Chapter 3

Crystal Binding and Elastic Constants

PHYS 432

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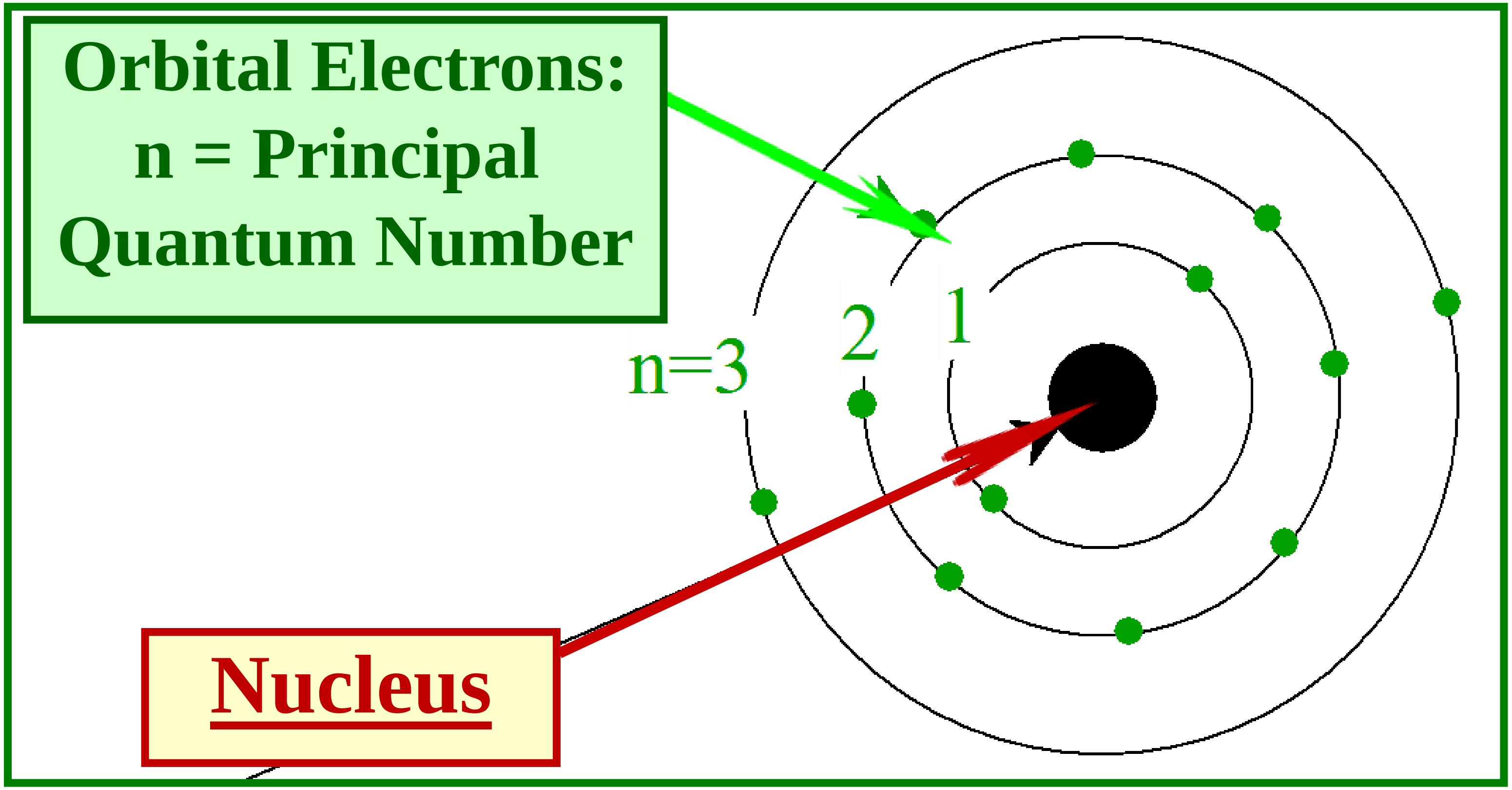
Chapter topics

- Crystals of inert gases
- Ionic crystals
- Covalent crystals
- Metals
- Hydrogen bonds
- Atomic radii
- Analysis of elastic strains
- Elastic compliance and stiffness constants
- Elastic waves in cubic crystals

The Bohr Model of the Atom

We know that ***this model is wrong in detail***, but it gives a ***qualitative understanding*** of electron orbits in atoms.

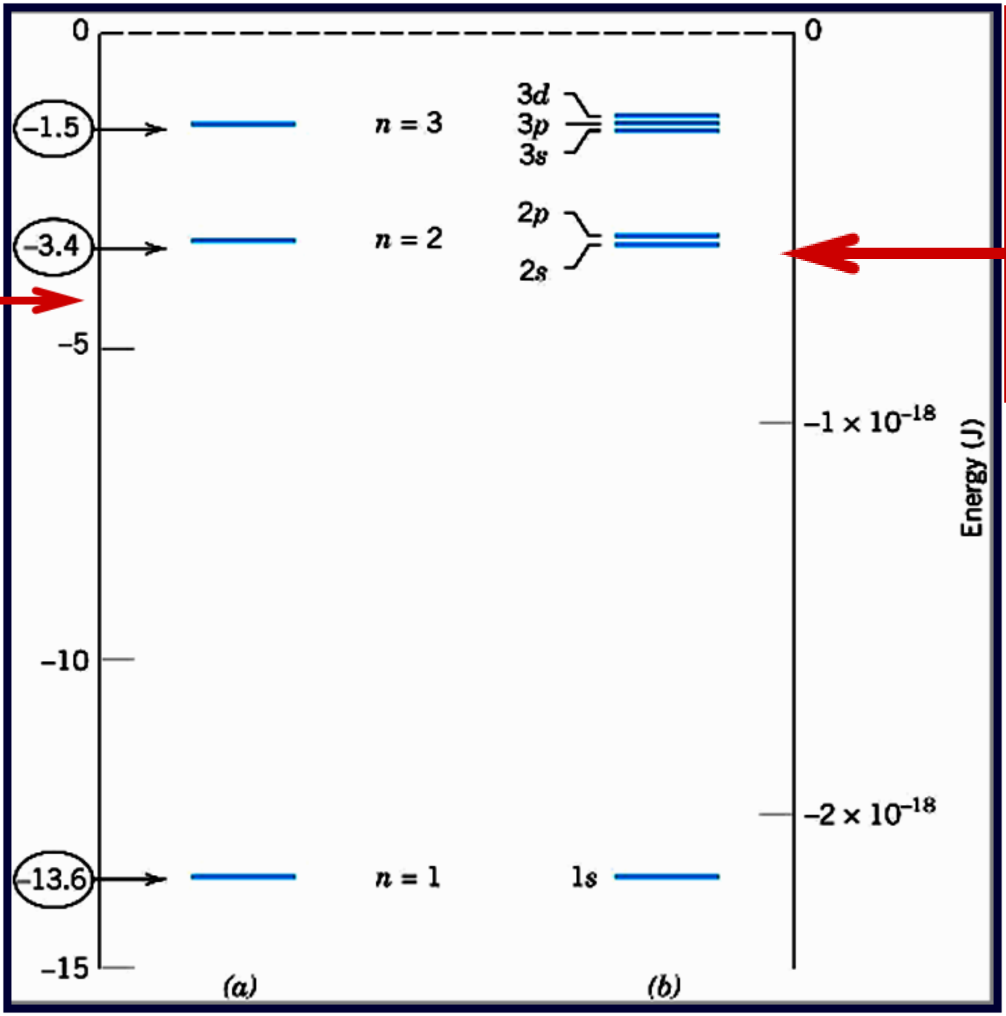


Orbital Electrons:
n = Principal
Quantum Number

Nucleus

Discrete Electron Energy Levels

- ***Discrete Energies*** of the atomic **s, p, & d electrons** are well-predicted by Quantum Mechanics (**Schrödinger's Equation**)



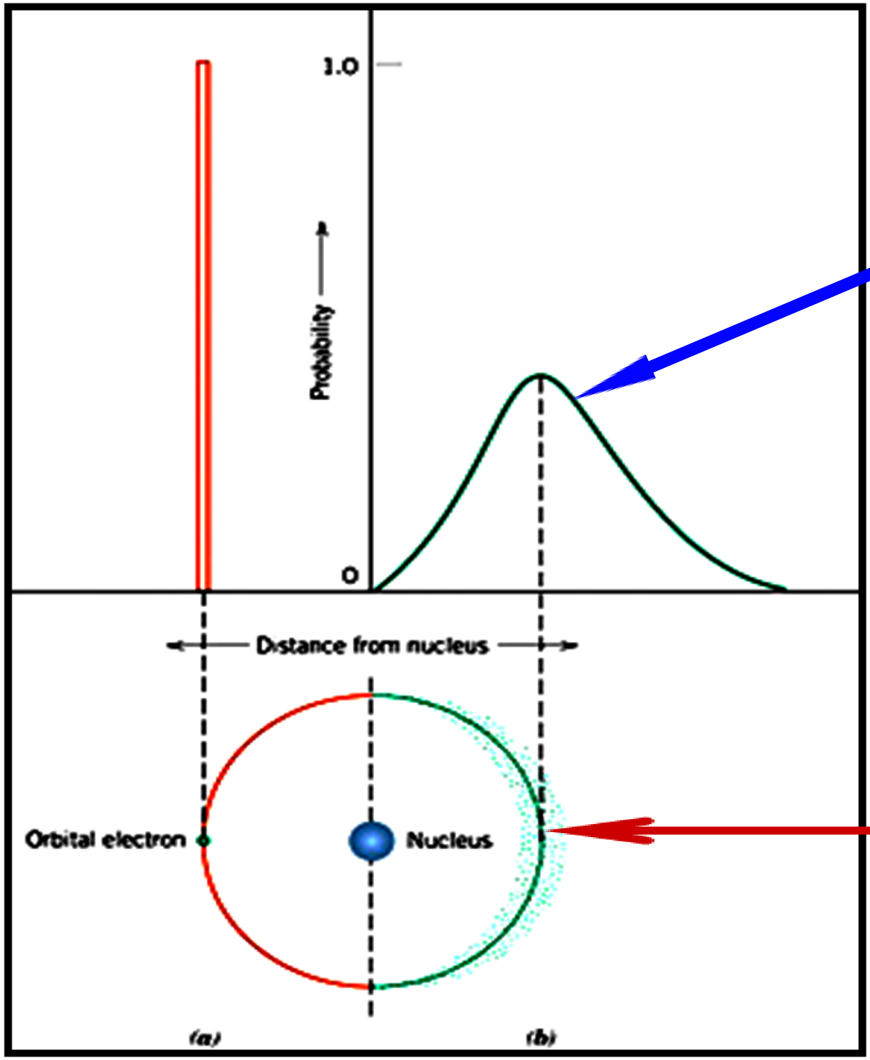
Bohr Model

Quantum Mechanics

(**Schrödinger's Equation**)

What is an Electron?

