Chapter 3:

Crystal Binding and Elastic Constants

electrostatic interaction between electrons (negatively charged) and nuclei (positively charged) defines cohesion of solids

- Not magnetic forces
- Not gravitation

electrostatic interaction

- exchange energy
- van der Waals forces
- covalent forces

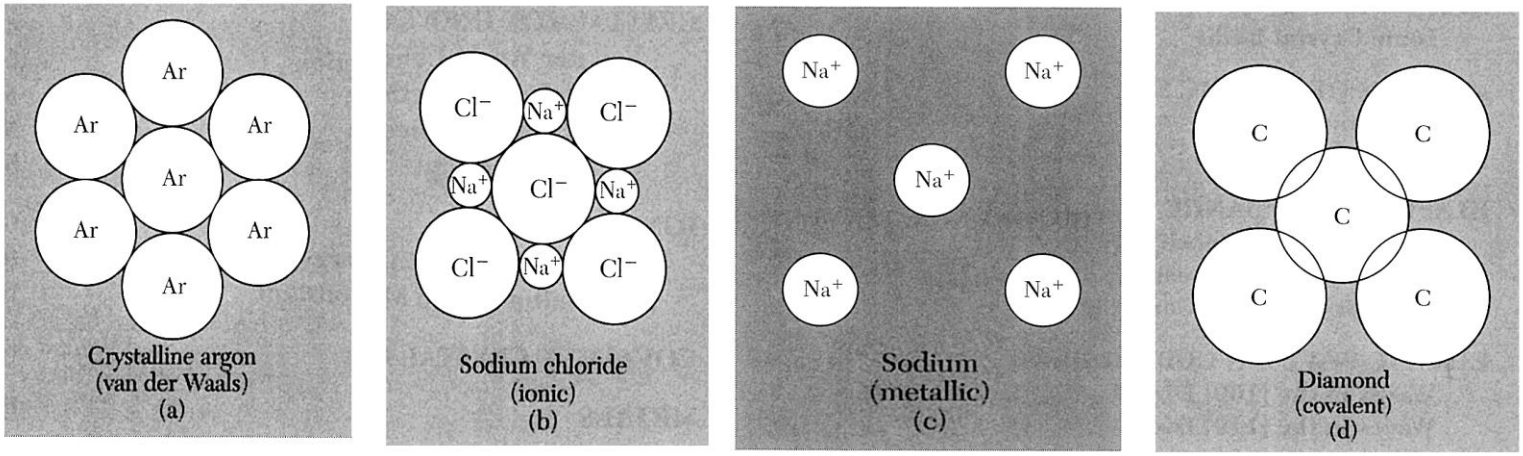


Figure 1 The principal types of crystalline binding. In (a) neutral atoms with closed electron shells are bound together weakly by the van der Waals forces associated with fluctuations in the charge distributions. In (b) electrons are transferred from the alkali atoms to the halogen atoms, and the resulting ions are held together by attractive electrostatic forces between the positive and negative ions. In (c) the valence electrons are taken away from each alkali atom to form a communal electron sea in which the positive ions are dispersed. In (d) the neutral atoms are bound together by the overlapping parts of their electron distributions.

Cohesive Energy:

The energy required to remove a single atom from the crystal

- the atom is neutral afterwards
- at infinite separation distance

Lattice energy:

The energy required to remove a single atom from an ionic crystal

- in an ionized state
- at infinite separation distance

Let us have a look at

- Cohesive Energy
- Melting Point
- Bulk Modulii

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.

kJ/mol
eV/atom
kcal/mol

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.											327.	446.	331.	275.	135.	7.74
1.113	1.51											3.39	4.63	3.43	2.85	1.40	0.080
25.67	34.7											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	134.7	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							

Table 2 Melting points, in K.

(After R. H. Lamoreaux)

Li 453.7	Be 1562											B 2365	C	N 63.15	O 54.36	F 53.48	Ne 24.56
Na 371.0	Mg 922											Al 933.5	Si 1687	P *w* 317 *r* 863	S 388.4	Cl 172.2	Ar 83.81
K 336.3	Ca 1113	Sc 1814	Ti 1946	V 2202	Cr 2133	Mn 1520	Fe 1811	Co 1770	Ni 1728	Cu 1358	Zn 692.7	Ga 302.9	Ge 1211	As 1089	Se 494	Br 265.9	Kr 115.8
Rb 312.6	Sr 1042	Y 1801	Zr 2128	Nb 2750	Mo 2895	Tc 2477	Ru 2527	Rh 2236	Pd 1827	Ag 1235	Cd 594.3	In 429.8	Sn 505.1	Sb 903.9	Te 722.7	I 386.7	Xe 161.4
Cs 301.6	Ba 1002	La 1194	Hf 2504	Ta 3293	W 3695	Re 3459	Os 3306	Ir 2720	Pt 2045	Au 1338	Hg 234.3	Tl 577	Pb 600.7	Bi 544.6	Po 527	At	Rn
Fr	Ra 973	Ac 1324															

Ce 1072	Pr 1205	Nd 1290	Pm	Sm 1346	Eu 1091	Gd 1587	Tb 1632	Dy 1684	Ho 1745	Er 1797	Tm 1820	Yb 1098	Lu 1938
Th 2031	Pa 1848	U 1406	Np 910	Pu 913	Am 1449	Cm 1613	Bk 1562	Cf	Es	Fm	Md	No	Lw

Table 3 Isothermal bulk modulii and compressibilities at room temperature

After K. Gschneidner, Jr., Solid State Physics 16, 275–426 (1964); several data are from F. Birch, in *Handbook of physical constants*, Geological Society of America Memoir 97, 107–173 (1966). Original references should be consulted when values are needed for research purposes. Values in parentheses are estimates. Letters in parentheses refer to the crystal form. Letters in brackets refer to the temperature:

[a] = 77 K; [b] = 273 K; [c] = 1 K; [d] = 4 K; [e] = 81 K.

Bulk modulus in units 10^{12} dyn/cm² or 10^{11} N/m²
Compressibility in units 10^{-12} cm²/dyn or 10^{-11} m²/N

H [d] 0.002 500																	He [d] 0.00 1168
Li 0.116 8.62	Be 1.003 0.997											B 1.78 0.562	C [d] 4.43 0.226	N [e] 0.012 80	O	F	Ne [d] 0.010 100
Na 0.068 14.7	Mg 0.354 2.82											Al 0.722 1.385	Si 0.988 1.012	P [b] 0.304 3.29	S [r] 0.178 5.62	Cl	Ar [a] 0.013 79
K 0.032 31.	Ca 0.152 6.58	Sc 0.435 2.30	Ti 1.051 0.951	V 1.619 0.618	Cr 1.901 0.526	Mn 0.596 1.68	Fe 1.683 0.594	Co 1.914 0.522	Ni 1.86 0.538	Cu 1.37 0.73	Zn 0.598 1.67	Ga [b] 0.569 1.76	Ge 0.772 1.29	As 0.394 2.54	Se 0.091 11.0	Br	Kr [a] 0.018 56
Rb 0.031 32.	Sr 0.116 8.62	Y 0.366 2.73	Zr 0.833 1.20	Nb 1.702 0.587	Mo 2.725 0.366	Tc (2.97) (0.34)	Ru 3.208 0.311	Rh 2.704 0.369	Pd 1.808 0.553	Ag 1.007 0.993	Cd 0.467 2.14	In 0.411 2.43	Sn [g] 1.11 0.901	Sb 0.383 2.61	Te 0.230 4.35	I	Xe
Cs 0.020 50.	Ba 0.103 9.97	La 0.243 4.12	Hf 1.09 0.92	Ta 2.00 0.50	W 3.232 0.309	Re 3.72 0.269	Os (4.18) (0.24)	Ir 3.55 0.282	Pt 2.783 0.359	Au 1.732 0.577	Hg [c] 0.382 2.60	Tl 0.359 2.79	Pb 0.430 2.33	Bi 0.315 3.17	Po (0.26) (3.8)	At	Rn
Fr (0.020) (50.)	Ra (0.132) (7.6)	Ac (0.25) (4.)															

Ce [γ] 0.239 4.18	Pr 0.306 3.27	Nd 0.327 3.06	Pm (0.35) (2.85)	Sm 0.294 3.40	Eu 0.147 6.80	Gd 0.383 2.61	Tb 0.399 2.51	Dy 0.384 2.60	Ho 0.397 2.52	Er 0.411 2.43	Tm 0.397 2.52	Yb 0.133 7.52	Lu 0.411 2.43
Th 0.543 1.84	Pa (0.76) (1.3)	U 0.987 1.01	Np (0.68) (1.5)	Pu 0.54 1.9	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Inert Gas Crystals (Xe, Ar, Kr, ...)

Outer electron shells are completely filled
Spherically symmetric distribution of outermost electrons

- Insulators (no free electrons)
- transparent (no low energy dipole transitions)
- weakly bond
- low melting point

- only van der Waals Forces (what are vd. Waals Forces ?)

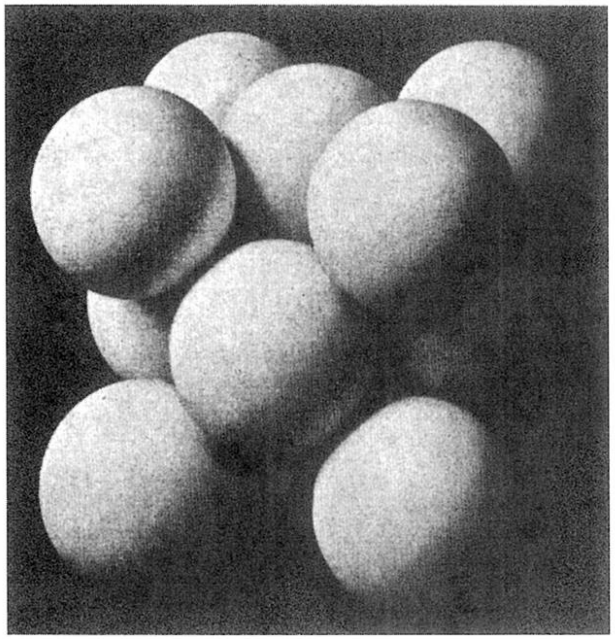


Figure 2 Cubic close-packed (fcc) crystal structure of the inert gases Ne, Ar, Kr, and Xe. The lattice parameters of the cubic cells are 4.46, 5.31, 5.64, and 6.13 Å, respectively, at 4 K.

What is the Lennard-Jones Potential ?

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

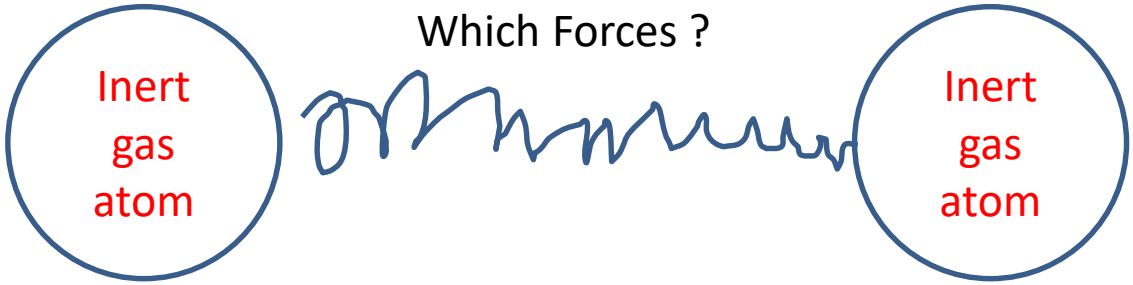
R_o

~ about only 1 % of ionization potential

σ

$R_o/\sigma \sim 1.09$

Van der Waals – London Interaction



neutral atom

neutral atom

No Coulomb Forces ! ..... ?

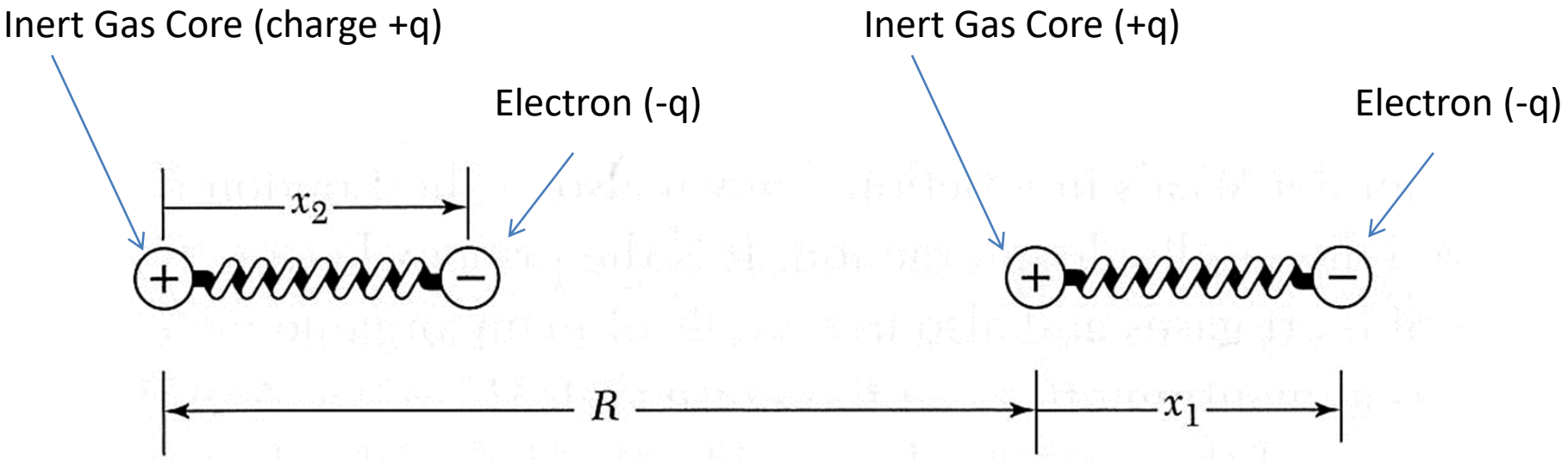


Figure 3 Coordinates of the two oscillators.

Two identical, linear, harmonic oscillators 1 and 2

$$\mathcal{H}_0 = \frac{1}{2m} p_1^2 + \tfrac{1}{2} C x_1^2 + \frac{1}{2m} p_2^2 + \tfrac{1}{2} C x_2^2 \ . \qquad (1)$$

Coulomb Interaction

(CGS)
$$\mathcal{H}_1 = \frac{e^2}{R} + \frac{e^2}{R + x_1 - x_2} - \frac{e^2}{R + x_1} - \frac{e^2}{R - x_2} \ ; \qquad (2)$$

$$|x_1|, |x_2| \ll R \quad \Rightarrow \quad \mathcal{H}_1 \cong -\frac{2e^2 x_1 x_2}{R^3} \ . \tag{3}$$

symmetric mode asymmetric mode

$$x_s \equiv \frac{1}{\sqrt{2}}(x_1 + x_2) \ ; \qquad x_a \equiv \frac{1}{\sqrt{2}}(x_1 - x_2) \ , \tag{4}$$

in coordinates of 1 and 2

$$x_1 = \frac{1}{\sqrt{2}}(x_s + x_a) \ ; \qquad x_2 = \frac{1}{\sqrt{2}}(x_s - x_a) \ . \tag{5}$$

$$p_1 \equiv \frac{1}{\sqrt{2}}(p_s + p_a) \ ; \qquad p_2 \equiv \frac{1}{\sqrt{2}}(p_s - p_a) \ . \tag{6}$$

$$\mathcal{H} = \left[\frac{1}{2m}p_s^2 + \frac{1}{2}\left(C - \frac{2e^2}{R^3}\right)x_s^2\right] + \left[\frac{1}{2m}p_a^2 + \frac{1}{2}\left(C + \frac{2e^2}{R^3}\right)x_a^2\right] \quad . \tag{7}$$

ω_0 given by $(C/m)^{1/2}$.

$$\omega = \left[\left(C \pm \frac{2e^2}{R^3}\right)\Big/ m\right]^{1/2} = \omega_0\left[1 \pm \frac{1}{2}\left(\frac{2e^2}{CR^3}\right) - \frac{1}{8}\left(\frac{2e^2}{CR^3}\right)^2 + \cdots\right] , \tag{8}$$

Zero-Point Energy of interacting system: $\frac{1}{2}\hbar(\omega_s + \omega_a)$

Zero-Point Energy of a non-interacting system: $\frac{1}{2}\hbar\omega_0$

$$\Delta U = \tfrac{1}{2}\hbar(\Delta\omega_s + \Delta\omega_a) = -\hbar\omega_0 \cdot \frac{1}{8}\left(\frac{2e^2}{CR^3}\right)^2 = -\frac{A}{R^6} \quad . \tag{9}$$

