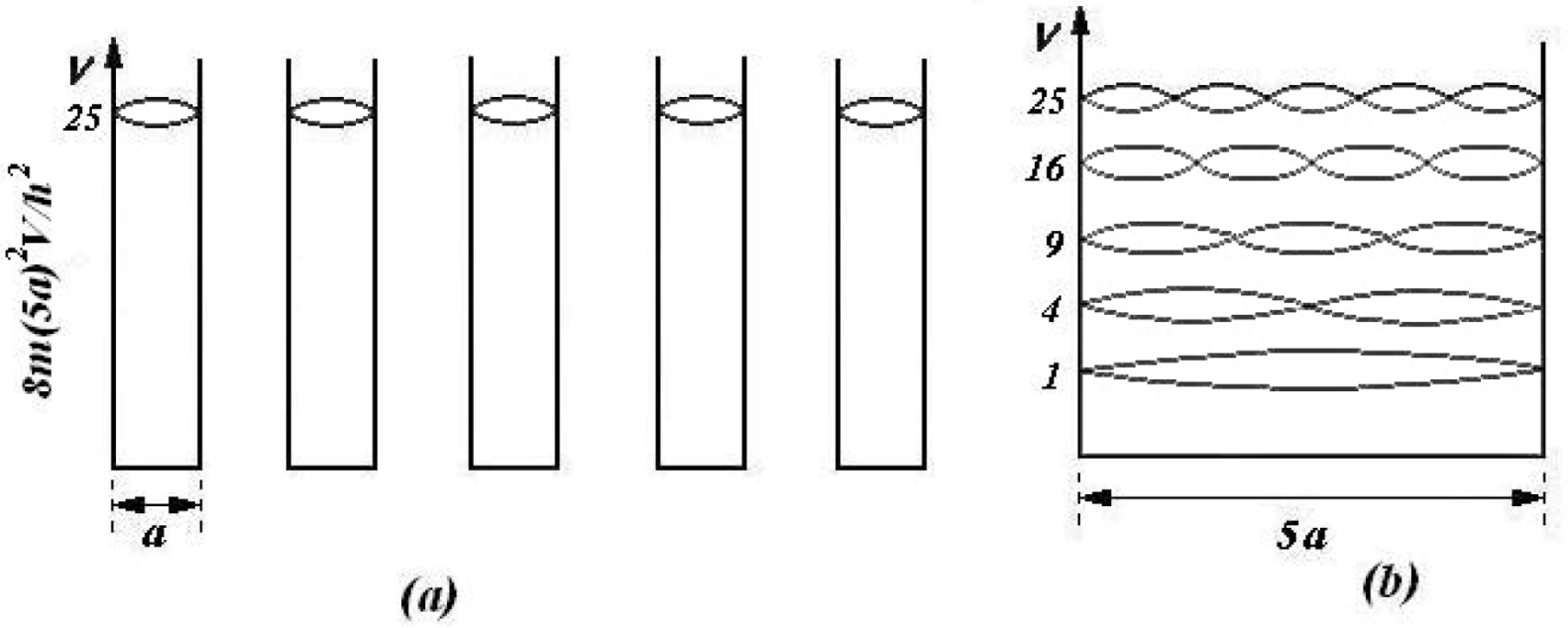
- ❖ Metallic bond arises from the electrostatic attractive force between a cloud (or “sea”) of delocalized electrons and positively charged metal ions.



Chapter 2.2.3: Metallic Binding (金属型结合)

➢ Metallic Bond (金属键)

- ❖ The **"delocalization" of electrons** in metallic bonding can significantly reduce the total energy of metals.



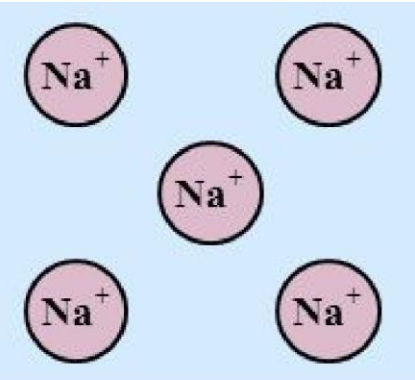
A quantum-well model comparing 5 localized electrons (a) with 5 delocalized electrons (b)

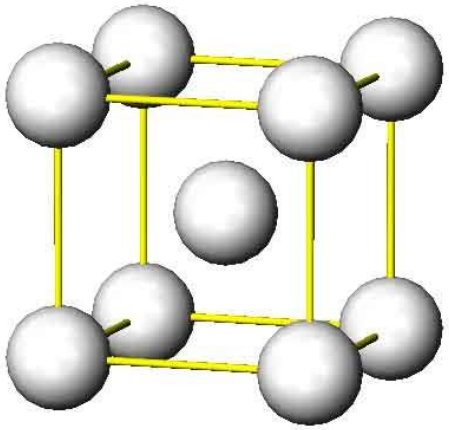
Chapter 2.2.3: Metallic Binding (金属型结合)