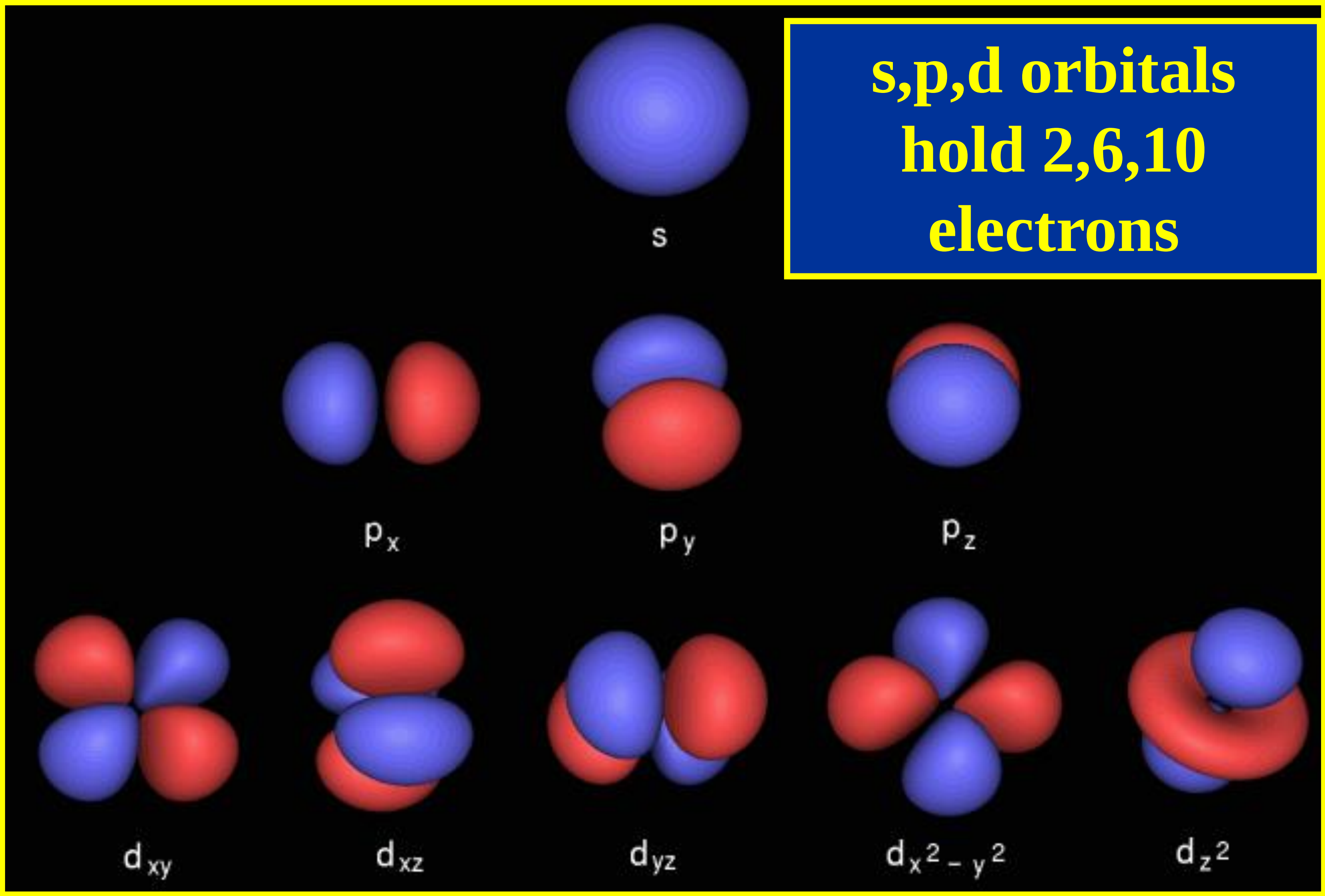
Diffraction & Wave/Particle Duality



Electron Probability Density

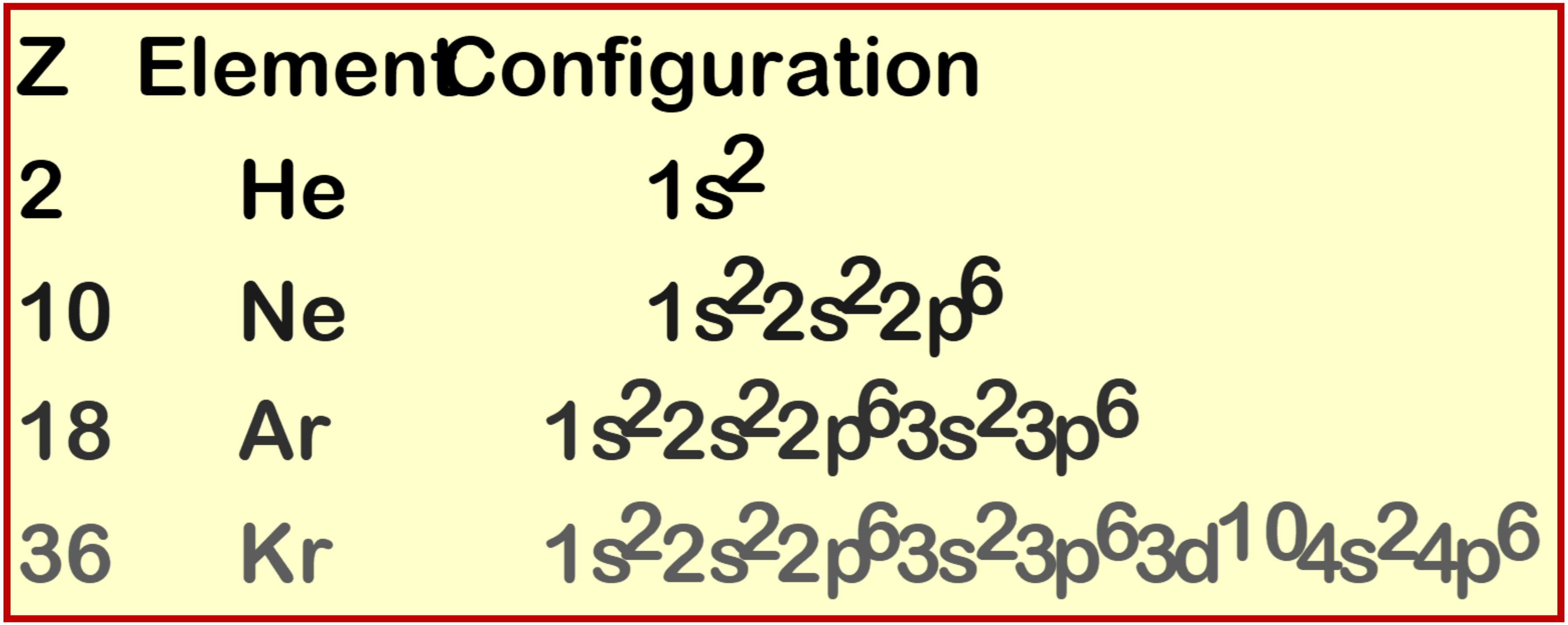
Electron Orbit

Electronic Structure in Atoms



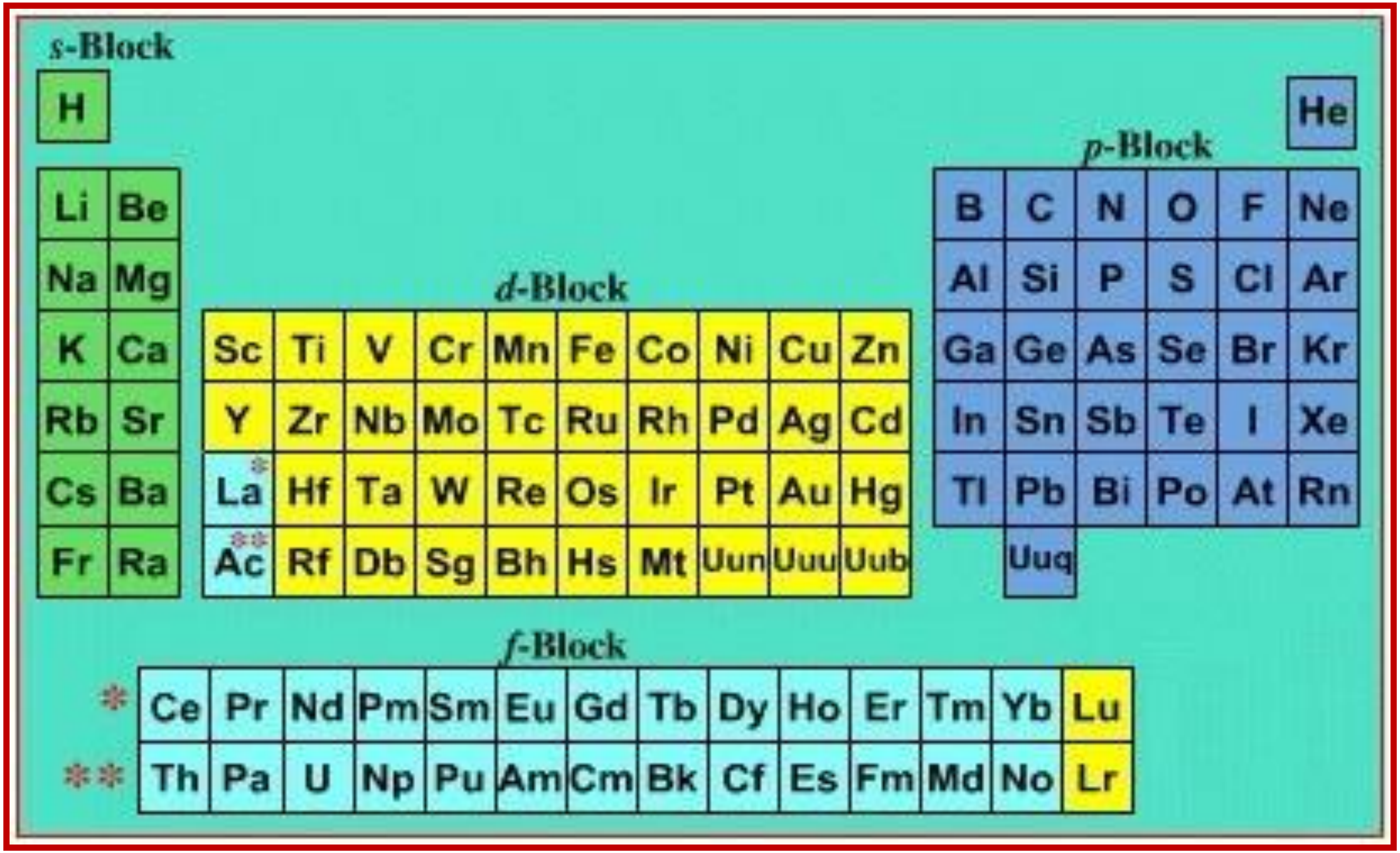
s,p,d orbitals hold 2,6,10 electrons

Electronic Energy States



Z	Element	Configuration
2	He	$1s^2$
10	Ne	$1s^2 2s^2 2p^6$
18	Ar	$1s^2 2s^2 2p^6 3s^2 3p^6$
36	Kr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$

Orbitals & the Periodic Table



s-Block

p-Block

d-Block

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac**	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub		Uuq				

f-Block

*	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
**	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Chemical Bonding Types

Bond Type	Bond Energy	Material Type
Van der Waals	Smallest	Solid Inert Gases Polymers
Ionic	Large	Ceramics, Salts
Covalent	Variable Large in Diamond Small in Bismuth	Polymers Semiconductors
Metallic	Variable Large in Tungsten Small in Mercury	Metals
Hydrogen	Variable	Water, hydrogen difluoride etc.

Van der Waals Bonding

- **Primary bonds** are formed when the bonding process involves a transfer or sharing of electrons i.e. ionic, covalent, and metallic bonds.

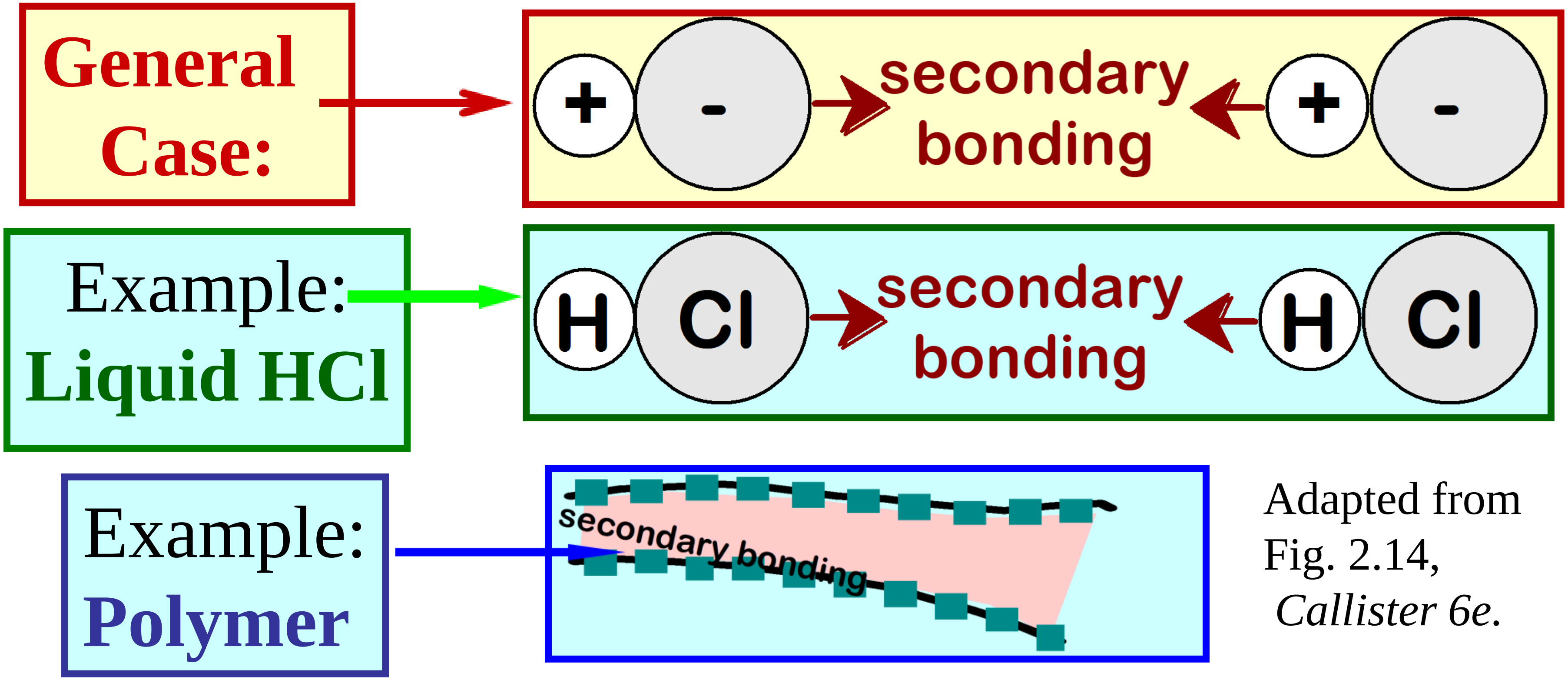
- **Secondary bonds** are formed from the subtle attraction forces between positive and negative charges. There is no transfer or sharing of electrons involved in a secondary bond i.e. **Van der Waals bond.**

- **Van der Waals bonds** are a result of an asymmetrical distribution of positive and negative charges inside each bonded atoms/molecule, which creates in a dipole.

- A dipole could be permanent or induced by an external charge.

Van der Waals Bonding

- The Van der Waals bonds tend to be weak compared to the primary bonds, but they can play an important role in determining the properties of polymeric materials & other molecular solids.



General Case:

Example: **Liquid HCl**

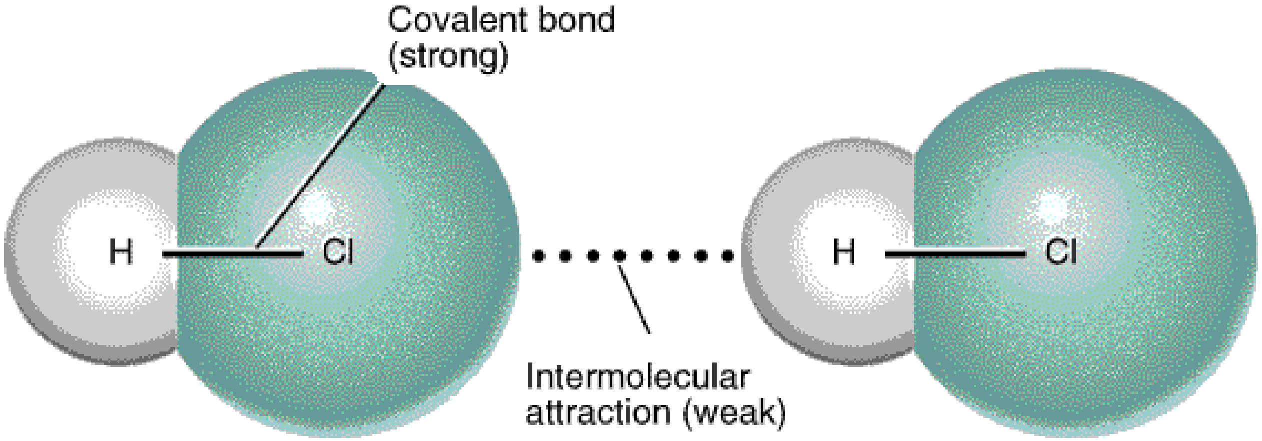
Example: **Polymer**

Adapted from Fig. 2.14, *Callister 6e.*

Dipole-Dipole Interactions

Dipole-dipole interactions exist between molecules which are permanent dipole. They tend to orientate themselves such that the attractive forces between molecules are maximized while repulsive forces are minimized.

In the illustration : the H end of HCl is permanently slightly positive charge. The Cl end of HCl has a permanent slight negative charge, the "H" in one molecule is attracted to the "Cl" in a neighbor.



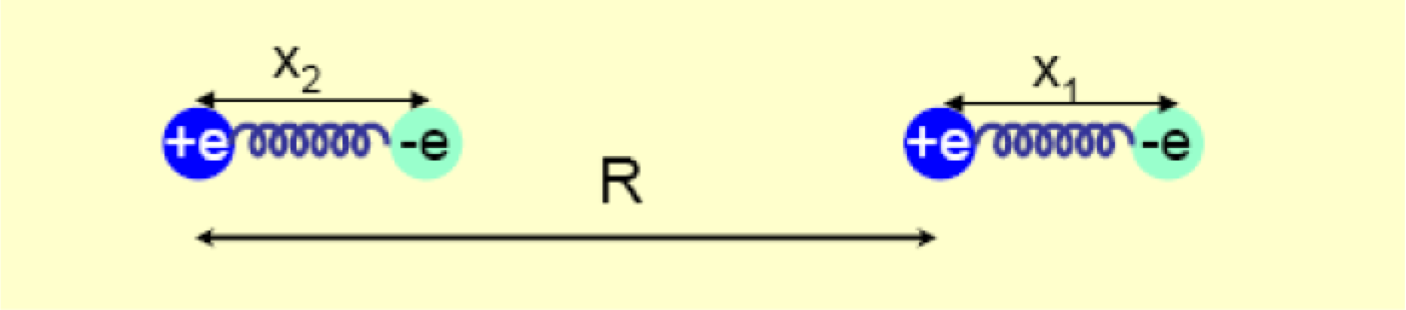
Instantaneous Dipole-Induced Dipole Interactions

- It is also known as London forces or Dispersion Forces. Instantaneous dipole-induced dipole Interactions exist in non-polar molecules. These forces result from temporary charge imbalances.

- These temporary charges in one molecule or atom attract opposite charges in nearby molecules or atoms. A local slight positive charge δ+ in one molecule will be attracted to a temporary slight δ- negative charge in a neighboring molecule.

- It is also known as induction force. When a polar molecule approaches a nonpolar molecule, the permanent dipole on the polar molecule can distort the electron cloud of the nonpolar molecule, forming an induced dipole.

Model for inert gases



Hamiltonian for the unperturbed system – no Coulomb interaction is given by the equation

$$H_o = \frac{p_1^2}{2m} + \frac{1}{2}Cx_1^2 + \frac{p_2^2}{2m} + \frac{1}{2}Cx_2^2$$

where p_1 and p_2 are the momenta of these two oscillators and C is the force constant. The energy of the two **uncoupled oscillators** is

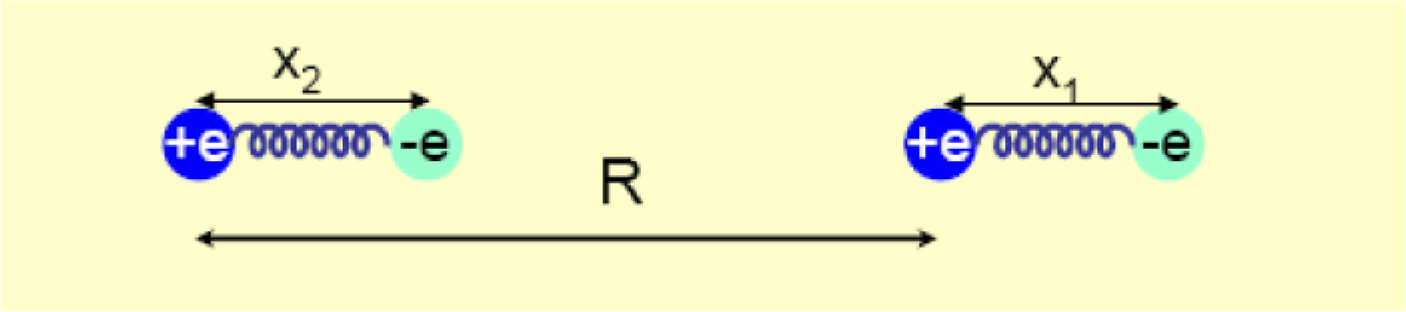
$$E = (n_1 + \frac{1}{2})\hbar\omega_o + (n_2 + \frac{1}{2})\hbar\omega_o$$

Where

$$\omega_o = \sqrt{\frac{C}{m}}$$

Model for inert gases

Coulomb interactions of the system are treated as a perturbation to H_0.



$$H_1 = \frac{e^2}{R} + \frac{e^2}{R + x_1 - x_2} - \frac{e^2}{R + x_1} - \frac{e^2}{R - x_2}$$

$$= \frac{e^2}{R}\left[1 + \left(1 + \frac{x_1}{R} - \frac{x_2}{R}\right)^{-1} - \left(1 + \frac{x_1}{R}\right)^{-1} - \left(1 - \frac{x_2}{R}\right)^{-1}\right]$$

Since $R \gg x_1 , R \gg x_2$ and $(1 + \varepsilon)^{-1} = 1 - \varepsilon + \varepsilon^2 + \cdots$

Taylor series

$$\sum_{n=0}^{\infty} \frac{f^{(n)}(a)}{n!}(x - a)^n$$

$$H_1 = -\frac{2e^2 x_1 x_2}{R^3}$$

Model for inert gases

$$H_{total} = \frac{P_1^2}{2m} + \frac{P_2^2}{2m} + \frac{1}{2}Cx_1^2 + \frac{1}{2}Cx_2^2 - \frac{2e^2 x_1 x_2}{R^3}$$

This equation can be solved by normal mode transformation -- symmetric (s) and anti-symmetric (a) modes. p_s and p_a are momenta associated with the two modes.

$$x_1 \equiv \frac{1}{\sqrt{2}}(x_s + x_a) \quad x_2 \equiv \frac{1}{\sqrt{2}}(x_s - x_a)$$

$$P_1 \equiv \frac{1}{\sqrt{2}}(P_s + P_a) \quad P_2 \equiv \frac{1}{\sqrt{2}}(P_s - P_a)$$

This is a standard method to solve two coupled oscillator problem. It converts the coupled simple harmonic oscillator problem on the previous page into a two independent SHO.

Model for inert gases

$$H_{Total} = \frac{\frac{1}{2}(P_s^2 + P_a^2 + 2P_sP_a)}{2m} + \frac{\frac{1}{2}(P_s^2 + P_a^2 - 2P_sP_s)}{2m}$$

$$+\frac{1}{2}C(x_s^2 + x_a^2 + 2x_sx_a) + \frac{1}{2}C(x_s^2 + x_a^2 - 2x_sx_a)$$

$$-\frac{2e^2\frac{1}{2}(x_s^2 - x_a^2)}{R^3}$$

$$H_{Total} = \frac{P_s^2}{2m} + \frac{P_a^2}{2m} + \frac{1}{2}C(x_s^2 + x_a^2) - \frac{e^2x_s^2}{R^3} + \frac{e^2x_a^2}{R^3}$$

$$= \frac{P_s^2}{2m} + \frac{1}{2}\left(C - \frac{2e^2}{R^3}\right)x_s^2 + \frac{P_a^2}{2m} + \frac{1}{2}\left(C + \frac{2e^2}{R^3}\right)x_a^2$$

Model for inert gases

The two frequencies of the coupled oscillators in the modes of symmetric (s) and anti-symmetric (a) are given below:

$$\omega_s = \sqrt{\frac{1}{m}(C - \frac{2e^2}{R^3})} = \omega_o \left[1 - \frac{1}{2}\frac{2e^2}{CR^3} - \frac{1}{8}\left(\frac{2e^2}{CR^3}\right)^2 + \ldots \right]$$

$$\omega_a = \sqrt{\frac{1}{m}(C + \frac{2e^2}{R^3})} = \omega_o \left[1 + \frac{1}{2}\frac{2e^2}{CR^3} - \frac{1}{8}\left(\frac{2e^2}{CR^3}\right)^2 + \ldots \right]$$

Model for inert gases

The energy of the two **coupled oscillators** is

$$E = (n_1 + \frac{1}{2})\hbar\omega_s + (n_2 + \frac{1}{2})\hbar\omega_a$$

The zero-point energy is

$$E = \frac{1}{2}\hbar\omega_s + \frac{1}{2}\hbar\omega_a = \hbar\omega_0 - \frac{1}{8}\left(\frac{2e^2}{CR^3}\right)^2 \hbar\omega_0$$

Therefore, the zero point energy of the coupled oscillators is lowered from the uncoupled oscillators by

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

It is an attractive interaction.