The interacting system has a lower energy by ΔU
because of charge fluctuations (van der Waals Force)
also called London Interaction or induced dipole-dipole interaction

$$\Delta U = \tfrac{1}{2}\hbar(\Delta\omega_s + \Delta\omega_a) = -\hbar\omega_0 \cdot \frac{1}{8}\left(\frac{2e^2}{CR^3}\right)^2 = -\frac{A}{R^6} \ . \qquad (9)$$

approximately: A = $\hbar\omega_0\alpha^2$

strongest optical absorption line

electronic polarizability (Chapter 15)

attractive van der Waals Interaction

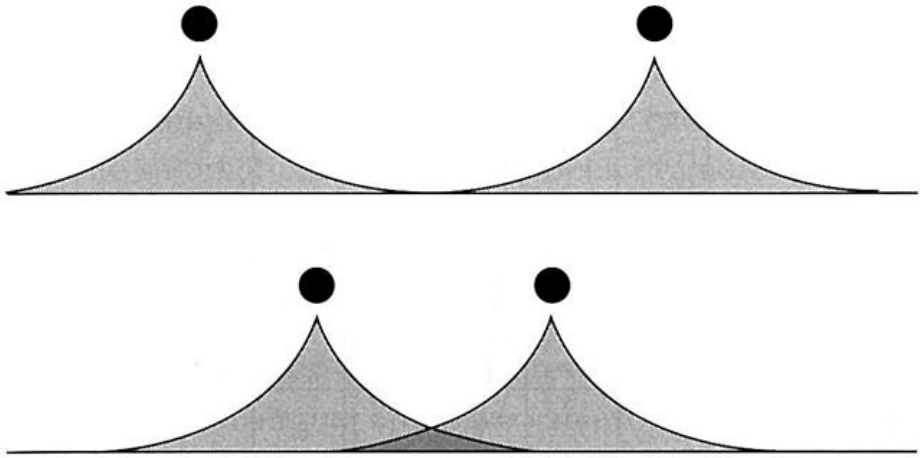


Figure 4 Electronic charge distributions overlap as atoms approach. The solid circles denote the nuclei.

repulsive interaction due to overlap of charge density (Pauli exclusion principle)

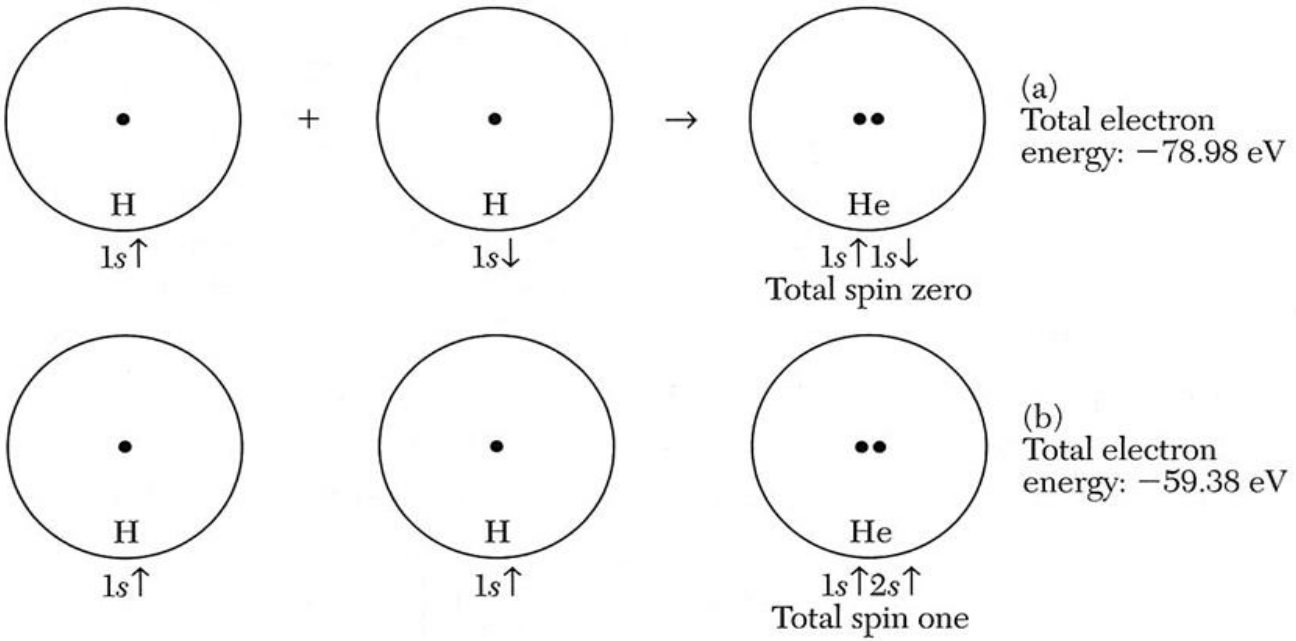


Figure 5 The effect of Pauli principle on the repulsive energy: in an extreme example, two hydrogen atoms are pushed together until the protons are almost in contact. The energy of the electron system alone can be taken from observations on atomic He, which has two electrons. In (a) the electrons have antiparallel spins and the Pauli principle has no effect: the electrons are bound by −78.98 eV. In (b) the spins are parallel: the Pauli principle forces the promotion of an electron from a 1s ↑ orbital of H to a 2s ↑ orbital of He. The electrons now are bound by -59.38 eV, less than (a) by 19.60 eV. This is the amount by which the Pauli principle has increased the repulsion. We have omitted the repulsive coulomb energy of the two protons, which is the same in both (a) and (b).

Lennard-Jones Potential (approximate description)

attractive van der Waals forces

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

repulsive interaction

Force between two atoms: $F = - dU / dR$

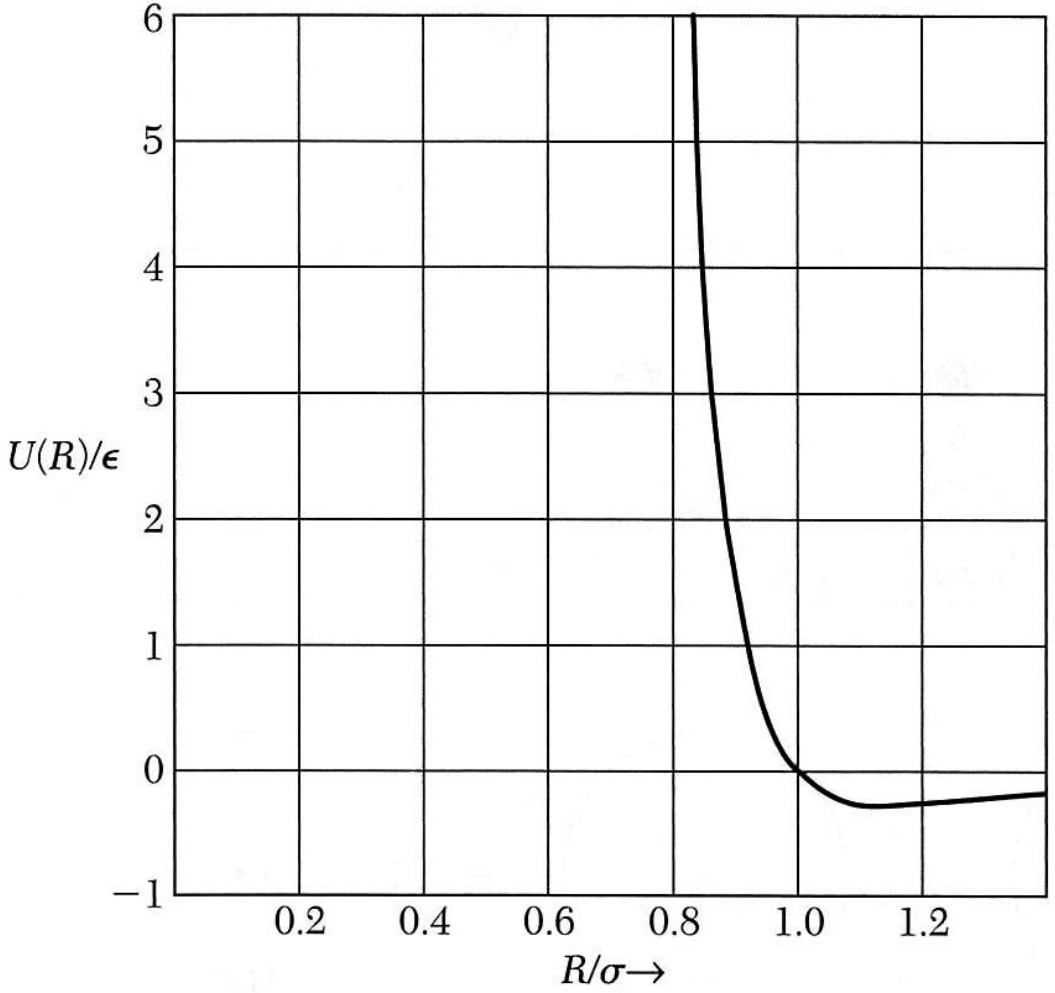


Figure 6 Form of the Lennard-Jones potential (10) which describes the interaction of two inert gas atoms. The minimum occurs at $R/\sigma = 2^{1/6} \cong 1.12$. Notice how steep the curve is inside the minimum, and how flat it is outside the minimum. The value of U at the minimum is $-\epsilon$; and $U = 0$ at $R = \sigma$.

Equilibrium Lattice Constant

N atoms in the crystal

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

double counting

distance between atom i and j in units of nearest neighbour distance R

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

close to 12 (number of neighbors – which dominate the interaction)

Minimum distance (Force = 0)

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

$$R_0/\sigma = 1.09 \ ,$$

	Ne	Ar	Kr	Xe
$R_0/\boldsymbol{\sigma}$	1.14	1.11	1.10	1.09

Variations due to zero-point quantum effects

Cohesive Energy (at T = 0K, 0 Pressure)

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

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

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

The heavier the atom, the smaller the quantum correction.

Ionic Crystals

- Ionic crystals are made of positively and negatively charged ions and result from respective Coulomb Forces

- ions donate or accept an electron from the counterpart to completely fill all electronic shells – similar to inert gas

- charge is basically spherically symmetrically distributed with minor deformations due to the neighbors

Li: $1s^2\ 2s^1$ F: $1s^2\ 2s^2\ 2p^5$ => Li+: $1s^2$ and F-: $1s^2\ 2s^2\ 2p^6$

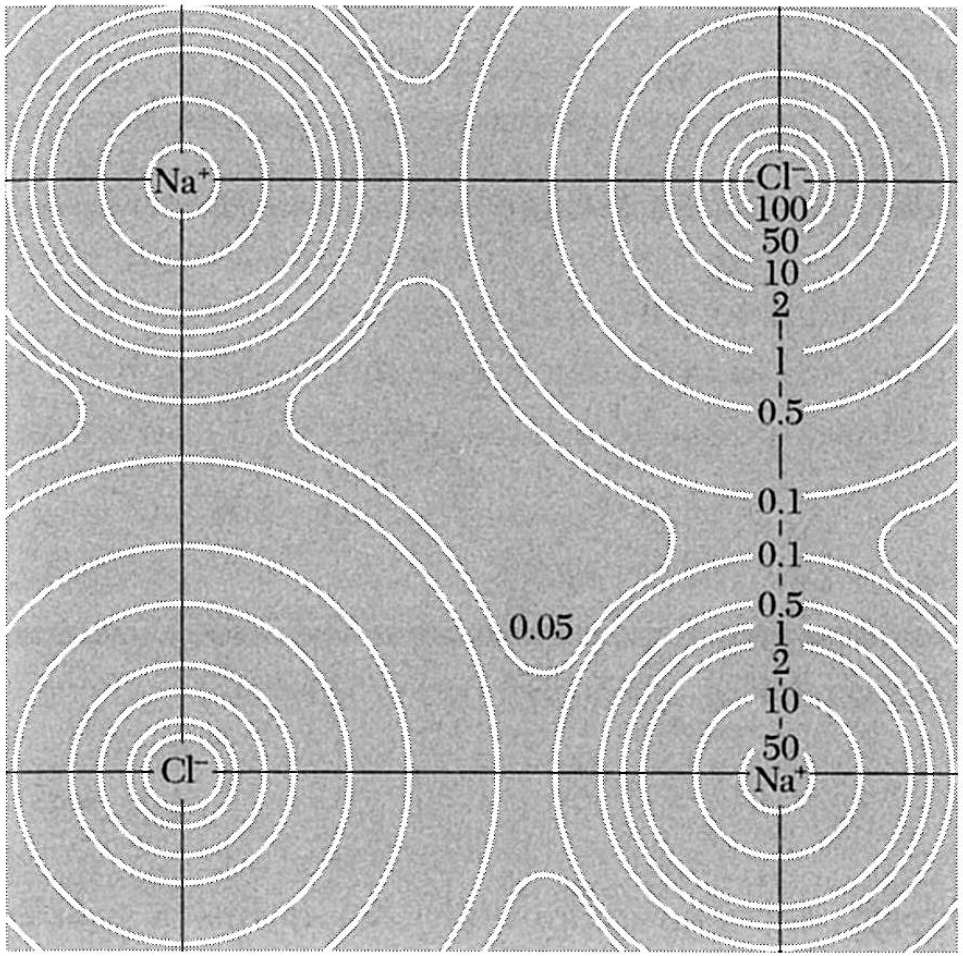


Figure 7 Electron density distribution in the base plane of NaCl, after x-ray studies by G. Schoknecht. The numbers on the contours give the relative electron concentration.

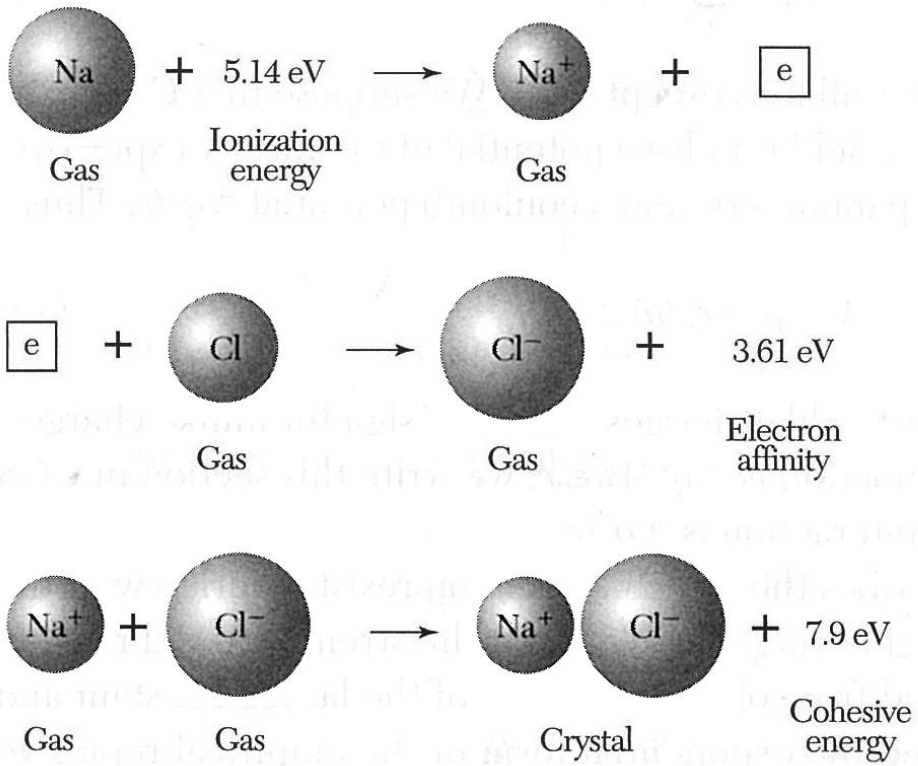


Figure 8 The energy per molecule unit of a crystal of sodium chloride is $(7.9 - 5.1 + 3.6) = 6.4$ eV lower than the energy of separated neutral atoms. The lattice energy with respect to separated ions is 7.9 eV per molecule unit. All values on the figure are experimental. Values of the ionization energy are given in Table 5, and values of the electron affinity are given in Table 6.

Table 6 Electron affinities of negative ions

The electron affinity is positive for a stable negative ion.

Atom	Electron affinity energy eV	Atom	Electron affinity energy eV
H	0.7542	Si	1.39
Li	0.62	P	0.74
C	1.27	S	2.08
O	1.46	Cl	3.61
F	3.40	Br	3.36
Na	0.55	I	3.06
Al	0.46	K	0.50

Source: H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data 4, 539 (1975).

