

# PHYS 342/555

## Condensed Matter in a Nutshell

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Instructor: Dr. Pengcheng Dai

Professor of Physics

The University of Tennessee

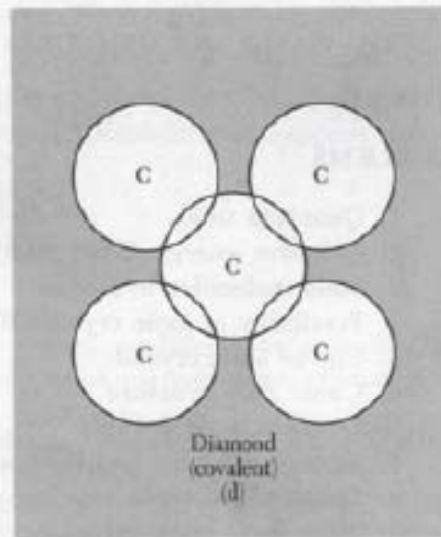
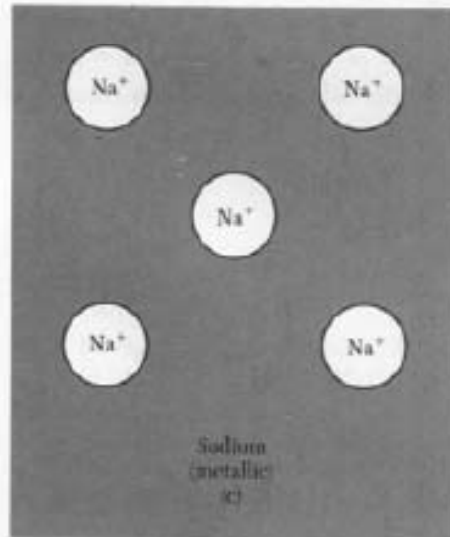
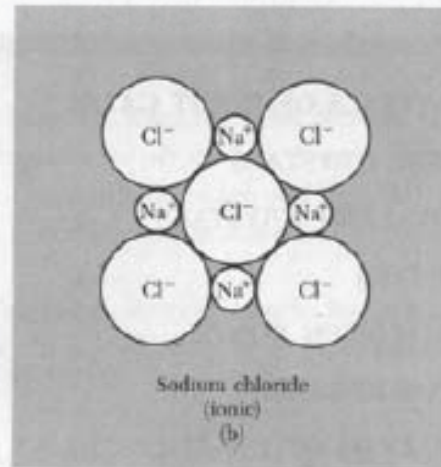
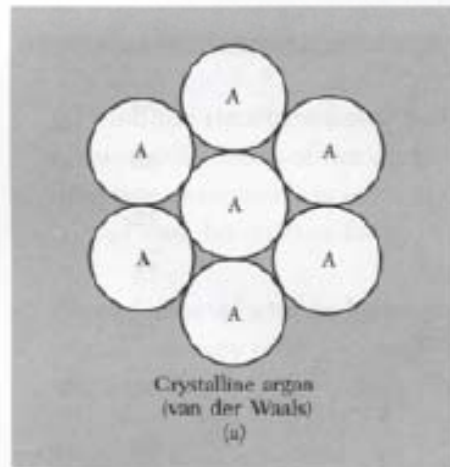
(Room 407, Nielsen, 974-1509)

(Office hours: after class)

Chapter 3: Crystal bindings

Lecture in pdf format will be available at:

<http://www.phys.utk.edu>

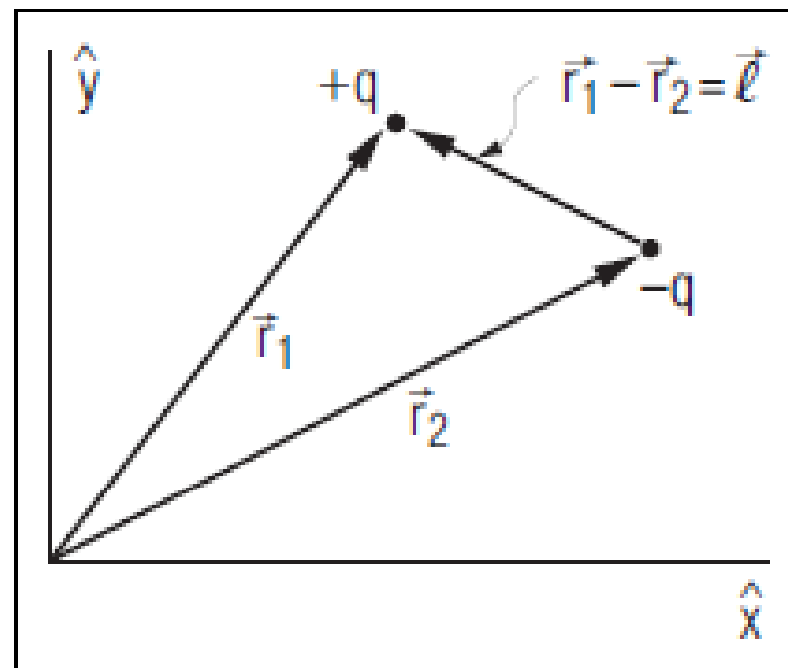


**Crystal binding:**  
**The cohesive energy of a crystal is defined as the energy that must be added to the crystal to separate its components into neutral free atoms at rest, at infinite separation, with the same electronic configuration. Lattice energy is the energy required to separate its component ions into free ions.**

**2b. Definition of A Dipole.** “A dipole” is defined as a system consisting of two equal but oppositely charged point charges:  $q_1 = q$  and  $q_2 = -q$ . For that case the dipole moment,  $\vec{p}$ , is:

$$\vec{p} = q_1\vec{r}_1 + q_2\vec{r}_2 = q\vec{r}_1 - q\vec{r}_2 = q(\vec{r}_1 - \vec{r}_2) = q\vec{\ell}, \quad (2)$$

where  $\vec{r}_1 - \vec{r}_2 = \vec{\ell}$ , the vector separation of the charges, points from the negative charge ( $-q$ ) to the positive charge ( $+q$ ) (see Fig. 2). Note that

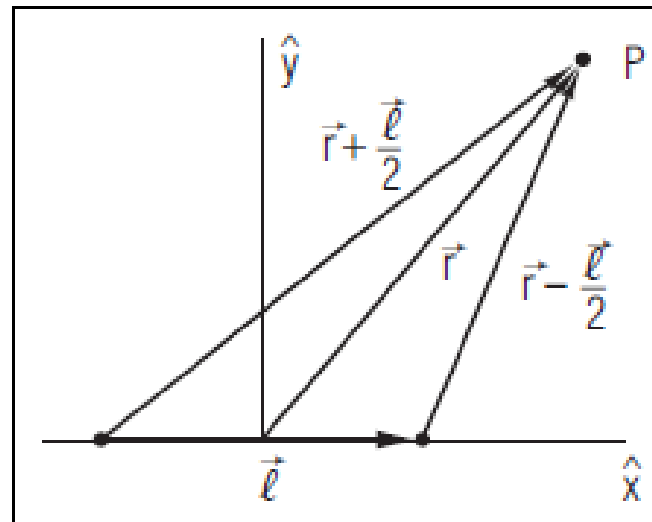


**Figure 2.** Vectors used to define an electric dipole.

**2c. Electric Field Due to a Dipole.** The electric field and the electric potential at any point in the vicinity of a dipole can be straightforwardly calculated just by adding the contributions due to each of the charges. For example, consider a dipole whose center is at the origin (Fig. 3). At point  $P$  you can calculate the field due to the two charges. The answer is:

$$\vec{E}(\vec{r}) = k_e q \left[ \frac{\vec{r} - \vec{\ell}/2}{|\vec{r} - \vec{\ell}/2|^3} - \frac{\vec{r} + \vec{\ell}/2}{|\vec{r} + \vec{\ell}/2|^3} \right], \quad (3)$$

where  $\vec{r}$  is the vector from the origin to  $P$ .

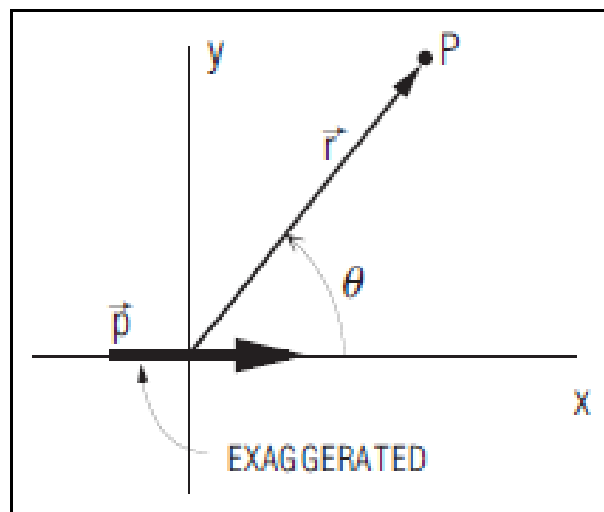


**Figure 3.** Position vectors for the electric field of a dipole.

**2d. Electric Field Due to a “Point” Dipole.** An interesting result occurs if we take the dipole to be “very small.” Here we mean that the dipole has a spatial size,  $\ell$ , that is negligible compared with the distance  $r$  to the point  $P$  where the field of the dipole is observed. The result is that the field at  $P$  due to the point dipole at the origin is well-approximated by:<sup>1</sup>

$$\vec{E}(\vec{r}) = k_e \left[ \frac{(3\vec{r} \cdot \vec{p}) \vec{r}}{r^5} - \frac{\vec{p}}{r^3} \right] \quad (\ell \ll r)$$

Note that there is one component in the  $\vec{r}$  direction and another in the  $\vec{p}$  direction. The expression becomes the exact answer for  $\vec{E}$  as the ratio  $\ell/r$  becomes vanishingly small, regardless of whether  $\vec{p}$  and  $\vec{E}$  become small or not.