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

- This is called the Van der Waals interaction, also known as the London interaction or the induced dipole-dipole interaction.

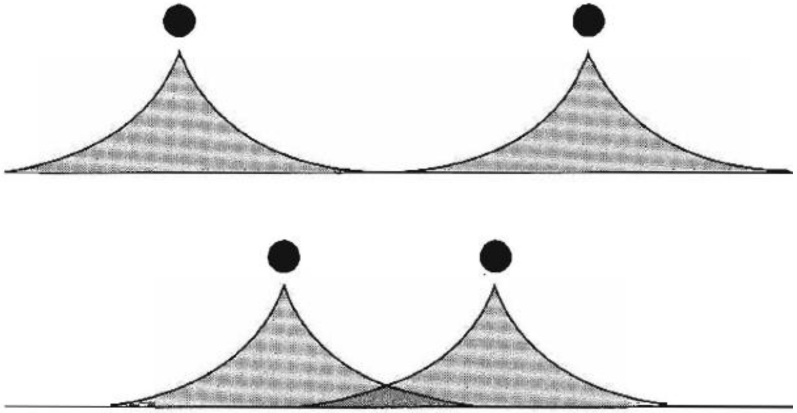
- It is the principal attractive interaction in crystals of inert gases and also in crystals of many organic molecules.

- The interaction is a quantum effect, in the sense that $\Delta U \rightarrow 0$ as $\hbar \rightarrow 0$.

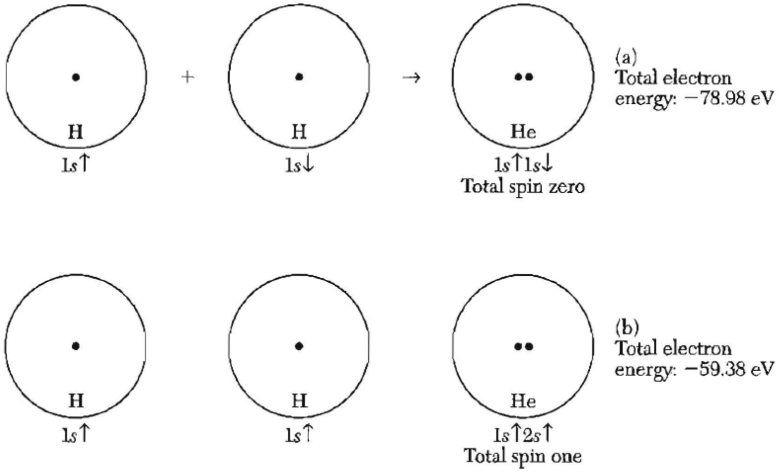
- The Van der Waals interaction does not depend for its existence on any overlap of the charge densities of the two atoms.

Repulsive Interaction

- As the two atoms are brought together, their charge distributions gradually overlap.
- At sufficiently close separations the overlap energy is repulsive, in large part because of the Pauli exclusion principle.



- We make no attempt here to evaluate the repulsive interaction from first principles.
- Experimental data on the inert gases can be fitted well by an empirical repulsive potential of the form $\mathbf{B}/\mathbf{R}^{12}$, where **B** is a positive constant.



The Lennard-Jones Potential

By combining the Van der Waals interaction and the repulsive interaction, we obtain Lennard Jones Potential.

$$U(R) = \frac{B}{R^{12}} - \frac{A}{R^{6}}$$

$$B = 4\epsilon\sigma^{12}, \mathrm{A} = 4\epsilon\sigma^{6}$$

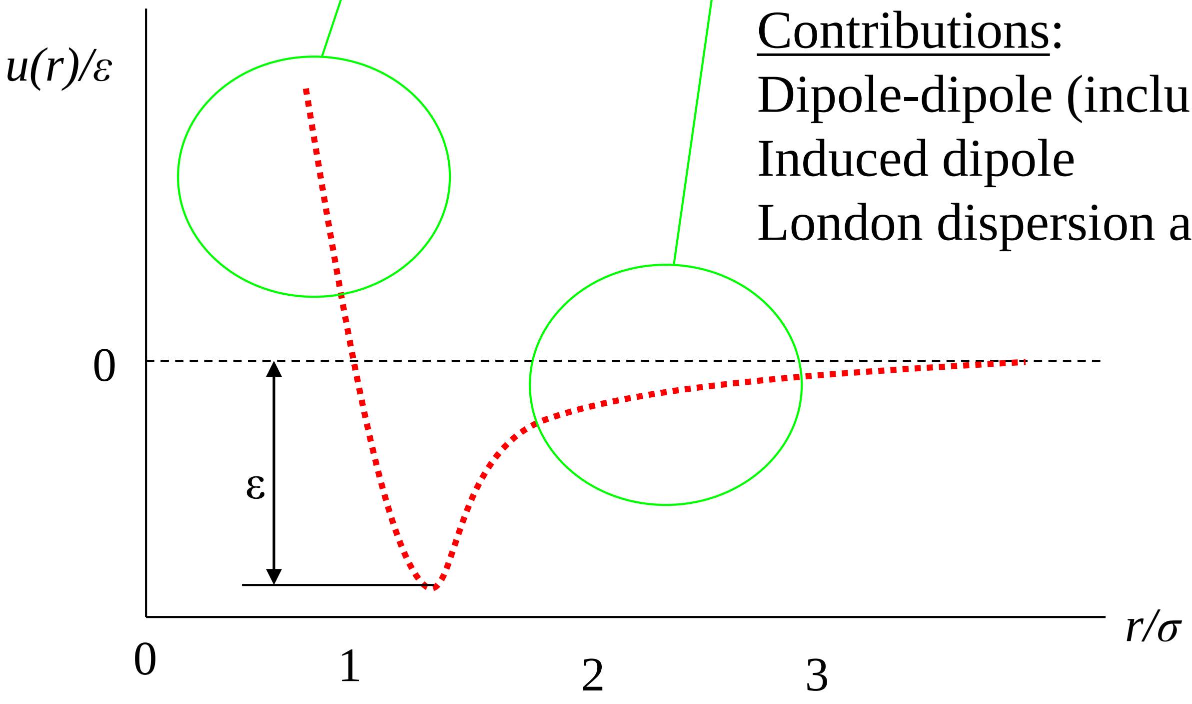
This potential is known as the **Lennard-Janes potential**.

The Lennard-Jones Potential

$$u(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

The short range 1/r^{12} repulsive term

The long range 1/r^{6} attractive term



Contributions:
Dipole-dipole (including H-bonding)
Induced dipole
London dispersion attraction

- **Cohesive Energy**
- **Ionic crystals**
- **Evaluation of Madelung Constant**

Cohesive Energy

- If we neglect the kinetic energy of the inert gas atoms, the **cohesive energy** of an inert gas crystal is given by summing the Lennard-Jones potential over all pairs of atoms in the crystal.

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

- **The distance between reference atom *i* and any other atom *j* is $p_{ij}R$**, which is expressed in terms of the nearest-neighbor distance R. The factor N/2 represents the pairs of atoms in the crystal.

- The summations for fcc crystal structure have been evaluated, which are

$$\sum_j \left(\frac{1}{p_{ij}}\right)^{12} = 12.13188, \qquad \sum_j \left(\frac{1}{p_{ij}}\right)^{6} = 14.45392.$$

Cohesive Energy

At equilibrium, U_{tot} is minimum with respect to variations in the nearest-neighbor distance R:

$$\frac{dU_{\mathrm{tot}}}{dR} = 0 = -2N\epsilon\left[(12)(12.13)\frac{\sigma^{12}}{R^{13}} - (6)(14.45)\frac{\sigma^{6}}{R^{7}}\right] ,$$

whence

$$R_0/\sigma = 1.09 ,$$

	Ne	Ar	Kr	Xe
R_0/σ	1.14	1.11	1.10	1.09

The agreement is remarkable.

The slight departure of R_0/σ for the lighter atoms from the universal value 1.09 predicted for inert gases can be explained by zero-point quantum effect.

Cohesive Energy

Using the value of $R_0/\sigma = 1.09$ in the equation of U_{tot}, we get

$$U_{tot}(R) = 2N\epsilon\left[(12.13)\left(\frac{\sigma}{R}\right)^{12} - (14.45)\left(\frac{\sigma}{R}\right)^{6}\right] ,$$

and, at $R = R_0$,

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

This is the calculated cohesive energy when the atoms are at rest/equilibrium position.

Quantum-mechanical corrections reduce the binding energy by 28, 10, 6, and 4 percent for Ne, Ar, Kr, and Xe, respectively.

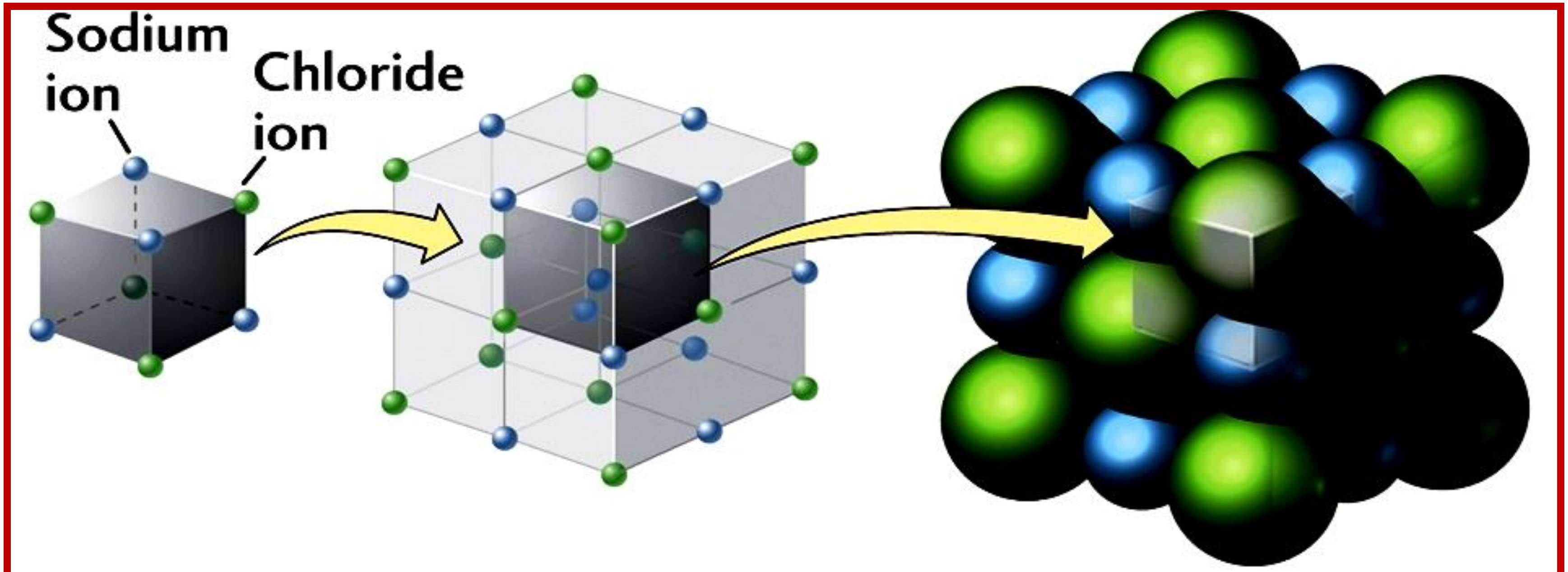
The heavier the atom, the smaller the quantum correction.

Ionic Bonding

Example: NaCl

$$\mathrm{Na}\ (1s^2 2s^2 2p^6 3s^1) \longrightarrow \mathrm{Na}^+\ (1s^2 2s^2 2p^6) + e^-$$

$$\mathrm{Cl}\ (1s^2 2s^2 2p^6 3s^2 3p^5) + e^- \longrightarrow \mathrm{Cl}^-\ (1s^2 2s^2 2p^6 3s^2 3p^6)$$



Ionic Crystals

Electrostatic or Madelung Energy

The long-range interaction between ions with charge ±q is the electrostatic interaction $\pm q^2/r$, attractive between ions of opposite charges and repulsive between the ions of same charge. For SI units multiply the Coulomb interaction energy by $\frac{1}{4\pi\epsilon_0}$.

The main contribution to the binding energy of ionic crystals is electrostatic and is called ***Madelung Energy***.

There are still van der Waal forces but they play much smaller part in the ionic crystals.

Electrostatic or Madelung Energy

If U_{ij} is the interaction between ions i and j, we define the sum U_i which includes all interactions involving the ion i:

$$U_i = \sum_j U_{ij}$$

Where the summation includes all ions except j = i.

The strong short-range core-core repulsive energy is due to the **Pauli principle** and is represented by exponential. Thus the interaction between two atoms i and j in a lattice is given by:

$$U_{ij} = \lambda e^{-r_{ij}/\rho} \pm q^2 / r_{ij}$$

Here the strength energy λ and the range of repulsive interaction ρ are treated as constants to be determined from observed values of compressibility and lattice constant. The constant ρ is typically ~ $0.1R_o$ (this is a very-short range interaction), and R_o is the equilibrium distance.

Electrostatic or Madelung Energy

We can write the total energy of the ionic crystal composed of N molecules or 2N ions as $U_{total} = N\,U_i$.

Here N, rather than 2N, occurs because we must count each *pair* of interactions only once or each bond only once.

The total lattice energy is defined as the energy required to decompose the crystal into individual ions at infinite distance.

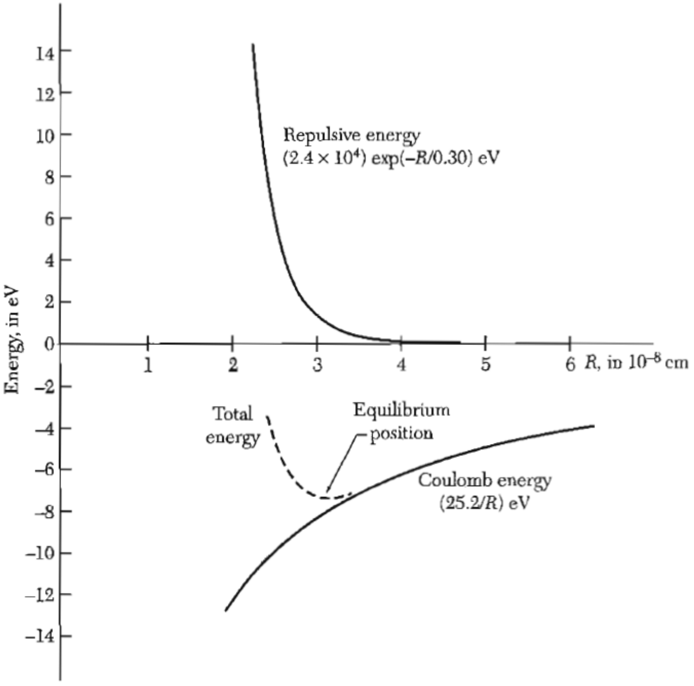


Figure 10 Energy per molecule of KCl crystal, showing Madelung (coulomb) and repulsive contributions.

Electrostatic or Madelung Energy

It is convenient to introduce quantity p_{ij}, such that $r_{ij} = p_{ij} R$, where R is the nearest neighbor distance in the crystal. If we include repulsive energy only among the nearest neighbors, then

$$U_{ij} = \begin{cases} \lambda e^{-R/\rho} - q^2 / p_{ij} R & \textit{Nearest neighbors} \\ \pm \dfrac{1}{p_{ij}} \dfrac{q^2}{R} & \textit{otherwise} \end{cases}$$

The total lattice energy is:

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

Where ***z*** is the number of nearest neighbors of any ion, and

$$\alpha = \sum_j \frac{(\pm)}{p_{ij}}$$ = ***Madelung constant***

Electrostatic or Madelung Energy

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

At the equilibrium the energy is minimum with respect to the separation between the ions i.e. $dU/dR = 0$.

$$-\frac{z\lambda}{\rho} e^{-R_o/\rho} + \frac{\alpha q^2}{R_o^2} = 0 \quad \rightarrow \quad z\lambda e^{-R_0/\rho} = \frac{\alpha\rho q^2}{R_0^2}$$

By substituting this value of $z\lambda e^{-R_0/\rho}$, the cohesive energy per atom of the ionic solid can be written as follows:

$$U_o = \frac{\alpha N\rho q^2}{R_o^2} - \frac{\alpha N q^2}{R_o} = -\frac{\alpha N q^2}{R_o}\left(1 - \frac{\rho}{R_o}\right)$$

The term $-\frac{N\alpha q^2}{R_0}$ is the Madelung energy.

Evaluation of the Madelung Constant

$$\alpha = \sum_{j} \frac{(\pm)}{p_{ij}}$$

The value of the Madelung constant is of central importance in ionic crystals.

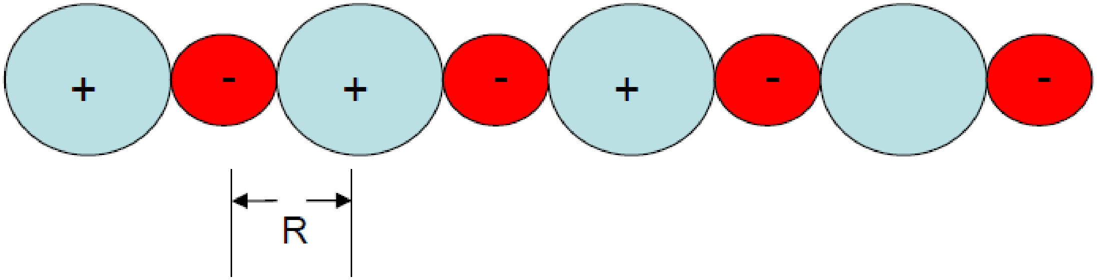
The Madelung Constant is specific to the crystal type (unit cell), but independent of interionic distances or ionic charges.