Electrostatic or Madelung Energy (Coulomb Force)

$$F \sim q_1 q_2 / r^2$$

- attractive electrostatic force (Madelung energy)
- van der Waals Forces are present but are very weak (1-2 %)
- repulsive forces are active (see inert gases)

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

Energy between ions i and j

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

central repulsive potential (r^{-12})

Note:
CGS: q^2/r_{ij}
SI: $q^2/4\pi\varepsilon_o r_{ij}$

It is convenient again to introduce quantities p_{ij} such that $r_{ij} \equiv p_{ij}R$, where R is the nearest-neighbor separation in the crystal. If we include the repulsive interaction only among nearest neighbors, we have

$$\text{(CGS)} \qquad U_{ij} = \begin{cases} \lambda \exp(-R/\rho) - \dfrac{q^2}{R} & \text{(nearest neighbors)} \\ \pm\dfrac{1}{p_{ij}}\dfrac{q^2}{R} & \text{(otherwise).} \end{cases} \tag{19}$$

Thus

number of nearest neighbors

$$\text{(CGS)} \qquad U_{\text{tot}} = NU_i = N\left(z\lambda e^{-R/\rho} - \frac{\alpha q^2}{R}\right), \tag{20}$$

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

Determine equilibrium separation (F = dU/dR = 0)

=>

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

very short range repulsive interaction
$\rho \sim 0.1\ R_0$

Madelung Energy

$$\alpha = \sum_j{}' \frac{(\pm)}{p_{ij}}$$

Definition of the Madelung Constant

To give a stable crystal: $\alpha > 0$

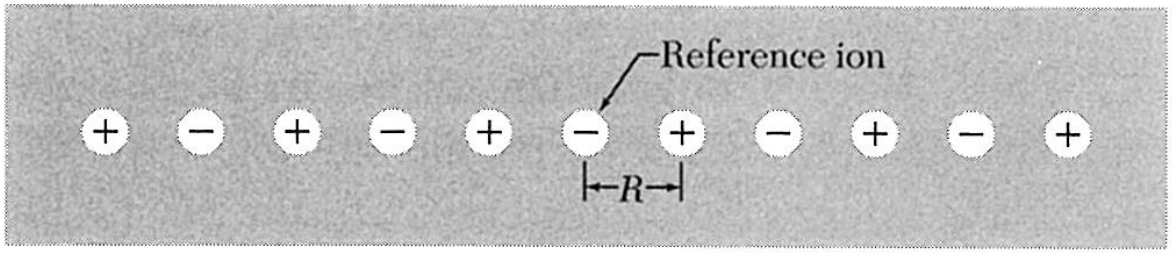


Figure 9 Line of ions of alternating signs, with distance R between ions.

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

For a 1D Chain:

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \cdots$$

α = 2 ln2

For 2D and 3D – very difficult to calculate .....

Typical values of the Madelung constant are listed below, based on unit charges and *referred to the nearest-neighbor distance:*

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

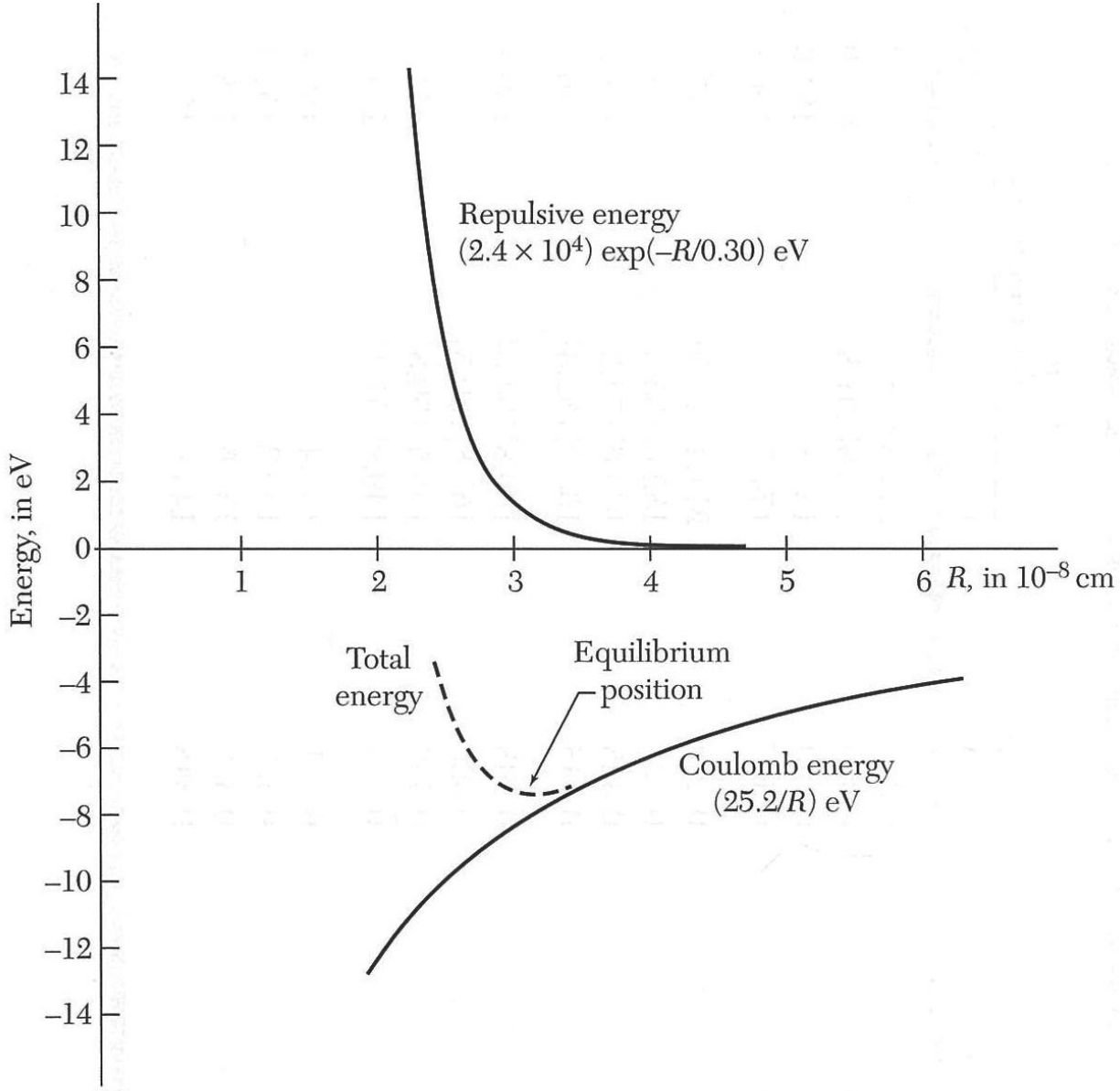


Figure 10 Energy per molecule of KCl crystal, showing Madelung (coulomb) and repulsive contributions.

Table 7 Properties of alkali halide crystals with the NaCl structure

All values (except those in square brackets) at room temperature and atmospheric pressure, with no correction for changes in R_0 and U from absolute zero. Values in square brackets at absolute zero temperature and zero pressure, from private communication by L. Brewer.

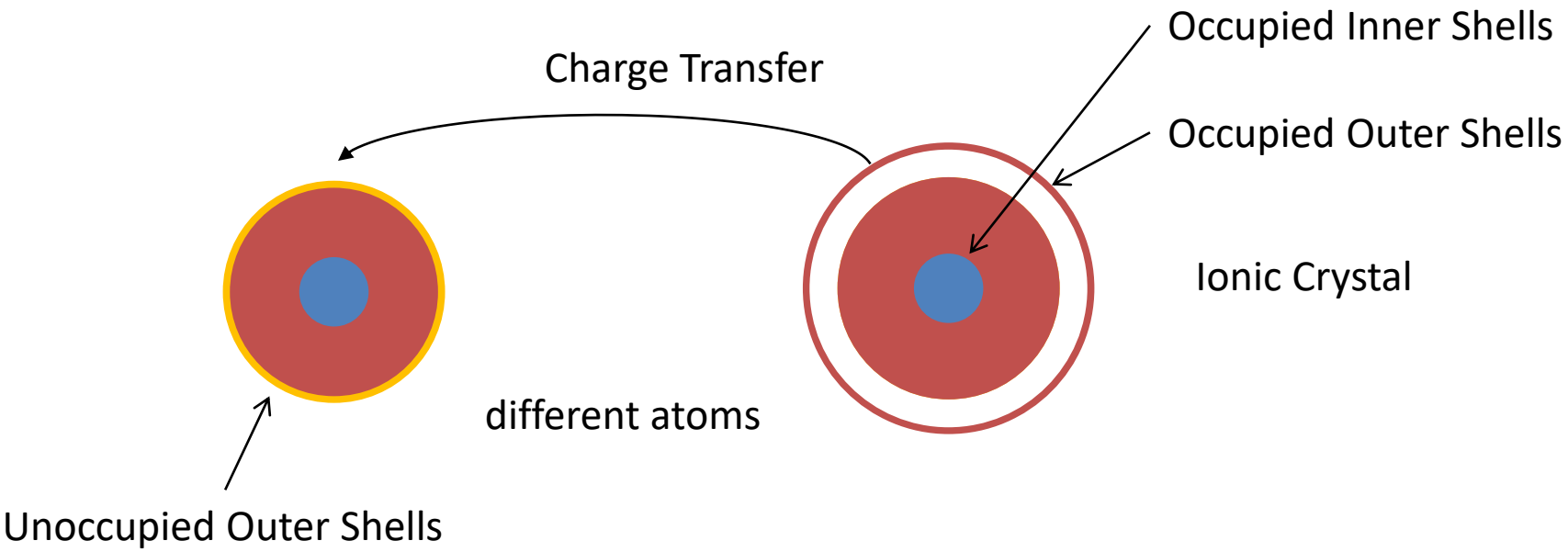
	Nearest-neighbor separation R_0 in Å	Bulk modulus B, in 10^{11} dyn/cm^2 or 10^{10} N/m^2	Repulsive energy parameter $z\lambda$, in 10^{-8} erg	Repulsive range parameter ρ, in Å	Lattice energy compared to free ions, in kcal/mol	
					Experimental	Calculated
LiF	2.014	6.71	0.296	0.291	242.3[246.8]	242.2
LiCl	2.570	2.98	0.490	0.330	198.9[201.8]	192.9
LiBr	2.751	2.38	0.591	0.340	189.8	181.0
LiI	3.000	(1.71)	0.599	0.366	177.7	166.1
NaF	2.317	4.65	0.641	0.290	214.4[217.9]	215.2
NaCl	2.820	2.40	1.05	0.321	182.6[185.3]	178.6
NaBr	2.989	1.99	1.33	0.328	173.6[174.3]	169.2
NaI	3.237	1.51	1.58	0.345	163.2[162.3]	156.6
KF	2.674	3.05	1.31	0.298	189.8[194.5]	189.1
KCl	3.147	1.74	2.05	0.326	165.8[169.5]	161.6
KBr	3.298	1.48	2.30	0.336	158.5[159.3]	154.5
KI	3.533	1.17	2.85	0.348	149.9[151.1]	144.5
RbF	2.815	2.62	1.78	0.301	181.4	180.4
RbCl	3.291	1.56	3.19	0.323	159.3	155.4
RbBr	3.445	1.30	3.03	0.338	152.6	148.3
RbI	3.671	1.06	3.99	0.348	144.9	139.6

R_o

Data from various tables by M. P. Tosi, Solid State Physics **16**, 1 (1964).

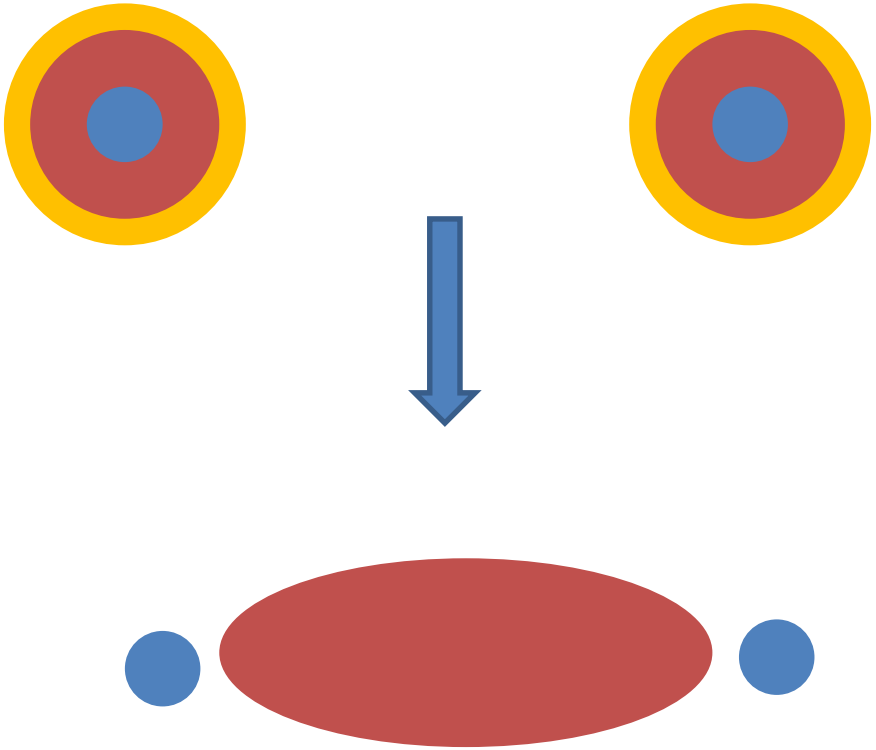
$\rho \sim 0.1 R_o$

Covalent Crystals



equal atoms

Si, Ge, ...



share electrons

Hydrogen System (1 electron)

$$\mathcal{H} = \frac{\hbar^2}{2m}\Delta - \frac{Ze^2}{4\epsilon_0 r_A} - \frac{Z'e^2}{4\epsilon_0 r_B} + \frac{ZZ'e^2}{4\epsilon_0 R}$$