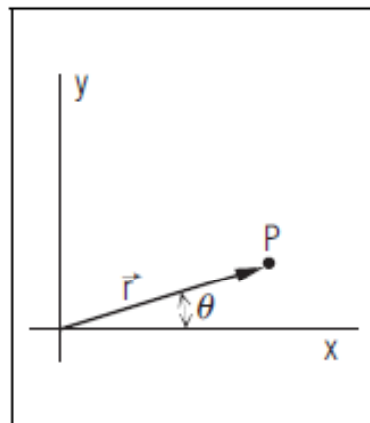


**Figure 4.** Symbols used to define the potential at a point  $P$  due to an electric dipole of moment  $\vec{p}$  at the origin.

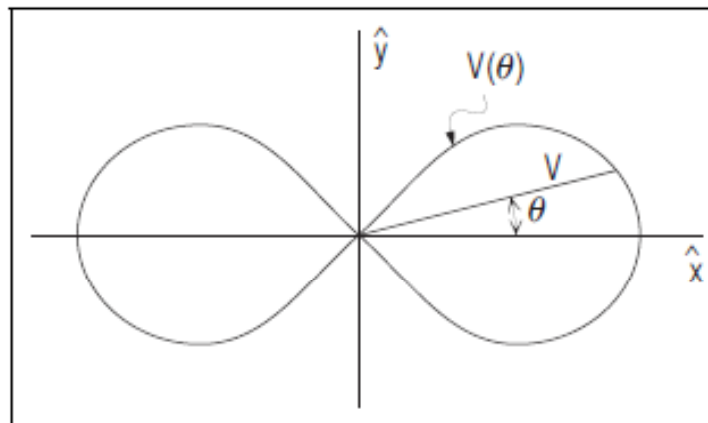
**2e. Potential Due to a “Point” Dipole.** The potential,  $V(r)$ , can be similarly determined, yielding (see Fig. 4 for symbols):<sup>2</sup>

$$V(r) = k_e \frac{\vec{p} \cdot \vec{r}}{r^3} = k_e \frac{p \cos \theta}{r^2}.$$

This is the potential at a distance  $r$  from a point-like dipole. The interesting thing about these expressions is that they depend neither on the charge nor the spatial size, but on the combination  $\vec{p}$ , the dipole moment. Notice also that the potential varies with  $\theta$ . For example, at any point on a line perpendicular to the direction of  $\vec{p}$  the potential  $V$  is zero. For a given value of  $r$ ,  $V$  has its maximum value for the point where  $r$  is in the direction of  $p$ . Contrast that with the potential due to a point charge at the origin: for that case,  $V$  has the same value for a fixed  $|\vec{r}|$ , no matter what the direction of  $\vec{r}$ .

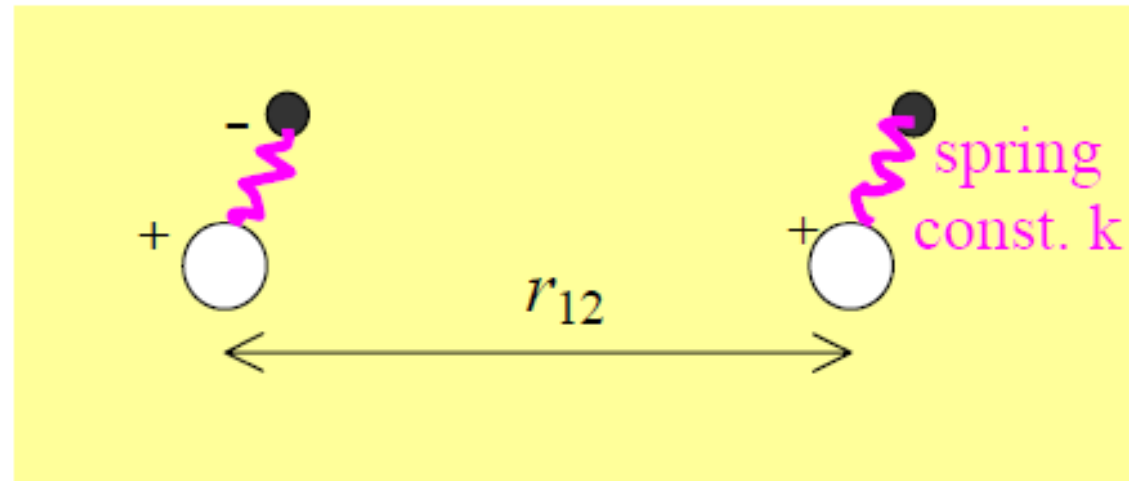


**Figure 5.** Coordinate-space symbol definitions for all points at constant radius.



**Figure 6.** Dipole potential-space symbols for points at constant radius, varying angle.

# Van der Waals interactions



The vibration frequency of the oscillator is related to the force constant  $k$  and the (reduced) mass of the electron  $m$  by  $k/m = \omega^2$ . We assume that the system is in its vibrational ground state. When the two dipoles are separated by an infinite distance ( $r_{12} \rightarrow \infty$ ), the total energy of the system will simply be the sum of their zero-point energies

$$(2.1) \quad E(r_{12} \rightarrow \infty) = \frac{1}{2} \hbar \omega + \frac{1}{2} \hbar \omega, \quad \omega = \sqrt{\frac{k}{m}}.$$

Obviously at his infinite separation the individual dipole moments will not affect each other and thus be zero on average. If we now want to compute the interactions between the two oscillators for finite separations, we need to write down their Hamiltonian. It will be the sum of the interactions of the two at rest (no correlations),  $H_0$ , and the contribution arising from the dipole-dipole interactions,  $U_{dd}$ :

$$(2.2) \quad H = H_0 + U_{dd}$$

$$(2.3) \quad H_0 = \frac{1}{2} m \dot{x}_1^2 + \frac{1}{2} m \dot{x}_2^2 + \frac{1}{2} k x_1^2 + \frac{1}{2} k x_2^2$$

the dipole-dipole interactions are

$$(2.4) \quad U_{dd} = \frac{3(\vec{p}_1 \cdot \hat{r}_{12})(\vec{p}_2 \cdot \hat{r}_{12}) - \vec{p}_1 \cdot \vec{p}_2}{4\pi\epsilon_0 r_{12}^3}.$$



For simplicity we only consider one direction for the moment. But keep in mind that we still have to average the end result over all orientations, which only changes the constant pre-factor. Thus  $\vec{x} \cdot \hat{r}_{12} = 0$ , for  $\vec{x} = \vec{x}_1$  and  $\vec{x} = \vec{x}_2$ . This simplifies the dipole-dipole interactions to

$$(2.5) \quad U_{dd} = -\frac{\vec{p}_1 \cdot \vec{p}_2}{r_{12}^3} = -\frac{e^2 x_1 x_2}{r_{12}^3}$$

where we have temporarily ignored the factor  $1/(4\pi\epsilon_0)$ . We can then write the Hamiltonian of the system as

$$(2.6) \quad H = \frac{1}{2}m\dot{x}_1^2 + \frac{1}{2}m\dot{x}_2^2 + \frac{1}{2}kx_1^2 + \frac{1}{2}kx_2^2 - \frac{e^2}{r_{12}^3}x_1x_2$$

What we are really interested in is the net-dipole-dipole interaction between the two oscillators at finite separation. In that case, the two harmonic oscillators are coupled and this leads to a change in the ground-state energy of the system. Let us denote the resonance frequencies of these coupled oscillators by  $\omega_1$  and  $\omega_2$  respectively. The zero point energy of the coupled system is  $\frac{1}{2}\hbar\omega_1 + \frac{1}{2}\hbar\omega_2$ . The change in energy due to the coupling is equal to this zero-point energy minus the zero-point energy of the oscillators at infinite separation:

$$\begin{aligned} \Delta E_{tot} &= E_{tot}(r_{12}) - E_{tot}(r_{12} \rightarrow \infty) = \frac{1}{2}\hbar(\omega_1 - \omega) + \frac{1}{2}\hbar(\omega_2 - \omega) \\ (2.7) \quad \Delta E_{tot} &= \frac{1}{2}\hbar\left(\frac{\omega_1}{\omega} - 1\right) + \frac{1}{2}\hbar\left(\frac{\omega_2}{\omega} + 1\right) \end{aligned}$$

Now we only need to calculate  $\omega_1$  and  $\omega_2$ . For this reconsider the Hamiltonian in equ. (2.6). The last three terms form a quadratic equation. Therefore, we can substitute the variables,  $x_1$  and  $x_2$  in the following way:

$$(2.8) \quad X = x_1 + x_2 \quad \text{and} \quad \Delta x = (x_1 - x_2)$$

$$\Rightarrow \quad x_1 = \frac{1}{2}(X + \Delta x) \quad \text{and} \quad x_2 = \frac{1}{2}(X - \Delta x) \quad \text{and} \quad x_1 x_2 = \left( \frac{X^2 - \Delta x^2}{4} \right)$$