In general it is not possible to compute the Madelung constant analytically. A powerful method for calculation of lattice sums was developed by Ewald, which is called *Ewald summation.*

This method is described in the appendix B in the text and can be used for the numerical evaluation of the Madelung constants in solids.

Evaluation of the Madelung Constant

As an example, let’s look at an infinite chain of ions of alternating sign:



We can pick a negative ion as a reference ion:

$$U_{ij} = \sum_j \pm \frac{1}{p_{ij}} \frac{q^2}{R} = \alpha \frac{q^2}{R} \qquad \alpha = \sum_j \frac{(\pm)}{p_{ij}}$$

$$\alpha = \sum_j \frac{\pm}{p_{ij}} = -2\left(\frac{1}{1} - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \ \dots\right)$$

2 is because there are two ions at the same distance from the reference ion, one to the right and one to the left

Evaluation of the Madelung Constant

$$\alpha = \sum_{j} \frac{\pm}{p_{ij}} = -2\left(\frac{1}{1} - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \ \ldots\right)$$

This is an infinite series and it is conditionally convergent! This means the order of the terms in the sum matters!

$$\ln(1 + x) = x - x^2/2 + x^3/3 - x^4/4 + \cdots$$

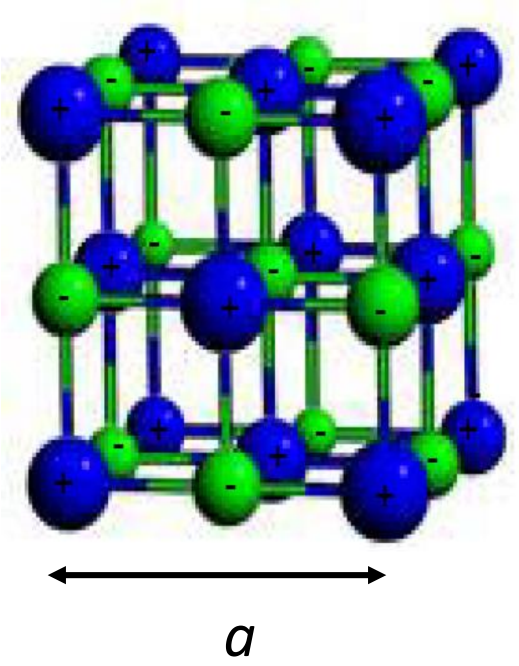
For $x = 1$, both series are the same.

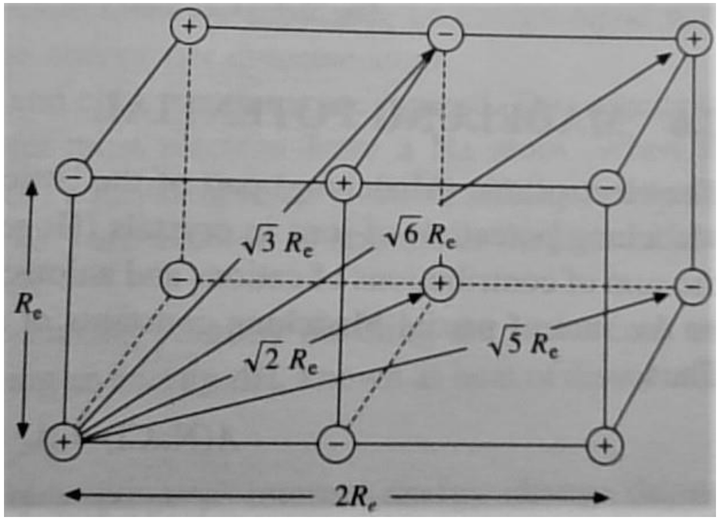
$$\alpha = -2\ln(1+1) = -2\ln(2)$$

In 3D, the sums become much more difficult. In order to converge at some reasonable rate, the positive and negative terms must nearly cancel.

Evaluation of the Madelung Constant

In NaCl, let’s choose Na$^+$ as our central atom and count the neighbors and their distance from the Na$^+$ ion

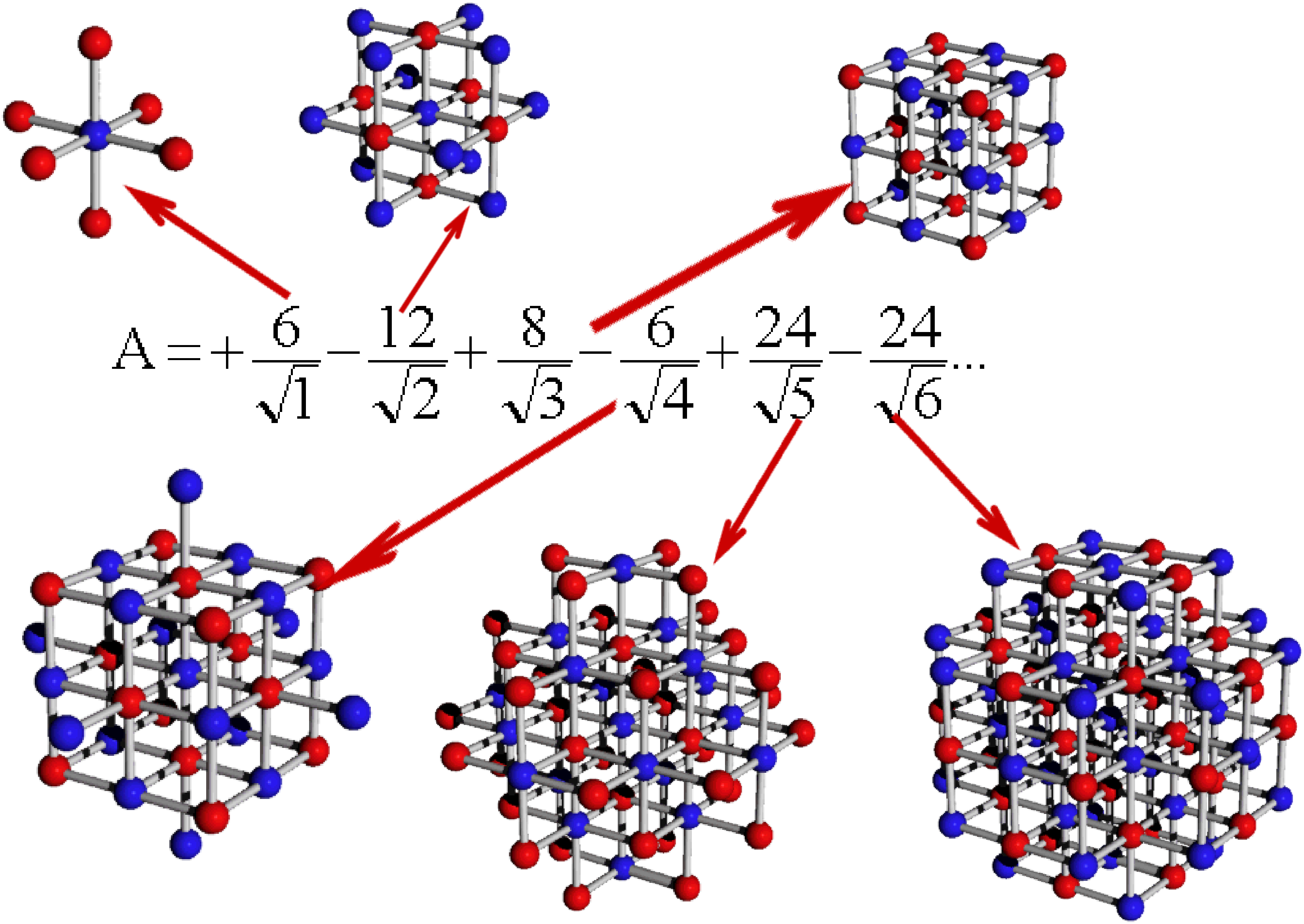




The attractive potential is:

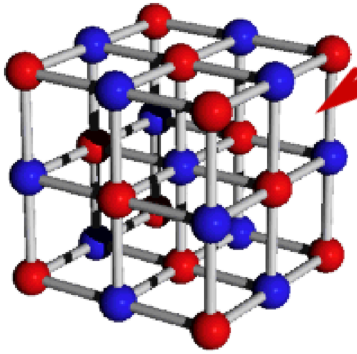
$$U = -\frac{q^2}{R_e}\left(\overbrace{\frac{6}{\sqrt{1}} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \ \dots}^{\text{Madelung constant}}\right)$$

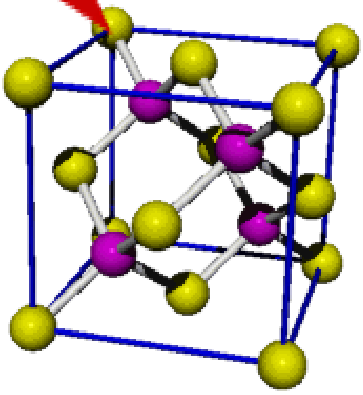
Origin of the Madelung Constant

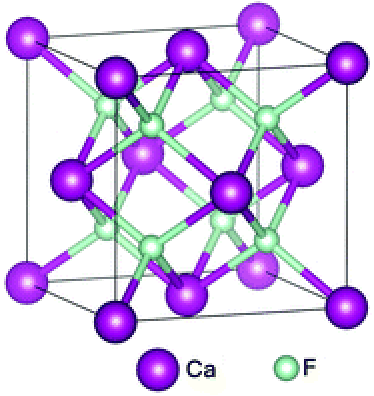


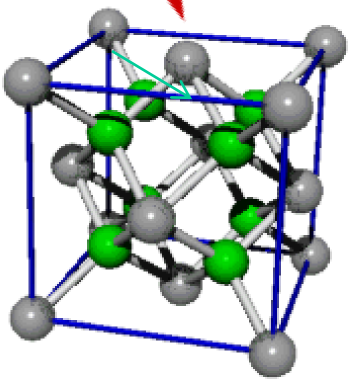
$$A = +\frac{6}{\sqrt{1}} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \frac{24}{\sqrt{5}} - \frac{24}{\sqrt{6}} \ldots$$

Crystal Structure	Madelung Constant
NaCl	1.748
CsCl	1.763
Zinc blende	1.638
Wurtzite	1.641
Fluorite	2.519
Rutile	2.408









- **Covalent Bonding**
- **Metallic Bonding**
- **Hydrogen bonds**
- **Atomic radii**

Covalent Bonding

- In a covalent bond, atoms share electrons so that both can assume states with a stable number of valence electrons.

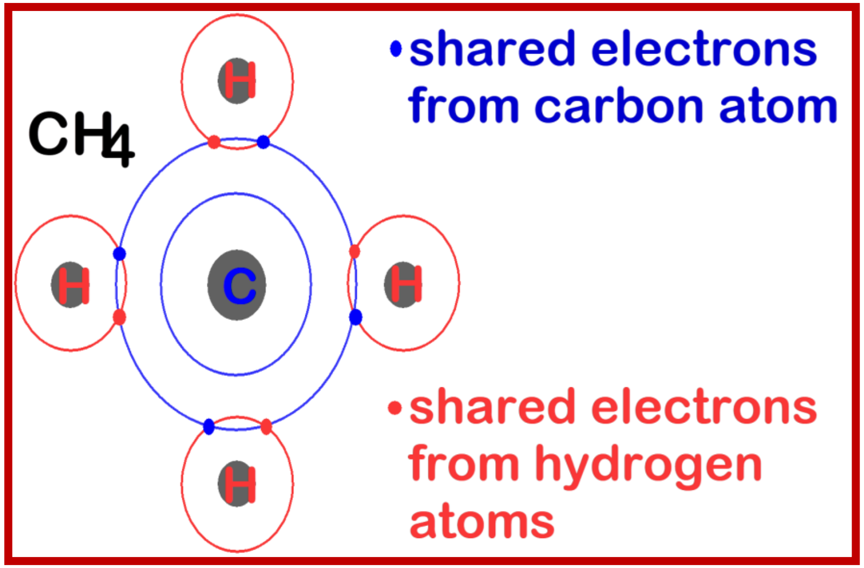
- Requires ***shared electrons***

Example: CH_4 :

C: has 4 valence e^-, needs 4 more

H: has 1 valence e^-, needs 1 more

Their electronegativities are comparable.



This is the primary bonding mechanism in many materials.

- Consider **2** close **Cl** atoms. Each has electronic shells

$$= 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$$

- If they move close until their outer orbitals overlap, the atoms can share **2 e^-** & "fill" the remaining **3p** shell of each **Cl**.
- The electronic energy there is lowered, which causes the orbitals to stay overlapped; resulting in a strong bond in **Cl_2** .

This is the covalent or shared electron bond.

- **Covalent Bonds** There is a “tug of war” for the electrons. There can be single, double & triple covalent bonds:

- **Single bond** – a bond in which 2 atoms share a pair of electrons.

- **Double bond** – bond that involves 2 shared pairs of e-.

- **Triple bond** – bond that involves 3 shared pairs of e-

- Combinations of atoms of non-metallic atoms are likely to form covalent bonds.

- Groups 4A, 5A, 6A, and 7A

- Summarized by G. Lewis in the ***octet rule*** sharing of e- occurs if atoms achieve noble gas configuration.

- H_2 is an exception to this rule.

Column (Group) Trends

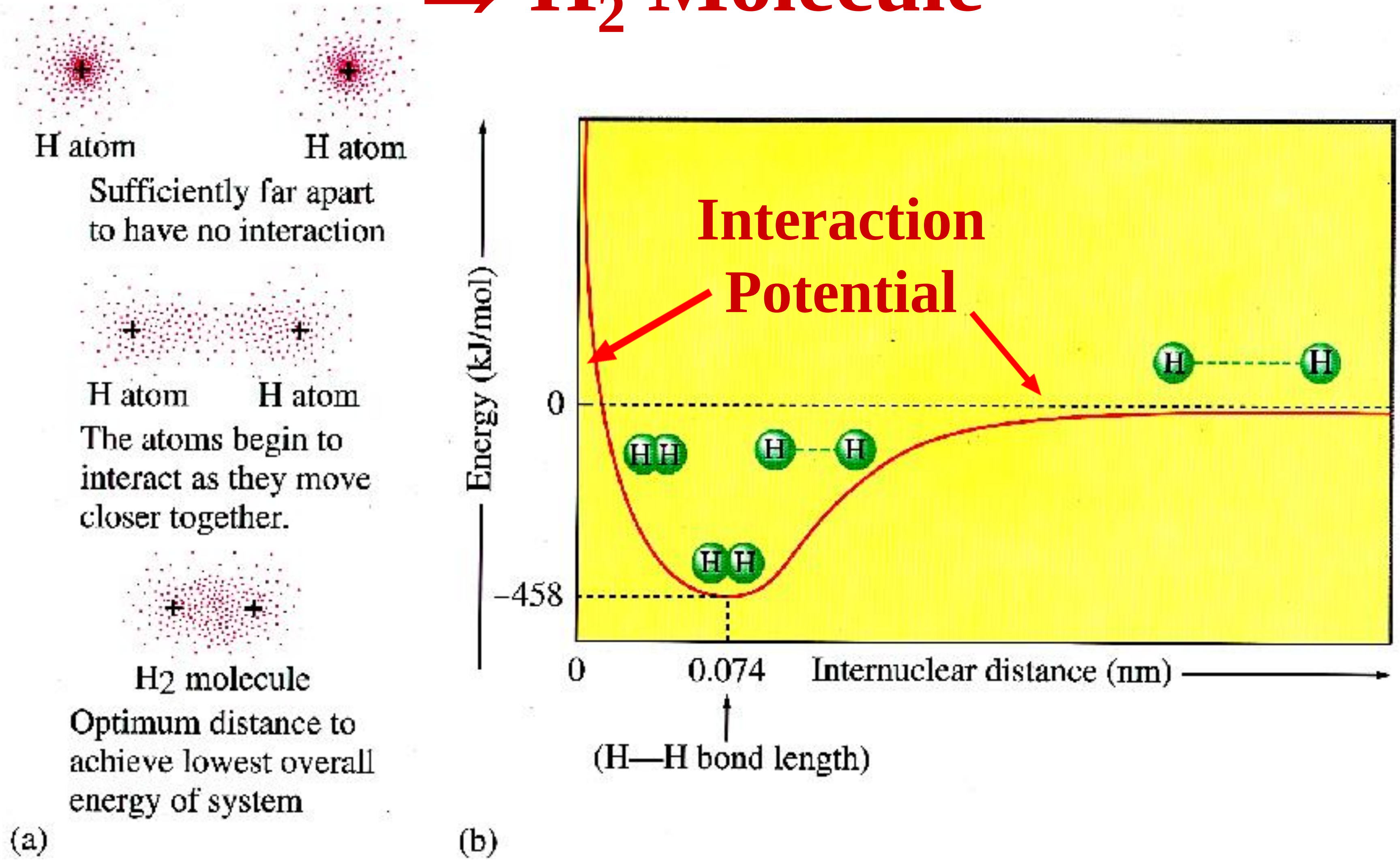
- **Halogens** form single covalent bonds in their diatomic molecules (ex: F – F).

- **Chalcogens** form double covalent bonds in their diatomic molecules (ex: O = O).

- **Phicogens/Pnictogens** form triple covalent bonds in their diatomic molecules (N ≡ N).

- The **Carbon group** tends to form 4 bonds with other atoms, (CH_4).