Kinetic Energy

electron-nuclei Coulomb Energy

nuclei-nuclei Coulomb Energy

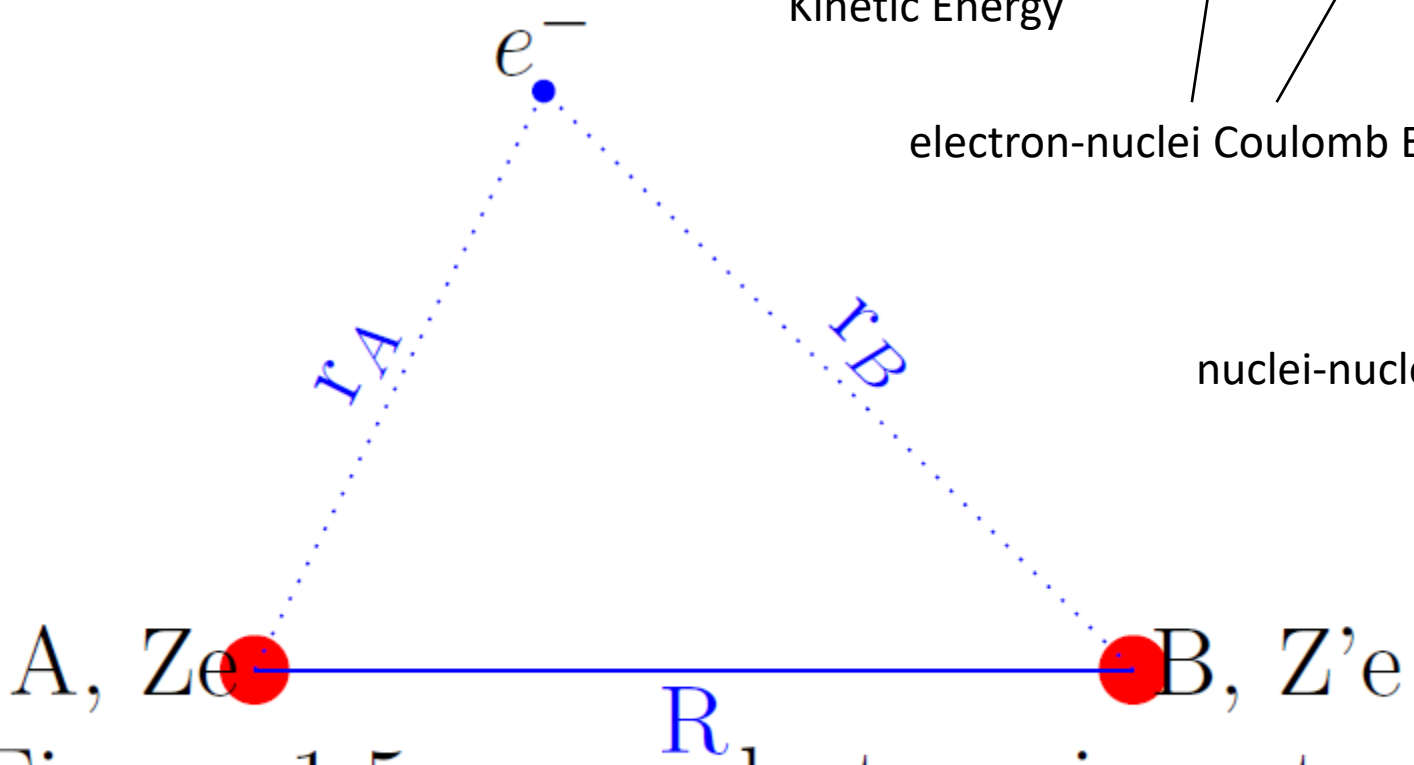


Figure 1.5: one electron in a two hydrogen system

Solve Schroedinger Equation $\mathcal{H}\Psi_{MO} = E\Psi_{MO}$

$$E = \frac{\int \Psi^* \mathcal{H} \Psi d\vec{r}}{\int \Psi^* \Psi d\vec{r}}$$

LCAO approximation (Linear Combination of Atomic Orbitals)

$$\Psi = c_A \Psi_A + c_B \Psi_B$$

Solution of 1-Atom Hydrogen System

$$H_{AB} = \int \Psi_A \mathcal{H} \Psi_B d\vec{r} \text{ exchange integral}$$

$$H_{AA} = \int \Psi_A \mathcal{H} \Psi_A d\vec{r}$$

$$E_{\pm} \lesssim E'_{\pm} = \frac{H_{AA} \pm H_{AB}}{1 \pm S}$$

$$S = \int \Psi_A \Psi_B d\vec{r} \text{ overlap integral}$$

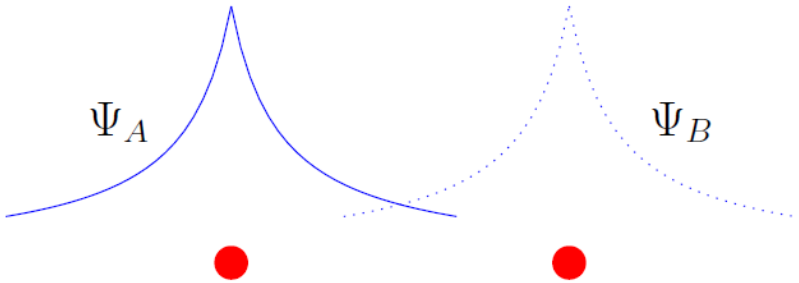


Figure 1.6: Two identical but isolated systems

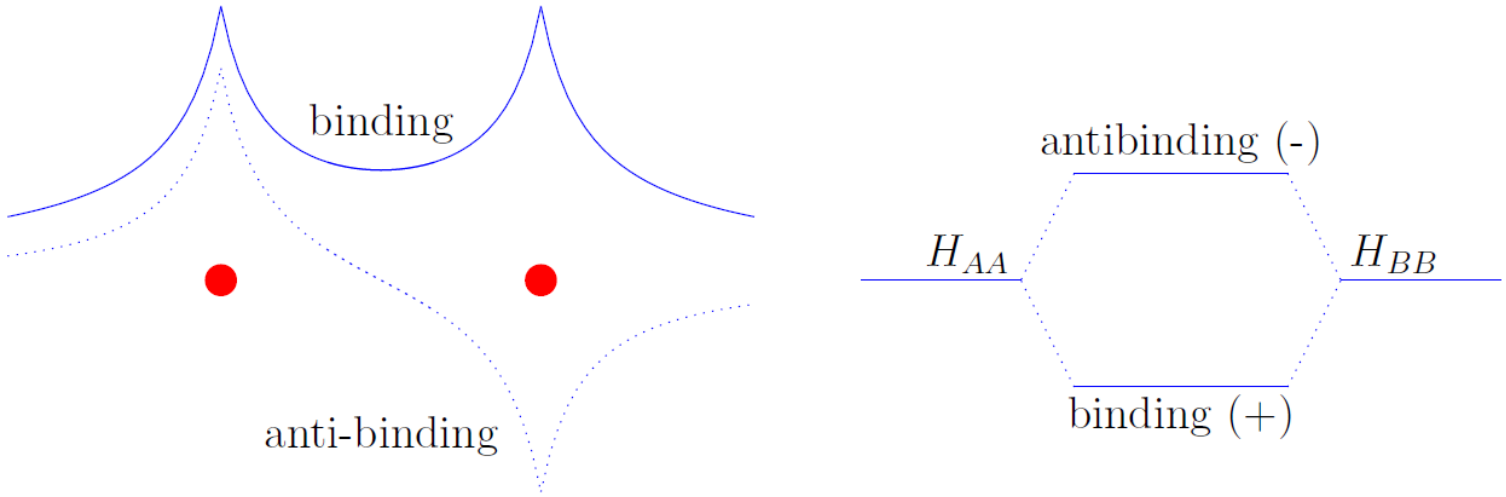
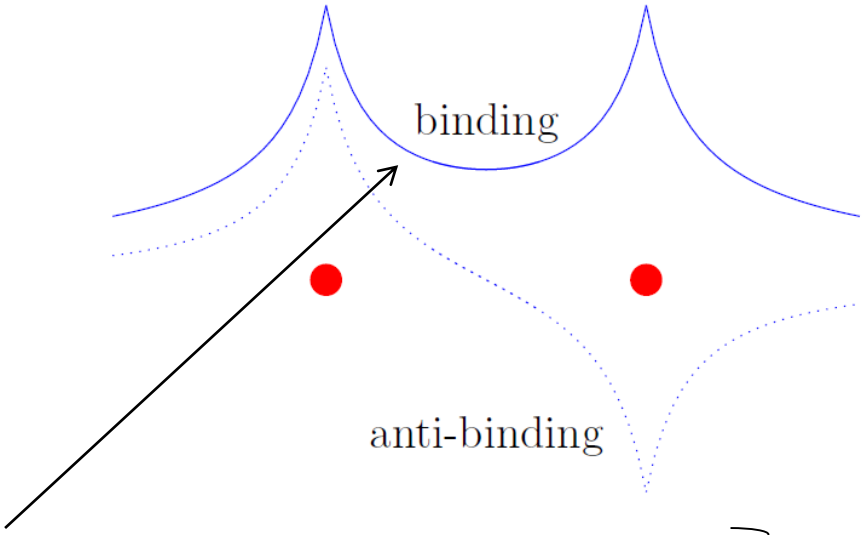


Figure 1.7: one electron in a two hydrogen system and results given by LCAO. (left) Amplitude of wave functions for the binding (+) and the anti-binding (-) case. (right) Result of the achieved delocalization of the electron over two atoms, is a lowered energy of the total system.

2 Hydrogen atoms
(with 2 electrons)



2 electrons in the same state (binding)
⇒ (Pauli Principle) s = +/- ½ ..... Total Spin S = 0
⇒ We loose Coulomb Energy (close proximity)
⇒ We gain Exchange Energy

2 electrons in different states (anti-binding)
⇒ S = 0,1
⇒ We gain Coulomb Energy
⇒ We loose Exchange Energy
⇒ 1 electron is in a higher state = loss of energy

The balance of Coulomb Energy and Exchange Energy determines if we have a magnetic state !
(see later Chapters)

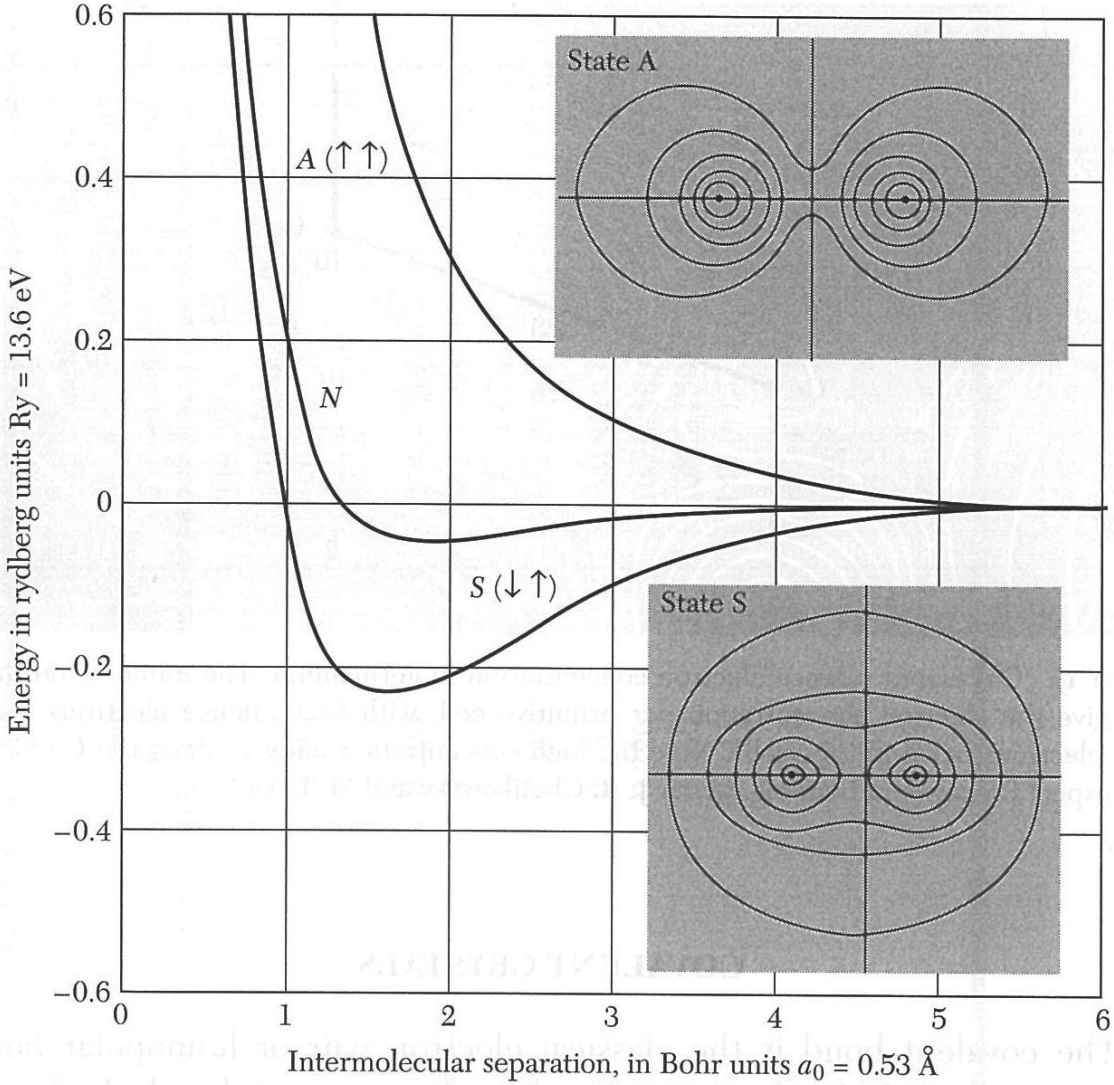


Figure 12 Energy of molecular hydrogen (H_2) referred to separated neutral atoms. A negative energy corresponds to binding. The curve *N* refers to a classical calculation with free atom charge densities; *A* is the result for parallel electron spins, taking the Pauli exclusion principle into account, and *S* (the stable state) for antiparallel spins. The density of charge is represented by contour lines for the states *A* and *S*.

C: $1s^2\ 2s^2\ 2p^2$ (equivalent for Si, Ge, Sn, ...)

↓ 2 occupied states in 6 different states
but: sp^3 hybridization

C: $1s^2\ 2s^1\ 2p^3$

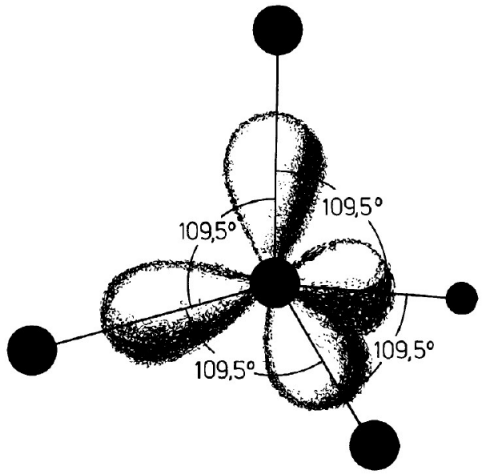
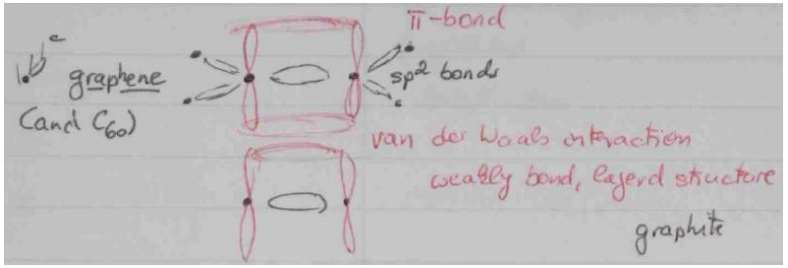


Figure 1.9: Coordination geometry for C, Si, Ge after sp^3

- (atom) $2s \rightarrow 2p$: loss of energy
- (crystal) $2s^1 2p^3 \rightarrow sp^3$: gain of energy via 4 binding states
- (structure) 3 dimensional
- (excitation) band gap = binding - anti-binding state
- (insulator) band gap > 3 eV
- (semiconductor) band gap < 3 eV

- sp^2: $2s^2 2p^2 \rightarrow [2s^1 2p_x 2p_y] 2p_z \rightarrow sp^2$ + half filled $2p_z$ [C, Si, Ge]
  - (structure) 2 dimensional
  - non-conductive in Carbon-plane
  - conductive in π-plane



- sp^2: $2s^2 2p^3 \rightarrow [2s^1 2p_x 2p_y] 2p_z^2 \rightarrow sp^2$ + filled $2p_z$ [P, As]
- sp: $2s^2 2p^4 \rightarrow [2s^1 2p_x] 2p_y^2 2p_z^2 \rightarrow sp$ [Te, Se]
  - (structure) 1 dimensional
- Bor-Nitrid: B $(2s^2 2p^1)$ N $(2s^2 2p^3)$ $\rightarrow$ charge transfer $\rightarrow$ B $(2s^2 2p^2)$ N $(2s^2 2p^2)$ $\rightarrow$ sp^3 bonds with ionic character.

electrons forming the bond are partly localized
in the region between the atoms.

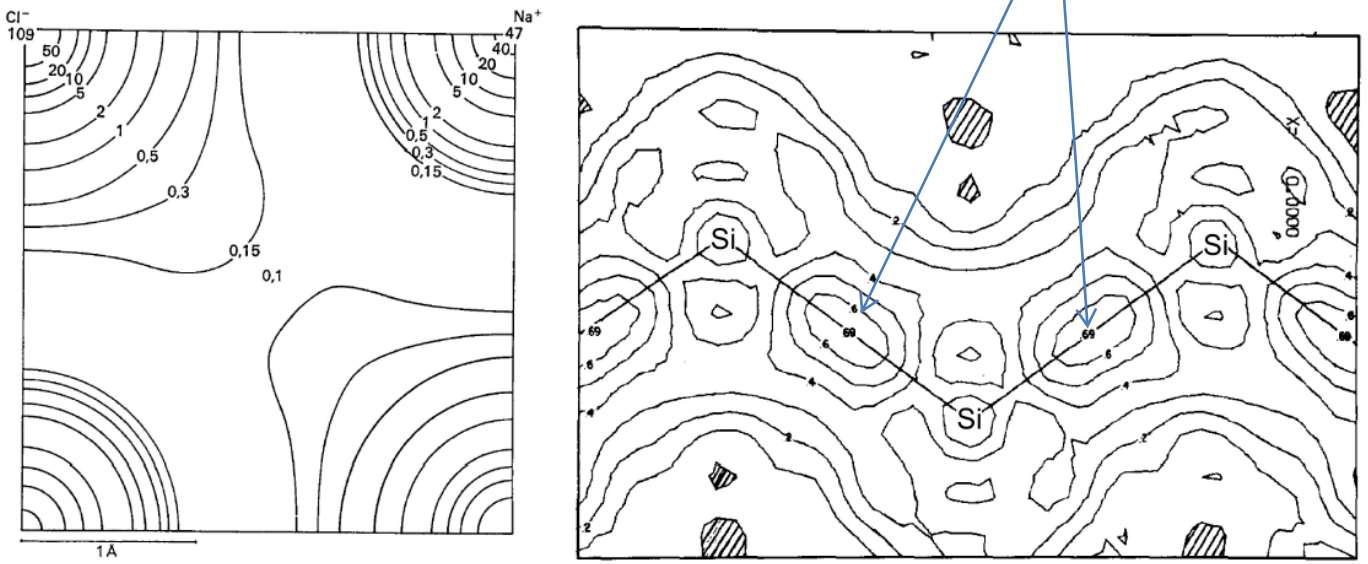


Figure 1.13: (a) Electron density distribution in a NaCl crystal. Electrons are localized near the atoms with a larger density at Cl. (S. Göttlicher, Acta Cryst. B 24, 122 (1968)). (b) Electron density distribution for a Si-crystal. Typical for a covalent system, large electron density is localized between the atoms (Y. W. Yang and P. Coppens, Solid State Commun. 15, 1555 (1974)).