So we can rewrite the quadratic terms in equ. (x.6) as

$$(2.9) \quad \frac{1}{2}k(X + \Delta x)^2 + \frac{1}{2}k(X - \Delta x)^2 - \frac{e^2}{r_{12}^3}(X^2 + \Delta x^2) = \frac{1}{2}k(2X^2 + 2\Delta x^2) - \frac{e^2}{r_{12}^3}(X^2 + \Delta x^2)$$

$$= \frac{1}{2} \left( 2k - \frac{e^2}{r_{12}^3} \right) X^2 + \frac{1}{2} \left( 2k + \frac{e^2}{r_{12}^3} \right) \Delta x^2$$

The time-derivatives of the variables,  $x_1$  and  $x_2$ , are

$$(2.10) \quad \dot{x}_1 = \dot{X} + \Delta \dot{x} \quad \text{and} \quad \dot{x}_2 = \dot{X} - \Delta \dot{x}$$

Inserting these and equ.(x.9) into the Hamiltonian, we obtain

$$(2.11) \quad H = \frac{1}{2}m(2\dot{X}^2) + \frac{1}{2} \left( 2k - \frac{e^2}{r_{12}^3} \right) X^2 + \frac{1}{2}m(2\Delta \dot{x}^2) + \frac{1}{2} \left( 2k + \frac{e^2}{r_{12}^3} \right) \Delta x^2$$

which represents the two harmonic oscillators with resonance frequencies

$$(2.12) \quad \omega_1 = \sqrt{\frac{k}{m} \left( 1 - \frac{e^2}{2kr_{12}^3} \right)} \quad \text{and} \quad \omega_2 = \sqrt{\frac{k}{m} \left( 1 + \frac{e^2}{2kr_{12}^3} \right)}$$

Now we can reconsider the difference in the total energy in equ.(x.7), where we wanted to compute  $\omega_1$  and  $\omega_2$ . We can now write

$$(2.13) \quad \frac{\omega_1}{\omega} = \sqrt{1 - \frac{e^2}{2kr_{12}^3}} \approx 1 - \frac{e^2}{4kr_{12}^3} - \frac{e^4}{32k^2r_{12}^6} + O(r_{12}^{-9})$$

and

$$\frac{\omega_2}{\omega} = \sqrt{1 + \frac{e^2}{2kr_{12}^3}} \approx 1 + \frac{e^2}{4kr_{12}^3} - \frac{e^4}{32k^2r_{12}^6} + O(r_{12}^{-9})$$

Inserting these expressions into  $\Delta E_{tot}$ , we obtain the famous  $r_{12}^{-6}$  power law behavior of the van der Waals dispersion forces:

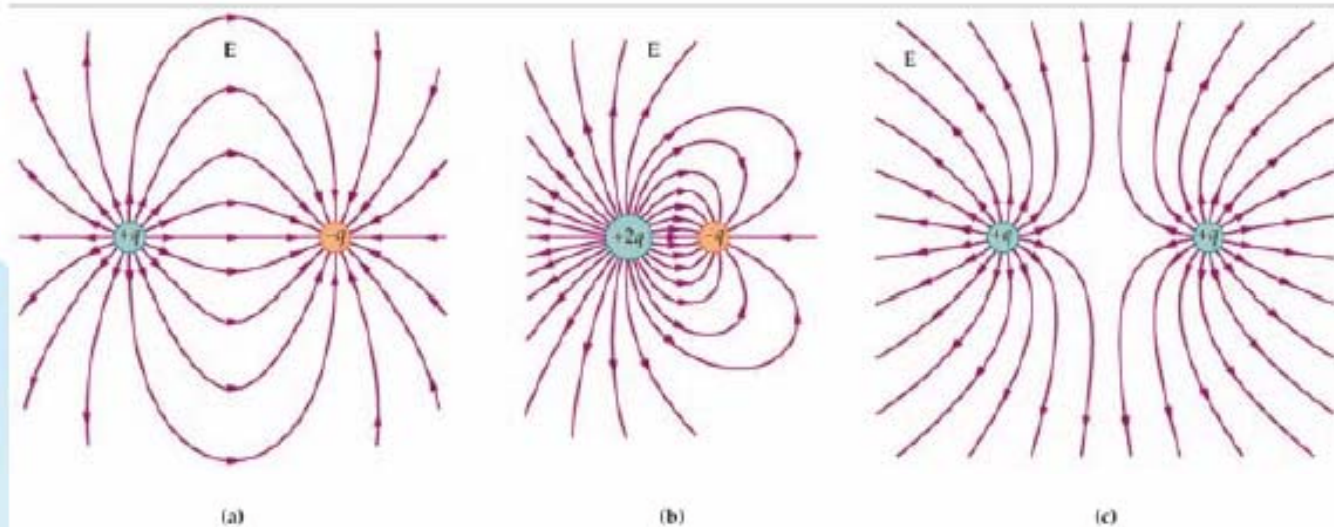
$$(2.14) \quad \Delta E_{tot} = \frac{1}{2} \hbar \omega \left( -\frac{e^4}{16k^2r_{12}^6} + O(r_{12}^{-9}) \right) \approx -\frac{\hbar \omega e^4}{32k^2r_{12}^6(4\pi\epsilon_0)^2} = -\frac{\hbar \omega \alpha^2}{32r_{12}^6(4\pi\epsilon_0)^2}$$

## Van de Waals-London interaction

Consider two atoms (1 and 2) separated by a distance  $r$ . If the instantaneous dipole moment of atom 1 is  $\vec{p}_1$ , then there will be an electric field proportional to  $p_1/r^3$  at a distance  $r$  from the atom. This will induce a dipole moment in atom 2 proportional to the field:

$$p_2 = \alpha E \sim \frac{\alpha p_1}{r^3}, \text{ where } \alpha \text{ is the polarizability of the atom.}$$





Since two dipoles have an energy of interaction proportional to the product of their moments divided by the cubic of the distance between them, there will be a lowering of energy of order

$$\frac{p_1 p_2}{r^3} \sim \frac{\alpha p_1^2}{r^6} \text{ associated with the induced moment.}$$

Since the energy drop depends on  $p_1^2$ , its time average does not vanish, even though the average value of  $p_1$  is zero.

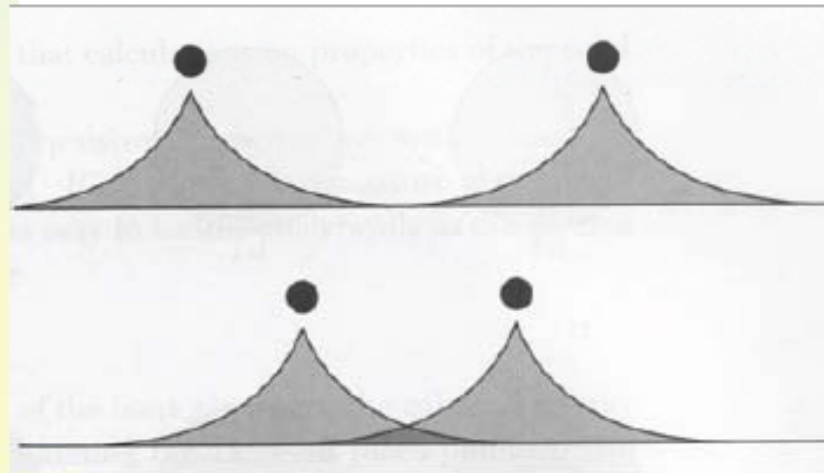
## Repulsive interaction

The Pauli exclusion principle prevents multiple occupancy, electron distributions of atoms with closed shells can overlap only if accompanied by the partial promotion of electrons to unoccupied high energy states of the atoms.

Experimentally, one finds Lennard-Jones potential,

$$U(R) = 4\varepsilon \left[ \left( \frac{\sigma}{R} \right)^{12} - \left( \frac{\sigma}{R} \right)^6 \right], \text{ where } \varepsilon \text{ and } \sigma \text{ are the new}$$

parameters with  $4\varepsilon\sigma^6 \equiv A$  and  $4\varepsilon\sigma^{12} \equiv B$ .



## Equilibrium lattice constants

If there are  $N$  atoms in the crystal, the total potential energy is:

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

where  $p_{ij}R$  is the distance between reference atom  $i$  and other atom  $j$  in terms of the nearest neighbor distance  $R$ .

For FCC structure,  $\sum_j p_{ij}^{-12} = 12.13188$ ,  $\sum_j p_{ij}^{-6} = 14.45392$

If there are  $N$  atoms in the crystal, the total potential energy is:

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

therefore  $R_0 / \sigma = 1.09$ .

