

An equation to calculate internuclear distances of covalent, ionic and metallic lattices

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Abstract

This paper briefly describes the many different sets of ionic and covalent radii available. A simple model of ionic and covalent bonding is proposed and an equation to calculate internuclear distances of covalent, ionic and metallic lattices is described. Derivation of covalent radii and the use of a proposed model of metallic structure and bonding to derive ionic radii are discussed. A brief summary of the development of the simple equation for calculating internuclear distances of ionic compounds is provided. Values of internuclear distances calculated from the derived radii are compared to observed values give good agreement, showing strong evidence that ionic and covalent radii are not additive and electronegativity influence bonding and internuclear distances. Ionic radii derived from the proposed model are applied to calculate lattice energies which agree well with literature values/values calculated by the Born Haber cycle. Work functions of transition metals are shown to be simple inverse functions of the derived radii. Internuclear distances of inter-metallic compounds are calculated and compared with observed values to show good agreement. This work shows that the proposed model of metallic structure complements the band theory and expressions introduced in this work can be used to predict ionic and covalent bond lengths (in different environments) that have not yet been determined as well as being a method for resolving bond type.

Introduction

There is a proliferation of different series/sets of ionic and covalent radii in the open literature. Goldschmidt and Pauling used different methods to estimate ionic radii in the early part of the twentieth century¹. Amongst the various sets of ionic radii, one produced by Waddington² is fairly commonly quoted and a widely known set is put together by Shannon and Previt³ and later on improved by Shannon⁴. However, it was pointed out that there are some impressive discrepancies between these sets and they do not fare well on certain statistical tests⁵. Observed radii differ substantially from the commonly known sets of radii with a few exceptions. One of the essential differences is that cation radii are larger than previously believed whilst anion radii are correspondingly smaller. It is also evident that ionic radii are not additive since the ionic radius of two individual elements (say rubidium or caesium and fluorine) when added together does not match the observed internuclear distance between the two ions in the solid state.

As with ionic radii, there are many sets of covalent radii published. Sometimes it is unclear whether the radii refer to the solid or gaseous state. Recently, Cordero⁶ et al. undertook a large scale statistical exercise and published a set of solid state covalent radii deduced from crystallographic data. A set with completely different values was also produced by Pyykko and Atsumi⁷. Cordero (and her colleagues) discussed the need for covalent radii, the inconsistencies of some of the commonly used radii from the Cambridge Structural Database, the lack of covalent radii of some elements, uncertainties and limitations of some data and methodology used to derive the set. We have demonstrated that covalent radii are not additive⁸ and the covalent radius of an element in the gaseous state may be different from that in the solid state. The definition of metallic radii appears to be not as clear cut as ionic or covalent radii. Pauling⁹ produced a set of metallic radii and referred to them as single covalent bond radii.

Covalent and ionic radii are used in structural chemistry and molecular modelling. Reliable data of ionic or covalent radii (or internuclear distances) can serve as a rough guide to the magnitude of steric effects, how reactions may occur and on the stability of compounds. In this work we propose a simple equation for calculating internuclear distances of covalent, ionic and metallic lattices and show that internuclear separations calculated by this equation agree well with observed values. This equation is also used to derive ionic radii of transition metals. The derived radii are also used to calculate lattice energies and work functions of transition metals. Values calculated in this work are compared with observed data including values of bond lengths, lattice energies and work functions of metals to illustrate the reliability of this methodology.

Experimental Data

The *CRC Handbook of Chemistry and Physics*¹⁰ contains extensive and reliable compilations of ionization energies, lattice energies, work functions of metals, enthalpies of formation, observed covalent bond lengths of crystalline organic compounds and organometallic compounds and structure and bond lengths of free molecules in the gas phase. The structures, unit cell constants and internuclear separations of most of the elements in the solid state are provided in *The Structures of the Elements*¹¹. A comprehensive set of observed data of chemical bond lengths and unit cell dimensions in the solid state can be found in *Crystal Data Determinative Tables*¹² volumes One to Four, volumes One and Three contain data on organic compounds and volumes Two and Four contain data on inorganic compounds. *Structural Inorganic Chemistry*¹³ also contains reliable structural data with references to original work, including detailed discussions, of many compounds in the solid state as well as some data in the gaseous state. *The Journal Physical and Chemical Reference Data*¹⁴ also has structural data and unit cell dimensions of compounds at normal temperature/pressure as well as at elevated temperatures and pressures. *The Cambridge Structural Data Base* contains a vast quantity of crystallographic data, but most of the data are for complex inorganic or organic molecules whereas in this work our aim is to calculate internuclear distances of ionic, covalent or intermetallic lattices with fairly simple and regular structures.