➢ Metals (金属)

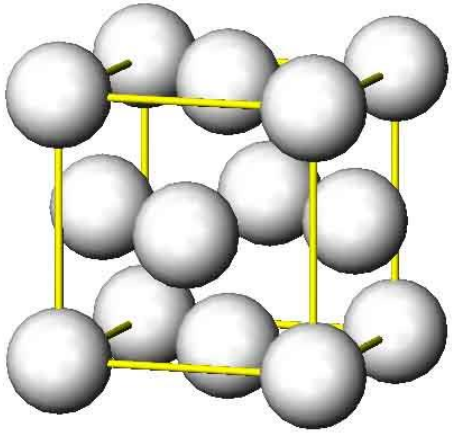
❖ Metals are the materials formed as a result of metallic binding.

❖ Typical metals include **alkali metals** (**碱金属** such as Li, Na, K, Rb, Cs, Fr) and **transition metals** (**过渡金属** such as Au, Ag, Cu, Zn, Ti…)

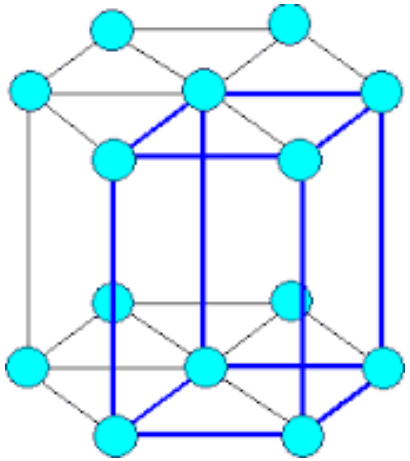




Na (Li, K) *bcc*



Au (Ag, Cu) *fcc*



Zn (Ti) *hcp*

Chapter 2.2.3: Metallic Binding (金属型结合)

➢ Binding Energy of Metals

❖ Similar to the case of covalent crystals, the analytical calculations of the binding energy of metallic crystals are also very difficult. Quantum chemistry methods (such as DFT and beyond) are very powerful in calculating the binding energies of metals.

典型金属的结合能、晶格常数和体积弹性模量

材　料	结合能/(Ry/原子)		晶格常数/原子单位		体积弹性模量/10^{11}Pa	
	实　验	理　论	实　验	理　论	实　验	理　论
Li	0.122	0.121	6.60	6.40	0.132	0.148
Be	0.244	0.294	6.02	5.93	1.15	1.35
Na	0.083	0.081	7.98	7.69	0.085	0.090
Mg	0.112	0.121	8.46	8.42	0.369	0.405
Al	0.244	0.282	4.60	7.59	0.880	0.801
K	0.069	0.066	9.90	9.57	0.040	0.044
Ca	0.134	0.164	10.52	10.0	0.152	0.167
Cu	0.257	0.309	6.81	6.79	1.42	1.58

1Ry ≈ 13.6 eV　　**1 ~ 4 eV**

*摘自朱建国等《固体物理学》, p52

Chapter 2.2.3: Metallic Binding (金属型结合)

➢ Characteristics of Metallic Binding (金属型结合的特点)

I. The **"delocalization" of electrons** is an important characteristic of metallic binding (电子的离域化).

II. Metals usually have **close packing and large coordination numbers**, such as 12 for transition metals with *fcc* and *hcp* lattice (密堆积与大配位数).