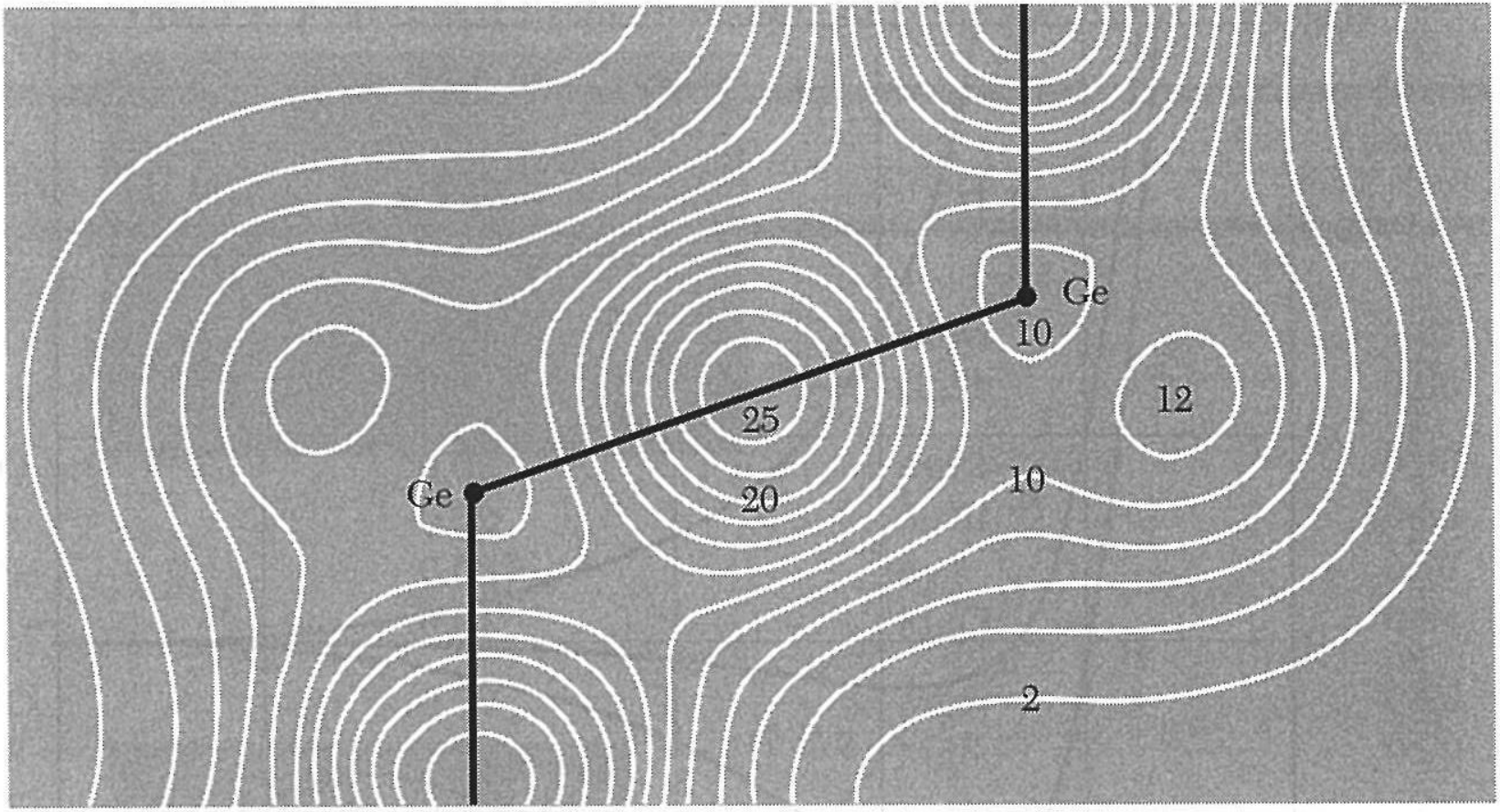


Figure 11 Calculated valence electron concentration in germanium. The numbers on the contours give the electron concentration per primitive cell, with four valence electrons per atom (eight electrons per primitive cell). Note the high concentration midway along the Ge-Ge bond, as we expect for covalent bonding. (After J. R. Chelikowsky and M. L. Cohen.)

The covalent bond has strong directional properties (Fig. 11). Thus carbon, silicon, and germanium have the diamond structure, with atoms joined to four nearest neighbors at tetrahedral angles, even though this arrangement gives a low filling of space, 0.34 of the available space, compared with 0.74 for a close-packed structure. The tetrahedral bond allows only four nearest neighbors, whereas a close-packed structure has 12. We should not overemphasize the similarity of the bonding of carbon and silicon. Carbon gives biology, but silicon gives geology and semiconductor technology.

The binding of molecular hydrogen is a simple example of a covalent bond. The strongest binding (Fig. 12) occurs when the spins of the two electrons are antiparallel. The binding depends on the relative spin orientation not because there are strong magnetic dipole forces between the spins, but because the Pauli principle modifies the distribution of charge according to the spin orientation. This spin-dependent coulomb energy is called the **exchange interaction**.

The Pauli principle gives a strong repulsive interaction between atoms with filled shells. If the shells are not filled, electron overlap can be accommodated without excitation of electrons to high energy states and the bond will be shorter. Compare the bond length (2 Å) of Cl_2 with the interatomic distance (3.76 Å) of Ar in solid Ar; also compare the cohesive energies given in Table 1. The difference between Cl_2 and Ar_2 is that the Cl atom has five electrons in the $3p$ shell and the Ar atom has six, filling the shell, so that the repulsive interaction is stronger in Ar than in Cl.

The elements C, Si, and Ge lack four electrons with respect to filled shells, and thus these elements (for example) can have an attractive interaction associated with charge overlap. The electron configuration of carbon is $1s^2 2s^2 2p^2$. To form a tetrahedral system of covalent bonds the carbon atom must first be promoted to the electronic configuration $1s^2 2s 2p^3$. This promotion from the ground state requires 4 eV, an amount more than regained when the bonds are formed.

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 (1,7)	0.85
ZnSe	0.63	AgI	0.77
ZnTe	0.61	MgO	0.84
(2,6)			
CdO	0.79	MgS (2,6)	0.79
CdS	0.69	MgSe	0.79
CdSe	0.70		
CdTe	0.67	LiF	0.92
		NaCl (1,7)	0.94
InP	0.42	RbF	0.96
InAs (3,5)	0.36		
InSb	0.32		

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

Metals:

- high electrical conductivity
- large number of available electrons to move freely (typ. 1 – 2 electrons / atom)

- these electrons are called “conduction electrons”

Metallic bonds are important for electron transport. From a theoretical point of view, they have the same origin as covalent bonds, i. e. the overlap of electron wave functions from different atoms. This overlap we call a covalent bond, when mainly electrons of only two atoms form a new electronic states. This is different for bonds which we call metallic bonds. Fig. 1.14 gives an illustration.

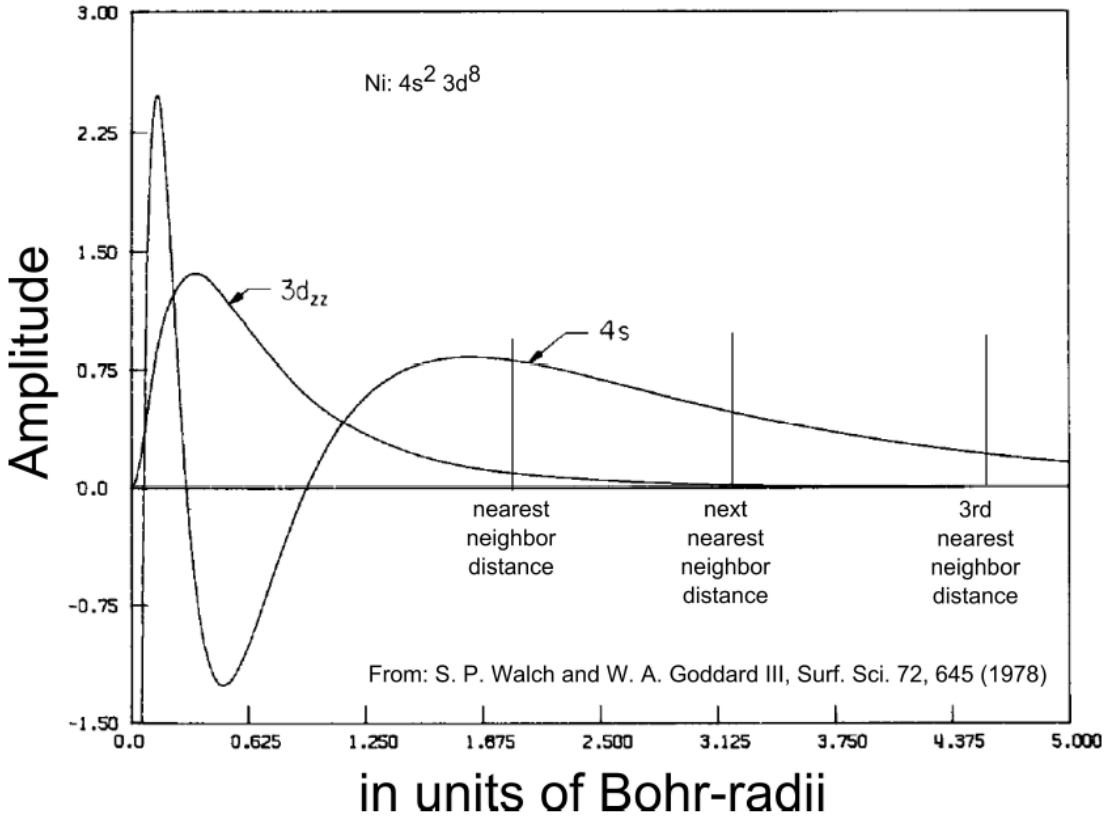


Figure 1.14: Amplitude of wave functions with distance for Ni.

Nickel has $4s^2, 3d^8$ outer shells - the inner shells lay much deeper in energy and are less relevant for bonding processes. The $3d$ shell is localized near the core and extends up to a distant of the nearest neighbor. Electrons from further away atoms do not interfere. The $4s$ shell has a very high electron density very close to the core (due to the stronger attractive Coulomb interaction the $4s$ shells is lower in energy than the $3d$ shell). The $4s$ shell also has a high electron density very far away from the atom and in Ni-crystal extends much beyond the nearest neighbor. The consequence is, that $4s$ electrons will start interacting with all electrons from more far away atoms.

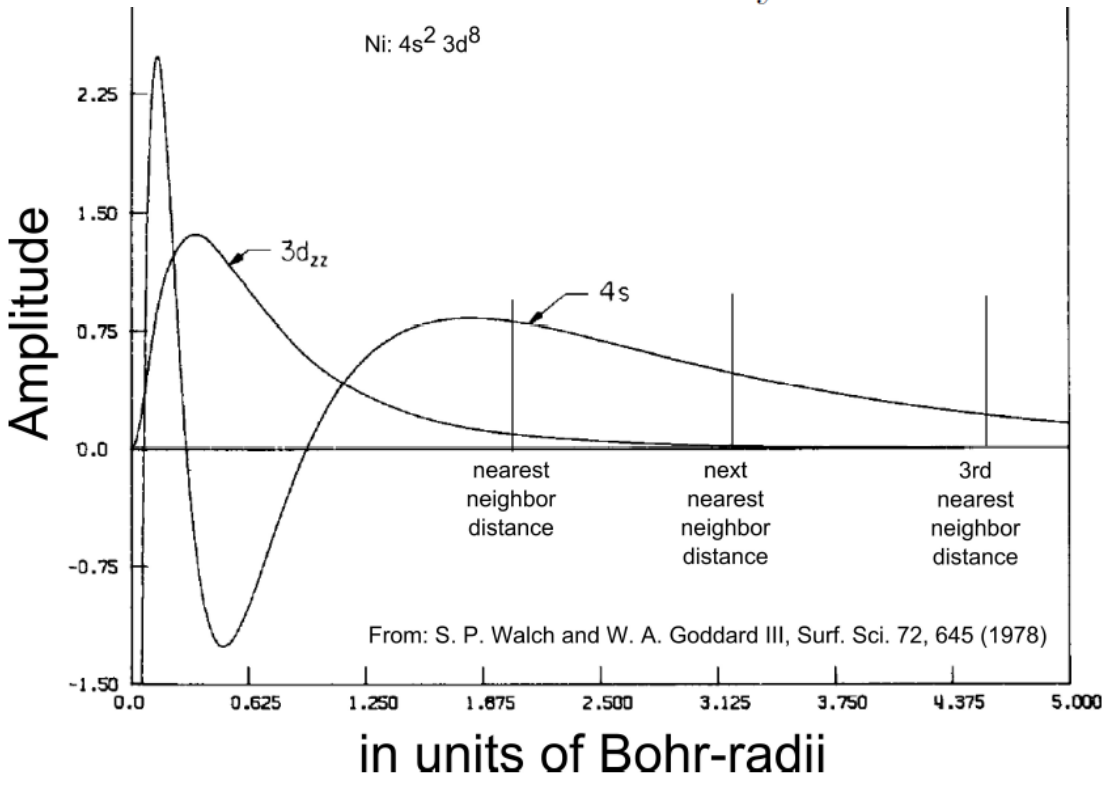


Figure 1.14: Amplitude of wave functions with distance for Ni.

The $3d$ electrons will form covalent bonds with neighboring atoms and is directional. The $4s$ electrons will be smeared over a large area - therefore, the angular distribution of the wave function will play a much less important role.

Moreover, as the $4s$, $3p$, and the $3d$ shells are close in energy, all these electrons will form a quasi continuous energy range with available states. This we call an electronic band, which is partially filled.

- Alkali metals: Na, Li, K, Rb, Cs $\rightarrow$ s-bands
- Earth alkali metals: Be, Mg, Ca, Sr, Ba $\rightarrow$ sp-bands

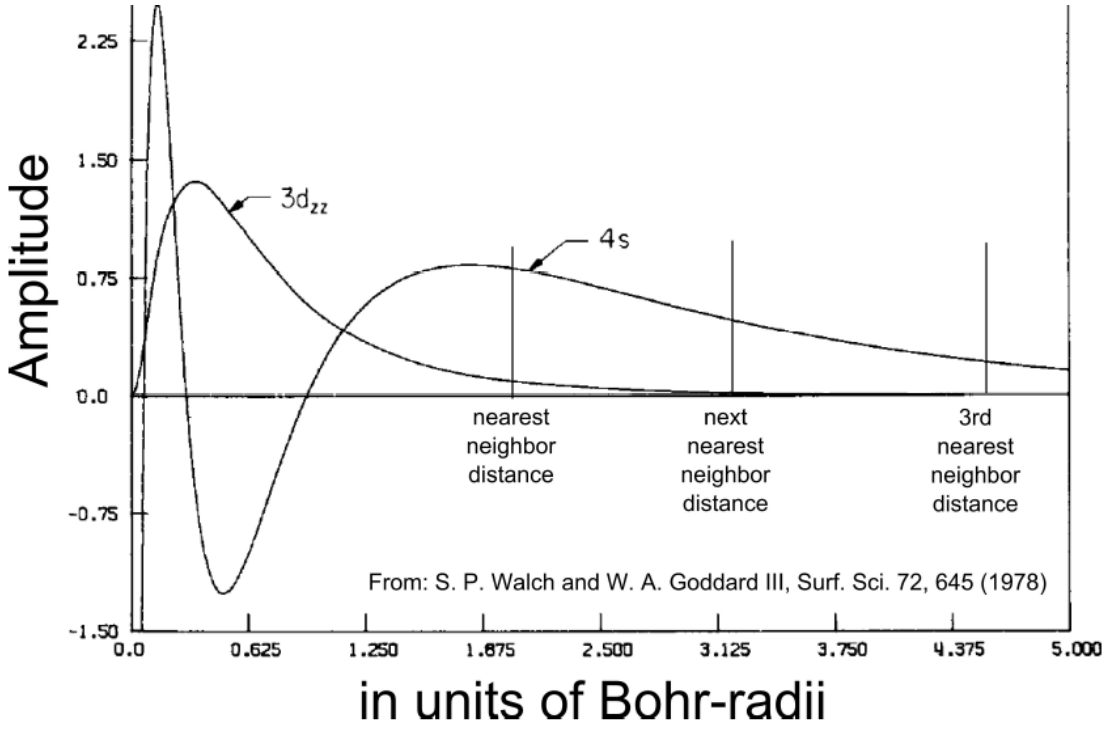


Figure 1.14: Amplitude of wave functions with distance for Ni.