Observed values of ionisation energies, lattice energies, enthalpies of formation, work functions, unit cell constants and internuclear distances/bond lengths used in this work are quoted from the above publications. Values of unit cell constants/internuclear distances provided by the above publications are often given to at least two and often three or four decimal places of an Angstrom (Å). We have examined many of the unit cell dimensions and internuclear distance listed in these publications and found that usually they agree well and in general if there are differences (in unit cell constants of particular compounds) they are less than 0.01 Å. There is no reason to doubt the reliability of the values in this these publications.

The Chemical Bond

On an elementary level, when two (identical or heteronuclear) atoms or two molecules approach each other an ionic bond is formed if one of the atoms donate one or more electrons and become a positive ion and the other atom accepts the electron(s) and becomes a negative ion. A covalent bond is formed if both share one or more pairs of electrons to form a chemical bond. Metallic bonds are formed when metal atoms condense into a regularly packed structure. However, in reality, many bonds are intermediate between ionic and covalent¹⁵. Although conduction in metals is well accounted for by quantum mechanical principles as described in band theory, the physical structure of metals is not completely understood. A popular description of “ions in a sea of electrons” or the “free electron” model proposed by Drude¹⁶ used to describe metallic bonding, structure and

properties has been shown to be inadequate¹⁷. It is obvious that a sea of delocalised electrons surrounding the ions can escape from a metal surface easily and does not require work functions which in some cases are higher than some ionisation energies. There are also discrepancies between the “free electron” model and other principles/calculations in physics¹⁸.

Electronegativity Effects on Chemical Bonding

Many ionic bonds formed between metals and non-metals possess covalent character. For example, most Group 1 hydrides are essentially ionic compounds, but lithium hydride shows significant covalent characteristics¹⁹. Secondly, covalent radii are not additive except when the two atoms forming the bond are homonuclear or (approximately additive) for elements belonging to the same group. Schomaker and Stevenson²⁰ suggested that these discrepancies originate from the partial ionic character of the bonds formed between different elements. Pauling²¹ discussed in detail in his works the dependence of bond length on the differences in electronegativity between the different elements which created the partial ionic character in the bonds. He was also the first to produce a practical electronegativity scale of the main group and transition elements. Covalent bonds possess ionic character when the difference in electronegativity between the elements forming the bond is large. We have devised a set of electronegativity values⁸ (see Table 13 of Appendix 1), which is slightly different from Pauling’s set. We use this set throughout this work to estimate ionic/covalent bond character. We have found that when this set of electronegativities is used for calculating internuclear distances there is good agreement between calculated and observed values.

It is obvious that a bond between a large electropositive atom and a smaller electronegative atom is more likely to be ionic than two atoms of similar size since it is easier for the smaller atom to draw the bonding electrons closer to itself. Since atoms of alkali and alkali earth metals are most electropositive and larger than atoms of other elements in the same period we may expect that bonds between these elements with elements of other Groups are ionic. However, beryllium has a fairly high ionization energy and high sublimation energy and it is the smallest atom in Group 2. As a result, its lattice and hydration energies are insufficient to provide complete charge separation and formation of simple Be^{2+} ions and there is covalent character in the some bonds involving beryllium²², such as BeH_2 . Besides LiH , MgH_2 also show covalent character²³. Transition metals are much less electropositive and binary compounds are likely to exhibit covalent character, for example, in the solid state, silver halides are progressively more covalent from fluoride to iodide. It is not surprising that silver and copper binary compounds form covalent lattices or exhibit covalent character since both elements also have high ionisation energies as well as higher electron affinities than most metals²⁴. Halides of some transition metals,

such as bromides and iodides, similar to selenides and tellurides, are in general much more covalent than fluorides or chlorides. Sulfides, selenides and tellurides of zinc, cadmium and mercury are also covalently bonded and form three dimensional covalent lattices in the solid state²⁵.