III. High electrical and thermal conductivity (高导电与导热性).

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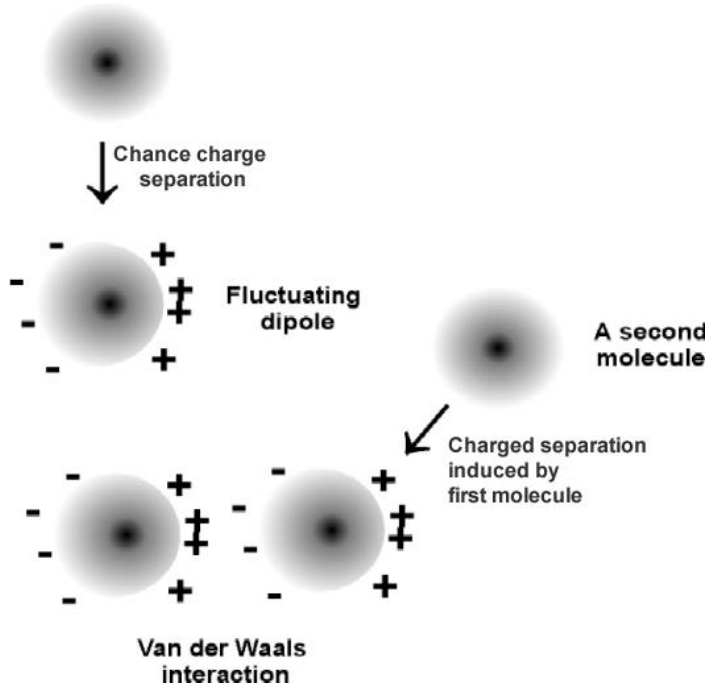
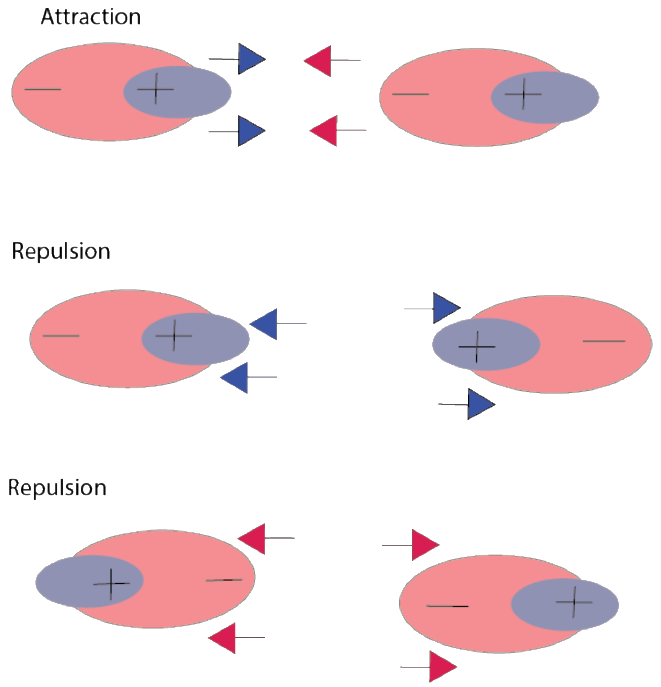
  - Hydrogen Binding (氢键型结合)
- **Chapter 2.3** Regularity of Crystal Binding (晶体结合的规律性)

Chapter 2.2.4: van der Waals Binding (范德瓦耳斯型结合)

➢ van der Waals Force (范德瓦尔斯力)

❖ van der Waals forces are **distance-dependent interactions** between atoms or molecules. They include both **attraction** and **repulsion**, caused by correlations in the **fluctuating polarizations** of nearby particles.





Chapter 2.2.4: van der Waals Binding (范德瓦耳斯型结合)

➢ van der Waals Force (范德瓦尔斯力)

❖ The three components that constitute to van der Waals forces:

Interaction Component	Origin of Interactions	Equation
Keesom	Dipole-dipole	$w(r) = -\frac{u_1^2 u_2^2}{3(4\pi\varepsilon_o\varepsilon_r)^2 k_B T} \frac{1}{r^6}$
Debye	Dipole – induced dipole	$w(r) = -\frac{u^2 \alpha_o}{(4\pi\varepsilon_o\varepsilon_r)^2} \frac{1}{r^6}$
London (Dispersion)	Induced Dipole – Induced Dipole	$w(r) = -\frac{3}{2} \frac{\alpha_{o1}\alpha_{o2}}{(4\pi\varepsilon_o)^2} \frac{I_1 I_2}{(I_1 + I_2)} \frac{1}{r^6}$

❖ **The London (dispersion) component is the most dominant.**

https://en.wikipedia.org/wiki/Van_der_Waals_force

Chapter 2.2.4: van der Waals Binding (范德瓦耳斯型结合)

➢ van der Waals Force (范德瓦尔斯力)

❖ Contribution of the London (dispersion) component to the total energy of interaction:

