北京航空航天大學
BEIHANG UNIVERSITY

Chaper 3 Crystal Binding

3.1 General descriptions

3.2 Crystal of inert gases

3.3 Ionic crystals

3.4 Covalent crystal

3.5 Metal and hydrogen bonds

3.1 General discription of crystal binding

I. Chemical Bonds

***PHYSICS*: The attractive electrostatic interaction between the *negative* charges of the electrons and the *positive* charges of the nuclei is *entirely responsible* for the cohesion of solids.**

Classification of Solids:

- ✓**According to the lattice symmetry (*7 crstal systems, etc*).**
- ✓**According to the chemical bonds (*ionic, covalent, etc*).**

II. Classification of Solid

According the spatial distribution of electrons, the chemical bonds can be devided into *five* classes:

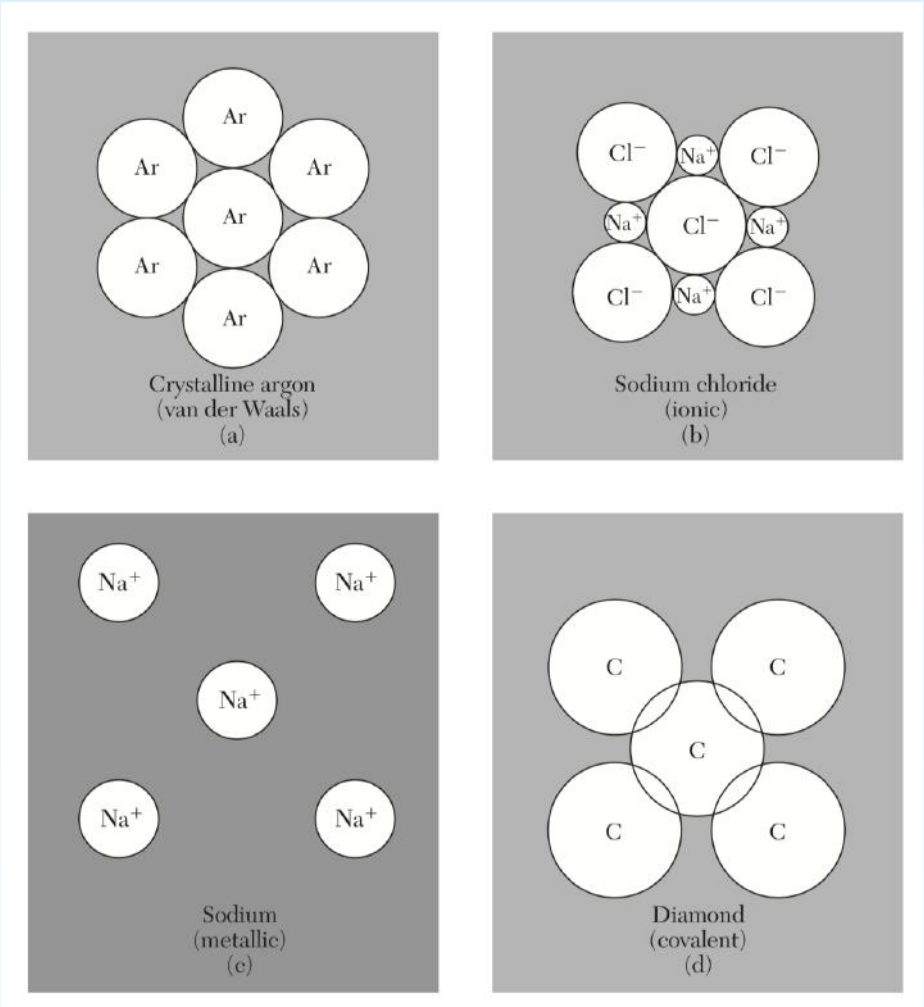
ionic bond, covalent bond, van der Waals bonding or molecular bond, hydrogen bond, metallic bond

1st-4th bonding types are usually found in *insulators*, the last type usually leads to *conductor (metal).*

(2) The principal types of crystalline binding

Neutral atoms with closed electron shells are bound together weakly by the van der Waals forces

The valence electrons are taken away from each alkali atom to form a communal electron sea.



Attractive electrostatic forces between the positive and negative ions

Neutral atoms, bound together by the overlapping parts of their electron distributions

III. cohesive energy

The energy that must be *added* to the crystal to separate its components into *neutral free* atoms *at rest*, *at infinite separation*, with the same electronic configuration.

Table 1 Cohesive energies

Energy required to form separated neutral atoms in their ground electronic state from the solid at 0 K at 1 atm. The data were supplied by Prof. Leo Brewer.

Li	Be											B	C	N	O	F	Ne
158.	320.											561	711.	474.	251.	81.0	1.92
1.63	3.32											5.81	7.37	4.92	2.60	0.84	0.020
37.7	76.5											134	170.	113.4	60.03	19.37	0.46
Na	Mg											Al	Si	P	S	Cl	Ar
107.	145.	← kJ/mol →										327.	446.	331.	275.	135.	7.74
1.113	1.51	← eV/atom →										3.39	4.63	3.43	2.85	1.40	0.080
25.67	34.7	← kcal/mol →										78.1	106.7	79.16	65.75	32.2	1.85
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
90.1	178.	376	468.	512.	395.	282.	413.	424.	428.	336.	130	271.	372.	285.3	237	118.	11.2
0.934	1.84	3.90	4.85	5.31	4.10	2.92	4.28	4.39	4.44	3.49	1.35	2.81	3.85	2.96	2.46	1.22	0.116
21.54	42.5	89.9	111.8	122.4	94.5	67.4	98.7	101.3	102.4	80.4	31.04	64.8	88.8	68.2	56.7	28.18	2.68
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
82.2	166.	422.	603.	730.	658	661.	650.	554.	376.	284.	112.	243.	303.	265.	211	107.	15.9
0.852	1.72	4.37	6.25	7.57	6.82	6.85	6.74	5.75	3.89	2.95	1.16	2.52	3.14	2.75	2.19	1.11	0.16
19.64	39.7	100.8	144.2	174.5	157.2	158.	155.4	132.5	89.8	68.0	26.73	58.1	72.4	63.4	50.34	25.62	3.80
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
77.6	183.	431.	621.	782.	859.	775.	788.	670.	564.	368.	65.	182.	196.	210.	144.		19.5
0.804	1.90	4.47	6.44	8.10	8.90	8.03	8.17	6.94	5.84	3.81	0.67	1.88	2.03	2.18	1.50		0.202
18.54	43.7	103.1	148.4	186.9	205.2	185.2	188.4	160.1	134	87.96	15.5	43.4	46.78	50.2	34.5		4.66
Fr	Ra	Ac															
	160.	410.															
	1.66	4.25															
	38.2	98.															

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
417.	357.	328.		206.	179.	400.	391.	294.	302.	317.	233.	154.	428.
4.32	3.70	3.40		2.14	1.86	4.14	4.05	3.04	3.14	3.29	2.42	1.60	4.43
99.7	85.3	78.5		49.3	42.8	95.5	93.4	70.2	72.3	75.8	55.8	37.1	102.2
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
598.		536.	456	347.	264.	385							
6.20		5.55	4.73	3.60	2.73	3.99							
142.9		128.	109.	83.0	63.	92.1							

***cohesive energy* is *very small* for <u>crystal of inert gases</u>**

3.2 Crystal of Inert Gases

(1) Basic Properties, Molecular Solid

Outermost electron shells of the atoms are *completely filled*, and is *spherically symmetric*.