METALS

Metals are characterized by high electrical conductivity, and a large number of electrons in a metal are free to move about, usually one or two per atom. The electrons available to move about are called conduction electrons. The valence electrons of the atom become the conduction electrons of the metal.

In some metals the interaction of the ion cores with the conduction electrons always makes a large contribution to the binding energy, but the characteristic feature of metallic binding is the lowering of the energy of the valence electrons in the metal as compared with the free atom.

There is a continuous range of crystals between the ionic and the covalent limits. It is often important to estimate the extent a given bond is ionic or covalent. A semiempirical theory of the fractional ionic or covalent character of a bond in a dielectric crystal has been developed with considerable success by J. C. Phillips, Table 8.

The binding energy of an alkali metal crystal is considerably less than that of an alkali halide crystal: the bond formed by a conduction electron is not very strong. The interatomic distances are relatively large in the alkali metals because the kinetic energy of the conduction electrons is lower at large interatomic distances. This leads to weak binding. Metals tend to crystallize in relatively close packed structures: hcp, fcc, bcc, and some other closely related structures, and not in loosely-packed structures such as diamond.

In the transition metals there is additional binding from inner electron shells. Transition metals and the metals immediately following them in the periodic table have large *d*-electron shells and are characterized by high binding energy.

HYDROGEN BONDS

Because neutral hydrogen has only one electron, it should form a covalent bond with only one other atom. It is known, however, that under certain conditions an atom of hydrogen is attracted by rather strong forces to two atoms, thus forming a **hydrogen bond** between them, with a bond energy of the order of 0.1 eV. It is believed that the hydrogen bond is largely ionic in character, being formed only between the most electronegative atoms, particularly F, O, and N. In the extreme ionic form of the hydrogen bond, the hydrogen atom loses its electron to another atom in the molecule; the bare proton forms the hydrogen bond. The atoms adjacent to the proton are so close that more than two of them would get in each other's way; thus the hydrogen bond connects only two atoms (Fig. 13).

The hydrogen bond is an important part of the interaction between H_2O molecules and is responsible together with the electrostatic attraction of the electric dipole moments for the striking physical properties of water and ice. It is important in certain ferroelectric crystals and in DNA.

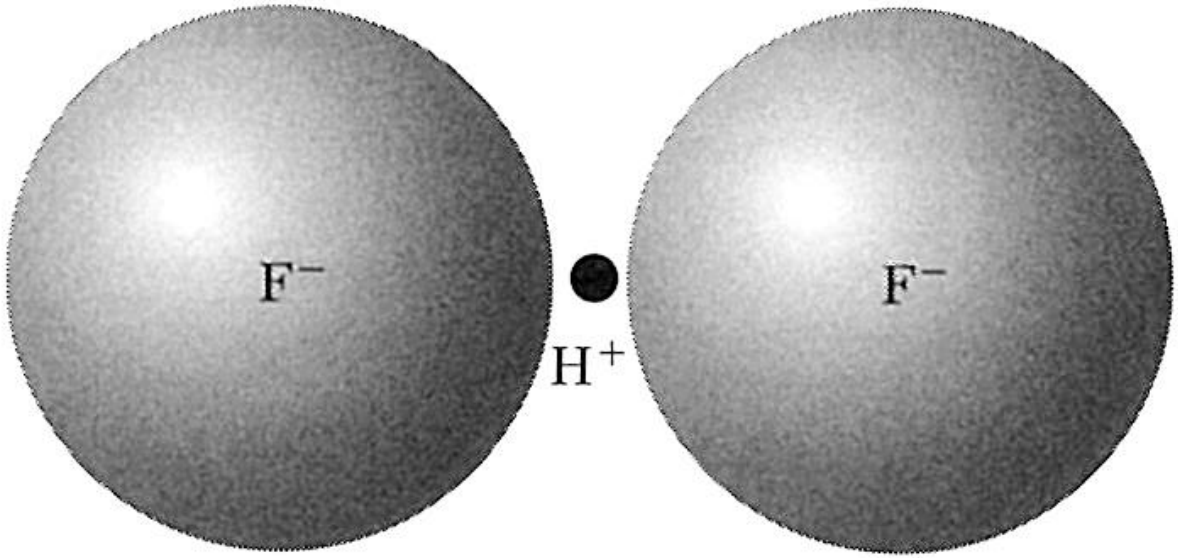


Figure 13 The hydrogen difluoride ion HF_2^- is stabilized by a hydrogen bond. The sketch is of an extreme model of the bond, extreme in the sense that the proton is shown bare of electrons.

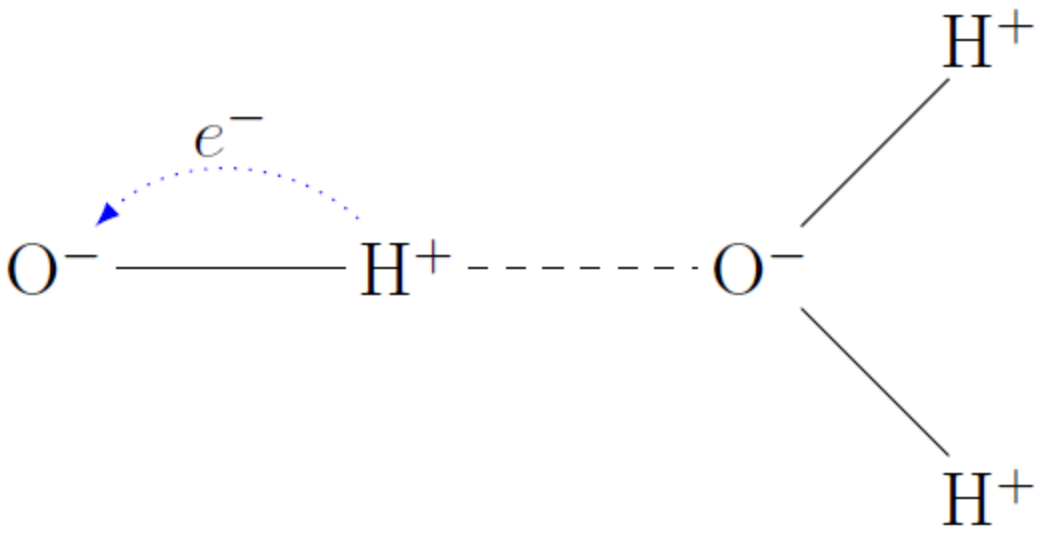
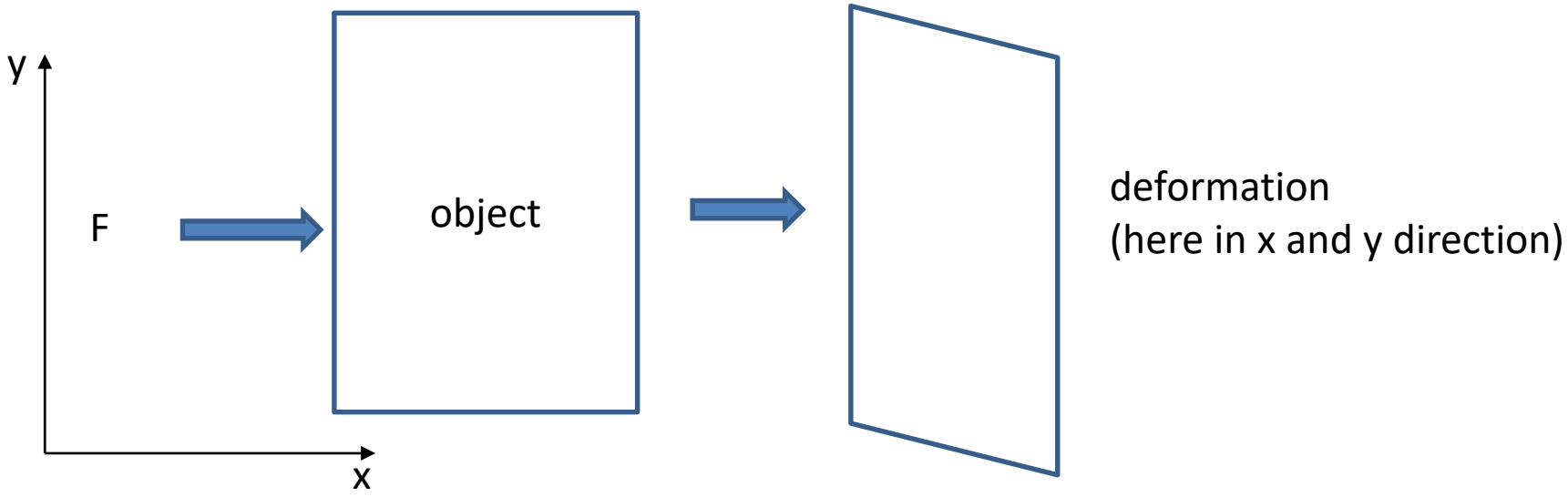


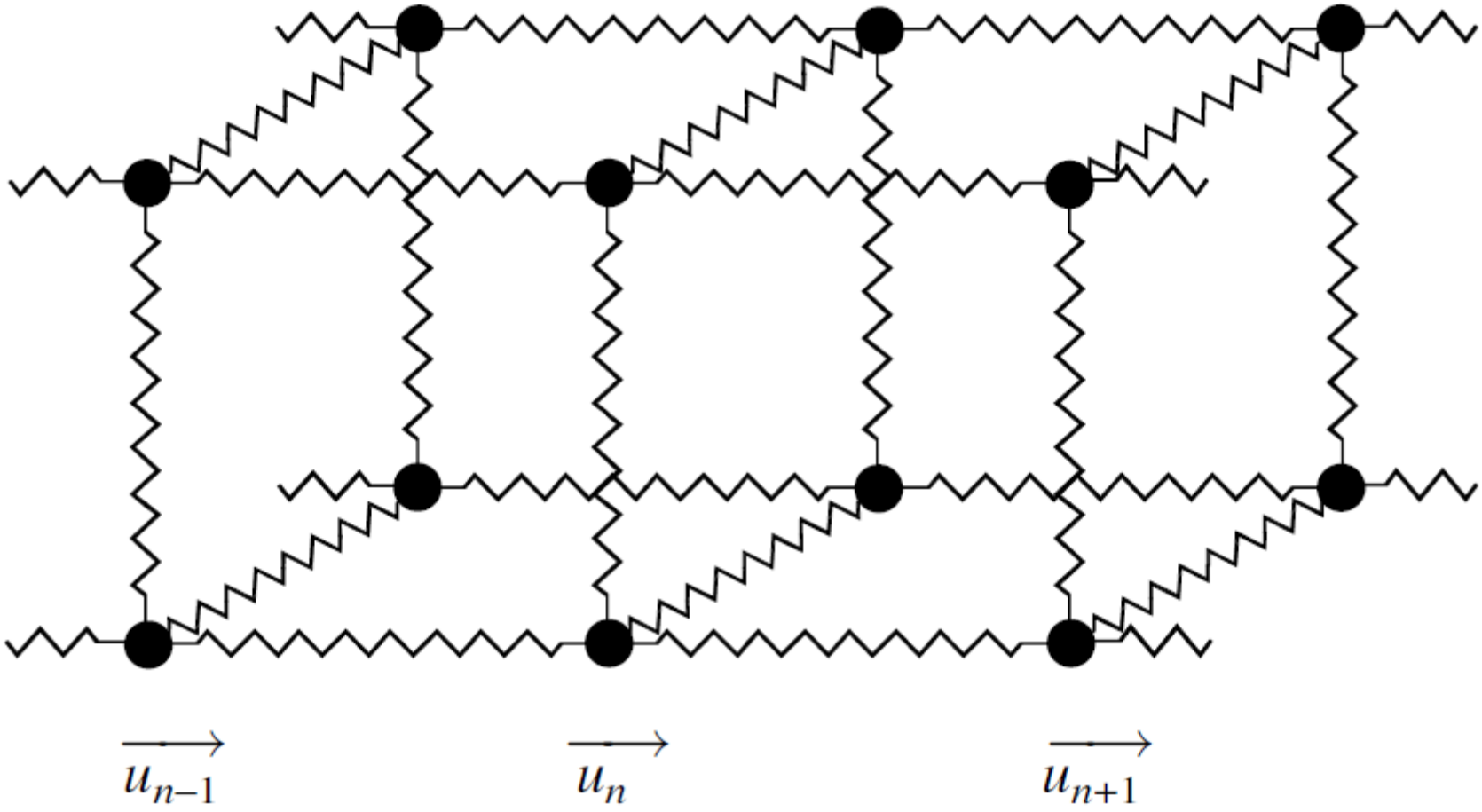
Figure 1.15: O-H is a covalent bond with a large charge transfer. As a result, H is covalently bond to one Oxygen and at the same time interacts with other charged Oxygen atoms.

Elastic Properties: Strain



- Continuum approximation:
  - crystal viewed as a homogeneous continuous medium
    (instead of a periodic array of atoms)
  - validity: elastic waves with $\lambda > 10$ nm ($f < 10^{11}$ Hz)
  - described by a (3 x 3) tensor ε_{ij} (or e_{ij} in Kittel's Book)
  - assume Hooke's Law & 2nd Newton's Law: ($F = - k \Delta x$, with k the spring constant)

spring constant f



a longitudinal wave in a cubic system:

$$M\ddot{u}_{n1} = f\left(u_{(n+1)1} - u_{n1}\right) - f\left(u_{n1} - u_{(n-1)1}\right)$$

$$M\ddot{u}_{n1} = f(u_{(n+1)1} - u_{n1}) - f(u_{n1} - u_{(n-1)1})$$

small displacement

$$(u_{(n+1)1} - u_{n1}) - (u_{n1} - u_{(n-1)1}) = a\frac{\partial u_1}{\partial x_1}\bigg|_{x=(n+1/2)a} - a\frac{\partial u_1}{\partial x_1}\bigg|_{x=(n-1/2)a}$$

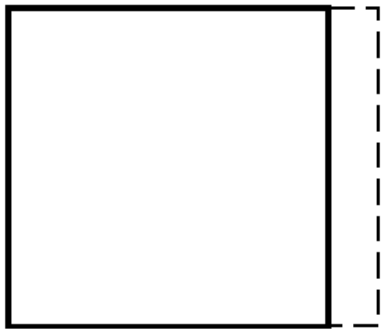
$$= a^2\frac{\partial^2 u_1}{\partial x_1^2}\bigg|_{x=na}.$$

$$\varepsilon_{11} = \frac{\partial u_1}{\partial x_1}$$

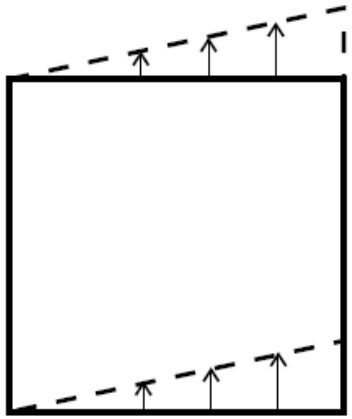
with $\varrho = M/a^3$ ⟹ $\varrho\ddot{u}_1 = c_{11}\frac{\partial^2 u_1}{\partial x_1^2}$ $\qquad c_{11} = \frac{f}{a}$ (elastic module)

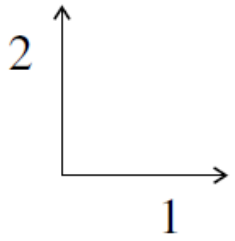
⟹ $c_L = \sqrt{\frac{c_{11}}{\varrho}}$ velocity of acoustic wave in a cubic crystal along one of the cubic axes.