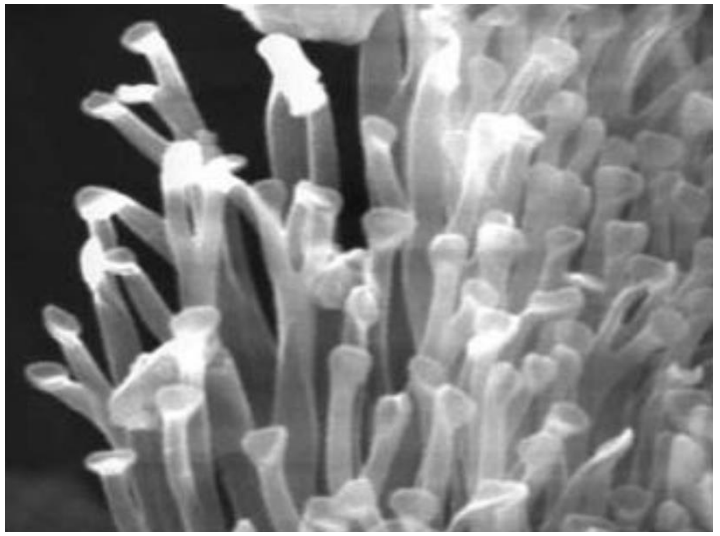
Molecule pair	% of the total energy of interaction
Ne-Ne	100
CH_4-CH_4	100
HCl-HCl	86
HBr-HBr	96
HI-HI	99
CH_3Cl-CH_3Cl	68
NH_3-NH_3	57
H_2O-H_2O	24
HCl-HI	96
H_2O-CH_4	87

https://en.wikipedia.org/wiki/London_dispersion_force

Chapter 2.2.4: van der Waals Binding (范德瓦耳斯型结合)

➢ van der Waals Force (范德瓦尔斯力)

❖ Examples of how van der Waals force holds things together:



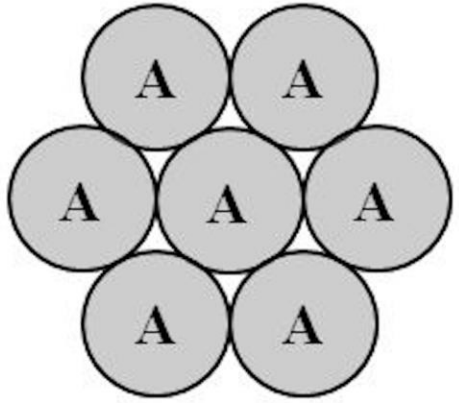
Geckos stick on wall as a result of van der Waals force!

K. Autumn *et al.*, **PNAS** 99, 12252 (2002).

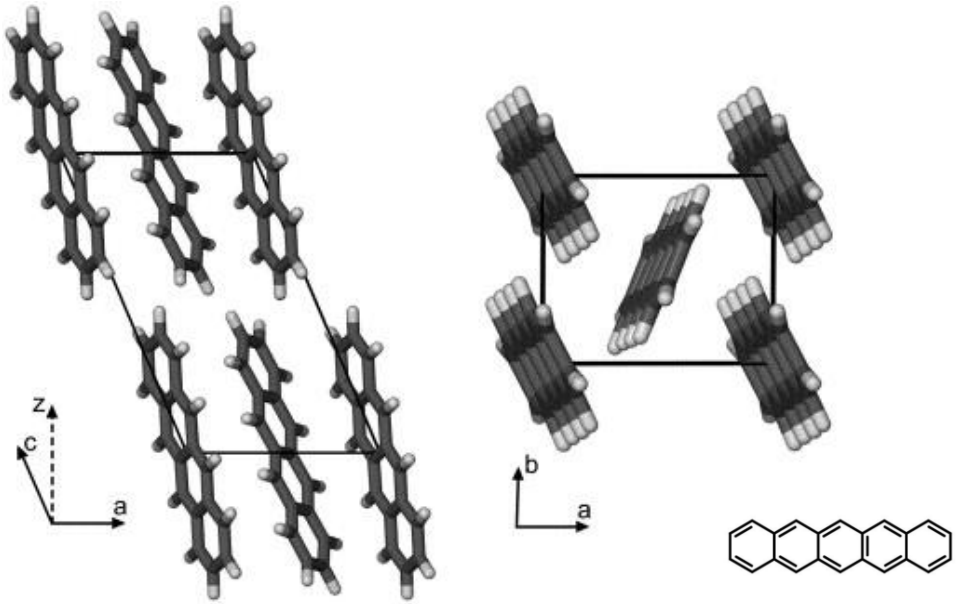
Chapter 2.2.4: van der Waals Binding (范德瓦耳斯型结合)

➢ Molecular Crystals (分子晶体)

- ❖ Molecular crystals are formed as a result of van der Waals force.
- ❖ Typical molecular crystals include crystals of inert gas atoms and organic molecules.



Crystals of inert gases
(van der Waals)



Organic Molecular Crystals (pentacene)

Chapter 2.2.4: van der Waals Binding (范德瓦耳斯型结合)

➢ Binding Energy of Molecular Crystals

❖ The binding energy of organic molecular crystals are very complex such that it is usually evaluated by means of quantum chemistry calculations.