Covalent Bonding of Two H Atoms $\Rightarrow$ H_2 Molecule



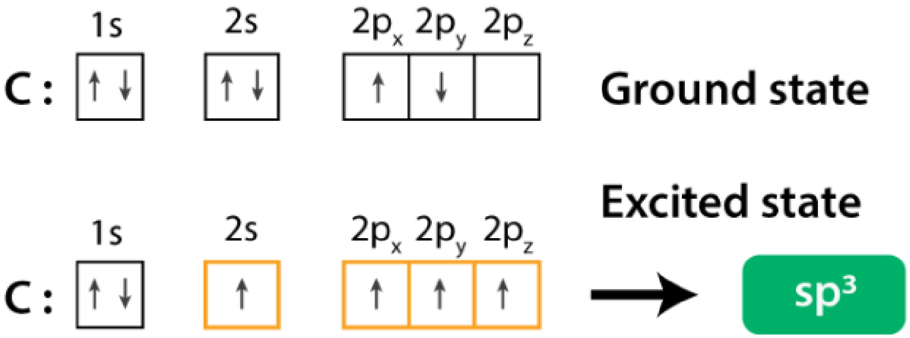
Interaction Potential

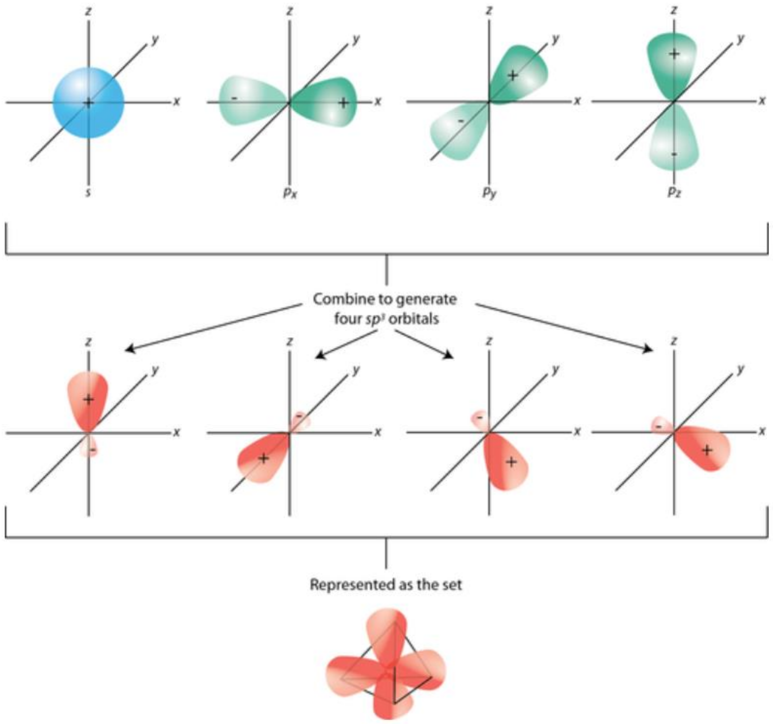
Bond Polarity

- Covalent bonds involve the sharing of electrons. However, they can differ in how the bonds are shared. It depends on the kind and number of atoms joined together.
- When electrons are shared equally, a nonpolar covalent bond is formed.
- When the atoms share the electron unequally, a polar covalent bond is formed.
- The more electronegative element will have the stronger electron attraction and will acquire a slightly negative charge.
- The less electronegative element will acquire a slightly positive charge

Hybrid Orbitals

In orbital hybridization, several atomic orbitals mix to form the same total number of equivalent hybrid orbitals. For example, sp^3 hybridization in carbon atom.



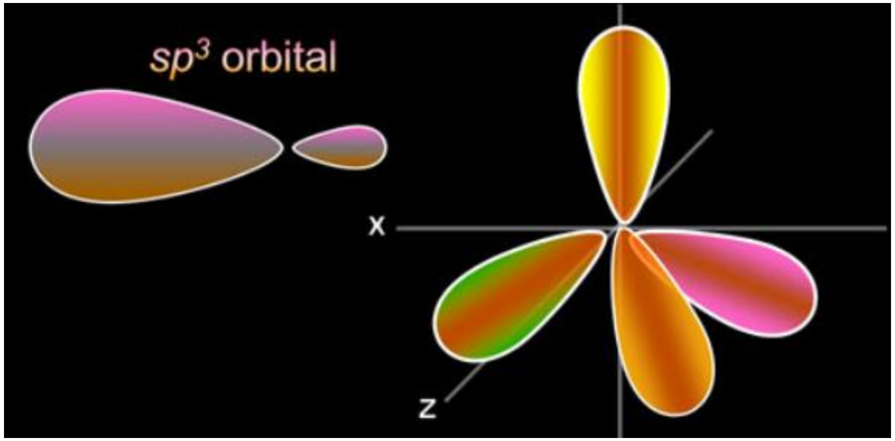


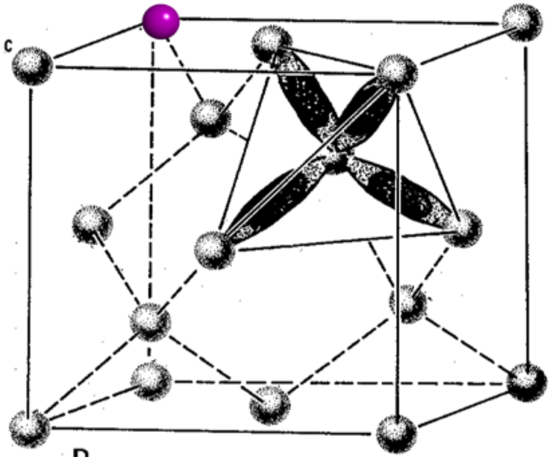
- The **sp^3** orbital is tetrahedrally shaped.

Larger Overlap ⇒ ***Stronger Bond***

Covalent Bonds are Directional

- Each **C** is tetrahedrally coordinated with 4 others (& each of them with 4 others as in the Diamond crystal.





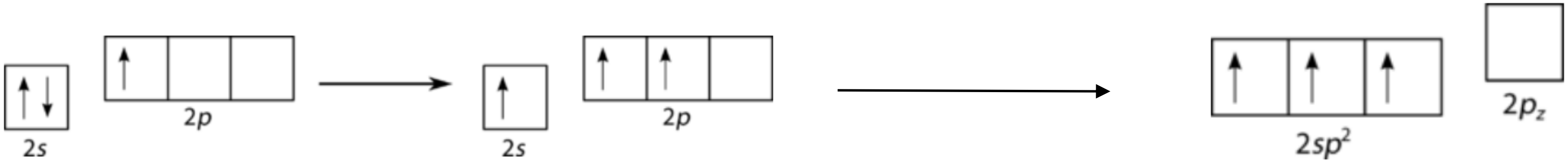
- The **C-C-C** bond angle is fixed at **109^{o} 28**' (max. overlap)
- Note the **Face-Centered Cubic lattice**

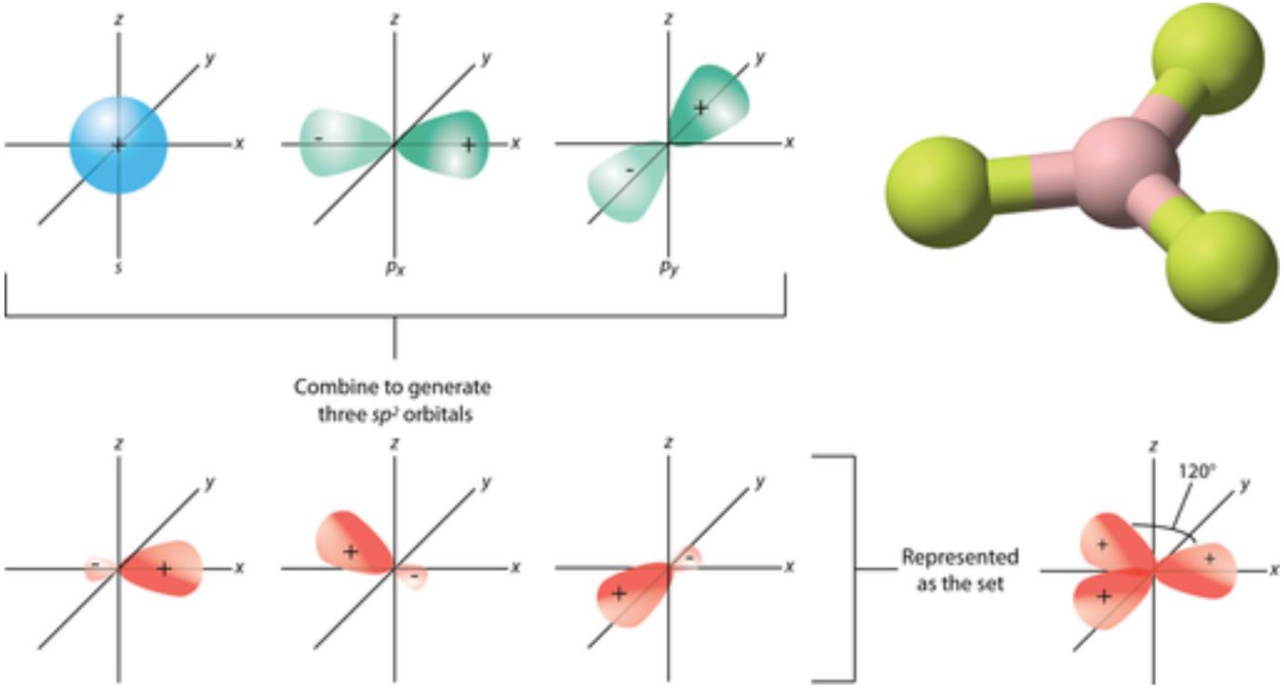
The directional character of the bonds,

⇒ *lower coordination & symmetry, density*

Hybrid Orbitals

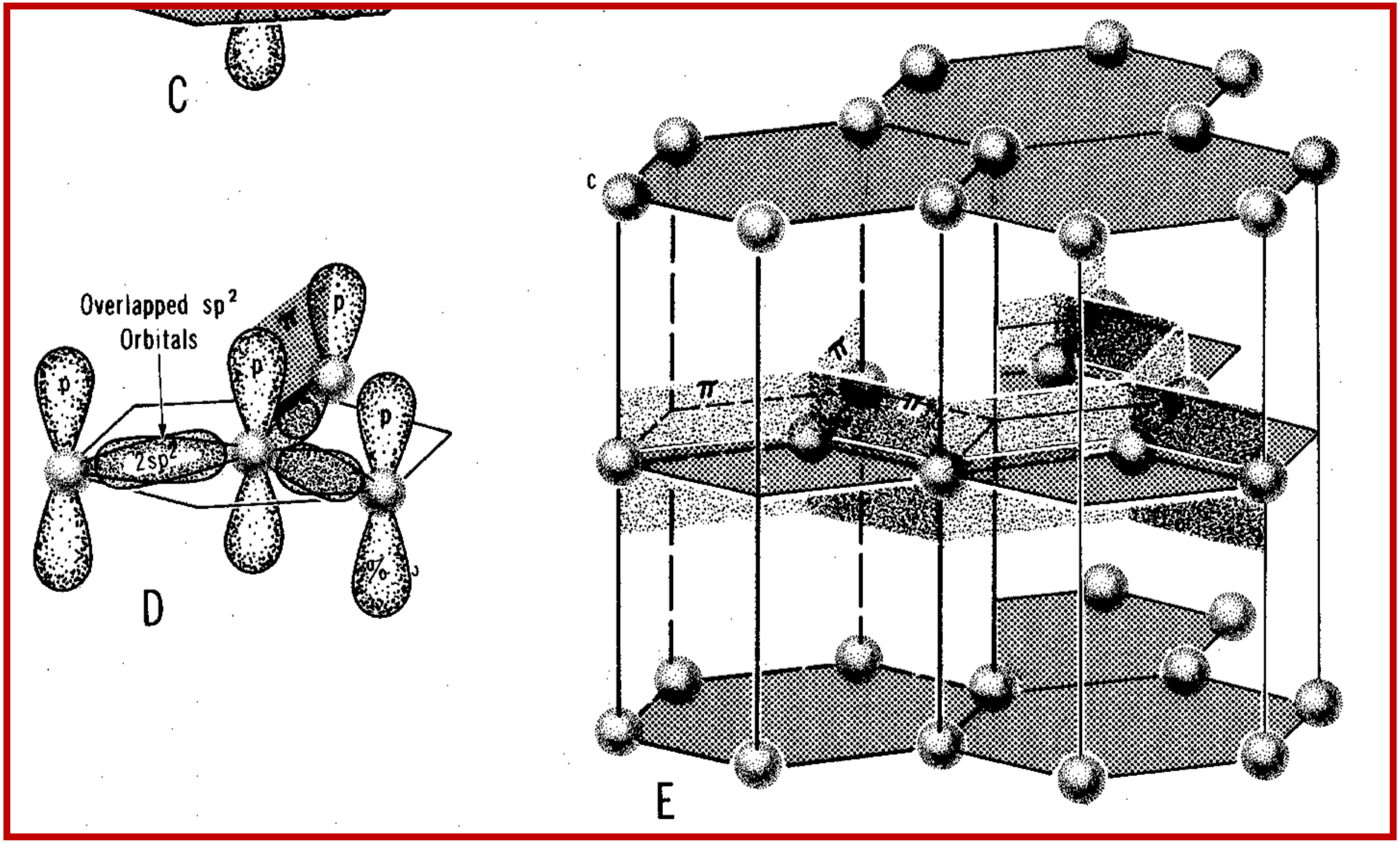
SP^2 hybridization in boron trifluoride (BF_3). The molecule has a trigonal planar geometry. First a paired 2s electron is promoted to the empty 2p$_y$ orbital.





SP^2 Hybridization

Graphite Structure



- The 3 **2(sp^2)** orbitals are coplanar & **120º** apart
- The orbital overlap is similar to that in diamond within the planes (strong too!).

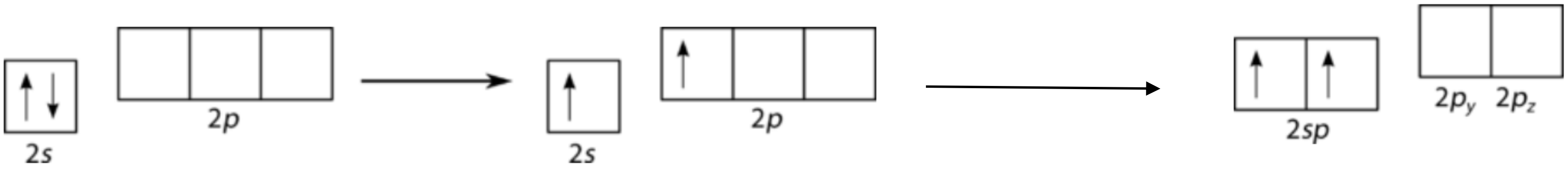
Belongs to the Hexagonal Crystal Class

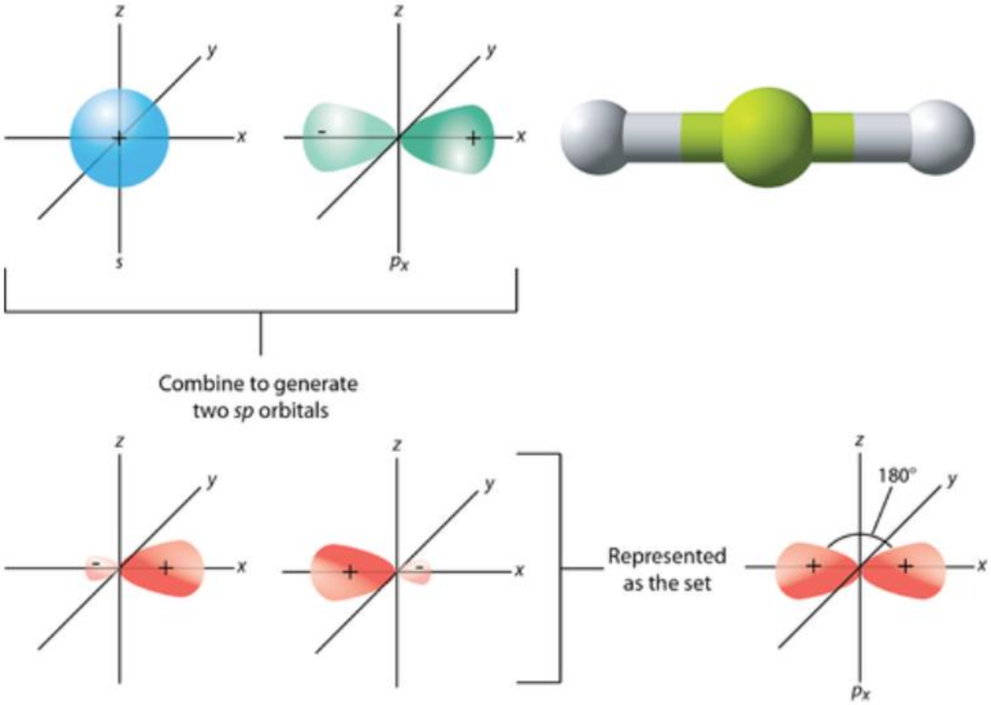
- Note the **p-bonding** between the remaining **2p's.** This results in **delocalized** e^- 's in **2p** orbitals which results in electrical conductivity only within sheets.

- There are other hybrids as well (${sp}^2$ in CuO- planar X) e^- may resonate in bonds of non-identical atoms & give a partial ionic character if one much more electronegative than the other.

Hybrid Orbitals

SP hybridization in beryllium hydride (BeH_2). The beryllium atom contains all paired electrons and so must also undergo hybridization. One of the 2s electrons is first promoted to the empty $2p_x$ orbital.

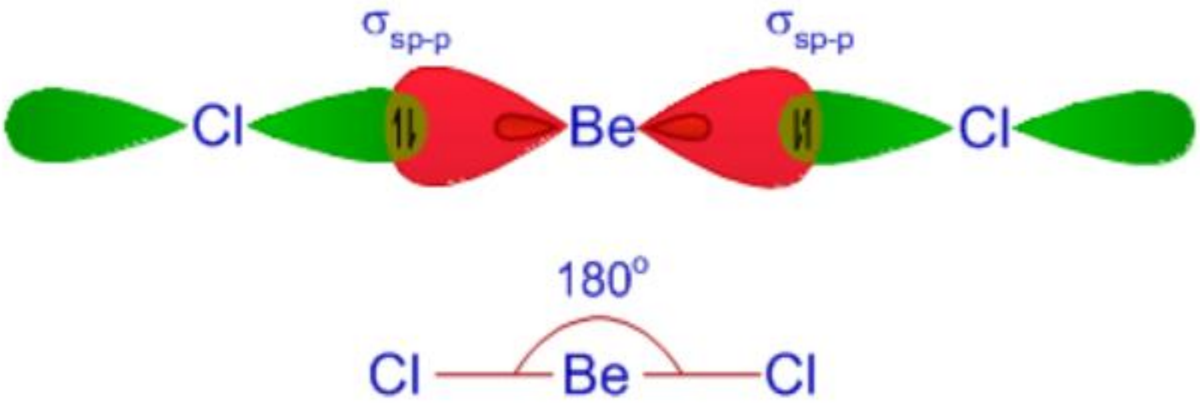




SP Hybridization

The electronic configuration of 'Be' in ground state is $1s^2$ $2s^2$. Since there are no unpaired electrons, it undergoes excitation by promoting one of its 2s electron into empty 2p orbital.