5 members

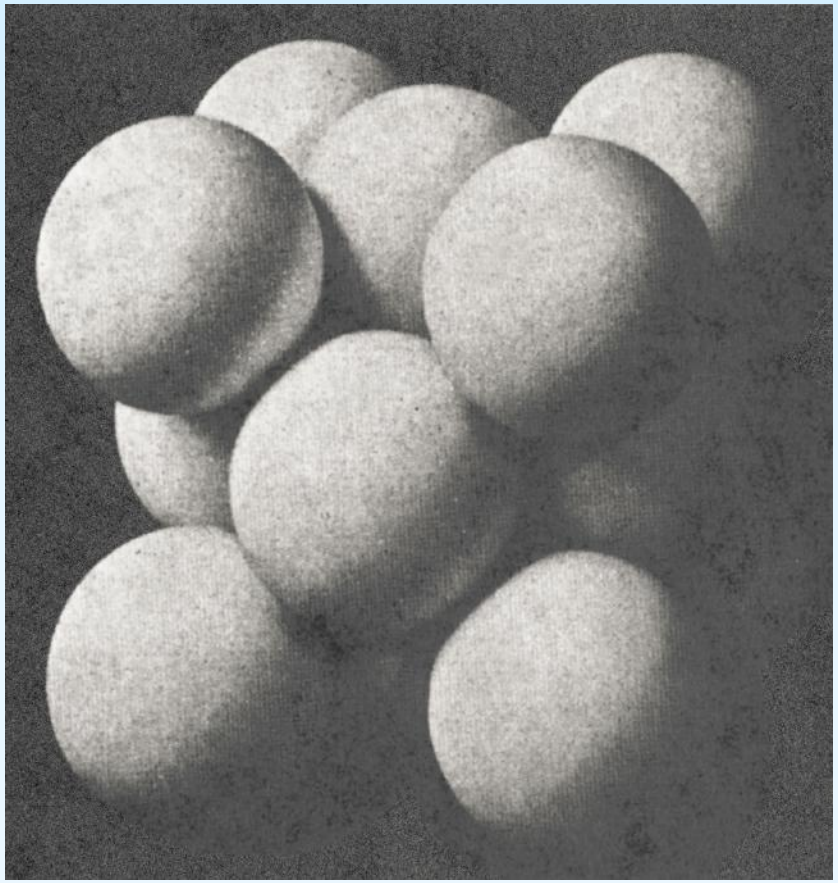
Helium
Neon
Argon
Krypton
Xenon

Table 4 Properties of inert gas crystals

(Extrapolated to 0 K and zero pressure)

	Nearest-neighbor distance, in Å	Experimental cohesive energy		Melting point, K	Ionization potential of free atom, eV	Parameters in Lennard-Jones potential, Eq. 10	
		kJ/mol	eV/atom			ϵ, in 10^{-16} erg	σ, in Å
He	(liquid at zero pressure)				24.58	14	2.56
Ne	3.13	1.88	0.02	24.56	21.56	50	2.74
Ar	3.76	7.74	0.080	83.81	15.76	167	3.40
Kr	4.01	11.2	0.116	115.8	14.00	225	3.65
Xe	4.35	16.0	0.17	161.4	12.13	320	3.98

3.2 Crystal of Inert Gases



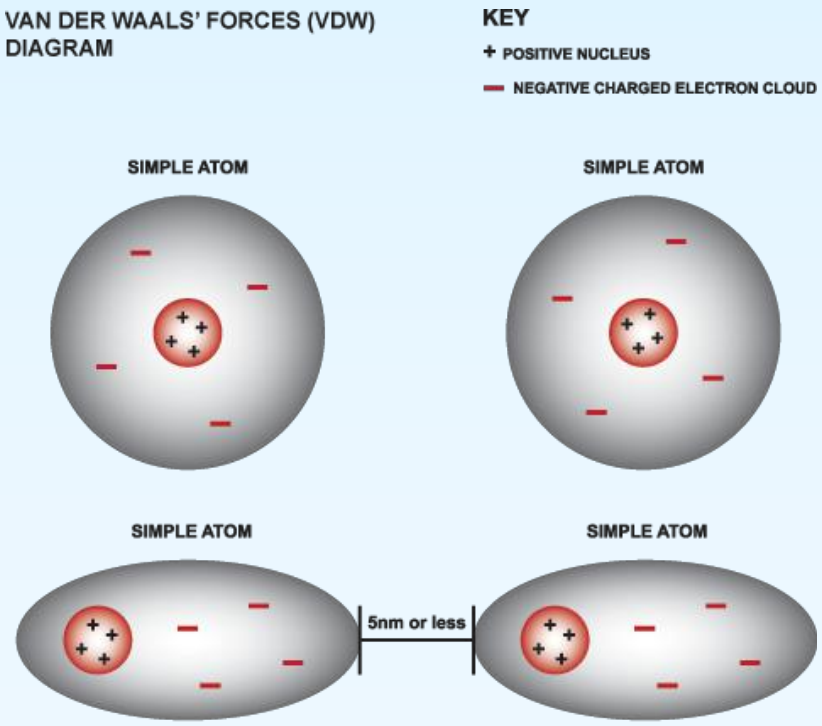
✓ The inert gas atoms pack together as closely as possible.

✓ Crystal structures are all cubic close-packed (fcc), except He^3 and He^4.

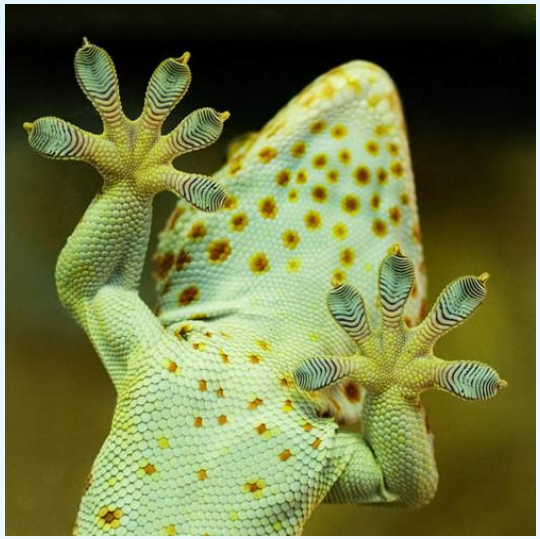
3.2 Crystal of Inert Gases

Van der Waals-London Interaction

Electron distribution in the crystal is slightly distorted → Intr. dipole moments in each other → An attractive interaction between the atoms



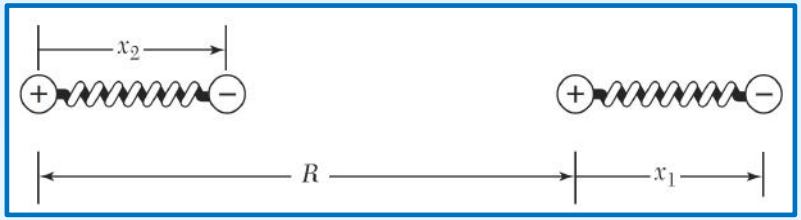
When two atoms come within 5 nanometers of each other, there will be a slight interaction between them, thus causing polarity and a slight attraction.



A Simple Model

Consider ***two identical linear harmonic oscillators*** 1 and 2 separated by R, with frequency ω_0.

$$\mathcal{H}_0 = \frac{1}{2m}p_1^2 + \tfrac{1}{2}Cx_1^2 + \frac{1}{2m}p_2^2 + \tfrac{1}{2}Cx_2^2$$



- ✓ The attractive interaction is called van der waals force.
- ✓ The zero point energy of the system is lowered by the ***dipole-dipole*** coupling.
- ✓ The interaction is a ***quantum effect***.

Colomb interaction: (since R » x_1,x_2)

$$\mathcal{H}_1 \cong -\frac{2e^2x_1x_2}{R^3}$$

$$x_1 = \frac{1}{\sqrt{2}}(x_s + x_a)\ ; \qquad x_2 = \frac{1}{\sqrt{2}}(x_s - x_a)$$

$$p_1 \equiv \frac{1}{\sqrt{2}}(p_s + p_a)\ ; \qquad p_2 \equiv \frac{1}{\sqrt{2}}(p_s - p_a)$$

$$\mathcal{H} = \left[\frac{1}{2m}p_s^2 + \frac{1}{2}\left(C - \frac{2e^2}{R^3}\right)x_s^2\right] + \left[\frac{1}{2m}p_a^2 + \frac{1}{2}\left(C + \frac{2e^2}{R^3}\right)x_a^2\right]$$

$$\Delta U = \tfrac{1}{2}\hbar(\Delta\omega_s + \Delta\omega_a) = -\hbar\omega_0 \cdot \frac{1}{8}\left(\frac{2e^2}{CR^3}\right)^2 = -\frac{A}{R^6}$$

(3) Pauli Exclusion Principle and Repulsive Interaction

✓ Two identical fermions ***cannot*** occupy the same quantum state simultaneously.