❖ The binding energy of inert gas crystals can be calculated analytically. The interatomic potential can be expressed in terms of the **Lennard-Jones potential ("兰纳-琼斯"势):**

$$u(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \qquad \sigma = \left(\frac{b}{a}\right)^{\frac{1}{6}}, \varepsilon = \frac{a^2}{4b}$$

❖ For a crystal with *N* inert gas atoms, the total potential is:

$$U(r) = 2N\varepsilon\left[A_{12}\left(\frac{\sigma}{r}\right)^{12} - A_6\left(\frac{\sigma}{r}\right)^{6}\right] \qquad A_{12} = \sum_{i(\neq j)} \frac{1}{a_i^{12}} \qquad A_6 = \sum_{i(\neq j)} \frac{1}{a_i^{6}}$$

Chapter 2.2.4: van der Waals Binding (范德瓦耳斯型结合)

➢ **Binding Energy of Molecular Crystals**

惰性气体元素的固体结合能

	$u_{实验}$ (eV/atom)	$u_{理论}$ (eV/atom)
Ne	-0.02	-0.027 (-0.019)
Ar	-0.08	-0.089 (-0.080)
Kr	-0.11	-0.120 (-0.113)
Xe	-0.17	-0.172

摘自黄昆书p70

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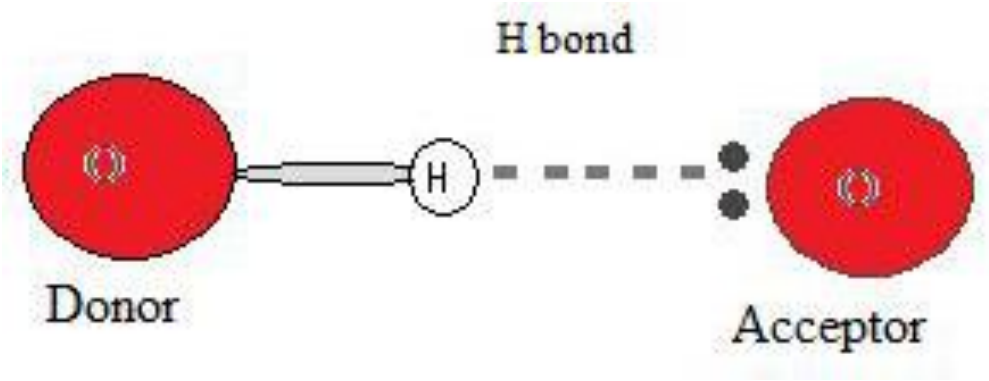
- **Chapter 2.3** Regularity of Crystal Binding (晶体结合的规律性)

Chapter 2.2.5: Hydrogen Binding (氢键型结合)

➢ Hydrogen Bond (氢键)

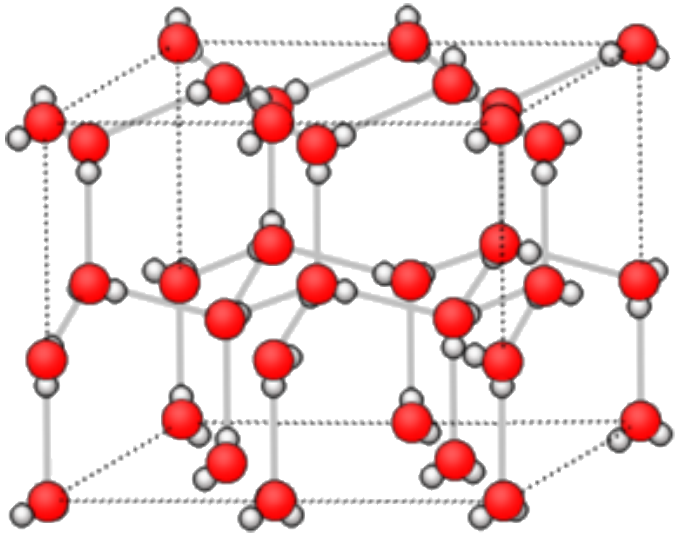
❖ A hydrogen bond is a partially electrostatic attraction between a hydrogen which is bound to a more electronegative atom (such as N, O, or F) and another adjacent atom bearing a **lone pair of electrons (孤对电子)**.