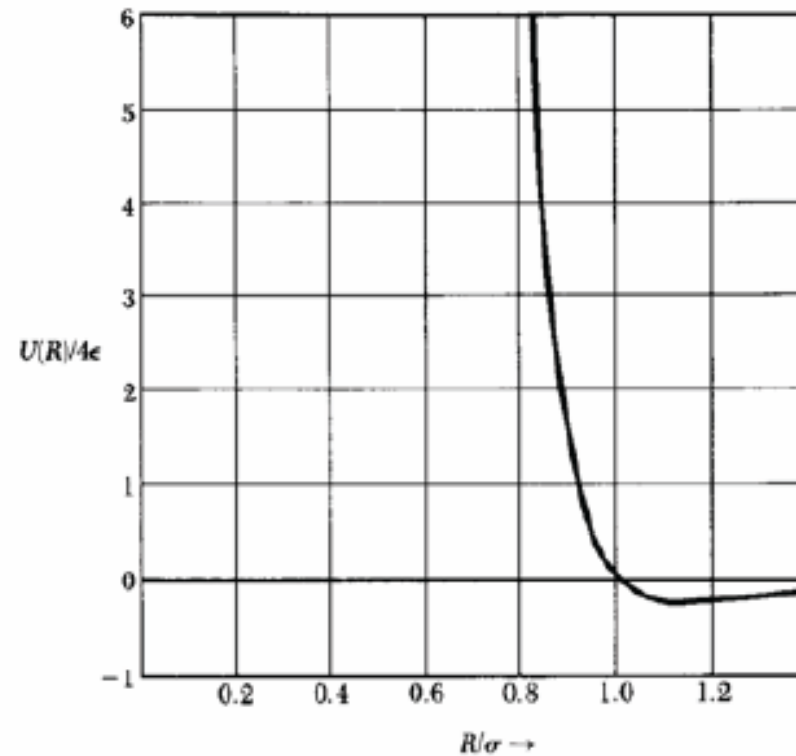


## Cohesive Energy

If there are  $N$  atoms in the crystal, the total potential energy is:

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

and, at  $R = R_0$ ,  $U_{total}(R_0) = -(2.15)(4N\varepsilon)$ .



**Table 4.1 Van der Waals summations for three lattices**

Crystal	$A_6$	$A_{12}$	$A_6^2/2A_{12}$
fcc	14.4519	12.1319	8.6078
hcp	14.4548	12.1353	8.6088
bcc	12.2519	9.1142	8.2349

The ground-state energy per atom is

$$E_G/N = 2\epsilon \left[ A_{12} \left( \frac{\sigma}{d} \right)^{12} - A_6 \left( \frac{\sigma}{d} \right)^6 \right] \quad (4.5)$$

The ratio  $(d/\sigma)$  is varied to find the nearest-neighbor spacing  $d$  with the lowest ground-state energy. Instead of varying  $d$ , choose another parameter  $Y$  to vary:

$$Y = \left( \frac{\sigma}{d} \right)^6 \quad (4.6)$$

$$E_G(Y)/N = 2\epsilon [A_{12} Y^2 - A_6 Y] \quad (4.7)$$

$$0 = \frac{1}{N} \frac{dE_G}{dY} = 2\epsilon [2A_{12} Y_0 - A_6] \quad (4.8)$$

$$Y_0 = \frac{A_6}{2A_{12}} \quad (4.9)$$

$$E_G(Y_0)/N = -\epsilon \frac{A_6^2}{2A_{12}} = -8.608\epsilon \quad (4.10)$$

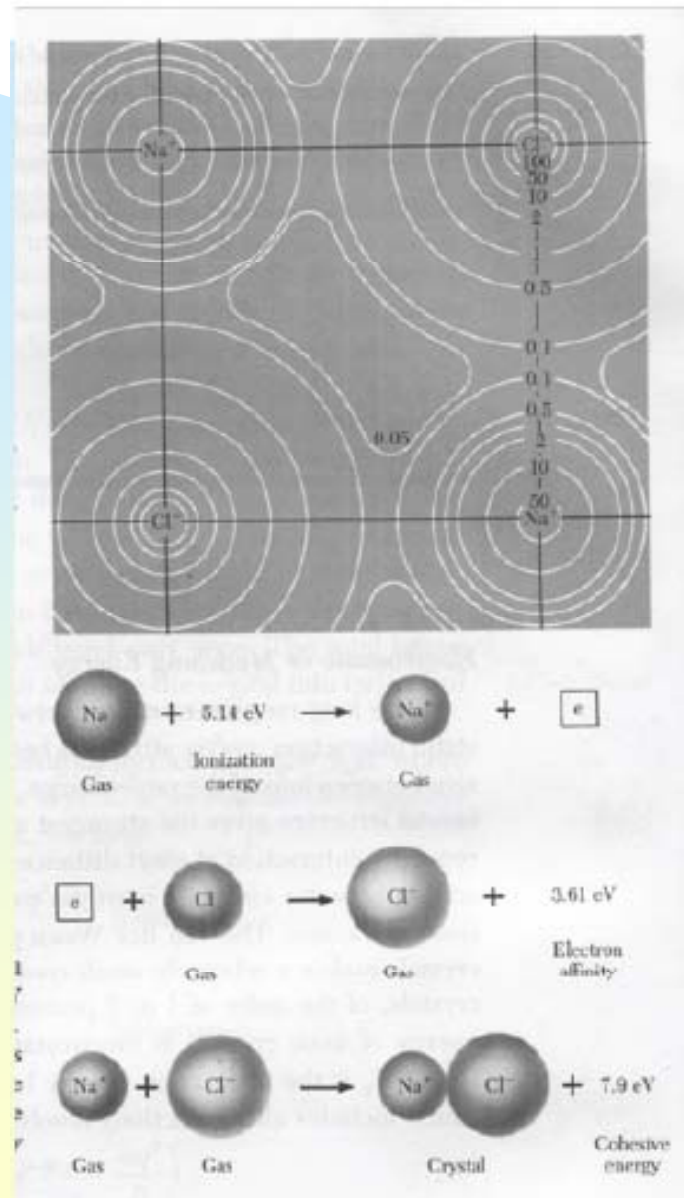
## Ionic crystals

**Ionic crystals are made up of positive and negative ions. The ionic bond results from the electrostatic interaction of oppositely charged ions.**

Cohesive energy is given by the potential energy of classical particles localized at the equilibrium positions. The total cohesive energy per ion pair is:

$U(r) = U^{core}(r) + U^{coul}(r)$ , where  $r$  is the nearest-neighbor distance.

$U^{core}(r) = \lambda \exp(-r_{ij} / \rho)$ , where  $\lambda$  and  $\rho$  are empirical parameters.



$U^{coul}(r) = \pm q^2 / r_{ij}$ , In NaCl structure, we have  $N$  molecules or  $2N$  ions. The total lattice energy is defined as the energy required to separate the crystal into individual ions.

If we define  $r_{ij} \equiv p_{ij}R$ , where  $R$  is the nearest-neighbor separation.

$$U_{ij} = \left\{ \begin{array}{l} \lambda \exp(-R / \rho) - q^2 / R \text{ (nearest neighbor)} \\ \pm \frac{q^2}{p_{ij}R} \text{ (otherwise)} \end{array} \right\}$$

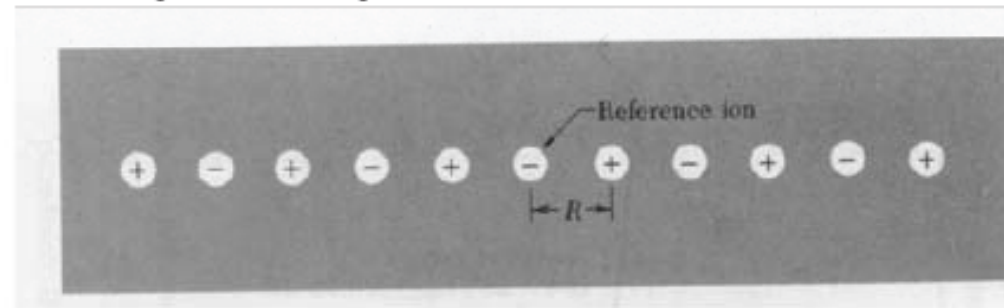
$$U_{tot} = N(z\lambda \exp(-R / \rho) - \alpha q^2 / R),$$

where  $z$  is # of nearest neighbors, and  $\alpha$  is Madelung

constant.  $\alpha \equiv \sum_j \frac{(\pm)}{p_{ij}}$ .

At equilibrium,  $\frac{dU_{tot}}{dR} = 0$ , or  $R_0^2 \exp(-R_0 / \rho) = \rho \alpha q^2 / z \lambda$ .