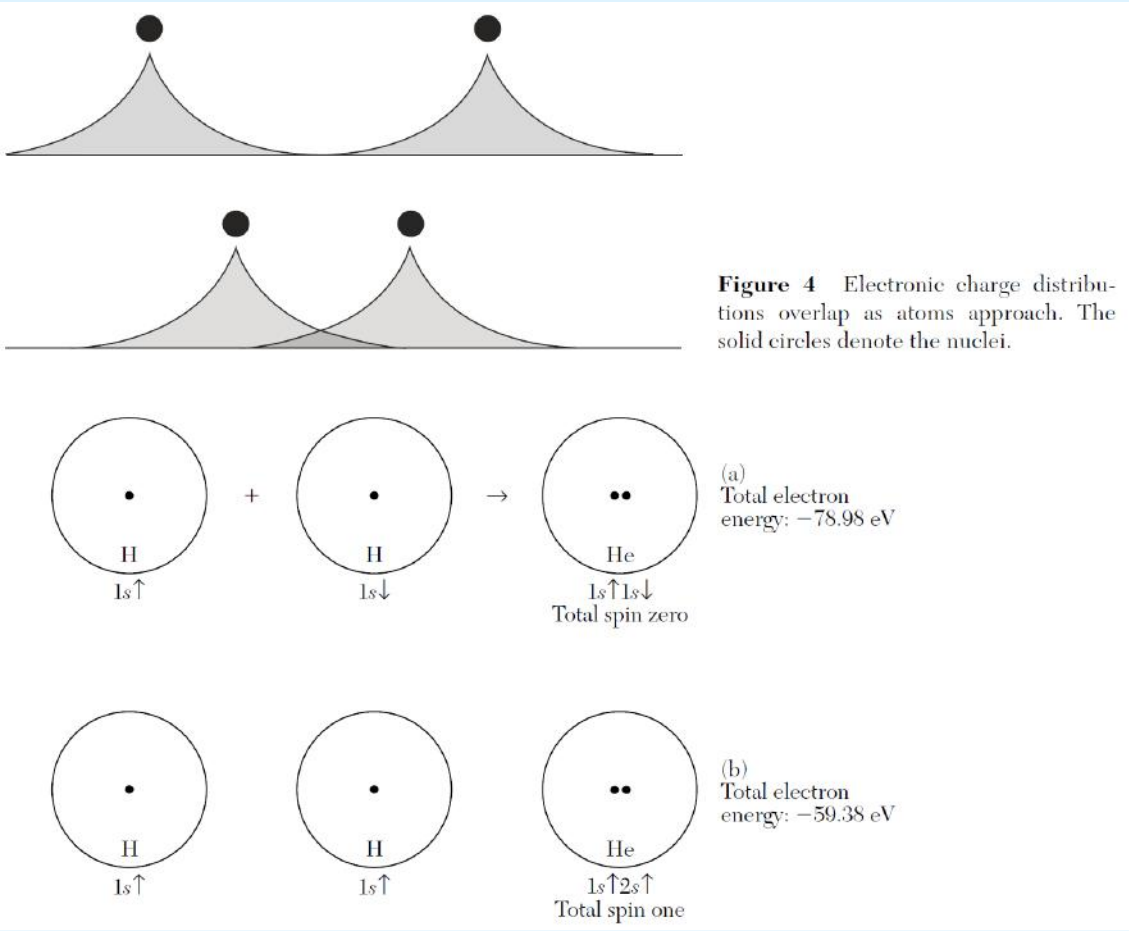


Figure 4 Electronic charge distributions overlap as atoms approach. The solid circles denote the nuclei.

✓ Electron overlap ***increases*** the total energy and gives a ***repulsive*** contribution to the interaction.

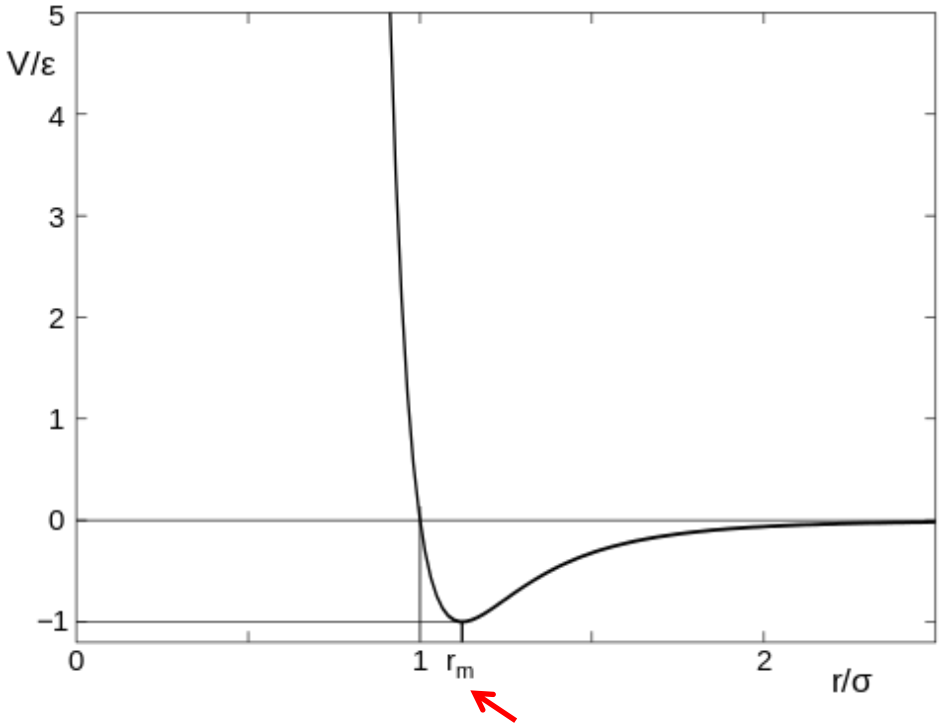
✓ ***Empirical*** repulsive potential of the form B/R^{12}, where B is a ***positive*** constant.

3.2 Crystal of Inert Gases

(4) Lenard-Jones potential

$$U(R) = 4\epsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right]$$

$$4\epsilon\sigma^6 = A \text{ and } 4\epsilon\sigma^{12} = B$$



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		kJ/mol	eV/atom	ϵ, in 10^{-16} erg	σ, in Å
He	(liquid at zero pressure)			14	2.56
Ne	3.13	1.88	0.02	50	2.74
Ar	3.76	7.74	0.080	167	3.40
Kr	4.01	11.2	0.116	225	3.65
Xe	4.35	16.0	0.17	320	3.98

$$U_{\text{tot}} = \tfrac{1}{2}N(4\epsilon)\left[\sum_j{}' \left(\frac{\sigma}{p_{ij}R}\right)^{12} - \sum_j{}' \left(\frac{\sigma}{p_{ij}R}\right)^{6}\right]$$

$$\sum_j{}' p_{ij}^{-12} = 12.13188 \; ; \qquad \sum_j{}' p_{ij}^{-6} = 14.45392$$

$$R_0/\sigma = 1.09$$

$$U_{\text{tot}}(R_0) = -(2.15)(4N\epsilon)$$

3.3 Ionic Crystal

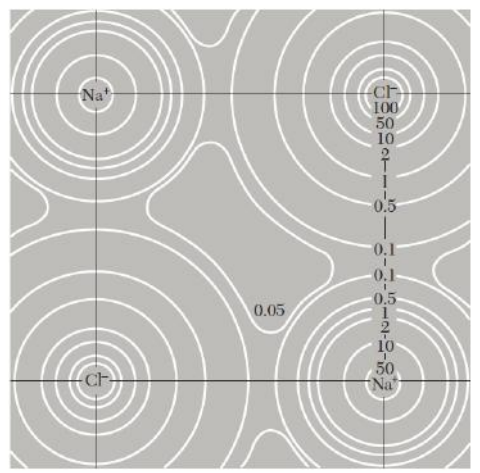
(1) Ionic Bond

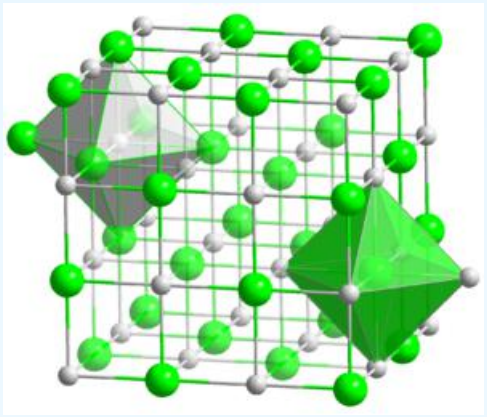
✓ ***Ionic bond:*** electrostatic interaction of oppositely charged ions. Two common examples: NaCl, CsCl.