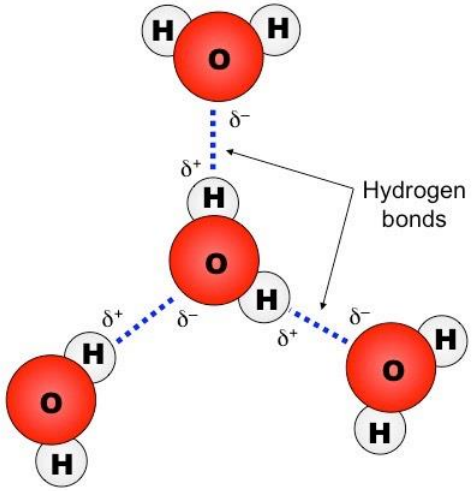
Chapter 2.2.5: Hydrogen Binding (氢键型结合)

➢ Solids with Hydrogen Bond (含有氢键的固体)

❖ Typical materials with hydrogen binding include some small molecules (H_2O, HF) and polymeric molecules (DNA, protein):



Ice (H_2O)



Chapter 2.2.5: Hydrogen Binding (氢键型结合)

➢ Solids with Hydrogen Bond (含有氢键的固体)

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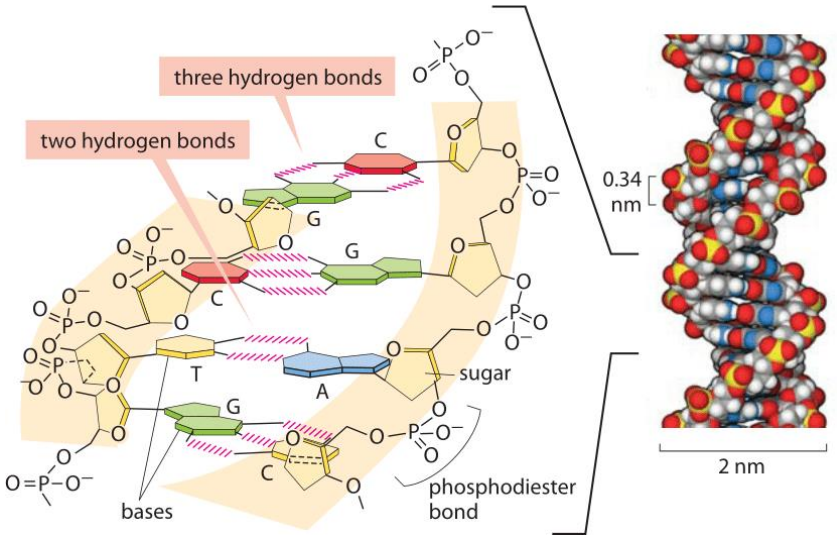

DNA molecules

Chapter 2.2.5: Hydrogen Binding (氢键型结合)

➢ Characteristics of Hydrogen Bonding (氢键型结合的特点)

I. Hydrogen bonding can occur between molecules (intermolecular) or between different parts of a single molecule (intramolecular).

II. There is no crystal consisting of only hydrogen binding.

III. Hydrogen binding usually works in crystals or molecules where other types of binding dominate.

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Chapter 2.3: Regularity of Crystal Binding (晶体结合的规律性)

➢ Comparison of Different Crystal Binding

❖ The binding energy of solids strongly depends on the **types of bonding**.

Bonding Type		Ionic Bond 离子键	Covalent Bond 共价键	Metallic Bond 金属键	Hydrogen Bond 氢键	Van der Waals Bond 范德瓦尔斯键
Binding Energy	kcal/mol	150 ~ 370	125 ~ 300	25 ~ 200	5 ~ 15	< 5
	eV	6.5 ~ 16.0	5.4 ~ 13.0	1.1 ~ 8.7	0.22 ~ 0.65	< 0.22

*摘自朱建国等《固体物理学》, p59

Chapter 2.3: Regularity of Crystal Binding (晶体结合的规律性)

➢ Comparison of Different Crystal Binding

❖ The binding in real crystals is usually **a combination of the 5 fundamental types**.

Bond	Strength	Directionality	Localization
Ionic	+	-	+
Covalent	+	+	+
Metallic	+	-	-
Van der Waals	-	no	N/A
Hydrogen	-	yes	N/A

Chapter 2.3: Regularity of Crystal Binding (晶体结合的规律性)

➢ Electronegativity of the Elements (元素的电负性)

- ❖ The nature of crystal binding is essentially determined by the ability that the atoms lose and obtain electrons, which can be evaluated by their **“electronegativity”.**

- ❖ There are several ways of defining electronegativity of the elements, such as the definitions by Mulliken, Pauling, and Philips.