Thus in the excited state, the electronic configuration of Be is $1s^2$ $2s^1$ $2p^1$.

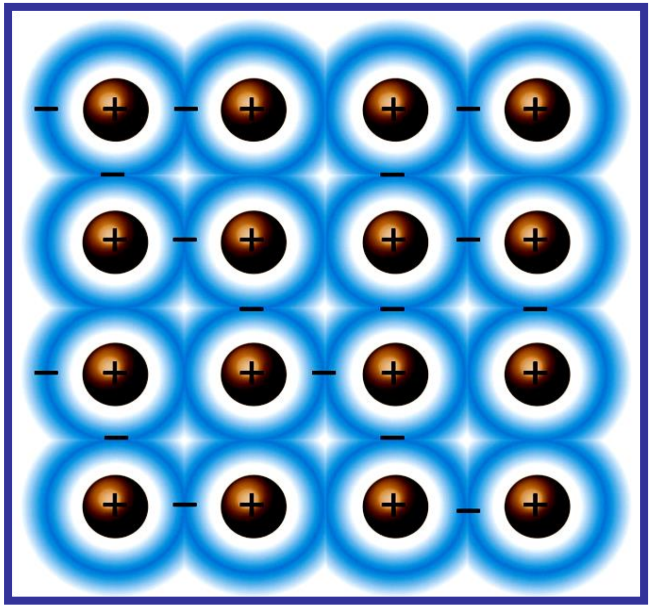


If the beryllium atom forms bonds using these pure orbitals, the molecule might be angular. However the observed shape of BeCl2 is linear. To account for this, sp hybridization was proposed as explained below.

Metallic Bonding

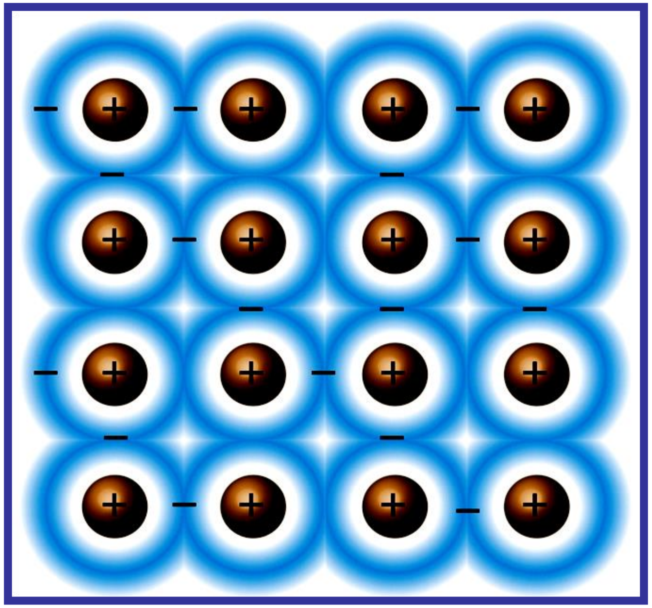
- Metal atoms have 1, 2,or 3 valence electrons that are loosely bound.

- In the solid metal, each atom will “give up” these electrons to all of the other atoms to form a “sea of free electrons”



Metallic Bonding

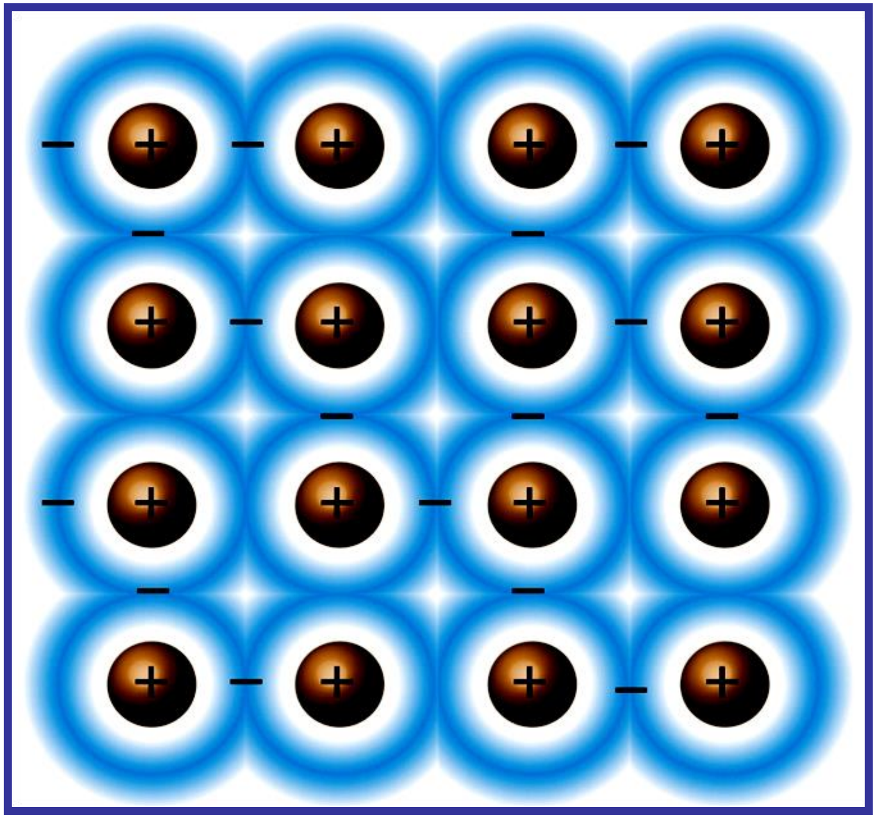
- The structure thus becomes a group of ionized metal atom cores embedded in the “electron sea”. The “free” electrons bind the cores together and shield them from each other.

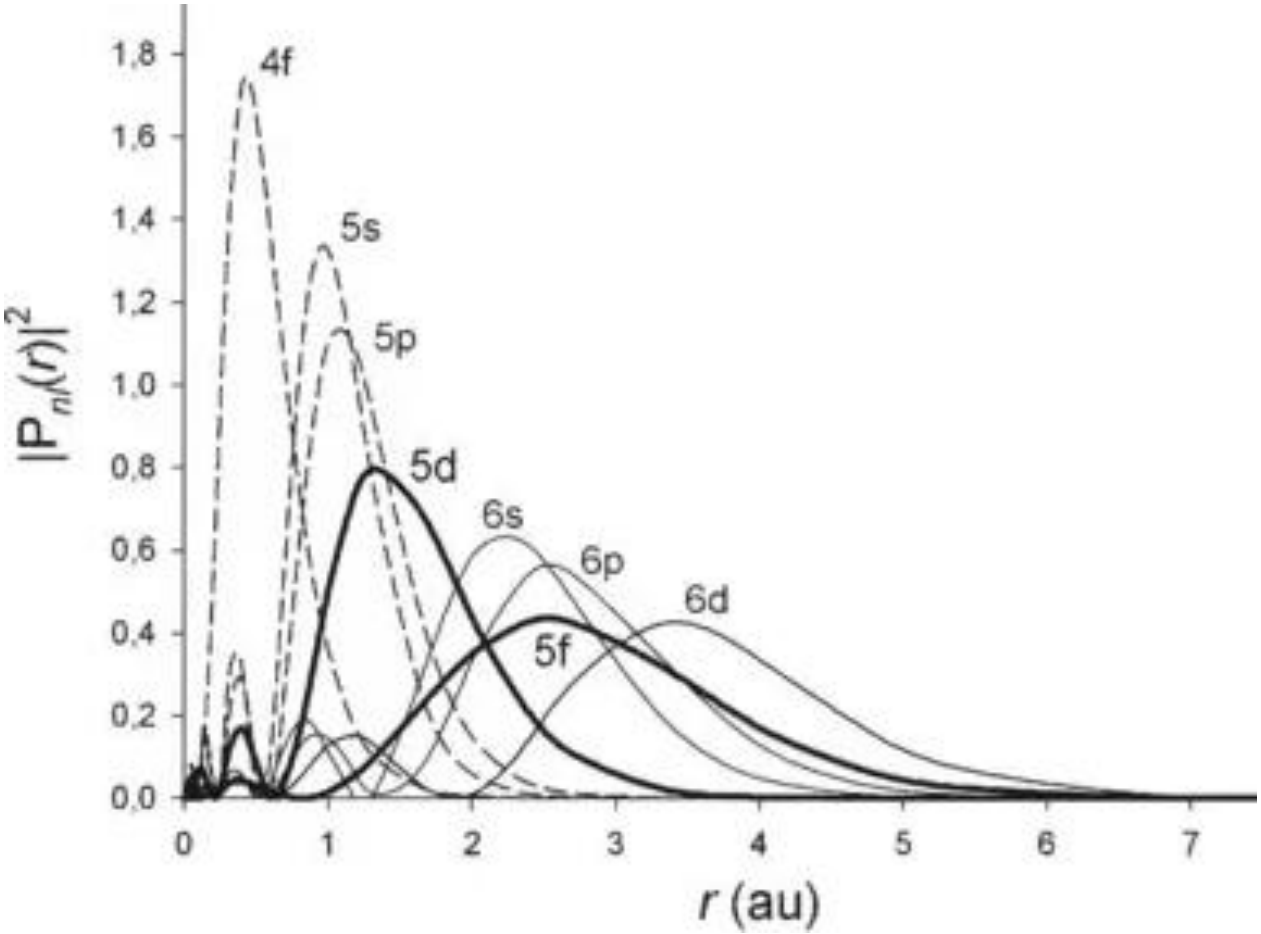


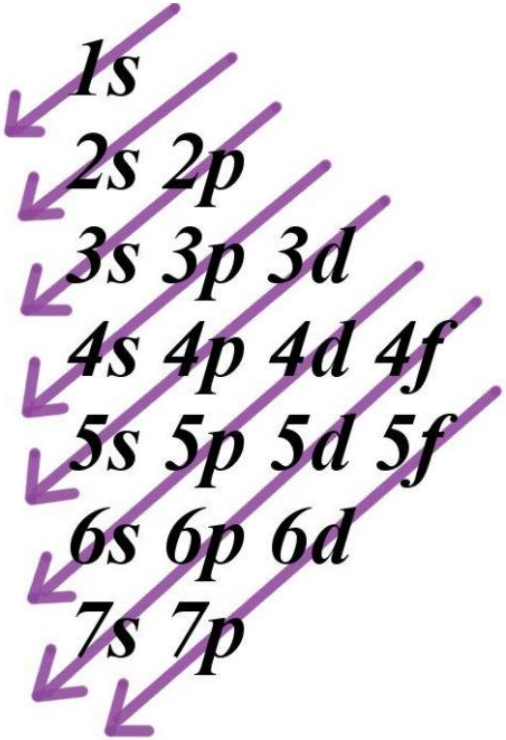
- We’re interested in how this free electron model affect the properties of the metals such as: **Electrical conductivity, Thermal Conductivity, Ductility, Strength, etc.**

Metallic crystals are not covalently bonded, but the attractions between atoms are too strong to be Van der Waals forces. In metals

the valence electrons are delocalized throughout the solid.







1s

2s 2p

3s 3p 3d

4s 4p 4d 4f

5s 5p 5d 5f

6s 6p 6d

7s 7p

Hydrogen Bond

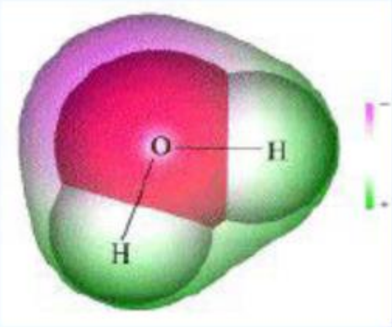
✓ The hydrogen atom loses its electron to an atom in the molecule (covalent); bare ***proton*** forms the ***hydrogen bond*** with another atom.

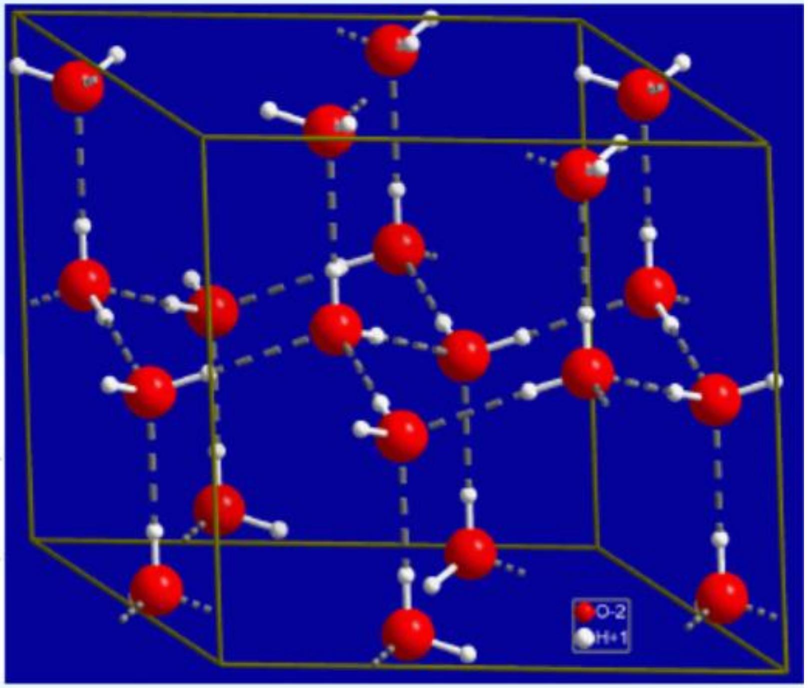
✓ Most ubiquitous and perhaps simplest example of a hydrogen bond is found between ***water*** molecules.

✓ Intermediate strength **~ 0.1 eV**.

surface of negative ions.

Ice Rule: large residual entropy





Atomic Radii

- There is no such thing as rigid spherical boundary for atoms, but the concept is of atomic radius is fruitful in predicting interatomic spacing.

- The electronic configuration of the constituent atoms can be inferred by comparing measured and predicted values of the lattice constants.

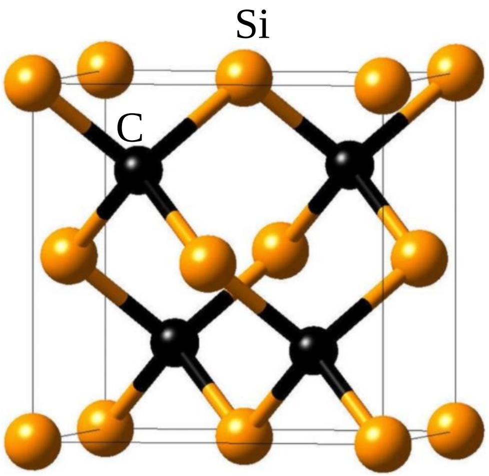
- Lattice constants can be estimated by adding atomic radii of the constituent atoms.

- The interatomic distance between C atoms in diamond is 1.54 Å; one-half of this is 0.77 Å, which is the radius of C in tetrahedral covalent bond.

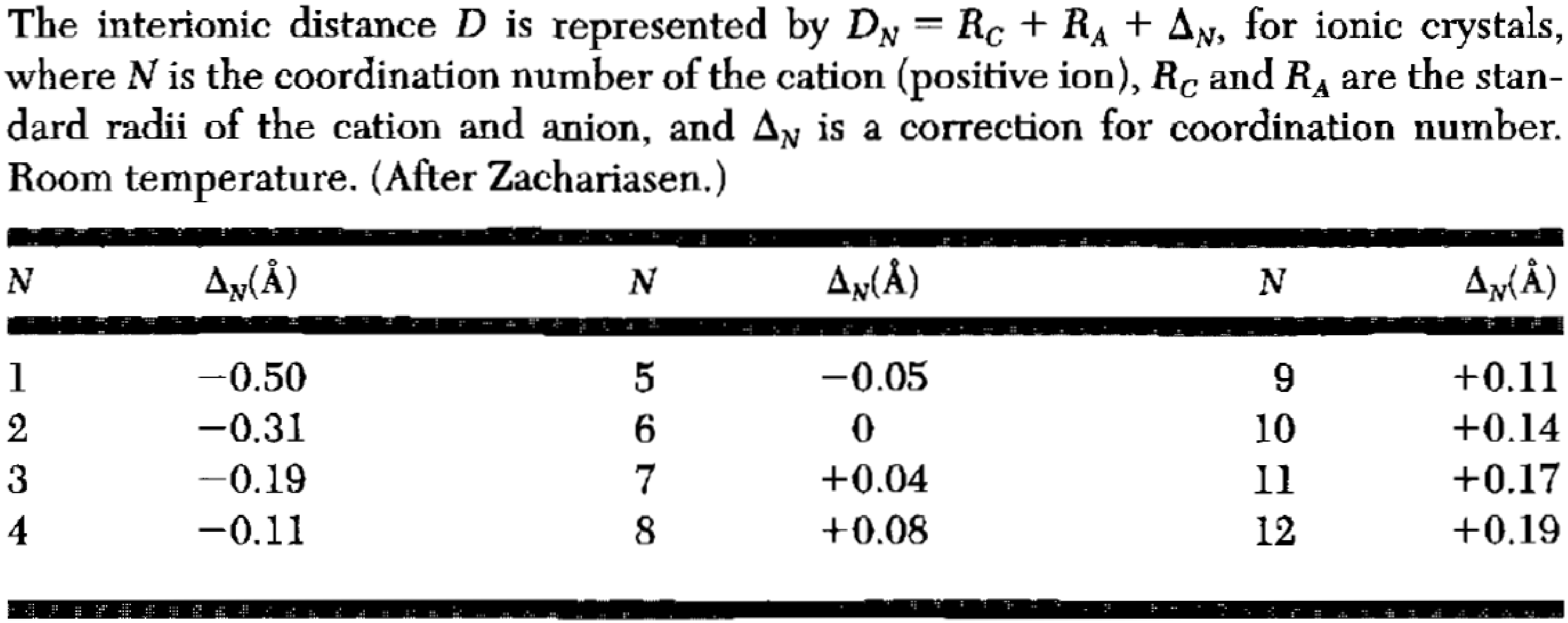
Atomic Radii

- Silicon also has diamond crystal structure, one-half the interatomic distance is 1.17 Å, which is the radius of C in tetrahedral covalent bond.