$\varepsilon_{ij} \cong \frac{\partial u_i}{\partial x_j}$; tensor of deformation

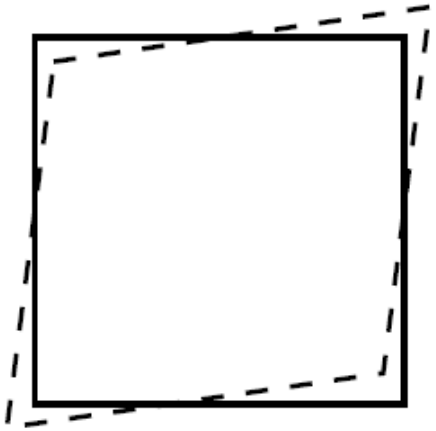


$$\varepsilon_{11} = \frac{\partial u_1}{\partial x_1}$$





$$\varepsilon_{21} = \frac{\partial u_2}{\partial x_1}$$



$$\varepsilon_{21} = \varepsilon_{12} = \frac{1}{2}\left(\frac{\partial u_2}{\partial x_1} + \frac{\partial u_1}{\partial x_1}\right)$$

Tensor of Deformation:

$$\begin{aligned}
\mathbf{x}' &= (1+\epsilon_{xx})\hat{\mathbf{x}} + \epsilon_{xy}\hat{\mathbf{y}} + \epsilon_{xz}\hat{\mathbf{z}} \ ; \\
\mathbf{y}' &= \epsilon_{yx}\hat{\mathbf{x}} + (1+\epsilon_{yy})\hat{\mathbf{y}} + \epsilon_{yz}\hat{\mathbf{z}} \ ; \\
\mathbf{z}' &= \epsilon_{zx}\hat{\mathbf{x}} + \epsilon_{zy}\hat{\mathbf{y}} + (1+\epsilon_{zz})\hat{\mathbf{z}} \ .
\end{aligned}$$

uniform deformation (26)

ε_{ij} : dimensionless, << 1

$$\Rightarrow \quad \mathbf{x}' \cdot \mathbf{x}' = 1 + 2\epsilon_{xx} + \epsilon_{xx}^2 + \epsilon_{xy}^2 + \epsilon_{xz}^2 \ ,$$

whence $x' \cong 1 + \epsilon_{xx} + \cdots$. The fractional changes of length of the $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, and $\hat{\mathbf{z}}$ axes are ϵ_{xx}, ϵ_{yy}, ϵ_{zz}, respectively, to the first order.

$\vec{r} = x\,\hat{x} + y\,\hat{y} + z\,\hat{z}$

uniform deformation

$\vec{r} = x\,x' + y\,y' + z\,z'$

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

$= (x\varepsilon_{xx} + y\varepsilon_{yx} + z\varepsilon_{zx})\,\hat{x} + \ldots\ldots$

This may be written in a more general form by introducing u, v, w such that the displacement is given by

$$\mathbf{R}(\mathbf{r}) = u(\mathbf{r})\hat{\mathbf{x}} + v(\mathbf{r})\hat{\mathbf{y}} + w(\mathbf{r})\hat{\mathbf{z}} \ . \qquad (29)$$

If deformation is nonuniform – u,v,w are related to local strains.:

$x\varepsilon_{xx} \cong x \frac{\partial u}{\partial x}$; etc,

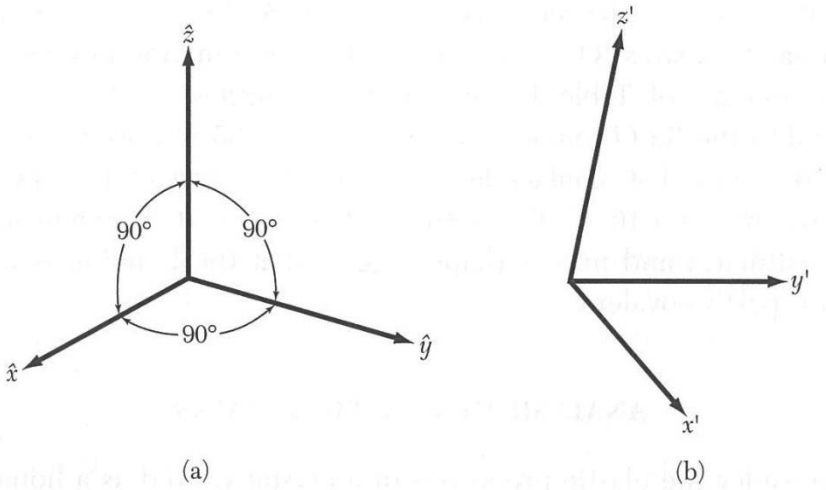


Figure 14 Coordinate axes for the description of the state of strain; the orthogonal unit axes in the unstrained state (a) are deformed in the strained state (b).

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

$$\begin{aligned} e_{xy} &\equiv \mathbf{x}' \cdot \mathbf{y}' \cong \epsilon_{yx} + \epsilon_{xy} = \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \ ; \\ e_{yz} &\equiv \mathbf{y}' \cdot \mathbf{z}' \cong \epsilon_{zy} + \epsilon_{yz} = \frac{\partial v}{\partial z} + \frac{\partial w}{\partial y} \ ; \\ e_{zx} &\equiv \mathbf{z}' \cdot \mathbf{x}' \cong \epsilon_{zx} + \epsilon_{xz} = \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \ . \end{aligned} \tag{32}$$

Dilation

The fractional *increase* of volume associated with a deformation is called the dilation. The dilation is negative for hydrostatic pressure. The unit cube of edges $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, $\hat{\mathbf{z}}$ has a volume after deformation of

$$V' = \mathbf{x}' \cdot \mathbf{y}' \times \mathbf{z}' \ , \tag{33}$$

by virtue of a well-known result for the volume of a parallelepiped having edges $\mathbf{x}'$, $\mathbf{y}'$, $\mathbf{z}'$. From (26) we have

$$\mathbf{x}' \cdot \mathbf{y}' \times \mathbf{z}' = \begin{vmatrix} 1+\epsilon_{xx} & \epsilon_{xy} & \epsilon_{xz} \\ \epsilon_{yx} & 1+\epsilon_{yy} & \epsilon_{yz} \\ \epsilon_{zx} & \epsilon_{zy} & 1+\epsilon_{zz} \end{vmatrix} \cong 1 + e_{xx} + e_{yy} + e_{zz} \ . \tag{34}$$

Products of two strain components have been neglected. The dilation δ is then given by

$$\boxed{\delta \equiv \frac{V' - V}{V} \cong e_{xx} + e_{yy} + e_{zz} \ .} \tag{35}$$

Stress (force):

$X_x, X_y, X_z, Y_x, Y_y, Y_z, Z_x, Z_y, Z_z$: Stress Components (in force per unit area)

The normal of the plane, the force is applied to

The direction of the force

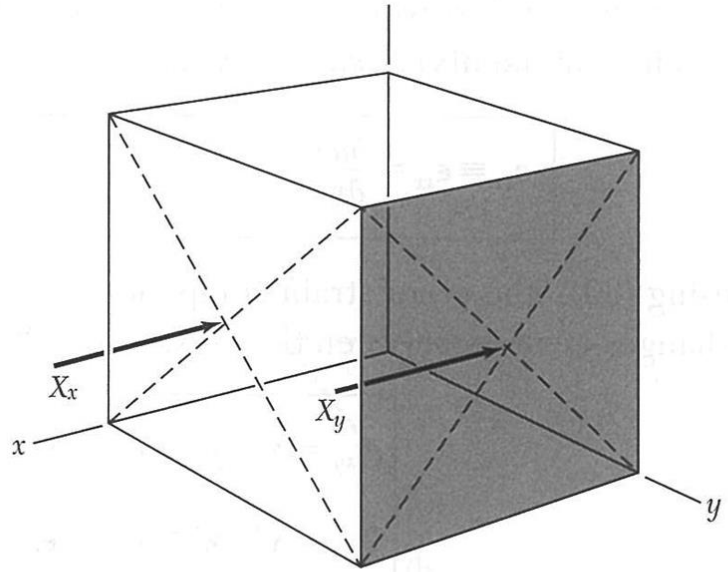


Figure 15 Stress component X_x is a force applied in the x direction to a unit area of a plane whose normal lies in the x direction; X_y is applied in the x direction to a unit area of a plane whose normal lies in the y direction.

The number of independent components reduces from 9 to 6 (the total torque must be zero)

$$Y_z = Z_y \ ; \qquad Z_x = X_z \ ; \qquad X_y = Y_x \ . \tag{36}$$

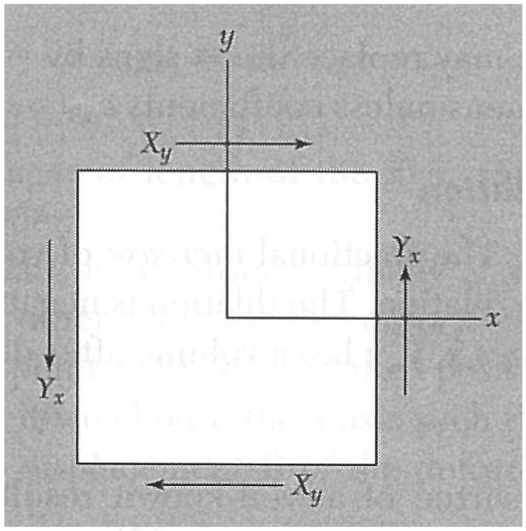


Figure 16 Demonstration that for a body in static equilibrium $Y_x = X_y$. The sum of the forces in the x direction is zero. The sum of the forces in the y direction is also zero. The total force vanishes. The total torque about the origin is also zero if $Y_x = X_y$.

Elastic Energy Density

$$U = \frac{1}{2} \sum_{\lambda=1}^{6} \sum_{\mu=1}^{6} \tilde{C}_{\lambda\mu} e_\lambda e_\mu \ , \tag{39}$$

with:

$$1 \equiv xx \ ; \quad 2 \equiv yy \ ; \quad 3 \equiv zz \ ; \quad 4 \equiv yz \ ; \quad 5 \equiv zx \ ; \quad 6 \equiv xy \ . \tag{40}$$

ELASTIC COMPLIANCE AND STIFFNESS CONSTANTS

Hooke's law states that for sufficiently small deformations the strain is directly proportional to the stress, so that the strain components are linear functions of the stress components:

$$
\begin{aligned}
e_{xx} &= S_{11}X_x + S_{12}Y_y + S_{13}Z_z + S_{14}Y_z + S_{15}Z_x + S_{16}X_y \ ; \\
e_{yy} &= S_{21}X_x + S_{22}Y_y + S_{23}Z_z + S_{24}Y_z + S_{25}Z_x + S_{26}X_y \ ; \\
e_{zz} &= S_{31}X_x + S_{32}Y_y + S_{33}Z_z + S_{34}Y_z + S_{35}Z_x + S_{36}X_y \ ; \\
e_{yz} &= S_{41}X_x + S_{42}Y_y + S_{43}Z_z + S_{44}Y_z + S_{45}Z_x + S_{46}X_y \ ; \\
e_{zx} &= S_{51}X_x + S_{52}Y_y + S_{53}Z_z + S_{54}Y_z + S_{55}Z_x + S_{56}X_y \ ; \\
e_{xy} &= S_{61}X_x + S_{62}Y_y + S_{63}Z_z + S_{64}Y_z + S_{65}Z_x + S_{66}X_y \ .
\end{aligned}
\tag{37}
$$

For six strain components

36 S_{xy} and 36 C_{xy}

$$
\begin{aligned}
X_x &= C_{11}e_{xx} + C_{12}e_{yy} + C_{13}e_{zz} + C_{14}e_{yz} + C_{15}e_{zx} + C_{16}e_{xy} \ ; \\
Y_y &= C_{21}e_{xx} + C_{22}e_{yy} + C_{23}e_{zz} + C_{24}e_{yz} + C_{25}e_{zx} + C_{26}e_{xy} \ ; \\
Z_z &= C_{31}e_{xx} + C_{32}e_{yy} + C_{33}e_{zz} + C_{34}e_{yz} + C_{35}e_{zx} + C_{36}e_{xy} \ ; \\
Y_z &= C_{41}e_{xx} + C_{42}e_{yy} + C_{43}e_{zz} + C_{44}e_{yz} + C_{45}e_{zx} + C_{46}e_{xy} \ ; \\
Z_x &= C_{51}e_{xx} + C_{52}e_{yy} + C_{53}e_{zz} + C_{54}e_{yz} + C_{55}e_{zx} + C_{56}e_{xy} \ ; \\
X_y &= C_{61}e_{xx} + C_{62}e_{yy} + C_{63}e_{zz} + C_{64}e_{yz} + C_{65}e_{zx} + C_{66}e_{xy} \ .
\end{aligned}
\tag{38}
$$

For six stress components

The quantities S_{11}, S_{12} . . . are called **elastic compliance constants** or elastic constants; the quantities C_{11}, C_{12}, . . . are called the **elastic stiffness constants** or moduli of elasticity. The S's have the dimensions of [area]/[force] or [volume]/[energy]. The C's have the dimensions of [force]/[area] or [energy]/[volume].

I. 1st consideration

The stress components are found from the derivative of U with respect to the associated strain component. This result follows from the definition of potential energy. Consider the stress X_x applied to one face of a unit cube, the opposite face being held at rest:

From Eq. 38

$$X_x = \frac{\partial U}{\partial e_{xx}} \equiv \frac{\partial U}{\partial e_1} = \tilde{C}_{11} e_1 + \frac{1}{2} \sum_{\beta=2}^{6} (\tilde{C}_{1\beta} + \tilde{C}_{\beta 1}) e_\beta \quad . \qquad (41)$$

Note that only the combination $\frac{1}{2}(\tilde{C}_{\alpha\beta} + \tilde{C}_{\beta\alpha})$ enters the stress-strain relations. It follows that the elastic stiffness constants are symmetrical:

$$C_{\alpha\beta} = \tfrac{1}{2}(\tilde{C}_{\alpha\beta} + \tilde{C}_{\beta\alpha}) = C_{\beta\alpha} \quad . \qquad (42)$$

Thus the thirty-six elastic stiffness constants are reduced to twenty-one.

Reduce C's from 36 down to 21 !

II. 2nd Consideration

Elastic Stiffness Constants of Cubic Crystals

The number of independent elastic stiffness constants is reduced further if the crystal possesses symmetry elements. We now show that in cubic crystals there are only three independent stiffness constants.

Only C_{11} C_{12} C_{44}

We assert that the elastic energy density of a cubic crystal is

$$U = \tfrac{1}{2}C_{11}(e_{xx}^2 + e_{yy}^2 + e_{zz}^2) + \tfrac{1}{2}C_{44}(e_{yz}^2 + e_{zx}^2 + e_{xy}^2) + C_{12}(e_{yy}e_{zz} + e_{zz}e_{xx} + e_{xx}e_{yy}) \quad (43)$$

For cubic crystals only

and that no other quadratic terms occur; that is,

$$(e_{xx}e_{xy} + \cdots) \; ; \qquad (e_{yz}e_{zx} + \cdots) \; ; \qquad (e_{xx}e_{yz} + \cdots) \quad (44)$$

do not occur.

The minimum symmetry requirement for a cubic structure is the existence of four three-fold rotation axes. The axes are in the [111] and equivalent directions (Fig. 17). The effect of a rotation of $2\pi/3$ about these four axes is to interchange the x, y, z axes according to the schemes

$$\begin{aligned} &x \to y \to z \to x \ ; \qquad -x \to z \to y \to -x \ ; \\ &x \to z \to -y \to x \ ; \qquad -x \to y \to z \to -x \ , \end{aligned} \tag{45}$$

according to the axis chosen. Under the first of these schemes, for example,

$$e_{xx}^2 + e_{yy}^2 + e_{zz}^2 \to e_{yy}^2 + e_{zz}^2 + e_{xx}^2 \ ,$$

and similarly for the other terms in parentheses in (43). Thus (43) is invariant under the operations considered. But each of the terms exhibited in (44) is odd in one or more indices. A rotation in the set (45) can be found which will change the sign of the term, because $e_{xy} = -e_{x(-y)}$, for example. Thus the terms (44) are not invariant under the required operations.