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



## Evaluation of the Madelung constant

$\frac{\alpha}{R} \equiv \sum_j \frac{(\pm)}{R_j}$ . For one-dimensional NaCl, one have

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

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \dots \text{ and } \alpha = 2 \ln 2.$$

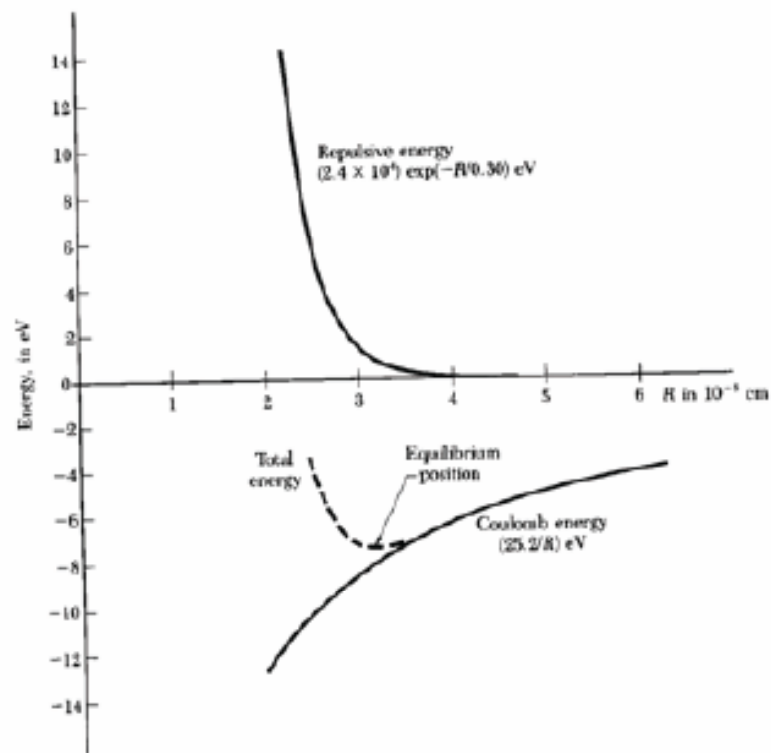


Figure 10 Energy per molecule of KCl crystal, showing Madelung and repulsive contributions.

Structure

$\alpha$

NaCl

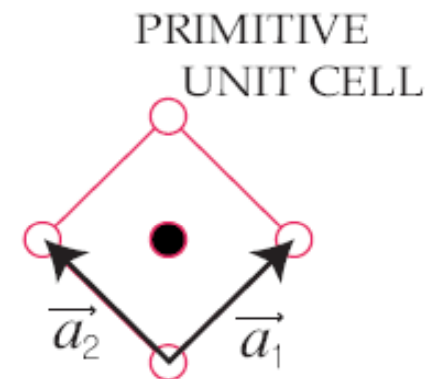
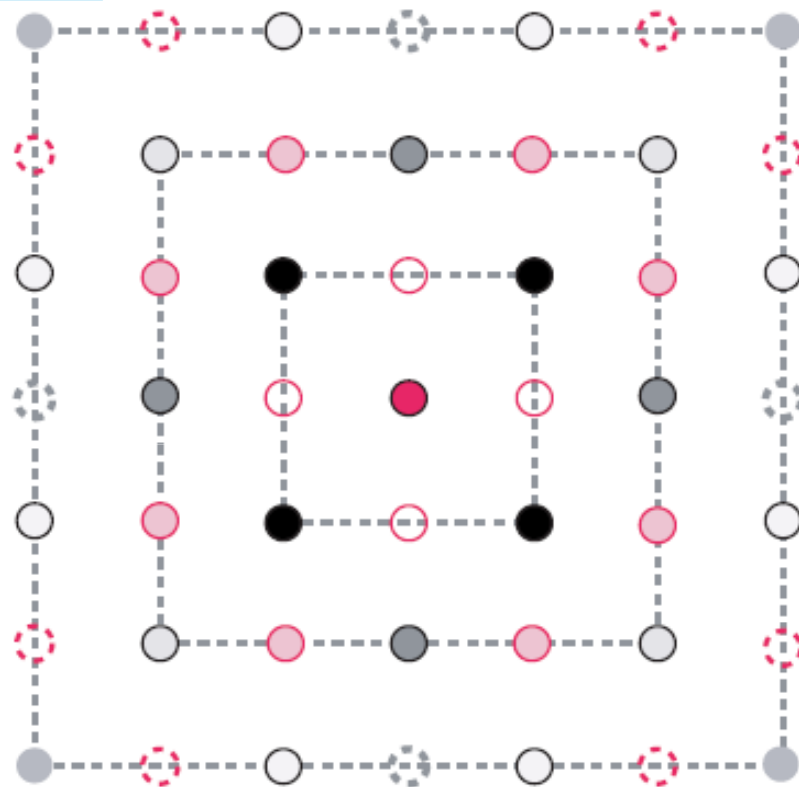
1.747565


CsCl

1.762675

## Evjen's Method

We will illustrate **Evjen's method**<sup>2</sup> by considering a simple square lattice in two dimensions with two atoms per unit cell, one at  $(0,0)$  and one at  $(\frac{1}{2}, \frac{1}{2})$ . The crystal structure is illustrated in Figure 1.25. The calculation is carried out as follows:



- 
1. One considers the charges associated with different shells where the first shell is everything inside the first square, the second is everything outside the first but inside the second square, etc.
  2. An ion on a face is considered to be half inside and half outside the square defined by that face; a corner atom is one quarter inside and three quarters outside.
  3. The total Madelung constant is given by  $\alpha = \alpha_1 + \alpha_2 + \alpha_3 + \dots$ , where  $\alpha_j$  is the contribution from the  $i^{\text{th}}$  shell.



As an example, let us evaluate the total charge on the first few shells. The first shell has four atoms on faces, all with the opposite charge to the atom at the origin and four corner atoms all with the same charge as the atom at the origin. Therefore the charge of shell number one is

$$Q_1 = 4 \left(\frac{1}{2}\right) - 4 \left(\frac{1}{4}\right) = 1. \quad (1.55)$$

Doing the same for the second shell gives

$$Q_2 = 4 \left(\frac{1}{2}\right) - 4 \left(\frac{3}{4}\right) - 4 \left(\frac{1}{2}\right) + 8 \left(\frac{1}{2}\right) - 4 \left(\frac{1}{4}\right) = 0. \quad (1.56)$$

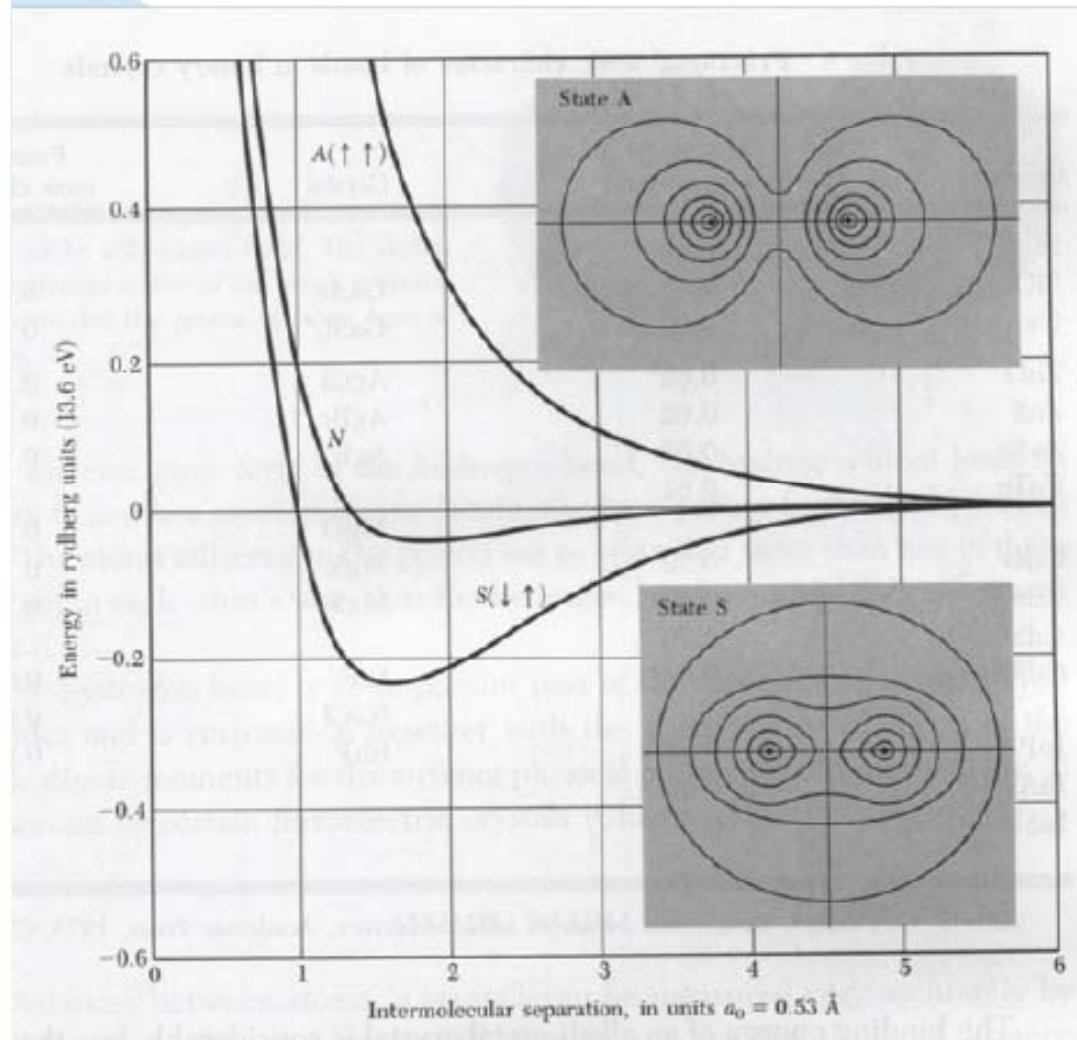
Here the first two terms come from the remainder of the atoms on the outside of the first square; the next three terms come from the atoms on the inside of the second square. To get  $\alpha_1$  and  $\alpha_2$  we simply divide the individual charges by their separations from the origin. This gives

$$\alpha_1 = \frac{4 \left(\frac{1}{2}\right)}{1} - \frac{4 \left(\frac{1}{4}\right)}{\sqrt{2}} \simeq 1.293, \quad (1.57)$$

$$\alpha_2 = \frac{4 \left(\frac{1}{2}\right)}{1} - \frac{4 \left(\frac{3}{4}\right)}{\sqrt{2}} - \frac{4 \left(\frac{1}{2}\right)}{2} + \frac{8 \left(\frac{1}{2}\right)}{\sqrt{5}} + \frac{4 \left(\frac{1}{4}\right)}{2\sqrt{2}} \simeq 0.314. \quad (1.58)$$

This gives  $\alpha \simeq \alpha_1 + \alpha_2 \sim 1.607$ . The readers should be able to evaluate  $\alpha_3$  for themselves.