✓ Ions have ***closed shell*** structures (approximately spherical symmetric), just like those of inert atoms.

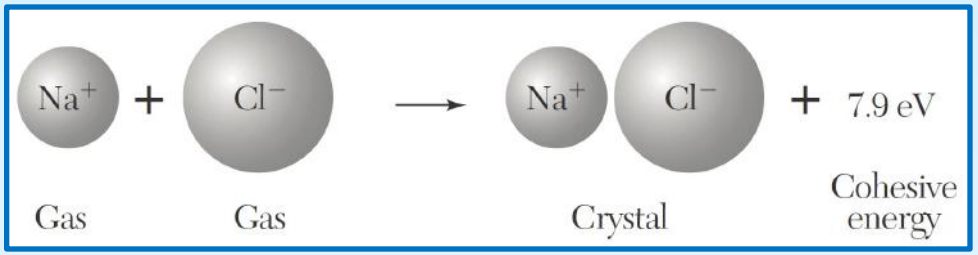
$$\text{Li: } 1s^2 2s,\ \text{F: } 1s^2 2s^2 2p^5 \Rightarrow \text{Li}^+ : 1s^2,\ \text{F}^- : 1s^2 2s^2 2p^6$$

helium **neon**





(2) Madelung Energy



- ✓ Simple Estimate shows the binding energy mainly comes from the ***electrostatic*** interactions. [electrostatic energy between a pair of Na & Cl (*distance* 2.81Å) ~ **5.1eV**].

- ✓ The van der Waals part of the attractive interaction makes a relatively small contribution (%1~2), the rest part is electrostatic contribution, called ***Madelung*** energy.

$$U_{ij} = \lambda \exp(-r_{ij}/\rho) \pm q^2/4\pi\epsilon_0 r$$

Repulsive Interaction, short distance

Attractive electrostatic inter. long distance

(3) Madelung Constant

✓ Restricting repulsive interaction ***within N.N.***:

$$U_{ij} = \begin{cases} \lambda \exp(-R/\rho) - \dfrac{q^2}{R} & \text{(nearest neighbors)} \\ \pm\dfrac{1}{p_{ij}}\dfrac{q^2}{R} & \text{(otherwise).} \end{cases}$$

$$r_{ij} \equiv p_{ij}R$$

✓ Negalecting surface effect, the Madelung energy:

$$U_{\text{tot}} = NU_i = N\left(z\lambda e^{-R/\rho} - \frac{\alpha q^2}{R}\right)$$

NB! 2N ions, to avoid overcounting

$$\alpha \equiv \sum_j{}' \frac{(\pm)}{p_{ij}} \equiv \textbf{Madelung constant}$$

✓ The value of the ***Madelung constant*** is of central **importance**!

(4) Equilibrium position and Total energy

$$N\frac{dU_i}{dR} = -\frac{Nz\lambda}{\rho}\exp(-R/\rho) + \frac{N\alpha q^2}{R^2} = 0$$

$$R_0^2 \exp(-R_0/\rho) = \rho\alpha q^2/z\lambda$$

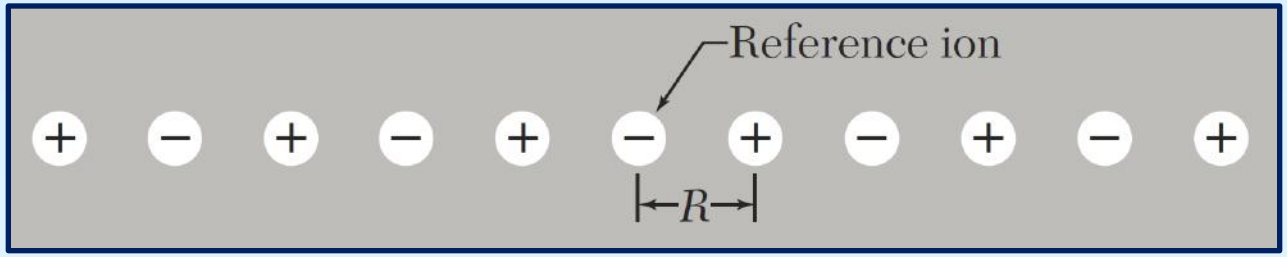
$$U_{\text{tot}} = -\frac{N\alpha q^2}{R_0}\left(1 - \frac{\rho}{R_0}\right)$$

Madelung Energy

Short-range Repulsive Energy

$\rho \sim 0.1R_0$

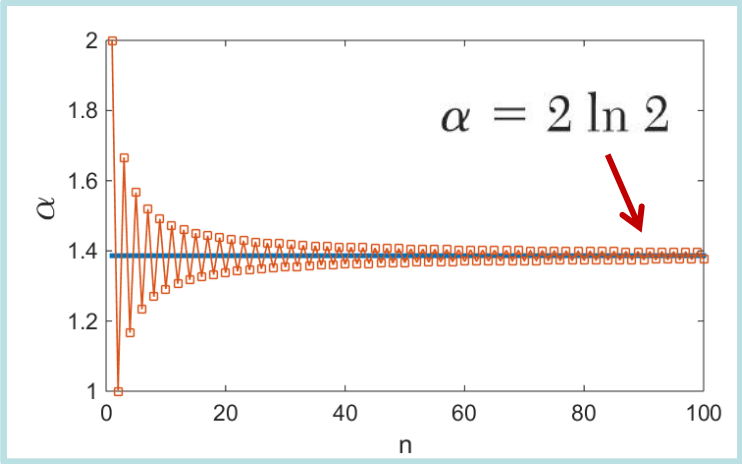
(5) Example: Evaluation of Madelung Constant in a Chain



Remember: $\alpha \equiv \sum_j{}' \frac{(\pm)}{p_{ij}} \equiv$ **Madelung constant**

✓ Take the reference ion as a negative charge, **plus** sign should be chosen for the N.N. and **negative** for N.N.N. and so on...

$$\alpha = 2\left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \cdots\right]$$

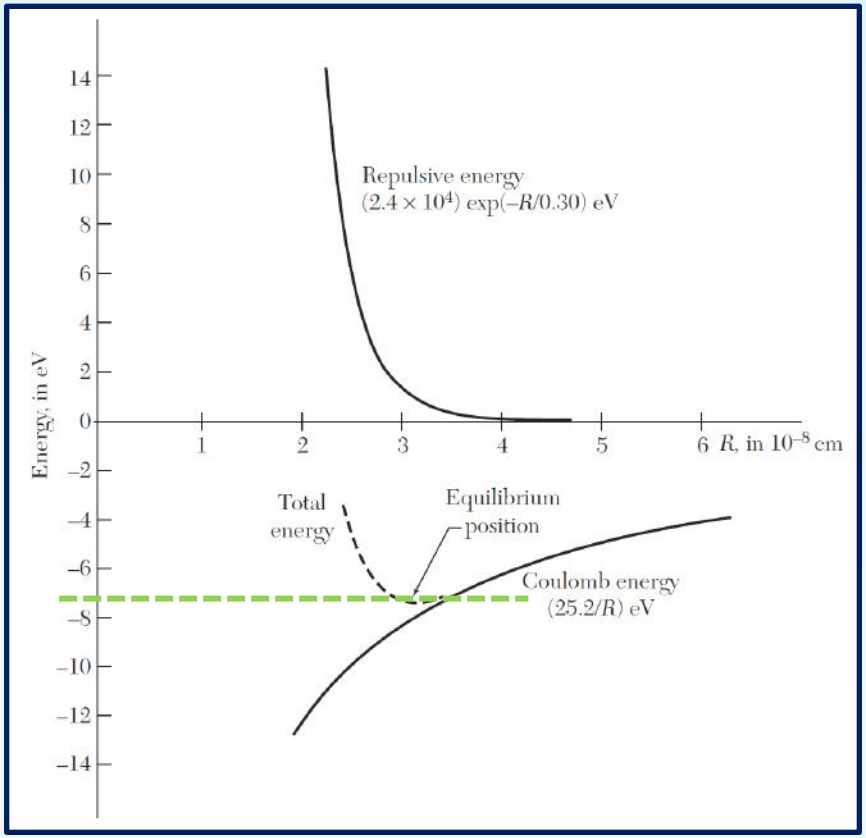


3.3 Ionic Crystal

(6) 3D lattices (alkali halide)

- ✓ The evaluation of Madlung const. in 3D is more difficult.
- ✓ The total, repulsive, and Madelung energies in KCl.
- ✓ Cohesion energy is very strong (~-8eV) per atom.
- ✓ Insulator, high melting temperature, high hardness.