Definition of Bond Type

We initially assumed that ionic radii may be additive and used existing sets of ionic/covalent radii (such as those proposed by Pauling and Shannon and Previt to compare calculated and observed internuclear distances of many binary inorganic compounds. It was found that the calculated and observed differ in some cases by more than 5%. We then, by trial and error, produced a set of ionic radii for the alkali metals, alkali earth metals and some transition metals as well as halogens and chalcogens. We compared the calculated and observed internuclear distances and discovered that within a certain range of compounds the ions do behave like hard spheres where the internuclear separation is equal to the sum of the cationic and anionic radii. Some examples of these results are shown Table 1 below. However, for many compounds, such as those involving transition metals, the observed bond lengths are very much different from the sum of cationic and anionic radii. These simple calculations and previous results²⁶ also show that when the co-ordination number is different, the radii of the cation and anion are different.

Table 1. Examples of internuclear distances where ionic radii are additive.

Compound	Radii and internuclear distances (in Angstrom)				
	Radii		Internuclear separation		
	Cation	Anion	(Cation+Anion)	Observed	Abs % difference
CaS	1.279	1.571	2.850	2.851	0.0
CaSe	1.279	1.682	2.961	2.962	0.0
CaTe	1.279	1.884	3.163	3.186	0.7
SrS	1.437	1.571	3.008	3.012	0.1
SrSe	1.437	1.682	3.119	3.123	0.1
SrTe	1.437	1.884	3.321	3.333	0.4
BaS	1.609	1.571	3.180	3.184	0.1
BaSe	1.609	1.682	3.291	3.295	0.1
BaTe	1.609	1.884	3.493	3.500	0.2
KF	1.502	1.179	2.681	2.672	0.3

KCl	1.502	1.662	3.164	3.146	0.5
KBr	1.502	1.807	3.309	3.300	0.3
KI	1.502	2.033	3.535	3.533	0.1
RbF	1.646	1.179	2.825	2.827	0.1
RbCl	1.646	1.662	3.308	3.295	0.4
RbBr	1.646	1.807	3.453	3.434	0.5
RbI	1.646	2.033	3.679	3.670	0.2

In the above table, column one lists the compounds, the cationic radii, anionic radii, calculated and observed internuclear separations and absolute % difference are shown in columns two to six respectively. In every case the difference between observed and calculated is less than 1%. These results show that Groups 1 and 2 ions, as well as halide and chalcogen ions (when bonded to Groups 1 or 2 cations), usually behave like hard spheres. This is strong evidence that ions can be truly ionic and with little or no covalent character and not polarisable. After analysing all the data together with earlier work⁸ and examining electronegativity differences between the cations and anions we concluded the following (a) bonds between Groups 1 or 2 metals with halogens/chalcogens are purely ionic (with little or no covalent character and this is reflected in their behaviour like hard spheres). (b) Bonds between other metals with non-metals (mainly fluorides) are also mainly ionic when the difference in electronegativity between the two atoms is two or higher. If the difference in electronegativity between the anion and cation forming the bond is from one to two then the particular ionic bond are easily polarised and exhibit “covalent” character. (c) But, if the difference in electronegativity is one or less than one then the bond is covalent (more covalent than ionic) but exhibiting “some ionic character”. (d) Bonds between non-metals are covalent with no ionic character when the difference in electronegativity between them is one or less than one. (d) Otherwise, we assume that covalently bonded compounds between non-metals may possess “some ionic character” if the difference in electronegativity is one or higher. Further examination of the gradual transformation of bond type from ionic to covalent is provided in the *Discussion* section.

Bonds in intermetallic compounds are mainly covalent because the difference in electronegativity between the two metallic atoms is always less than one, in many cases equal to 0.5 or less and when the electronegativity difference is so small it is difficult for one metal to attract one or more electrons from the other to become a negative ion. In addition to the set of electronegativity values of elements, we have made the assumption that

the electronegativity values of functional groups such as (OH), (SO₄) and (NO₃) are equivalent to a value of 4.0 and that of (COOH), (CN) and CO(NH₂) are equivalent to 2.8. These are included because they are fairly common parts of simple covalent molecules.

Equation to calculate internuclear distances

Quantum mechanics show that when two atoms approach each other to form a bond their equilibrium internuclear distance is reached when the energy is at a minimum. The Bohr radius of a hydrogen atom is 0.5292 Å (to 4 figures). Condon approximated the internuclear separation of two hydrogen atoms in H₂ to be 0.73 Å. Heitler & London and others²⁷ using approximate wave functions worked out the binding energy and the equilibrium internuclear separation to be about 0.743 Å. This was confirmed by experiment²⁸. A hydrogen atom has only one electron, so unlike other atoms we do not need to consider factors such as screening constants. Therefore, we consider that when two hydrogen atoms bond the overlap between the two atoms to be biggest, i.e. the compression or reduction in size of the two hydrogens is greatest. In a hydrogen molecule, the radius of each hydrogen is reduced by 30%.