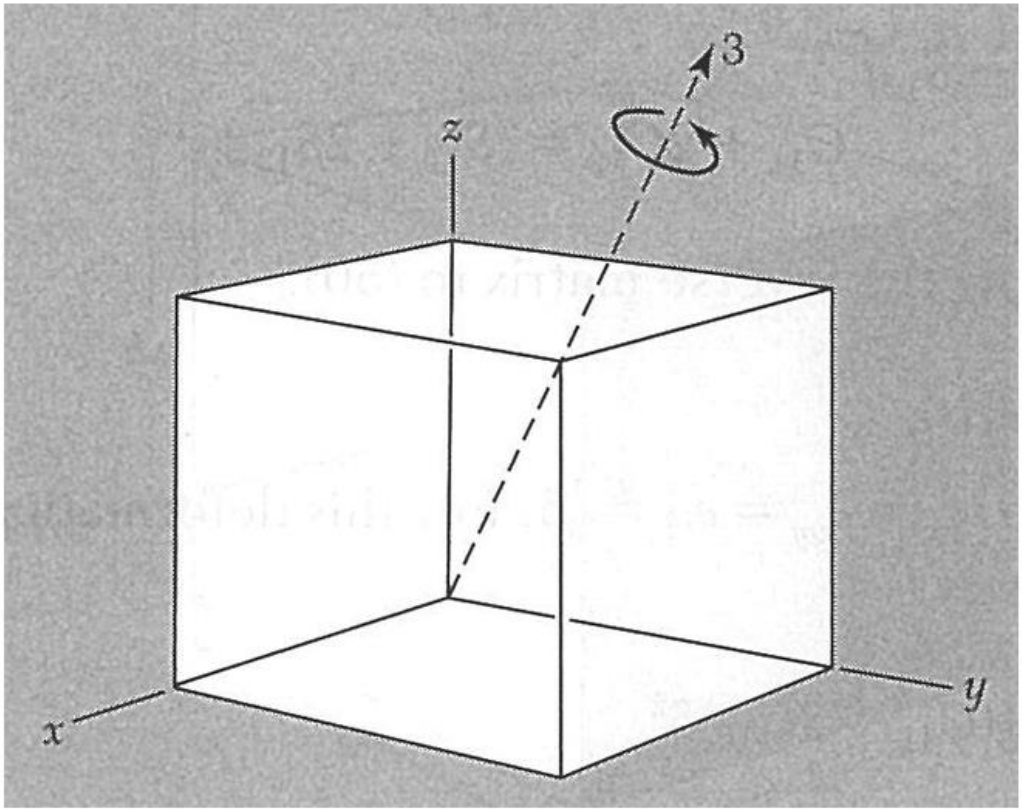


Figure 17 Rotation by $2\pi/3$ about the axis marked 3 changes $x \to y$; $y \to z$; and $z \to x$.

It remains to verify that the numerical factors in (43) are correct. By (41),

$$\partial U/\partial e_{xx} = X_x = C_{11}e_{xx} + C_{12}(e_{yy} + e_{zz}) \ . \qquad (46)$$

The appearance of $C_{11}e_{xx}$ agrees with (38). On further comparison, we see that

$$(1)\ C_{12} = C_{13} \ ; \quad (2)\ C_{14} = C_{15} = C_{16} = 0 \ . \qquad (47)$$

(1) Because *y* is equivalent to *z* for a cubic crystal
(2) This is due to the basic definitions of C_{14}, C_{15}, C_{16}

Further, from (43),

$$\partial U/\partial e_{xy} = X_y = C_{44}e_{xy} \ ; \qquad (48)$$

on comparison with (38) we have

$$(3)\ C_{61} = C_{62} = C_{63} = C_{64} = C_{65} = 0 \ ; \quad (4)\ C_{66} = C_{44} = C_{55} \qquad (49)$$

Thus from (43) we find that the array of values of the elastic stiffness constants is reduced for a cubic crystal to the matrix

	e_{xx}	e_{yy}	e_{zz}	e_{yz}	e_{zx}	e_{xy}
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}

(50)

Thus we have only C_{11}, C_{12}, C_{44}

For cubic crystals the stiffness and compliance constants are related by

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

$$C_{11} + 2C_{12} = (S_{11} + 2S_{12})^{-1} . \qquad (51)$$

These relations follow on evaluating the inverse matrix to (50).

Bulk Modulus and Compressibility

See eq. 35

Consider the uniform dilation $e_{xx} = e_{yy} = e_{zz} = \frac{1}{3}\delta$. For this deformation the energy density (43) of a cubic crystal is

$$U = \tfrac{1}{6}(C_{11} + 2C_{12})\delta^2 \ . \tag{52}$$

We may define the **bulk modulus** B by the relation

$$U = \tfrac{1}{2}B\delta^2 \ , \tag{53}$$

which is equivalent to the definition $-V\,dp/dV$. For a cubic crystal,

$$B = \tfrac{1}{3}(C_{11} + 2C_{12}) \ . \tag{54}$$

The **compressibility** K is defined as $K = 1/B$. Values of B and K are given in Table 3.

Elastic Waves in Cubic Crystals

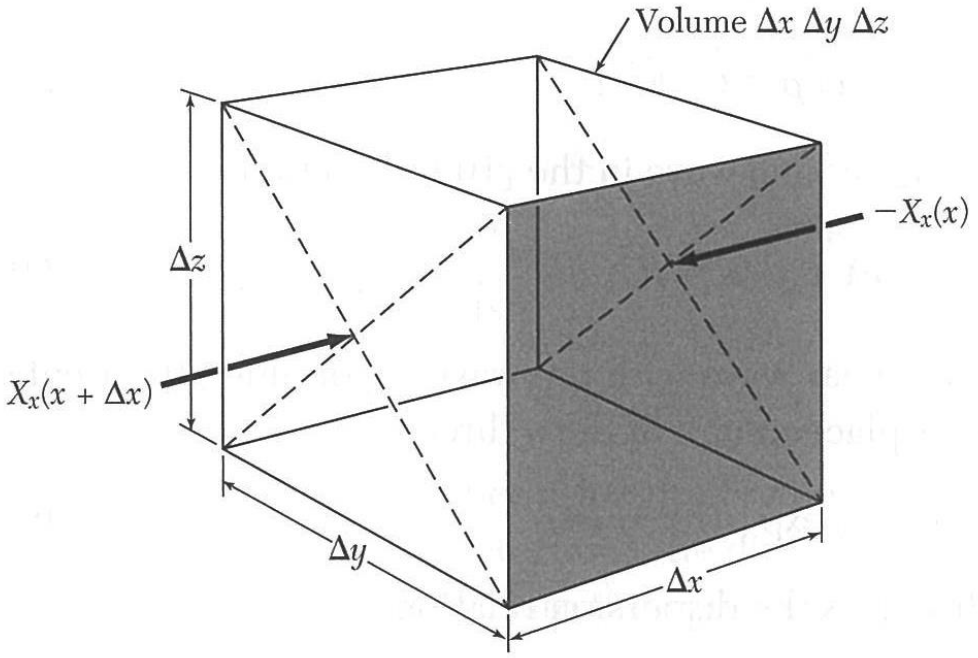


Figure 18 Cube of volume $\Delta x\ \Delta y\ \Delta z$ acted on by a stress $-X_x(x)$ on the face at x, and $X_x(x + \Delta x) \simeq X_x(x) + \dfrac{\partial X_x}{\partial x}\ \Delta x$ on the parallel face at $x + \Delta x$. The net force is $\left(\dfrac{\partial X_x}{\partial x}\ \Delta x\right)\Delta y\ \Delta z$. 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 $\partial^2 u/\partial t^2$.

$$F_x = \left(\frac{\partial X_x}{\partial x} + \frac{\partial X_y}{\partial y} + \frac{\partial X_z}{\partial z}\right) \Delta x\, \Delta y\, \Delta z \;=\; \Delta x\, \Delta y\, \Delta z \quad \rho \frac{\partial^2 u}{\partial t^2} = \frac{\partial X_x}{\partial x} + \frac{\partial X_y}{\partial y} + \frac{\partial X_z}{\partial z}\; \Delta x\, \Delta y\, \Delta z$$

displacement in x-direction

The X_x, X_y, and X_z are substituted from eqs. (38) and (50) as:

$X_x = C_{11}e_{xx} + C_{12}e_{yy} + C_{12}e_{zz}$

$Y_y = C_{44}e_{xy}$

$X_z = Z_x = C_{44}e_{zx}$

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

from eq. 31 & 32

$e_{xx} = \partial u/\partial x$

$e_{yy} = \partial v/\partial y$

$e_{zz} = \partial w/\partial z$

$e_{xy} = \partial u/\partial y + \partial v/\partial x$

$e_{xz} = \partial u/\partial z + \partial w/\partial x$

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

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

$$\rho \frac{\partial^2 v}{\partial t^2} = C_{11} \frac{\partial^2 v}{\partial y^2} + C_{44} \left(\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial z^2} \right) + (C_{12} + C_{44}) \left(\frac{\partial^2 u}{\partial x \, \partial y} + \frac{\partial^2 w}{\partial y \, \partial z} \right) ; \quad (57b)$$

$$\rho \frac{\partial^2 w}{\partial t^2} = C_{11} \frac{\partial^2 w}{\partial z^2} + C_{44} \left(\frac{\partial^2 w}{\partial x^2} + \frac{\partial^2 w}{\partial y^2} \right) + (C_{12} + C_{44}) \left(\frac{\partial^2 u}{\partial x \, \partial z} + \frac{\partial^2 v}{\partial y \, \partial z} \right) . \quad (57c)$$

Longitudinal Wave (solution of eq. 57a):

$$u = u_0 \exp \left[i(Kx - \omega t) \right] , \qquad (58)$$

$K = 2\pi/\lambda$ Wavevector

$\omega = 2\pi\nu$ Angular Frequency

$\Rightarrow$ $\omega^2 \rho = C_{11} K^2$ $\qquad v_s = \nu\lambda = \omega/K = (C_{11}/\rho)^{1/2}$

Transversal Wave (wavevector along x direction, displacement along y direction)

$$v = v_0 \exp\left[i(Kx - \omega t)\right]$$

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

$$v_s = (C_{44}/\rho)^{1/2}$$

Waves in the [110] Direction

a) Transversal Waves: propagates in xy plane, displacement in z direction

$$w = w_0 \exp\left[i(K_x x + K_y y - \omega t)\right]$$

$$\omega^2 \rho = C_{44}\,(K_x^2 + K_y^2) = C_{44} K^2$$

b) propagation in xy plane, displacement in xy direction

$$u = u_0 \exp\left[i(K_x x + K_y y - \omega t)\right] \; ; \qquad v = v_0 \exp\left[i(K_x x + K_y y - \omega t)\right] \; . \tag{66}$$

From (57a) and (57b),

$$\begin{aligned} \omega^2 \rho u &= (C_{11} K_x^2 + C_{44} K_y^2) u + (C_{12} + C_{44}) K_x K_y v \; ; \\ \omega^2 \rho v &= (C_{11} K_y^2 + C_{44} K_x^2) v + (C_{12} + C_{44}) K_x K_y u \; . \end{aligned} \tag{67}$$

$$K_x = K_y = K/\sqrt{2}$$

$$\begin{vmatrix} -\omega^2\rho + \tfrac{1}{2}(C_{11}+C_{44})K^2 & \tfrac{1}{2}(C_{12}+C_{44})K^2 \\ \tfrac{1}{2}(C_{12}+C_{44})K^2 & -\omega^2\rho + \tfrac{1}{2}(C_{11}+C_{44})K^2 \end{vmatrix} = 0 \ . \qquad (68)$$

This equation has the roots

$$\omega^2\rho = \tfrac{1}{2}(C_{11}+C_{12}+2C_{44})K^2 \ ; \qquad \omega^2\rho = \tfrac{1}{2}(C_{11}-C_{12})K^2 \ . \qquad (69)$$

u = v

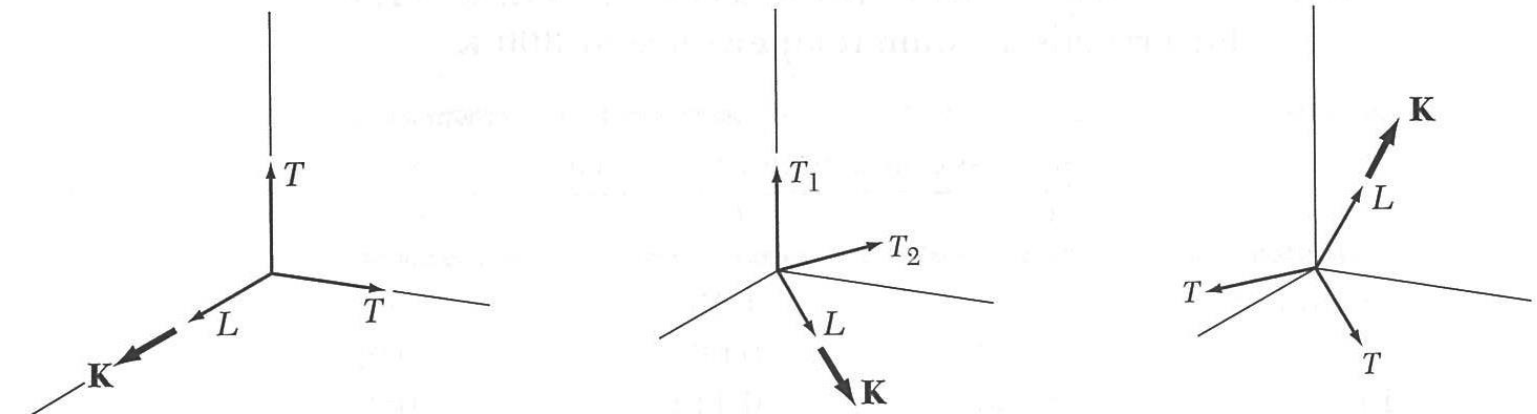
u = -v

longitudinal wave (displacement along [110] and || K

$$\tfrac{1}{2}(C_{11}+C_{12}+2C_{44})K^2u = \tfrac{1}{2}(C_{11}+C_{44})K^2u + \tfrac{1}{2}(C_{12}+C_{44})K^2v \ , \qquad (70)$$

transversal wave (displacement along [1-10] and perpendicular to K

$$\tfrac{1}{2}(C_{11}-C_{12})K^2u = \tfrac{1}{2}(C_{11}+C_{44})K^2u + \tfrac{1}{2}(C_{12}+C_{44})K^2v \ ;$$



Wave in [100] direction
$L : C_{11}$
$T : C_{44}$

Wave in [110] direction
$L : \frac{1}{2}(C_{11} + C_{12} + 2C_{44})$
$T_1 : C_{44}$
$T_2 : \frac{1}{2}(C_{11} - C_{12})$

Wave in [111] direction
$L : \frac{1}{3}(C_{11} + 2C_{12} + 4C_{44})$
$T : \frac{1}{3}(C_{11} - C_{12} + C_{44})$

Figure 20 Effective elastic constants for the three modes of elastic waves in the principal propagation directions in cubic crystals. The two transverse modes are degenerate for propagation in the [100] and [111] directions.

Selected values of the adiabatic elastic stiffness constants of cubic crystals at low temperatures and at room temperature are given in Table 11. Notice the general tendency for the elastic constants to decrease as the temperature is increased. Further values at room temperature alone are given in Table 12.

Table 11 Adiabatic elastic stiffness constants of cubic crystals at low temperature and at room temperature

The values given at 0 K were obtained by extrapolation of measurements carried out down to 4 K. The table was compiled with the assistance of Professor Charles S. Smith.

Crystal	Stiffness constants, in 10^{12} dyne/cm^2 (10^{11}N/m^2)			Temperature, K	Density, g/cm^3
	C_{11}	C_{12}	C_{44}		
W	5.326	2.049	1.631	0	19.317
	5.233	2.045	1.607	300	—
Ta	2.663	1.582	0.874	0	16.696
	2.609	1.574	0.818	300	—
Cu	1.762	1.249	0.818	0	9.018
	1.684	1.214	0.754	300	—
Ag	1.315	0.973	0.511	0	10.635
	1.240	0.937	0.461	300	—
Au	2.016	1.697	0.454	0	19.488
	1.923	1.631	0.420	300	—
Al	1.143	0.619	0.316	0	2.733
	1.068	0.607	0.282	300	—
K	0.0416	0.0341	0.0286	4	
	0.0370	0.0314	0.0188	295	
Pb	0.555	0.454	0.194	0	11.599
	0.495	0.423	0.149	300	—
Ni	2.612	1.508	1.317	0	8.968
	2.508	1.500	1.235	300	—
Pd	2.341	1.761	0.712	0	12.132
	2.271	1.761	0.717	300	—