Structure	α
Sodium chloride, NaCl	1.747565
Cesium chloride, CsCl	1.762675
Zinc blende, cubic ZnS	1.6381



(7) A Subtle Example: NaCl structure

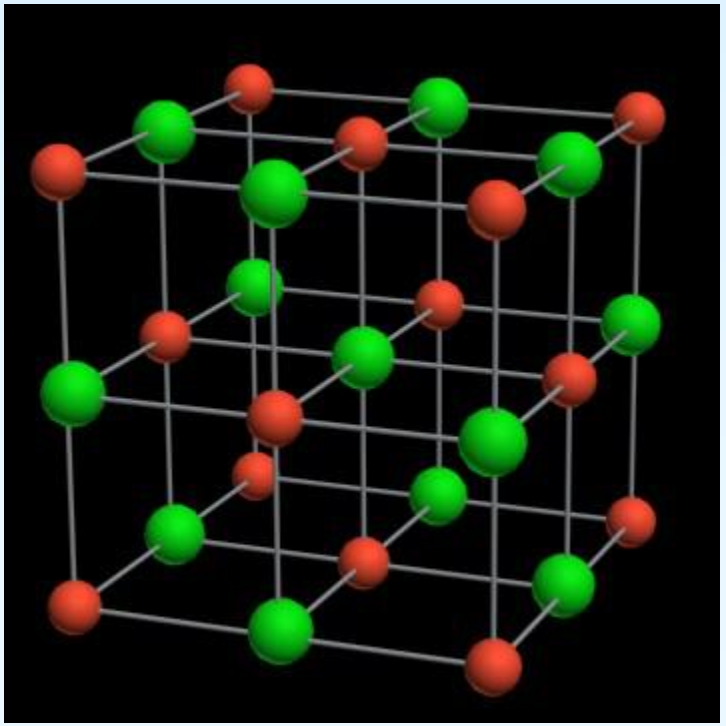
R —— **distance between nearest neighbors**

Coordination of other ions:

$$(n_1R, n_2R, n_3R)$$

$$R_{1j} = \sqrt{n_1^2 + n_2^2 + n_3^2}\,R = P_jR$$

$$P_j = \sqrt{n_1^2 + n_2^2 + n_3^2}$$

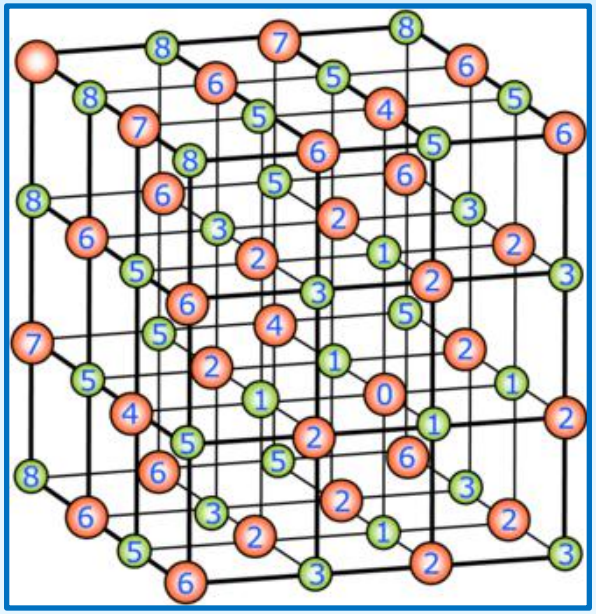


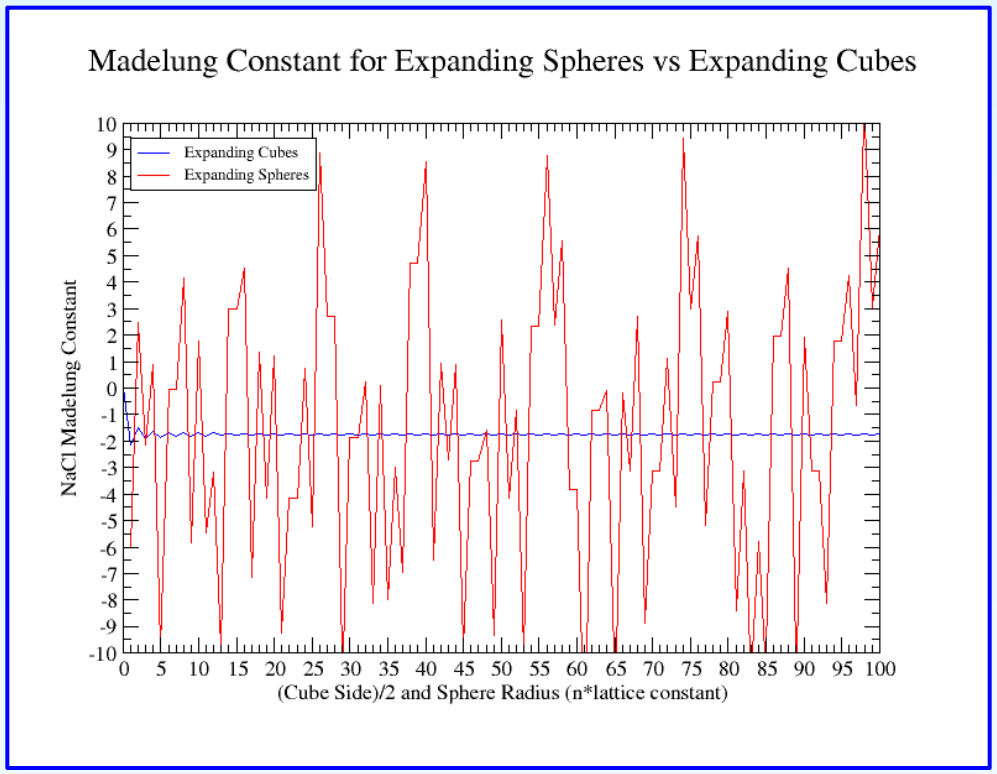
3.3 Ionic Crystal

Expanding Spheres

$$M_{\mathrm{Na}} = -M_{\mathrm{Cl}} = \sum_{j,k,\ell=-\infty}^{\infty}{}' \frac{(-1)^{j+k+\ell}}{(j^2+k^2+\ell^2)^{1/2}}.$$

$$M = -6 + 12/\sqrt{2} - 8/\sqrt{3} + 6/2 - 24/\sqrt{5} + \cdots = -1.74756\ldots$$



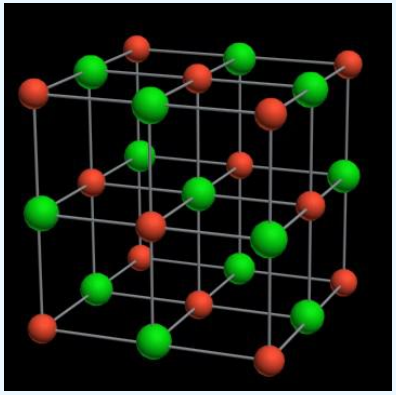


NOT Converging!

Expanding Cubes

	# of ions	P_j	contrib. factor
N.N	$6(+)$	1	$1/2$
N.N.N	$12(-)$	$\sqrt{2}$	$1/4$
3rd N.N.	$8(+)$	$\sqrt{3}$	$1/8$

$$\alpha = \frac{6}{2} - \frac{12}{4\sqrt{2}} + \frac{8}{8\sqrt{3}} = 1.457$$



Include more cubes, ones gets accurate & converging estimate of Madelung constant.