To formulate an equation to calculate internuclear distances of binary compounds we assumed that atoms, when forming a bond, behave (as with hydrogen atoms) more like soft compressible spheres which can be deformed/compressed and the amount of compressibility/deformation depends on the bond. Atoms behave in such a way because only a minority of bonds are purely ionic or covalent. Most bonds, ionic or covalent, are polarisable and the atoms forming the polarised bond change shape and size (deformable and compressible). For convenience and to differentiate the radii derived/used for calculation in this work from other sets of radii, we use to term “soft-sphere” radii to describe them in the remainder of this work. We found that a very simple expression to calculate the internuclear separation in an ionic bond can take the form of:

$$L[AB] = \{[A]^k + [B]^k\}^{1/k} \dots\dots\dots[1a]$$

In the above equation, L[AB] is the internuclear distance between atoms A and B when they form a truly ionic bond. [A] and [B] are the hypothetical radii of each individual ion in isolation. For an equation of this type, the value of k is just over 2.0 for a reduction in the length of the radii by 30% (i.e. L[AB] is equal to the sum of 0.7[A] and 0.7[B]).

When the bond between A and B is mainly covalent, the two atoms/spheres just come into contact. In most cases, the electronegativity values of the two atoms may be different. In such cases the atom with the higher electronegativity draws the electron density slightly closer to it and the other atom becomes a smaller sphere because of a loss of electron density. The bond length is then shorter than the sum of the two covalent radii

because one of the soft spheres has reduced in size. The decrease in bond length or internuclear separation is then a simple function of the difference in electronegativity and the expression becomes:

$$L[AB] = \{[A]^l + [B]^l\} - C[\text{abs}(x_a - x_b)^r] \dots\dots\dots[1b]$$

The electronegativity values of atoms A and B are x_a and x_b respectively and r and C are constants. In many cases, the two atoms A and B can approach each other to form a bond which is not completely ionic, as discussed above if the difference in electronegativity between the anion and cation is between one and two, the particular ionic bond will exhibit “covalent” character. The internuclear distance between A and B can be calculated by the following:

$$L[AB] = \{[A]^k + [B]^k\}^{1/k} - C[\text{abs}(x_a - x_b)^r] \dots\dots\dots[1c]$$

Whether we use [1a], [1b] or [1c] to calculate bond length depends on the definition of bond type discussed above. For example, the internuclear separation of a mainly ionic bond (such as one formed between an alkali earth metal and a halogen or where the difference in electronegativity between the elements is two or higher), can be calculated by [1a]. However, when a bond is not predominately ionic or covalent, as A and B approach each other to form a bond, both spheres A and B will overlap and the spheres may also change in size and become compressed/deformed. The above discussion assumes that the bonds between A and B are all equidistant such as in the NaCl or CsCl structures. However, in other structures such as the rutile structure²⁹, not all the bonds are equidistant and the calculated results will not mirror the true internuclear distances as accurately.

Derivation of values of k and other constants

We began deriving values of k for Group 1 binary compounds and noticed that the majority possess the NaCl structure and some possess the CsCl structure. Ammonium halides also possess these two structures. Table 2 lists the radii of caesium and ammonium ions which possess NaCl and CsCl structures together with Group 2 fluorides with the CaF₂ structure.

Table 2. Differences between NaCl, CsCl and CaF₂ structures.

Compound	Radii and internuclear distances (in Angstrom)				
	Cation	Anion	(Cation+Anion)	Observed	Abs % difference
CsF*	1.804	1.179	2.983	3.001	0.5
CsCl	1.857	1.710	3.566	3.569	0.1

CsBr	1.857	1.860	3.717	3.720	0.1
CsI	1.857	2.092	3.949	3.955	0.2
NH ₄ Cl	1.652	1.710	3.362	3.357	0.1
NH ₄ Br	1.652	1.860	3.512	3.515	0.1
NH ₄ I*	1.606	2.033	3.639	3.630	0.2
CaF ₂	1.225	1.143	2.368	2.365	0.1
SrF ₂	1.375	1.143	2.519	2.509	0.3
BaF ₂	1.540	1.143	2.683	2.683	0.0

NH₄I and CsF possess the NaCl structure (6 co-ordination) and the others, excepting the last three with CaF₂ structure, possess the CsCl structure (eight co-ordination). From the above, it is evident that the radius of the same ion is bigger when in eight co-ordination than six co-ordination. In the fluorite structure, each fluorine has only four nearest neighbours (four co-ordination) and the radii of both fluorine and the cation are smaller than in six co-ordination, as shown in Table 1.