## Covalent crystals

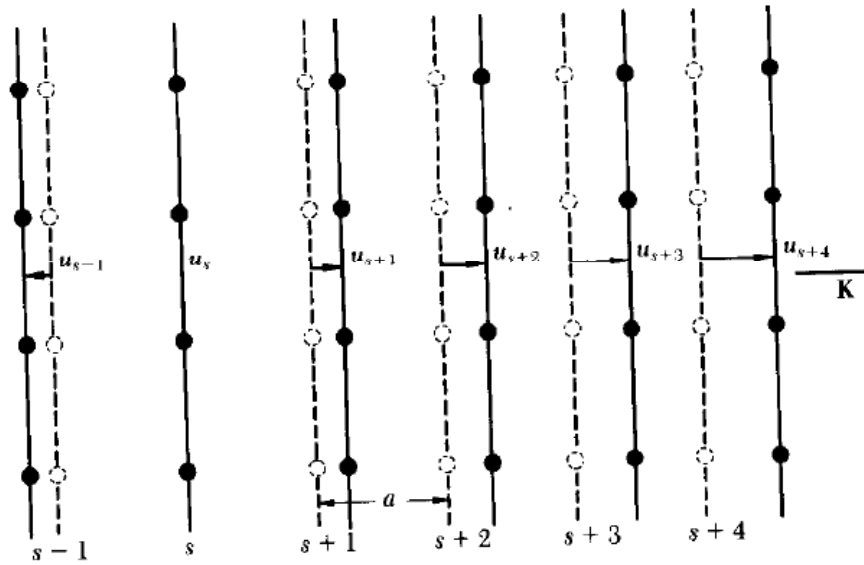


The binding of molecular hydrogen is a covalent bond. The strongest binding occurs when the spins of the two electrons are antiparallel because of the Pauli contribution to the repulsion is reduced in antiparallel spins. The spin-dependent coulomb energy is called the exchange interaction.

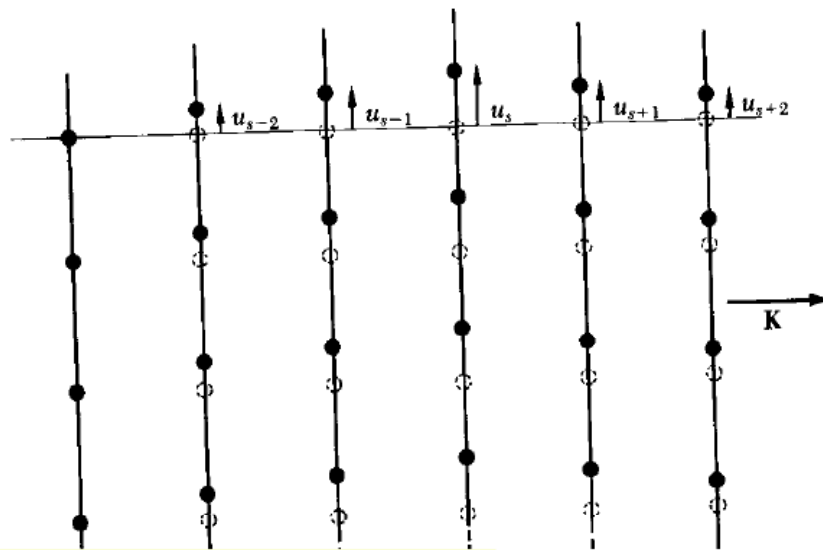
## Vibrations of crystals with monatomic basis

Our goal is to find the frequency of an elastic wave in terms of the wavevector that describes the wave and in terms of the elastic constants.

Longitudinal and transverse waves. When a wave propagates along one of the high symmetry directions ( $[100]$ ,  $[110]$ , and  $[111]$ ), entire planes of atoms move in phase with displacement either parallel or perpendicular to the direction of the wavevector.

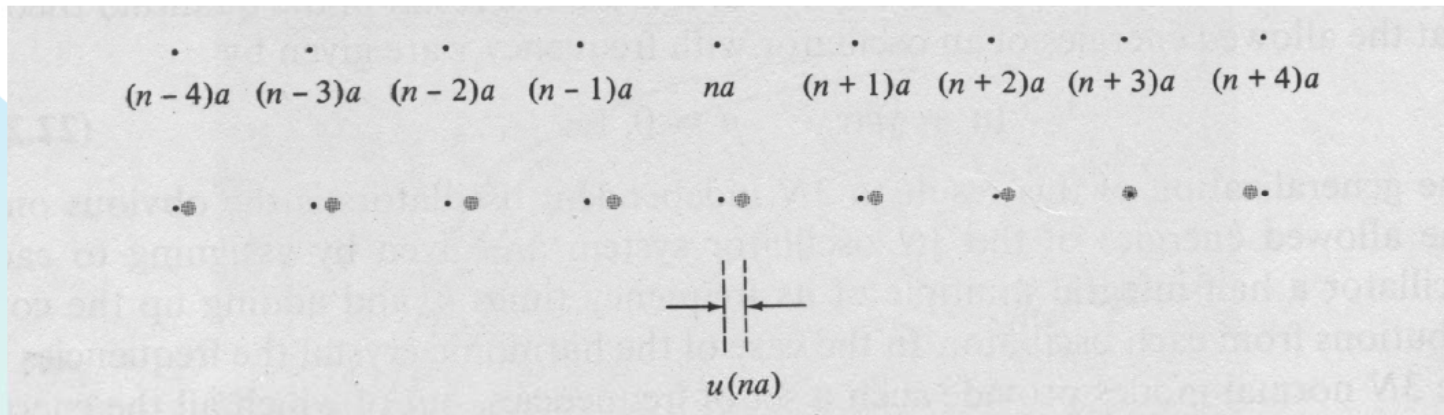


Longitudinal phonon wave



Transverse phonon wave

## Normal modes of a 1-D monatomic Bravais Lattice

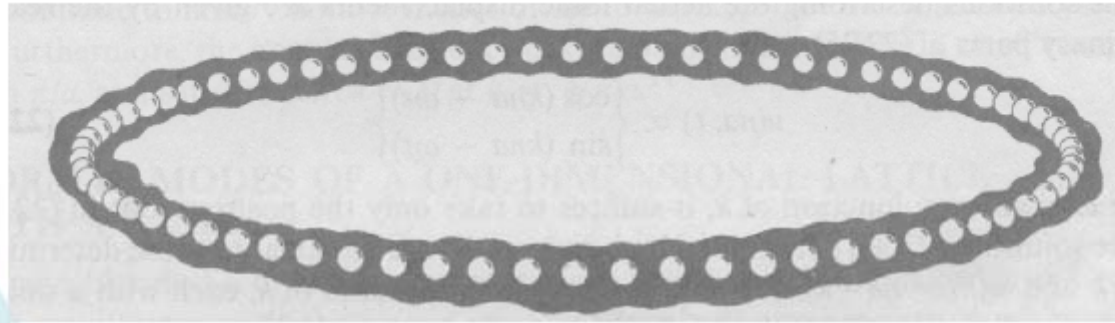


Consider a set of ions  $M$  separated by a distance  $a$ ,  
 $\vec{R} = na$  for integral  $n$ . Let  $u(na)$  be the displacement.  
 Assuming only neighboring ions interact, we have

$$U^{harm} = \frac{1}{2} C \sum_n [u(na) - u([n+1]a)]^2,$$

Newton's second law  $F = Ma$  or

$$M \frac{du(na)}{dt^2} = - \frac{\partial U^{harm}}{\partial u(na)} = -C [2u(na) - u([n-1]a) - u([n+1]a)]$$



If the chain of ions has number,  $N$ , and  $N$  is large, we can join the two remote ends of the chain back together with  $u([N + 1]a) = u(a); u(0) = u(Na)$ .

This is called Born-von Karman (periodic) boundary condition.

We seek solution of the form:  $u(na, t) \propto \exp[i(kna - \omega t)]$ .