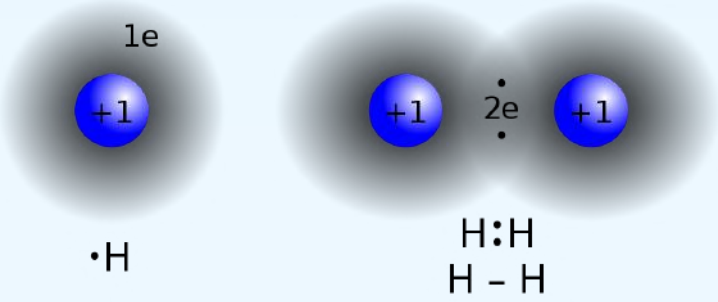
3.4 Covalent Crystal

(1) Covalent Bond

- ***Electron Pair:*** formed from ***two*** electrons, one from each atom, partly ***localized*** in the region between the two atoms, with ***antiparallel*** spin orientations.

- ***Strong Bond:*** bond between two carbon atoms in diamond (7.37 eV/atom), as strong as ionic bond.

- ***Directional:*** strong directional properties (spatially annisotropic)

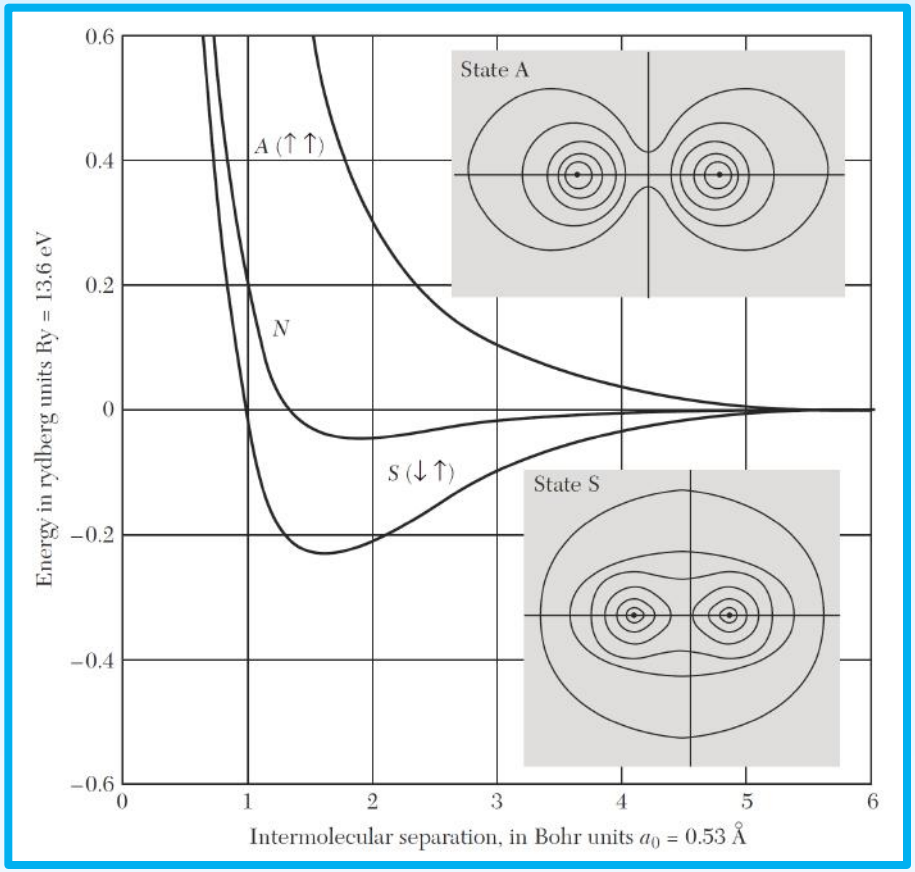


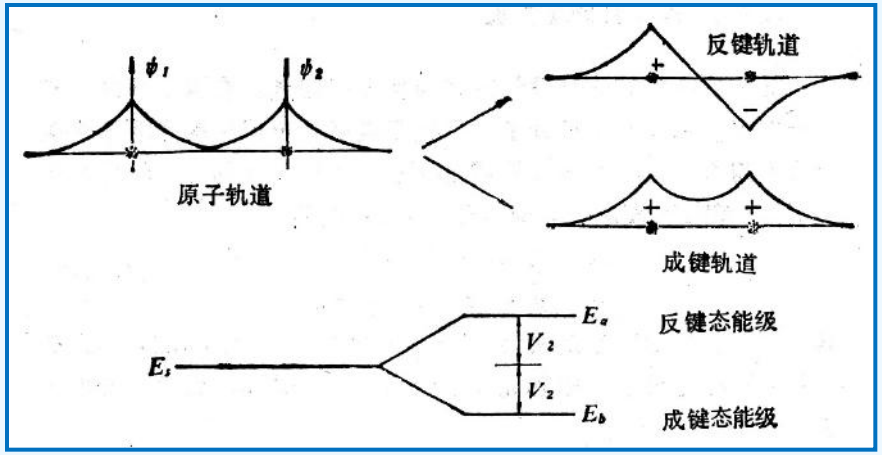
3.4 Covalent Crystal

(2) Example I: valence bond in hydrogen molecule

- ✓ The binding depends on the ***relative spin orientation***, this spin-dependent coulomb energy is called the ***exchange interaction***.

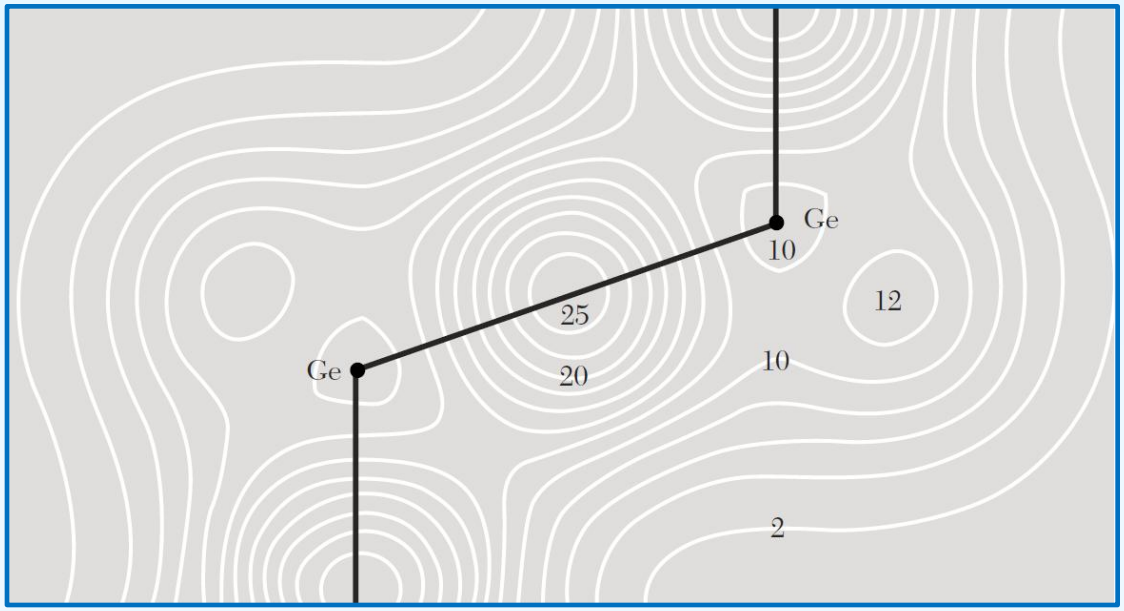
- ✓ Two electrons form a singlet pair (***antisymmetric spin wavefunc.***), and have symmetric real space wavefunc.