- In SiC each atom is surrounded by four atoms of the opposite kind. If we add the C and Si radii just given, we predict 1.94 Å for the length of the C-Si bond, in fair agreement with the observed for the bond length of 1.89 Å.



Ionic Crystal Radii



The interionic distance D is represented by $D_N = R_C + R_A + \Delta_N$, for ionic crystals, where N is the coordination number of the cation (positive ion), R_C and R_A are the standard radii of the cation and anion, and Δ_N is a correction for coordination number. Room temperature. (After Zachariasen.)

N	Δ_N(Å)	N	Δ_N(Å)	N	Δ_N(Å)
1	−0.50	5	−0.05	9	+0.11
2	−0.31	6	0	10	+0.14
3	−0.19	7	+0.04	11	+0.17
4	−0.11	8	+0.08	12	+0.19

Ionic Crystal Radii

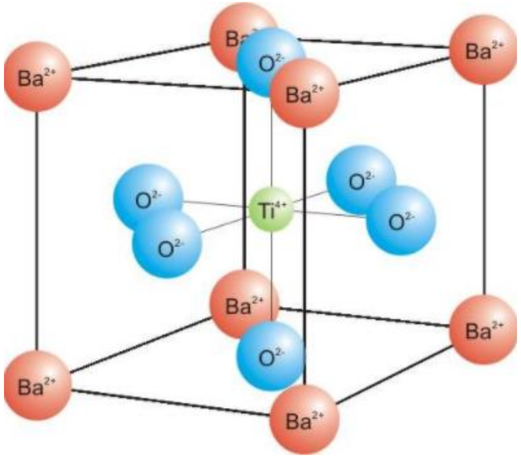
- Consider $BaTiO_3$, with a lattice constant of 4.004 Å at room temperature.

- Each Ba^{++} ion has 12 nearest O^{--} ions, so that the coordination number is 12 and the correction Δ_{12} of Table 10 applies.

- If we suppose that the structure is determined by the Ba-O contacts, we have $D_{12} = 1.35 + 1.40 + 0.19 = 2.94$ Å or a = 4.16 Å.

- If the Ti-O contact determines the structure, we have D, = 0.68 + 1.40 = 2.08 Å or a = 4.16 Å.

- The actual lattice constant of 4.004 Å is somewhat smaller than the estimates and may perhaps suggest that the bonding is not purely ionic, but is partly covalent.



- **Analysis of elastic strains**
- **Elastic compliance and stiffness constants**
- **Elastic Energy Density**
- **Elastic waves in cubic crystals**

- **What is the difference between stress and strain?**

- **What is tensile strain and Young’s modulus?**

- **What is bulk modulus?**

- **What is shear modulus?**

Analysis of Elastic Strains

- We consider the elastic properties of a crystal viewed as a homogeneous continuous medium rather than as a periodic array of atoms. The continuum approximation is usually valid for elastic waves of wavelengths longer than $10^{-6}cm$, which means for frequencies below 10^{11} or 10^{12} Hz**.**

- Here we will be discussing **Hooke's law** ($\boldsymbol{F = -kx}$) and **Newton's second law** ($\boldsymbol{F = ma}$) and treat infinitesimal strains only $\Delta x <<$.

- We shall not distinguish in our notation between isothermal (constant temperature) and adiabatic (constant entropy) deformations. The small differences between the isothermal and adiabatic elastic constants are not often of importance at room temperature and below.

Analysis of Elastic Strains

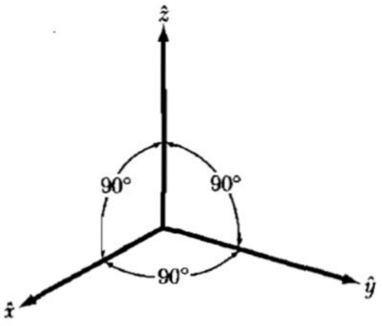
After a small uniform deformation of a solid, the axes are distorted in orientation and in length. The old axes $\hat{x}$, $\hat{y}$, $\hat{z}$ and the new axes $\boldsymbol{x}'$, $\boldsymbol{y}'$, $\boldsymbol{z}'$ are related by the following equations.

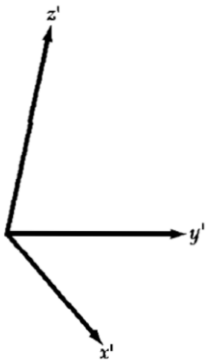
$$\boldsymbol{x}' = (1+\epsilon_{xx})\hat{x} + \epsilon_{xy}\ \hat{y}+\epsilon_{xz}\ \hat{z}$$

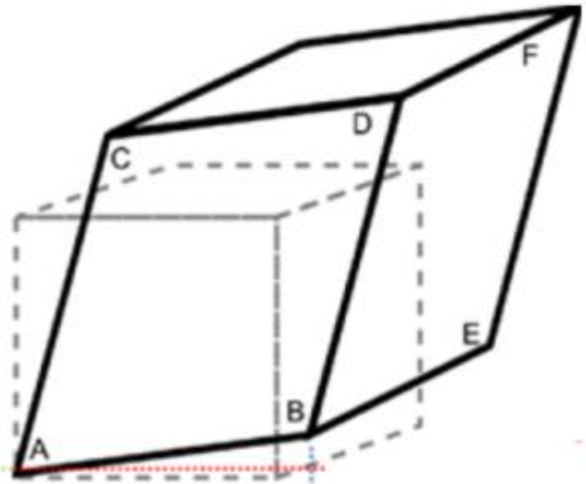
$$\boldsymbol{y}' = \epsilon_{yx}\ \hat{x} + (1+\epsilon_{yy})\hat{y}+\epsilon_{yz}\ \hat{z}$$

$$\boldsymbol{z}' = \epsilon_{zx}\ \hat{x}+\epsilon_{zy}\ \hat{y} + (1+\epsilon_{zz})\hat{z}$$

The coefficients $\epsilon_{\alpha\beta}$ (strain) define the deformation; they are dimensionless and have values $\ll 1$ if the strain is small.







Analysis of Elastic Strains

The original axes were of unit length, but the new axes will not necessarily be of unit length.

$$\boldsymbol{x}'.\boldsymbol{x}' = 1 + 2 \in_{xx} + \in_{xx}^2 + \in_{xy}^2 + \in_{xz}^2$$

With this deformation, an atom located at $\boldsymbol{r} = x\hat{x} + \mathrm{y}\hat{y} + z\hat{z}$ has moved to $\boldsymbol{r}' = x\boldsymbol{x}' + \mathrm{y}\boldsymbol{y}' + \mathrm{z}\boldsymbol{z}'$, so the displacement R is defined by

$$\boldsymbol{R} = \boldsymbol{r}' - \boldsymbol{r} = x(\boldsymbol{x}' - \hat{x}) + y(\boldsymbol{y}' - \hat{y}) + z(\boldsymbol{z}' - \hat{z})$$

$$\begin{aligned}\boldsymbol{R} = \boldsymbol{r}' - \boldsymbol{r} = &\left(x \in_{xx} + y \in_{yx} + z \in_{zx}\right)\hat{x} \\ &+\left(x \in_{xy} + y \in_{yy} + z \in_{zy}\right)\hat{y} \\ &+\left(x \in_{xz} + y \in_{yz} + z \in_{zz}\right)\hat{z}\end{aligned}$$

$$\boldsymbol{R} = \boldsymbol{r}' - \boldsymbol{r} = u(r)\hat{x} + v(r)\hat{y} + w(r)\hat{z}$$

$$x \in_{xx} = x\frac{\partial u}{\partial x} \qquad y \in_{yx} = y\frac{\partial u}{\partial y} \qquad \text{etc.}$$

Analysis of Elastic Strains

It is usual to work with coefficients $e_{\alpha\beta}$ rather than $\in_{\alpha\beta}$.

$$e_{xx} \equiv \in_{xx} = \frac{\partial u}{\partial x} \qquad e_{yy} \equiv \in_{yy} = \frac{\partial v}{\partial y} \qquad e_{zz} \equiv \in_{zz} = \frac{\partial w}{\partial z}$$

$$e_{xy} \equiv \mathbf{x}' \cdot \mathbf{y}' \cong \epsilon_{yx} + \epsilon_{xy} = \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x}$$

$$e_{yz} \equiv \mathbf{y}' \cdot \mathbf{z}' \cong \epsilon_{zy} + \epsilon_{yz} = \frac{\partial v}{\partial z} + \frac{\partial w}{\partial y}$$

$$e_{zx} \equiv \mathbf{z}' \cdot \mathbf{x}' \cong \epsilon_{zx} + \epsilon_{xz} = \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x}$$

The $\in_{\alpha\beta}^2$ terms and higher order terms are negligibly small because we are considering only **infinitesimal strains**.

The above six dimensionless coefficients completely define the strain.

Dilation

The fractional increase of volume associated with a deformation is called the dilation. Volume after the deformation is

$$\boldsymbol{V'} = xyz\,(\boldsymbol{x'}.\,\boldsymbol{y'} \times \boldsymbol{z'})$$

$$xyz\begin{vmatrix} 1+\in_{xx} & \in_{xy} & \in_{xz} \\ \in_{yx} & 1+\in_{yy} & \in_{yz} \\ \in_{zx} & \in_{zy} & 1+\in_{zz} \end{vmatrix} \cong xyz\left(1 + e_{xx} + e_{yy} + e_{zz}\right)$$

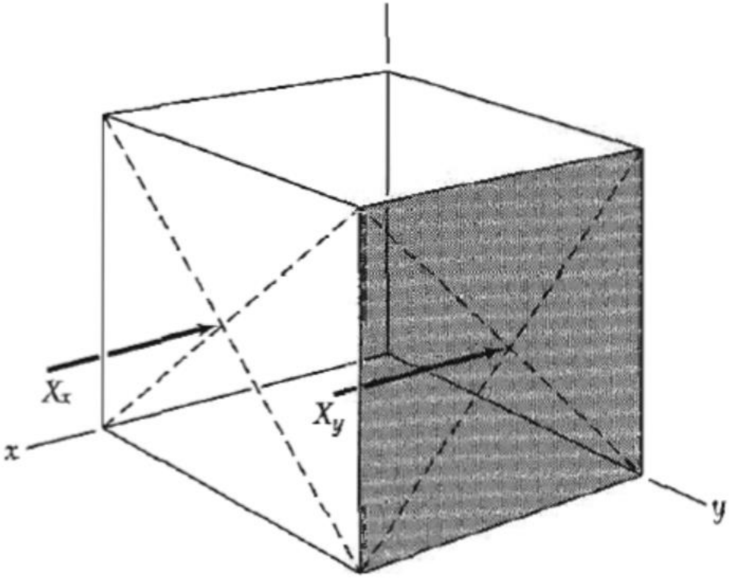
The $e_{\alpha\beta}^2$ terms neglected. The dilation δ is then given by

$$\delta = \frac{V' - V}{V} = \frac{xyz\left(e_{xx} + e_{yy} + e_{zz}\right)}{xyz} \cong e_{xx} + e_{yy} + e_{zz}$$

The δ represents strain.

Stress Components

- The force acting on a unit area in the solid is defined as the stress. It has dimensions of force/area or energy/volume.



- There are nine stress components: X_x, X_y, X_z, Y_x, Y_y, Y_z, Z_x, Z_y, Z_z.

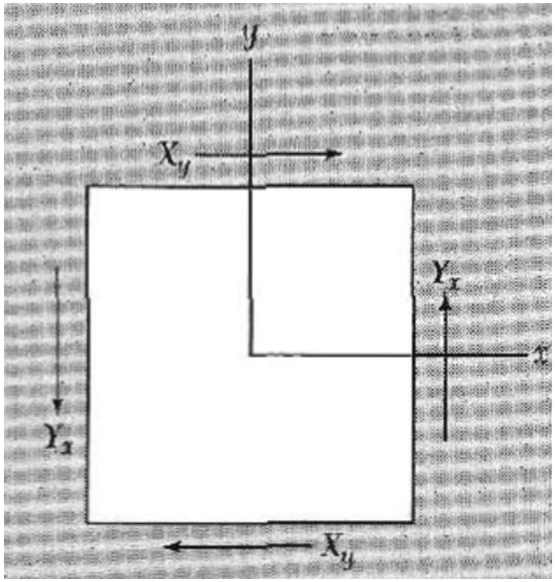
- All forces are equal in magnitude.

- The capital letter indicates the direction of the force, and the subscript indicates the normal to the plane to which the force is applied.

- Stress component X_y represents a force applied in the x-direction on a surface whose normal is in the y direction.

Stress Components

In static equilibrium, the following stresses are equivalent for a cubic symmetry and the torques produced by these forces also vanishes.



$$X_y = Y_x; \qquad Y_z = Z_y; \qquad Z_x = X_z$$

The cubic symmetry reduces the number of independent stress components from 9 to 6.

$$X_x, \qquad X_y, \qquad Y_y, \qquad Y_z, \qquad Z_x, \qquad Z_z$$

Associated with these 6 stresses, there are 6 independent stain components.

Elastic Compliance and Stiffness Constants

Hook’s law states that for sufficiently small deformation the strain is directly proportional to the stress; that is, the strain components are linear functions of the stress components.

Elastic modulus

$$\frac{F}{A_o} = E\,\frac{\Delta L}{L_o}$$

$$
\begin{aligned}
X_x &= C_{11}e_{xx} + C_{12}e_{yy} + C_{13}e_{zz} + C_{14}e_{yz} + C_{15}e_{zx} + C_{16}e_{xy}\\
Y_y &= C_{21}e_{xx} + C_{22}e_{yy} + C_{23}e_{zz} + C_{24}e_{yz} + C_{25}e_{zx} + C_{26}e_{xy}\\
Z_z &= C_{31}e_{xx} + C_{32}e_{yy} + C_{33}e_{zz} + C_{34}e_{yz} + C_{35}e_{zx} + C_{36}e_{xy}\\
Y_z &= C_{41}e_{xx} + C_{42}e_{yy} + C_{43}e_{zz} + C_{44}e_{yz} + C_{45}e_{zx} + C_{46}e_{xy}\\
Z_x &= C_{51}e_{xx} + C_{52}e_{yy} + C_{53}e_{zz} + C_{54}e_{yz} + C_{55}e_{zx} + C_{56}e_{xy}\\
X_y &= C_{61}e_{xx} + C_{62}e_{yy} + C_{63}e_{zz} + C_{64}e_{yz} + C_{65}e_{zx} + C_{66}e_{xy}
\end{aligned}
$$

C’s are called the elastic stiffness constants or moduli of elasticity and have dimensions of force/area.

$$1 \equiv xx\ ;\quad 2 \equiv yy\ ;\quad 3 \equiv zz\ ;\quad 4 \equiv yz\ ;\quad 5 \equiv zx\ ;\quad 6 \equiv xy$$

$$
\begin{aligned}
e_{xx} &= S_{11}X_x + S_{12}Y_y + S_{13}Z_z + S_{14}Y_z + S_{15}Z_x + S_{16}X_y\\
e_{yy} &= S_{21}X_x + S_{22}Y_y + S_{23}Z_z + S_{24}Y_z + S_{25}Z_x + S_{26}X_y\\
e_{zz} &= S_{31}X_x + S_{32}Y_y + S_{33}Z_z + S_{34}Y_z + S_{35}Z_x + S_{36}X_y\\
e_{yz} &= S_{41}X_x + S_{42}Y_y + S_{43}Z_z + S_{44}Y_z + S_{45}Z_x + S_{46}X_y\\
e_{zx} &= S_{51}X_x + S_{52}Y_y + S_{53}Z_z + S_{54}Y_z + S_{55}Z_x + S_{56}X_y\\
e_{xy} &= S_{61}X_x + S_{62}Y_y + S_{63}Z_z + S_{64}Y_z + S_{65}Z_x + S_{66}X_y
\end{aligned}
$$

S’s are called elastic compliance constants or elastic constants and have dimensions of area/force.

Eq. 1

Elastic Compliance and Stiffness Constants

- It has been tacitly assumed that the solid is isotropic. However, crystals are, in fact, anisotropic, and the effect of anisotropy on the elastic properties is readily demonstrated.

- This leads in general to the introduction of many more elastic constants (C’s) than the two needed for the isotropic solid: bulk modulus and shear modulus.

- Considerations of symmetry show, however, that many of these constants are interrelated, a fact which results in a substantial decrease in the number of independent elastic constants.

- **Elastic Energy Density**
- **Elastic waves in cubic crystals**

Elastic Energy Density

The elastic energy density U is a quadratic function of the strains, in the approximation of Hooke's law $\left(\mathrm{U} = \frac{1}{2}kx^2\right)$.

$$U = \frac{1}{2}\sum_{\lambda=1}^{6}\sum_{\mu=1}^{6}\tilde{C}_{\lambda\mu}e_\lambda e_\mu \quad ,$$

where the indices 1 through 6 are defined as:

$$1 \equiv xx \; ; \qquad 2 \equiv yy \; ; \qquad 3 \equiv zz \; ; \qquad 4 \equiv yz \; ; \qquad 5 \equiv zx \; ; \qquad 6 \equiv xy$$

$$U = \frac{1}{2}\left(\tilde{C}_{11}e_1e_1\right) + \frac{1}{2}\sum_{\lambda=2}^{6}\tilde{C}_{1\lambda}e_1e_\lambda + \frac{1}{2}\sum_{\mu=2}^{6}\tilde{C}_{\mu 1}e_\mu e_1 + \frac{1}{2}\sum_{\lambda=2}^{6}\sum_{\mu=2}^{6}\tilde{C}_{\lambda\mu}e_\lambda e_\mu$$

Derivative of the energy density with respect to stress will give us strain. (Similar to $|\mathrm{F}| = \frac{dU}{dr}$).