If we assume that atoms/ions are spheres (not completely hard but compressible), quantum mechanics shows that when two atoms come close together, on the one hand, the coulombic interaction between the electrons and the nuclei lowers the overall potential energy, but the kinetic energy increases as the internuclear distance is shortened and the electrons are compressed closer to the nuclei which tends to raise the overall energy. An equilibrium distance is reached when the total energy is at a minimum. In a slightly analogous way, when two ions approach very close each other, as in an ionic solid, electrostatic attraction between the opposite charges lower the total energy but the repulsion between the filled shells (electron orbitals) of the oppositely charged ions as they are “squeezed” into a smaller volume increases repulsive energy. Since the increase in repulsive energy is a function of the ionic spheres being “squeezed” into a smaller volume as they approach close to each other in a crystal, at equilibrium internuclear distance an optimum energy is reached. For eight co-ordination to take place, as in the CsCl structure, the total of the energy involved in compression of eight spheres by a certain percentage volume must not be larger than the sum of energy for compressing six spheres (in the case of six co-ordination) by some other volume change.

Let E_v be energy per unit volume change, r_1 be the radius of the ion in a hypothetical isolated state and r_x be the radius of the ion when it is in an ionic solid with another ion of opposite charge with co-ordination number x , the increase in repulsive energy when the volume is reduced from the decrease in radius is:

$$E_r(4\pi/3)[((r_1-r_x)/r_1)r_1]^3 \dots\dots\dots [2] \qquad \text{If}$$

the increase in repulsive energy for eight co-ordination is greater than for six co-ordination, then in energy terms eight co-ordination will not take place. As the increase in the total repulsive energy for eight co-ordination should not be bigger than for six co-ordination then $8E_r(4\pi/3)[((r_1-r_8)/r_1)r_1]^3$ should equal $6E_r(4\pi/3)[((r_1-r_6)/r_1)r_1]^3$ where r_8 and r_6 are the radii of the ion with the respective co-ordination numbers.

Assuming that the radii of the hypothetical (isolated) ions Cs^+ and NH_4^+ are 2.368 and 2.107 Å respectively²⁶, the increase in repulsive energies for Cs^+ in eight and six co-ordination become $8E_r(4\pi/3)[0.5115]^3$ and $6E_r(4\pi/3)[0.5635]^3$, which are $4.48E_r$ and $4.49E_r$ respectively. This calculation when repeated for NH_4^+ produces two very similar values of increase in repulsive energy. This means that for Group 1 elements, in eight co-ordination and six co-ordination the percentage decrease of the radii are 21.6 and 23.8% respectively.

Let the radii of the hypothetical (isolated) ions²⁶ Ca^{2+} , Sr^{2+} , Ba^{2+} and F^- to be 1.657, 1.861, 2.084 and 1.547 Å respectively. Using the simple formula [2] above, the repulsive energies of fluorine in four and six co-ordination are $1.102E_r$ and $1.102E_r$ respectively. For fluorine bonding with Group 2 elements, the percentage decrease in radii of fluorine, as well as Group 2 metals, in four and six co-ordination, are 26.1 and 22.8% respectively. A reduction of 21.6, 23.8, 22.8 and 26.1% in radii translate to k values of approximately 1.545, 1.667, 1.6 and 1.8 in expression [1a] (i.e. when k is 1.545, the internuclear separation $L[\text{AB}]$ is equal to the sum of $0.784[\text{A}]$ and $0.784[\text{B}]$ etc.).