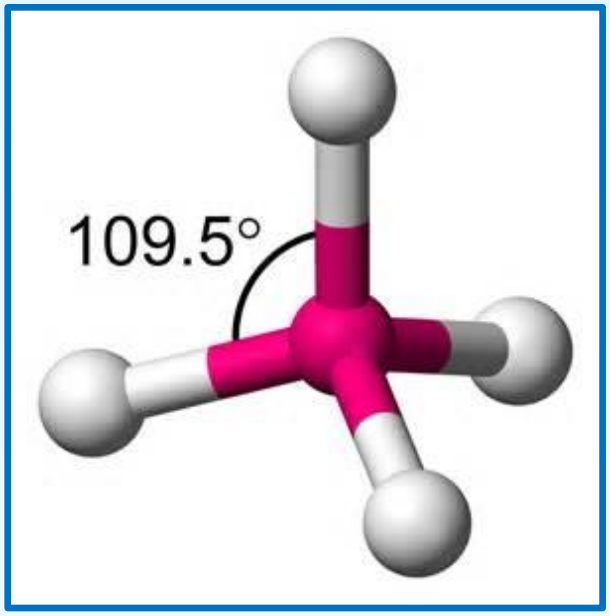




(3) Example II: Tetrahedral Bond

- ✓ Some common examples: ***carbon***, ***silicon***, and ***germanium*** having the diamond structure.
- ✓ Atoms joined to ***four*** nearest neighbors at tetrahedral angles.
- ✓ ***Low filling*** of space (ratio 0.34), due to small coordination number.

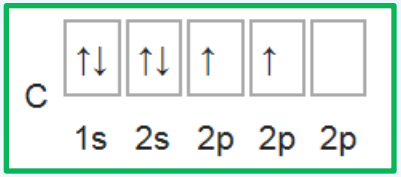


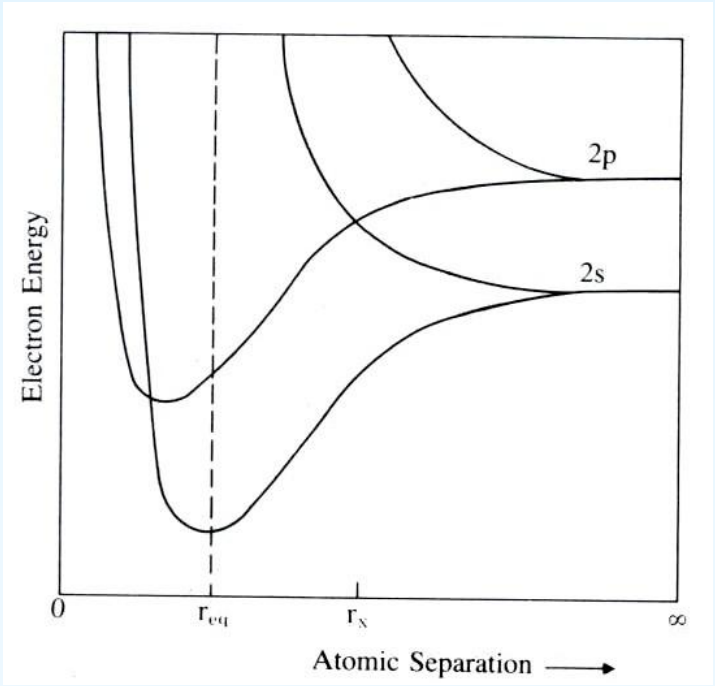


3.4 Covalent Crystal

(4) sp^3 hybridyzation

- ✓ The Pauli principle gives ***a strong repulsive interaction*** between atoms with filled shells.
- ✓ Unfilled shell can have ***an attractive interaction*** associated with charge overlap -- **valence bond theory**.
- ✓ C atom: $1s^2 2s^2 2p^2$ only ***two*** unpaired electrons.



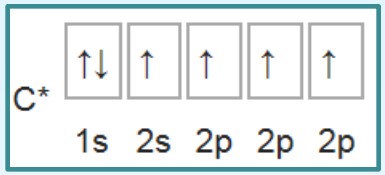


3.4 Covalent Crystal

✓ Promote one **2s** electron to **2p** orbital, with excitation energy **~4eV**.

$1s^2 2s^2 2p_x^1 p_y^1 p_z^0$(ground state) → $1s^2 2s^1 2p_x^1 p_y^1 p_z^1$(excited state)

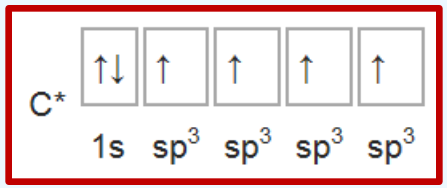
—— ***four*** **unpaired electrons.**



Four equivalent orbitals

—— **linear superpostion of *s*, p_x, p_y, p_z states.**

—— **dubbed as *hybrid orbital***



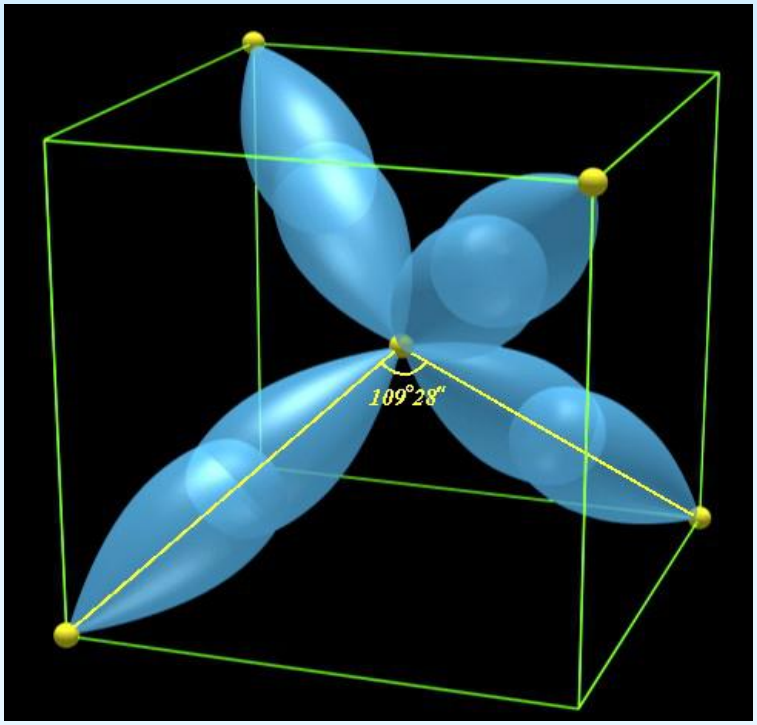
3.4 Covalent Crystal

$$|h_1\rangle = \frac{1}{2}\left(|s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle\right)$$

$$|h_2\rangle = \frac{1}{2}\left(|s\rangle + |p_x\rangle - |p\rangle_y - |p_z\rangle\right)$$

$$|h_3\rangle = \frac{1}{2}\left(|s\rangle - |p_x\rangle + |p_y\rangle - |p_z\rangle\right)$$

$$|h_4\rangle = \frac{1}{2}\left(|s\rangle - |p_x\rangle - |p_y\rangle + |p_z\rangle\right)$$



- ✓ **Four electron obitals are unfilled (*half filled*), pointing to four vertices of the cube.**
- ✓ **Four unpaired electrons can form valence bonds (*tetrahedral angle* between each other), energy lowers as *7.4 eV!***

(5) A Continuous Range of Crystal

covalent ⟺ **ionic**

Table 8 Fractional ionic character of bonds in binary crystals

Crystal	Fractional ionic character	Crystal	Fractional ionic character
Si	0.00		
SiC	0.18	GaAs	0.31
Ge	0.00	GaSb	0.26
ZnO	0.62	AgCl	0.86
ZnS	0.62	AgBr	0.85
ZnSe	0.63	AgI	0.77
ZnTe	0.61	MgO	0.84
CdO	0.79	MgS	0.79
CdS	0.69	MgSe	0.79
CdSe	0.70		
CdTe	0.67	LiF	0.92
		NaCl	0.94
InP	0.42	RbF	0.96
InAs	0.36		
InSb	0.32		