Chapter 2.3: Regularity of Crystal Binding (晶体结合的规律性)

➢ Electronegativity of the Elements (元素的电负性)

❖ The **Mulliken definination:**

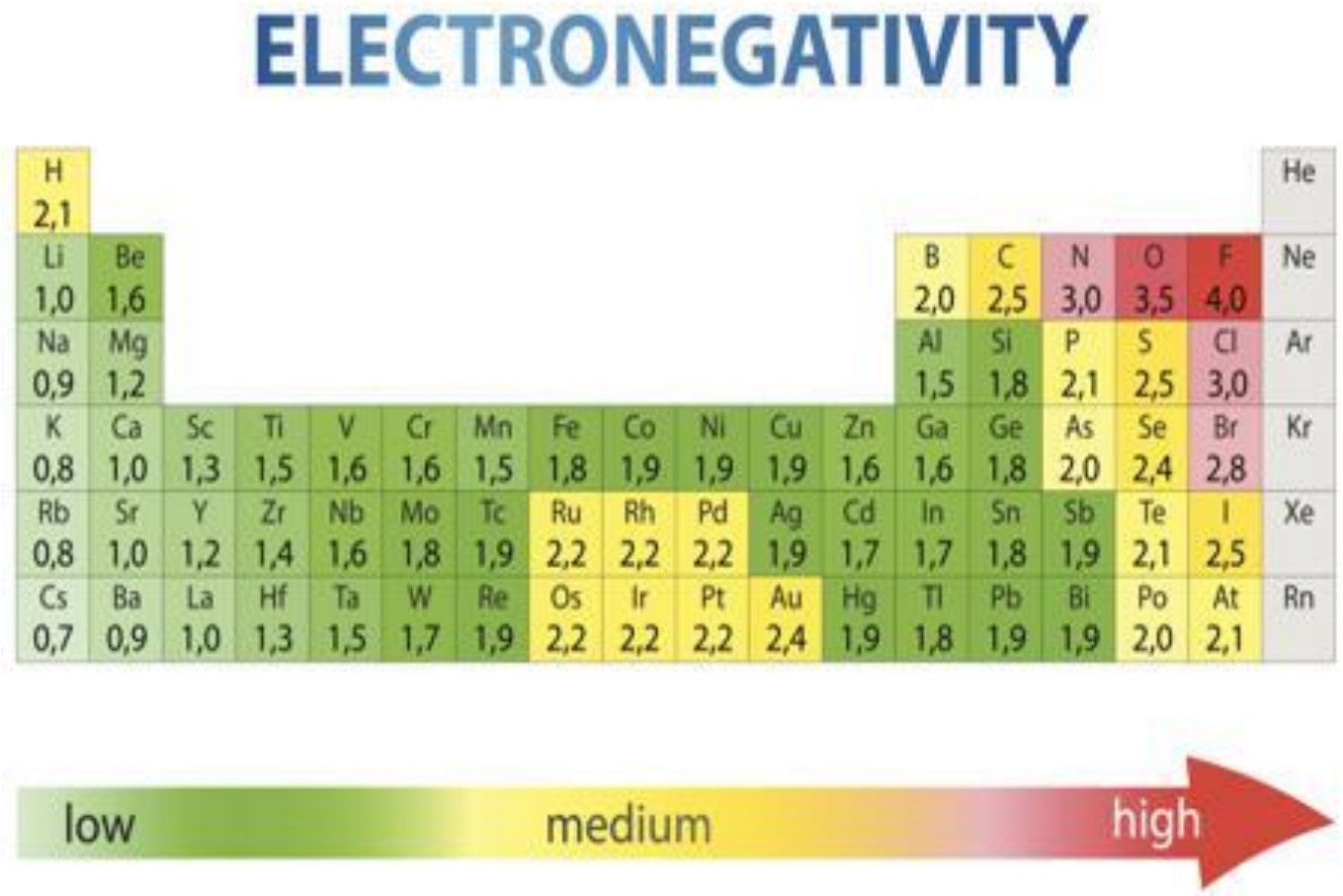
$$\chi_{\mathbf{Mulliken}} = \mathbf{0.18} \times (\boldsymbol{EA} + \boldsymbol{IP})$$