Elastic Energy Density

$$U = \frac{1}{2}\left(\tilde{C}_{11}e_1e_1\right) + \frac{1}{2}\sum_{\lambda=2}^{6}\tilde{C}_{1\lambda}e_1e_\lambda + \frac{1}{2}\sum_{\mu=2}^{6}\tilde{C}_{\mu 1}e_\mu e_1 + \frac{1}{2}\sum_{\lambda=2}^{6}\sum_{\mu=2}^{6}\tilde{C}_{\lambda\mu}e_\lambda e_\mu$$

The $\tilde{C}$ are related to C, *by*

$$X_x = \frac{\partial U}{\partial e_{xx}} \equiv \frac{\partial U}{\partial e_1} = \tilde{C}_{11}e_1 + \frac{1}{2}\sum_{\beta=2}^{6}(\tilde{C}_{1\beta} + \tilde{C}_{\beta 1})e_\beta$$

Comparison of this equation with the following stress equation (Eq. 1 on the previous slide) gives.

$$X_x = C_{11}e_{xx} + C_{12}e_{yy} + C_{13}e_{zz} + C_{14}e_{yz} + C_{15}e_{zx} + C_{16}e_{xy}$$

$$C_{12} = \frac{1}{2}\left(\tilde{C}_{12} + \tilde{C}_{21}\right) = C_{21}$$

$$C_{\alpha\beta} = \tfrac{1}{2}(\tilde{C}_{\alpha\beta} + \tilde{C}_{\beta\alpha}) = C_{\beta\alpha}$$

It reduces the independent elastic stiffness constants from 36 to 21.

Elastic Stiffness Constants of Cubic Crystals

For a cubic symmetry, there are only 3 independent stiffness constants.

$$U = \tfrac{1}{2}C_{11}(e_{xx}^2 + e_{yy}^2 + e_{zz}^2) + \tfrac{1}{2}C_{44}(e_{yz}^2 + e_{zx}^2 + e_{xy}^2) + C_{12}(e_{yy}e_{zz} + e_{zz}e_{xx} + e_{xx}e_{yy})$$

Eq. 2

The other quadratic strain terms do not occur.

It remains to verify that the numerical factors in Eq. 2 are correct.

From Eq. 2 → $\partial U/\partial e_{xx} = X_x = C_{11}e_{xx} + C_{12}(e_{yy} + e_{zz})$

From Eq. 1 → $X_x = C_{11}e_{xx} + C_{12}e_{yy} + C_{13}e_{zz} + C_{14}e_{yz} + C_{15}e_{zx} + C_{16}e_{xy}$

$C_{12} = C_{13}$ $\qquad$ $C_{14} = C_{15} = C_{16} = 0$

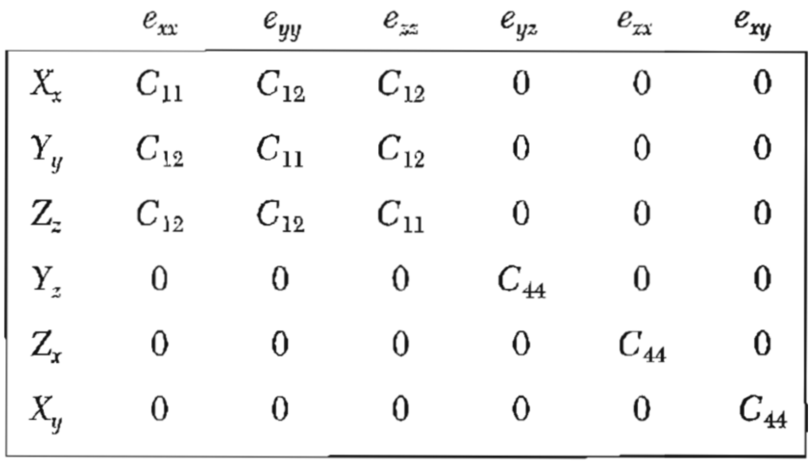
From Eq. 2 → $\partial U/\partial e_{xy} = X_y = C_{44}e_{xy}$

From Eq. 1 → $X_y = C_{61}e_{xx} + C_{62}e_{yy} + C_{63}e_{zz} + C_{64}e_{yz} + C_{65}e_{zx} + C_{66}e_{xy}$

$C_{44} = C_{66}$ $\qquad$ $C_{61} = C_{62} = C_{63} = C_{64} = C_{65} = 0$

Elastic Stiffness Constants of Cubic Crystals

The Eq.1 reduce to



$$\begin{array}{c|cccccc} & e_{xx} & e_{yy} & e_{zz} & e_{yz} & e_{zx} & e_{xy} \\ \hline X_x & C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ Y_y & C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ Z_z & C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ Y_z & 0 & 0 & 0 & C_{44} & 0 & 0 \\ Z_x & 0 & 0 & 0 & 0 & C_{44} & 0 \\ X_y & 0 & 0 & 0 & 0 & 0 & C_{44} \end{array}$$

Eq. 3

After determining the inverse matrix to Eq.3. The stiffness and compliance constants are related by:

$$C_{44} = 1/S_{44} \qquad C_{11} - C_{12} = (S_{11} - S_{12})^{-1} \ ;$$

$$C_{11} + 2C_{12} = (S_{11} + 2S_{12})^{-1}$$

Elastic Stiffness Constants of Cubic Crystals

- Physical interpretation of the three independent constants : C_{11}, C_{12}, and C_{44}.

- The constant $\mathbf{C_{11}}$ relates the **compression stress and strain** along the [100] direction, for example, the x-axis.

- The constant $\mathbf{C_{12}}$ relates the **compression stress in one direction to the strain in another**; these may, for instance, be the x- and y directions. It is related to the Poisson's ratio.

- The $\mathbf{C_{44}}$ relates the **shear stress and strain** in the same direction.

- The three constants are determined by measuring the sound velocities in certain directions in the crystal, which is discussed in the “Elastic Wave in Cubic Crystal” section below.

Bulk Modulus and Compressibility

For a uniform dilation in a cubic crystal $e_{xx} = e_{yy} = e_{zz} = \frac{1}{3}\delta$, and no shear deformation $e_{yz} = e_{zx} = e_{xy} = 0$, the energy density (Eq. 2) can be written as

$$U = \tfrac{1}{2}C_{11}(e_{xx}^2 + e_{yy}^2 + e_{zz}^2) + \tfrac{1}{2}C_{44}(e_{yz}^2 + e_{zx}^2 + e_{xy}^2) + C_{12}(e_{yy}e_{zz} + e_{zz}e_{xx} + e_{xx}e_{yy}) \qquad \text{Eq. 2}$$

$$U = \frac{1}{6}(C_{11} + 2C_{12})\delta^2$$

The bulk modulus B is determined by the following relation.

$$U = \frac{1}{2}B\delta^2 \qquad\qquad B = \frac{1}{3}(C_{11} + 2C_{12}) \cong -V\frac{dP}{dV}$$

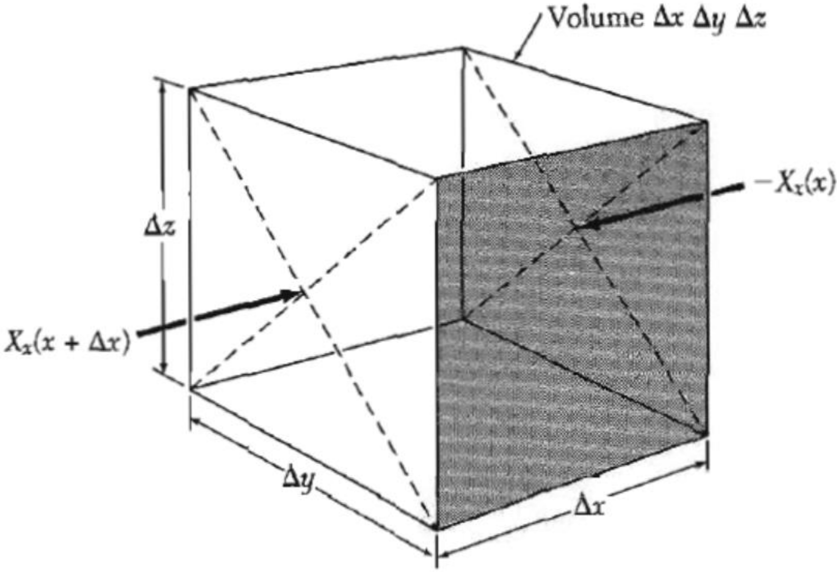
The compressibility K is defined as $K = 1/B$.

Elastic Waves in Cubic Crystals

Figure 18 Cube of volume $\Delta x\ \Delta y\ \Delta z$ acted on by a stress $-X_x(x)$ on the face at x, and $X_x(x+\Delta x) \simeq X_x(x) + \frac{\partial X_x}{\partial x}\Delta x$ on the parallel face at $x + \Delta x$. The net force is $\left(\frac{\partial X_x}{\partial x}\Delta x\right)\Delta y\ \Delta z$. Other forces in the x direction arise from the variation across the cube of the stresses X_y and X_z, which are not shown. The net x component of the force on the cube is

$$F_x = \left(\frac{\partial X_x}{\partial x} + \frac{\partial X_y}{\partial y} + \frac{\partial X_z}{\partial z}\right)\Delta x\ \Delta y\ \Delta z \ .$$

The force equals the mass of the cube times the component of the acceleration in the x direction. The mass is $\rho\ \Delta x\ \Delta y\ \Delta z$, and the acceleration is $\partial^2 u/\partial t^2$.



$$\rho\frac{\partial^2 u}{\partial t^2} = \frac{\partial X_x}{\partial x} + \frac{\partial X_y}{\partial y} + \frac{\partial X_z}{\partial z}$$

Elastic Waves in Cubic Crystals

$$\rho \frac{\partial^2 u}{\partial t^2} = \frac{\partial X_x}{\partial x} + \frac{\partial X_y}{\partial y} + \frac{\partial X_z}{\partial z}$$

$$\begin{aligned}
X_x &= C_{11}e_{xx} + C_{12}e_{yy} + C_{13}e_{zz} + C_{14}e_{yz} + C_{15}e_{zx} + C_{16}e_{xy} \\
Y_y &= C_{21}e_{xx} + C_{22}e_{yy} + C_{23}e_{zz} + C_{24}e_{yz} + C_{25}e_{zx} + C_{26}e_{xy} \\
Z_z &= C_{31}e_{xx} + C_{32}e_{yy} + C_{33}e_{zz} + C_{34}e_{yz} + C_{35}e_{zx} + C_{36}e_{xy} \\
Y_z &= C_{41}e_{xx} + C_{42}e_{yy} + C_{43}e_{zz} + C_{44}e_{yz} + C_{45}e_{zx} + C_{46}e_{xy} \\
Z_x &= C_{51}e_{xx} + C_{52}e_{yy} + C_{53}e_{zz} + C_{54}e_{yz} + C_{55}e_{zx} + C_{56}e_{xy} \\
X_y &= C_{61}e_{xx} + C_{62}e_{yy} + C_{63}e_{zz} + C_{64}e_{yz} + C_{65}e_{zx} + C_{66}e_{xy}
\end{aligned}$$

Eq. 1

Using Eq. 1, and Eq. 3, for complete set of equivalent constants.

$C_{12} = C_{13}$ $C_{44} = C_{66}$ $C_{14} = C_{15} = C_{16} = 0$

$X_y = Y_x;$ $Y_z = Z_y;$ $Z_x = X_z$ $C_{61} = C_{62} = C_{63} = C_{64} = C_{65} = 0$

$$\rho \frac{\partial^2 u}{\partial t^2} = C_{11}\frac{\partial e_{xx}}{\partial x} + C_{12}\left(\frac{\partial e_{yy}}{\partial x} + \frac{\partial e_{zz}}{\partial x}\right) + C_{44}\left(\frac{\partial e_{xy}}{\partial y} + \frac{\partial e_{zx}}{\partial z}\right)$$

Elastic Waves in Cubic Crystals

Using the following relations for the strain components.

$$e_{xx} = \frac{\partial u}{\partial x} \qquad e_{yy} = \frac{\partial v}{\partial y} \qquad e_{zz} = \frac{\partial w}{\partial z}$$

$$e_{xy} \equiv \mathbf{x}' \cdot \mathbf{y}' \cong \epsilon_{yx} + \epsilon_{xy} = \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x}$$

$$e_{yz} \equiv \mathbf{y}' \cdot \mathbf{z}' \cong \epsilon_{zy} + \epsilon_{yz} = \frac{\partial v}{\partial z} + \frac{\partial w}{\partial y}$$

$$e_{zx} \equiv \mathbf{z}' \cdot \mathbf{x}' \cong \epsilon_{zx} + \epsilon_{xz} = \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x}$$

We get:

$$\rho \frac{\partial^2 u}{\partial t^2} = C_{11} \frac{\partial^2 u}{\partial x^2} + C_{44} \left(\frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} \right) + (C_{12} + C_{44}) \left(\frac{\partial^2 v}{\partial x\, \partial y} + \frac{\partial^2 w}{\partial x\, \partial z} \right) \qquad \text{Eq. 3}$$

Similar equations of motion can also be derived for *v* and *w*.

$$\rho \frac{\partial^2 v}{\partial t^2} = C_{11} \frac{\partial^2 v}{\partial y^2} + C_{44} \left(\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial z^2} \right) + (C_{12} + C_{44}) \left(\frac{\partial^2 u}{\partial x\, \partial y} + \frac{\partial^2 w}{\partial y\, \partial z} \right) \qquad \text{Eq. 4}$$

$$\rho \frac{\partial^2 w}{\partial t^2} = C_{11} \frac{\partial^2 w}{\partial z^2} + C_{44} \left(\frac{\partial^2 w}{\partial x^2} + \frac{\partial^2 w}{\partial y^2} \right) + (C_{12} + C_{44}) \left(\frac{\partial^2 u}{\partial x\, \partial z} + \frac{\partial^2 v}{\partial y\, \partial z} \right) \qquad \text{Eq. 5}$$

Waves in [100] in a Cubic Crystal

The *x* displacement of a **longitudinal wave** can be determined by the following equation.

$$u = u_0 \exp[i(Kx - \omega t)]$$

Using this solution in Eq. 3, we determine a dispersion relation for the wave.

$$\omega^2 \rho = C_{11} K^2$$

$$v_s = \lambda f = \frac{\omega}{K} = \left(\frac{C_{11}}{\rho}\right)^{1/2}$$

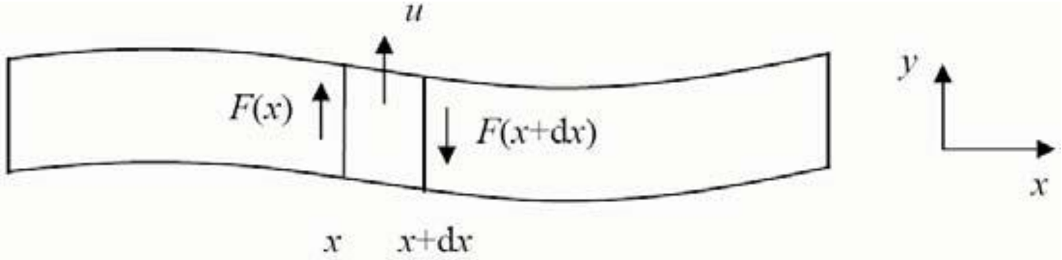
This is the velocity of a longitudinal wave.

$$v_s = \left(\frac{elastic\ property\ of\ the\ crystal\ (Elastic\ modulus)}{inertial\ property\ of\ the\ crystal\ (mass\ density)}\right)^{1/2}$$

Waves in [100] in a Cubic Crystal

Now consider a transverse wave which is controlled by shear stress and strain. The particle displacement *v (or w)* is in the y (or z) direction and wavevector along x-axis.

$$v = v_0 \exp[i(Kx - \omega t)] \qquad w = w_0 \exp[i(Kx - \omega t)]$$



Using this solution in Eq. 4 (Eq. 5), we determine a dispersion relation for the wave.

$$\omega^2 \rho = C_{44} K^2$$

$$v_s = \lambda f = \frac{\omega}{K} = \left(\frac{C_{44}}{\rho}\right)^{1/2}$$

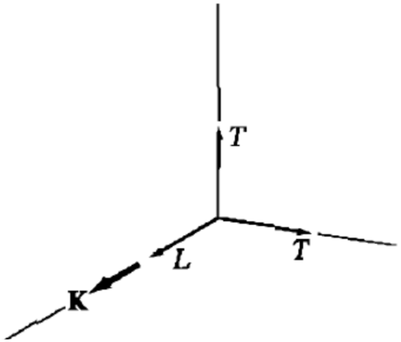
The is the velocity of the transverse wave and is same in both y and z directions.

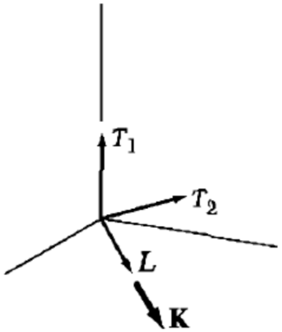
We determined velocities for **three normal modes** of oscillations: one longitudinal and two transverse.

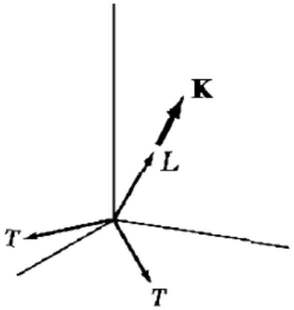
Waves in [110] and [111] in a Cubic Crystal

Calculations similar to the waves in [100] can be carried out to determine the longitudinal and transverse components of the sounds velocities in [110] and [111] directions. In all cases we need to calculate C_{eff}: an effective elastic constant to determine speed of sound in other directions.

$$v_s = \left(\frac{C_{eff}}{\rho}\right)^{1/2}$$







Mode of oscillation	**Wave in [100] direction**	**Wave in [110] direction**	**Wave in [111] direction**
Longitudinal	C_{11}	$\frac{1}{2}(C_{11}+C_{12}+2C_{44})$	$\frac{1}{3}(C_{11}+2C_{12}+4C_{44})$
Transverse 1	C_{44}	C_{44}	$\frac{1}{3}(C_{11}-C_{12}+C_{44})$
Transverse 2	C_{44}	$\frac{1}{2}(C_{11}-C_{12})$	$\frac{1}{3}(C_{11}-C_{12}+C_{44})$