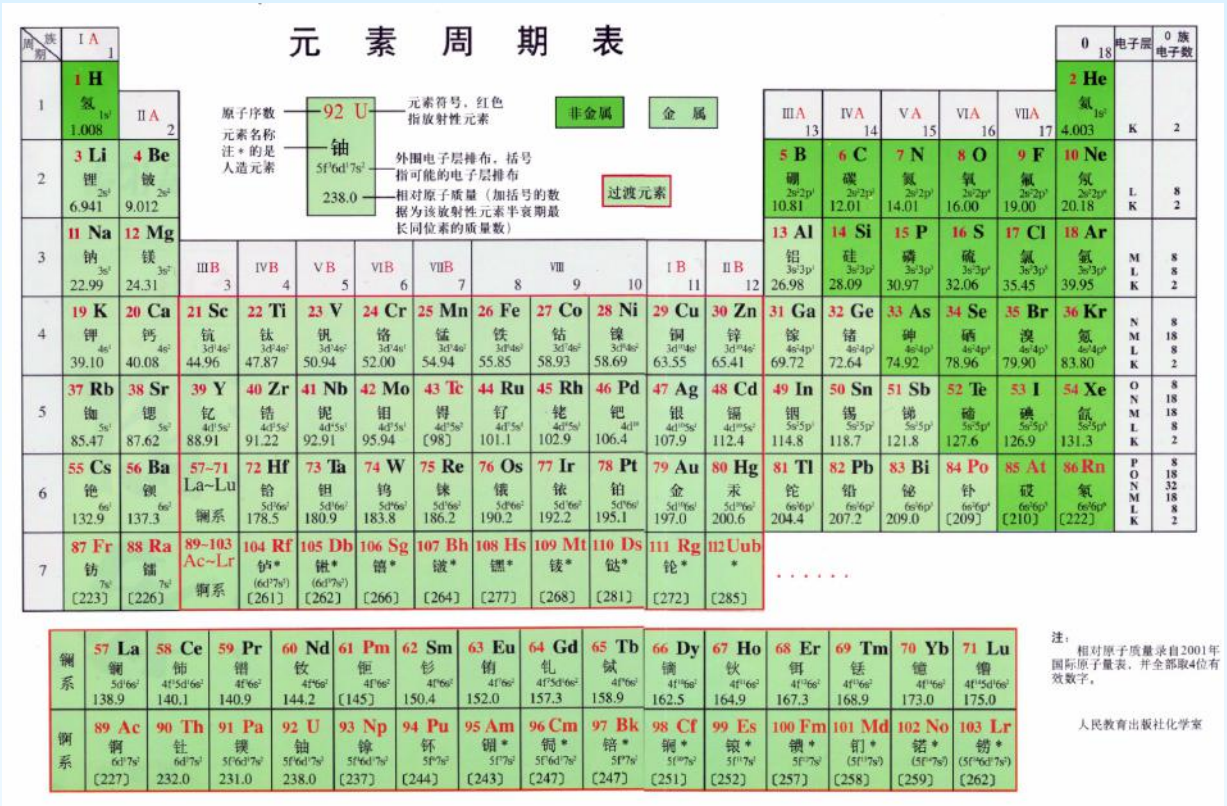
After J. C. Phillips, *Bonds and bands in semiconductors*.

✓ Semiempirical theory of the fractional ionic or covalent character.

3.5 Metals and Hydrogen Bond

(1) Metals

- characterized by ***high electrical conductivity,*** 1 or 2 ***free electrons*** per atom.
- a typical example is alkali metals, Li, Na, K, Rb, and Fr, ***weak bond***.
- Metallic bond: ions in the ***electron sea***, the latter gets ***lower*** energy.



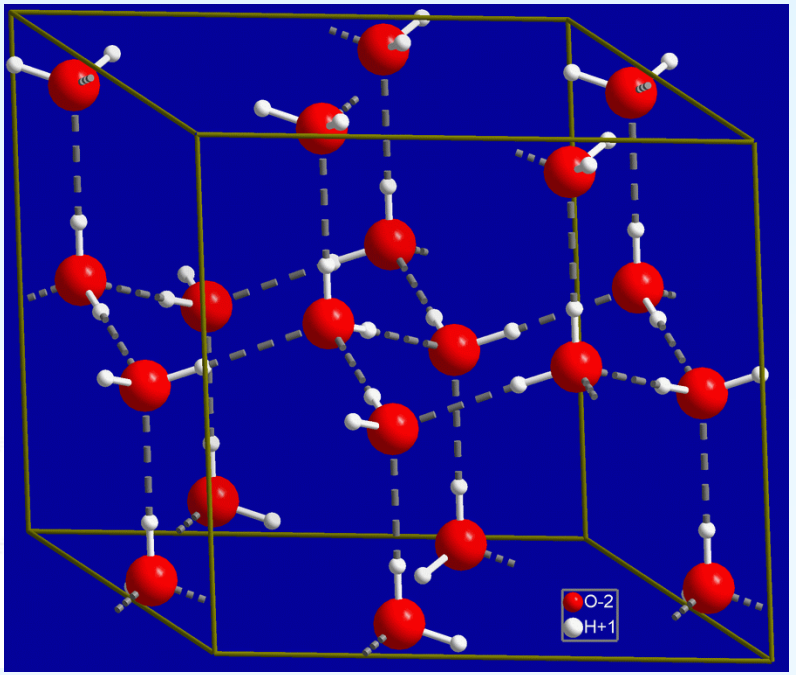
- Metallic bond is isotropic in spatial directions, leads to compact structures, hcp, fcc, or bcc.

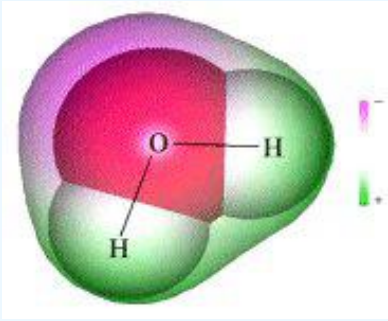
3.5 Metals and Hydrogen Bond

(2) Hydrogen Bond

- ✓ The hydrogen atom loses its electron to an atom in the molecule (covalent); bare ***proton*** forms the ***hydrogen bond*** with another atom.
- ✓ Most ubiquitous and perhaps simplest example of a hydrogen bond is found between ***water*** molecules.
- ✓ Intermediate strength **~ 0.1 eV**.
- ✓ Protons are so tiny, almost touch the ***surface*** of negative ions.

Ice Rule: large residual entropy

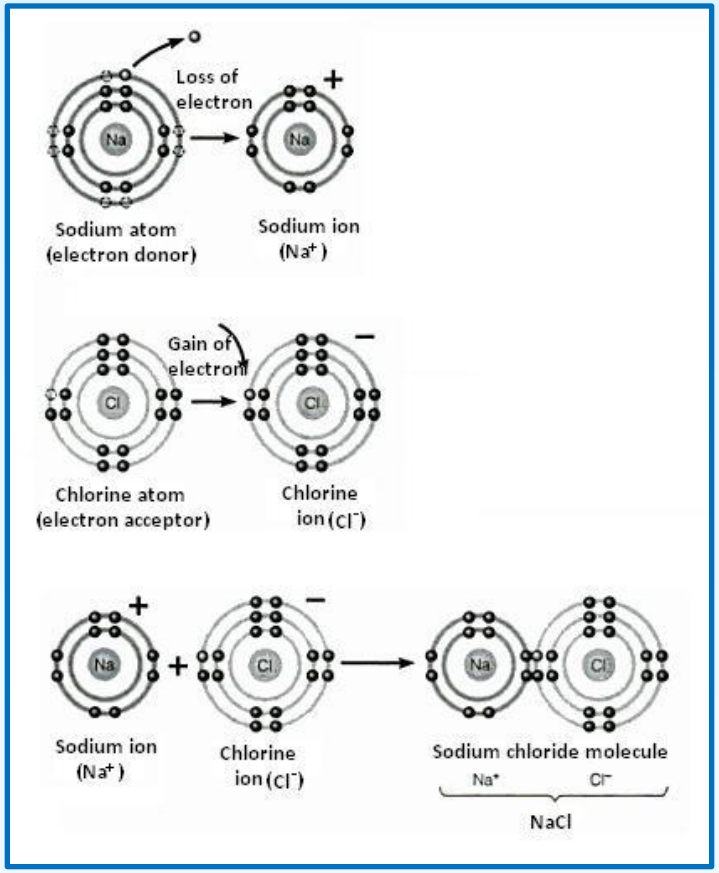




3.6 Atom Radii

✓ The existence and ***probable lattice constants*** of phases that have not yet been synthesized can be ***predicted*** from the ***additive*** properties of the atomic radii.

NaCl



0.97 Å

1.81 Å

1.81 + 0.97 = 2.78 Å

~ 2.81 Å