$\boldsymbol{EA}$: Electron Affinity (亲和势，或**亲和能**)　　中性原子＋（－e）⟶ 负离子

$\boldsymbol{IP}$: Ionization Potential (电离势，或**电离能**)　　正离子＋（－e）⟶ 中性原子

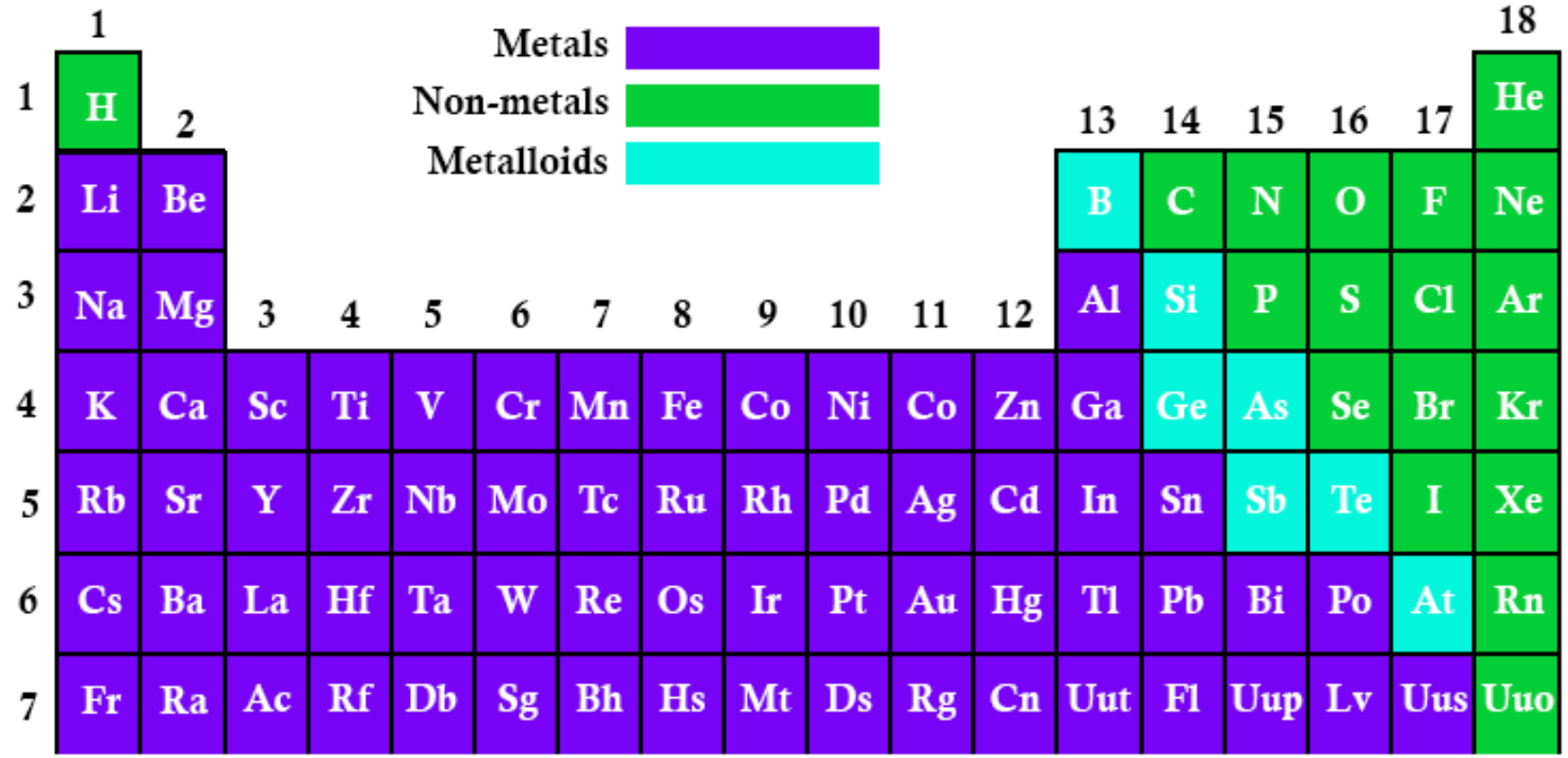
Chapter 2.3: Regularity of Crystal Binding (晶体结合的规律性)

- **Electronegativity of the Elements (元素的电负性)**



Chapter 2.3: Regularity of Crystal Binding (晶体结合的规律性)

➢ **Electronegativity of the Elements (元素的电负性)**



Chapter 2.3: Regularity of Crystal Binding (晶体结合的规律性)

➢ Regularity of Crystal Binding

- ❑ The elements with **low electronegativity** tend to form **metallic binding** (例如碱金属Li, Na, K…).
- ❑ The elements with **high electronegativity** tend to form **covalent binding** (例如IV族元素C, Si, Ge, Sn, Pb).
- ❑ The **combination** of different elements of **very low and very high electronegativity** tends to form **ionic binding** (例如碱金属和卤素的化合物NaCl, CsCl…).
- ❑ The **combination** of different elements with **similar electronegativity** tends to form **covalent binding** (例如III-V族化合物AlP, GaAs, InSb…)

Summary (总结)

➢ Summary (总结)

❖ The 5 fundamental types of crystal binding:

1) Ionic binding;

2) Covalent binding;

3) Metallic binding;

4) van der Waals binding;

5) Hydrogen binding.

❖ The regularity of crystal binding.