The periodic condition requires  $\exp(ikNa) = 1$ ,

or  $kNa = 2\pi n$ , where  $n$  is integer, or  $k = \frac{2\pi n}{Na}$

There are just  $N$  values of  $k$  yield distinct solutions.

$$M\omega^2 e^{i(kna-\omega t)} = -C \left[ 2 - e^{-ika} - e^{ika} \right] e^{i(kna-\omega t)} = -2C(1 - \cos ka) e^{i(kna-\omega t)},$$

Therefore we have

$$\omega(k) = \sqrt{\frac{2C(1 - \cos ka)}{M}} = 2\sqrt{\frac{C}{M}} \left| \sin \frac{1}{2} ka \right|$$

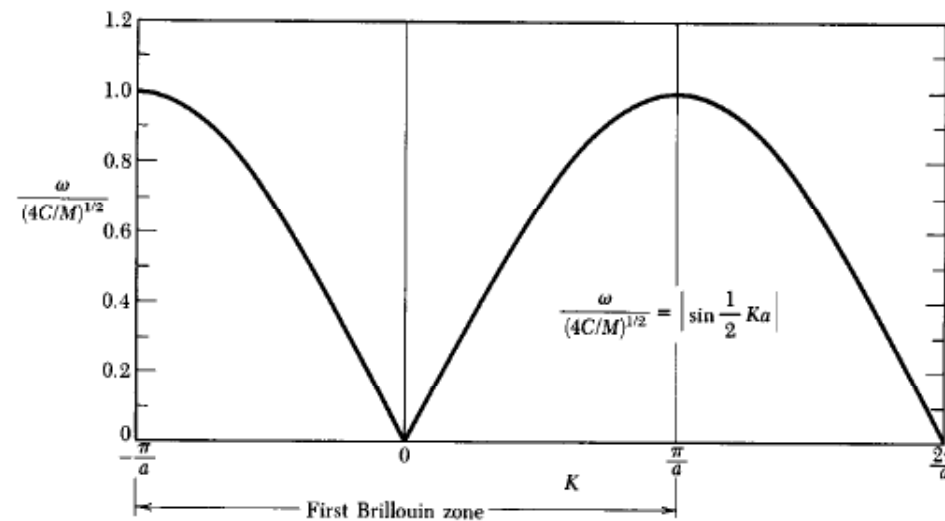
The solutions describing the actual ionic displacements are given by

$$u(na, t) \propto \begin{cases} \cos(kna - \omega t) \\ \sin(kna - \omega t) \end{cases}$$

Since  $\omega$  is an even function of  $k$ , solutions determined by  $k$  and  $-\omega(k)$  are identical to those determined by  $-k$  and  $\omega(k) = \omega(-k)$ .

There are  $N$  distinct values of  $k$ , each with a unique frequency  $\omega(k)$ , so we have  $2N$  independent solutions.

## First Brillouin zone

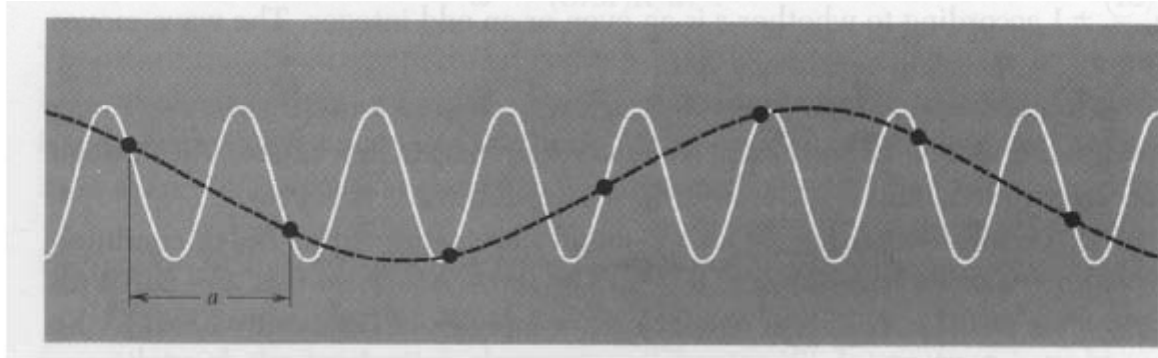


The boundary of the first Brillouin zone lies at  $k = \pm\pi / a$ . The slope of  $\omega$  versus  $k$  is zero at the zone boundary:

$$d\omega^2 / dk = (2Ca / M) \sin ka = 0.$$

An arbitrary motion of the chains is determined by specifying the  $N$  initial positions and  $N$  initial velocities of the ions. Since these can always be fit with a linear combination of the  $2N$  independent solutions, we have found a complete solution to the problem.





At the boundaries  $k_{\max} = \pm\pi / a$  of the first Brillouin zone the solution  $u(na, t) = u \exp(ikna) = u(-1)^n$ .

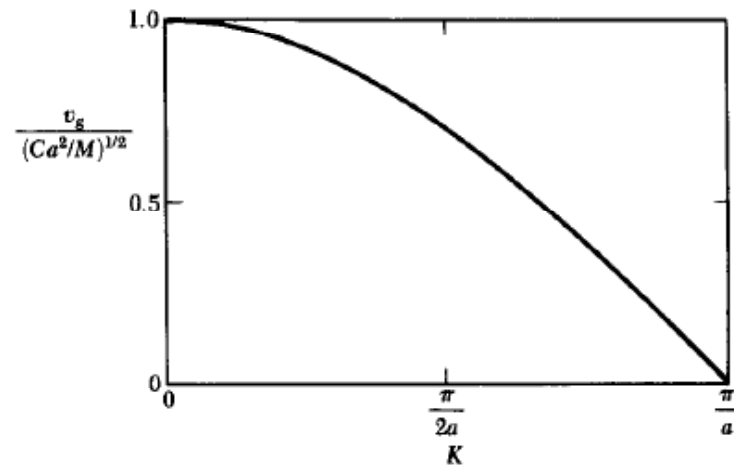
This is a standing wave: alternate atoms oscillate in opposite

## Group velocity

The transmission velocity of a wave packet is the group velocity, given as  $v_g = d\omega / dk$ . This is the velocity of energy propagation in the

medium. We find:  $v_g = (Ca^2 / M)^{1/2} \cos \frac{1}{2}ka$ . This is zero at the

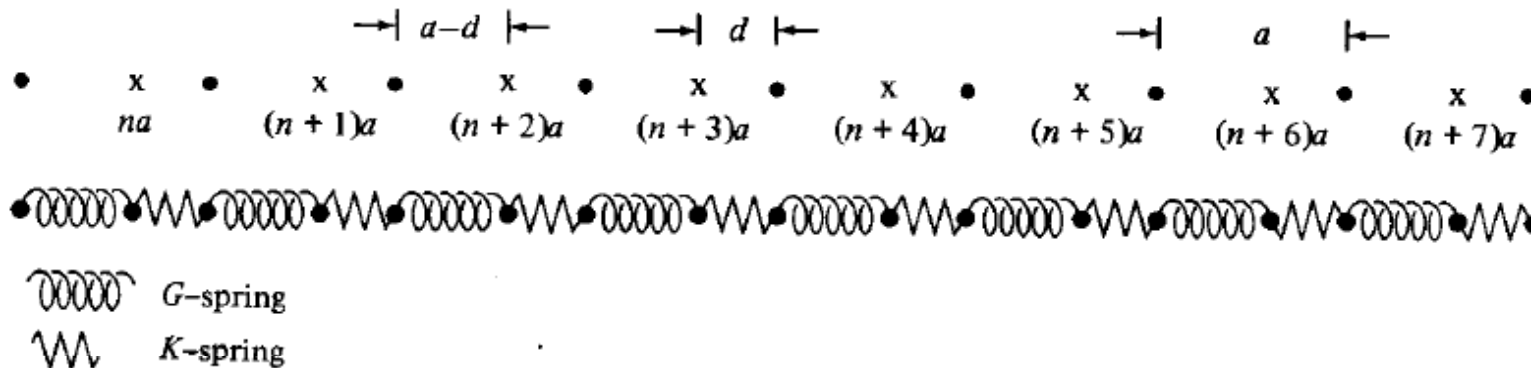
edge of the zone where  $k = \pi / a$ . The standing wave.



When  $ka \ll 1$  we have  $\cos ka \cong 1 - \frac{1}{2}(ka)^2$ , so that the dispersion relation becomes  $\omega^2 = (C/M)K^2 a^2$ .

If we drop the assumption that only nearest neighbors interact, very little changes. The functional dependence of  $\omega$  on  $k$  becomes more complex, but we continue to find  $N$  normal modes for the  $N$  allowed values of  $k$ . At small  $k$ ,  $\omega(k) \propto k$ .

## Normal modes of two atoms per primitive basis



The harmonic potential energy is:

$$U^{harm} = \frac{1}{2} K \sum_n [u_1(na) - u_2(na)]^2 + \frac{1}{2} G \sum_n [u_2(na) - u_1((n+1)a)]^2$$

where  $u_1(na)$  is the displacement around  $na$ ,  $u_2(na)$  the displacement around  $na + d$ . If  $d \leq a/2$ ,  $K \geq G$ .

$$M \frac{du_1(na)}{dt^2} = -\frac{\partial U^{harm}}{\partial u_1(na)} = -K [u_1(na) - u_2(na)] - G [u_1(na) - u_2((n-1)a)]$$

$$M \frac{du_2(na)}{dt^2} = -\frac{\partial U^{harm}}{\partial u_2(na)} = -K [u_2(na) - u_1(na)] - G [u_2(na) - u_1((n+1)a)]$$

We seek solution

$$u_1(na) = \varepsilon_1 \exp[i(kna - \omega t)]$$

$$u_2(na) = \varepsilon_2 \exp[i(kna - \omega t)]$$

Here  $\varepsilon_1$  and  $\varepsilon_2$  are constants that determine the relative amplitude and phase of the vibration of the ions within each primitive cell.

$$[M\omega^2 - (K + G)]\varepsilon_1 + (K + Ge^{-ika})\varepsilon_2 = 0$$

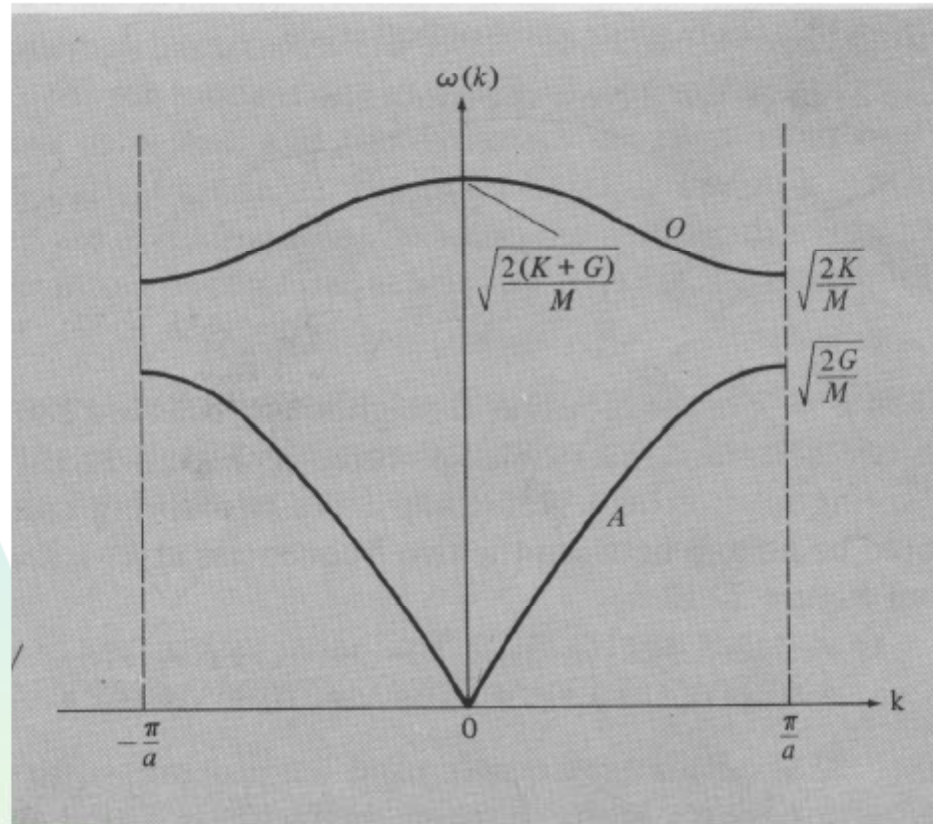
$$[M\omega^2 - (K + G)]\varepsilon_2 + (K + Ge^{-ika})\varepsilon_1 = 0$$

This pair of homogeneous equations will have a solution, if the determinant of the coefficients vanishes:

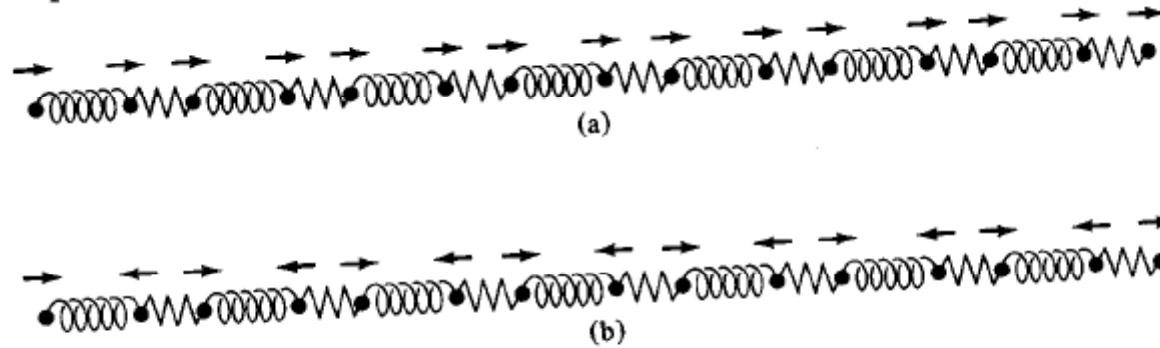
$$[M\omega^2 - (K + G)]^2 - |K + Ge^{-ika}|^2 = 0$$

$$\text{Two solutions: } \omega^2 = \frac{K + G}{M} \pm \frac{1}{M} \sqrt{K^2 + G^2 + 2KG \cos ka}$$

$$\text{with } \frac{\varepsilon_1}{\varepsilon_2} = \mp \frac{K + Ge^{-ika}}{|K + Ge^{-ika}|}$$



For each of the  $N$  values of  $k$  there are thus two solutions, leading to a total of  $2N$  normal modes. The two  $\omega$  vs  $k$  curves are two branches of the dispersion relation. Acoustic and optical branches.

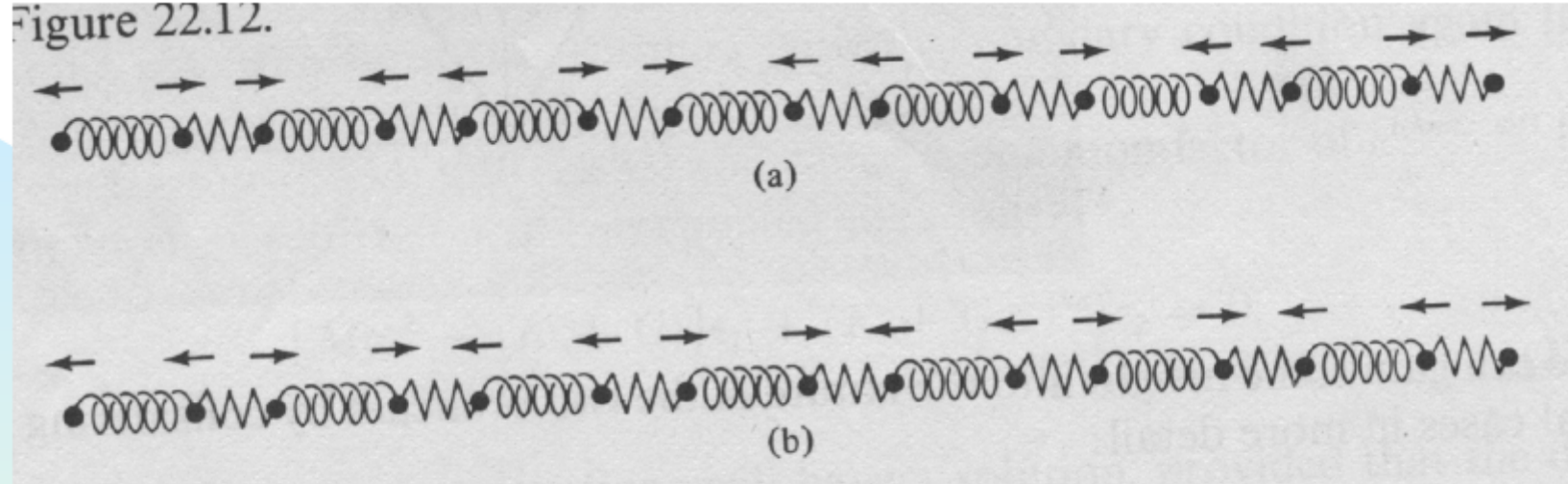


Case 1  $k \ll \pi / a$  Here  $\cos ka \approx 1 - (ka)^2 / 2$ , and

$$\omega = \sqrt{\frac{2(K+G)}{M}} - O(ka)^2$$

$$\omega = \sqrt{\frac{KG}{2M(K+G)}} ka \quad \text{When } k \text{ is very small, } \varepsilon_2 = \mp \varepsilon_1.$$

Figure 22.12.



Case 2  $k = \pi / a$

$$\omega = \sqrt{\frac{2K}{M}}, \varepsilon_1 = -\varepsilon_2$$

$$\omega = \sqrt{\frac{2G}{M}}, \varepsilon_1 = \varepsilon_2$$

When  $k = \pi / a$ , the motion in neighboring cells are 180 degrees out of phase, and therefore the two solutions are

Case 3  $K \gg G$  To leading order in  $G/K$  we have

$$\omega = \sqrt{\frac{2K}{M}} [1 + O(G/K)], \varepsilon_1 \approx -\varepsilon_2$$

$$\omega = \sqrt{\frac{2G}{M}} \left| \sin \frac{1}{2} ka \right| [1 + O(G/K)], \varepsilon_1 \approx \varepsilon_2$$

The optical branch now has a frequency that is independent of  $k$ , to leading order in  $G/K$ , and equal to the vibrational frequency of a single diatomic molecule composed of two mass  $M$  ions connected by a spring  $K$ . The acoustic branch is just that for a linear chain of atoms of mass  $2M$  coupled by the weak spring  $G$ .



An acoustic mode is one in which all ions within a primitive cell move essentially in phase and the dynamics are dominated by the interaction between cells; an optical mode is one in which the ions within each primitive cell are executing molecular vibratory mode.

Case 4  $K = G$

In this case we are really dealing with a monatomic Bravais lattice of lattice constant  $a/2$ .