We repeated the above exercise to obtain k values of other metal compounds (other than Groups 1 and 2). As expected, the reduction in radii for any particular structure/co-ordination number is not as clear cut as with Groups 1 and 2 and the percentage reduction in radii is much less. This is most likely that even when they are considered ionic there is still covalent character and the difference in electronegativity is much less than those of Groups 1 and 2 compounds. Secondly, d orbitals are involved and unlike Groups 1 and 2 the outer electron shell in many cases is not completely filled. Hence, it is not surprising that both the transition metal cations and anions ions behave more like “soft” spheres and their radii vary considerably from one binary compound to another. The structures we examined were the rutile structure where each anion is surrounded by three cations, the NaCl structure, the fluorite structure, and the CdI_2 structure, which like the rutile structure, has each anion is surrounded by only three cations. Some examples are shown in Table 3 below.

Table 3. “Compressible sphere” behaviour of some ions in binary ionic compounds.

Radii and internuclear distances (in Angstrom)

Compound	Radii		Internuclear separation		Abs % difference
	Cation	Anion	(Cation+Anion)	Observed	
CrO ₂	0.813	1.070	1.883	1.884	0.0
TiO ₂	0.915	1.042	1.957	1.960	0.1
VO ₂	0.840	1.114	1.954	1.953	0.1
TaO ₂	0.867	1.149	2.016	2.014	0.1
TiO	0.978	1.114	2.092	2.090	0.1
TaO	1.041	1.071	2.212	2.211	0.0
VO	0.917	1.143	2.060	2.060	0.0
VN	0.984	1.079	2.063	2.065	0.1
CrN	0.909	1.164	2.073	2.074	0.0

Since the transition metal ions do not behave exactly like hard spheres we are only able to find average k values which may not be exact fits. The best average k values are 1.667 for the rutile structure when fluorine is the anion and 1.6 for other anions, we suppose this is so because fluorine is most electronegative and the compounds are more ionic/compressible. The k values for NaCl, fluorite and CdI₂ structures are 1.3, 1.545 and 1.667 respectively.

We next considered the value of k for binary compounds between metals and non-metals that are more covalent than ionic and have electronegativity differences of one or less (such as CuCl, CuBr and CuI). Since the decrease in radii of the “hypothetical ions” in ionic solids vary from over 10% to about 30% we assume that the decrease in radii of those metallic compounds that are more covalent than ionic to be somewhere between 0% and 10% and the median is about 5%. A k value of 1.0667 equates to a reduction in radius of about 4.0 to 5%. We tried this value and it works fairly well. A summary of the k values we have used are given in Table 4 below.

Table 4. Values of k for ionic solids and covalent solids with some ionic character.

Structure	Group 1	Group 2	Other metal cations
NaCl	1.667	1.6	
CsCl	1.545		
CaF ₂		1.8	1.545
ZnS		1.8	

NaCl		1.3
Rutile (fluoride anion)		1.667
Rutile (other anion)		1.6
CdI ₂	1.8	1.667

The value of C is 0.1 and the value of r is 0.5. The values of these two constants have been discussed in detail in our earlier work²⁶ and not repeated here.

Co-ordination number and the radius ratio rules

The commonly known radius ratio rules do not always work and often cannot predict crystal structures correctly³⁰, such as with some Group 1 halides. We consider that the rules may not work, even if there is a perfect geometrical fit, for two reasons. First of all, the coulombic attractive energy of an ionic solid is a direct function of the Madelung constant and an inverse function of the internuclear separation. Hence the ratio:

$$(\text{Coulomb energy of structure A})/(\text{Coulomb energy of structure B}) = (M_A/M_B)(d_B/d_A) \dots [3]$$

M_A is the Madelung constant of structure A, M_B is Madelung constant of B. d_B is the internuclear separation in structure B and d_A is the internuclear separation in structure A. If $(M_A/M_B)(d_B/d_A)$ is bigger than one, then it is more favourable in terms of coulombic attractive energy to have structure A. Simple calculations first with “effective” ionic radii derived by Shannon substituted in [3] and repeated with radii derived by us showed that some rubidium and caesium halides possess the NaCl rather than the CsCl structure because in terms of coulomb potential energy it is more favourable with the NaCl structure. However, these simple calculations also show that CsCl and CsBr have the NaCl structure on coulombic potential energy grounds. But, eight co-ordination is favoured over six co-ordination because as indicated by the radius ratio rules and as discussed above the compressive energy marginally is less for eight than six co-ordination. Therefore we believe that the radius ratio rules can only predict the correct structure of an ionic solid if both (a) the coulombic attractive energy and (b) the energy to compress the ions are favourable.

Calculation of internuclear distances of covalent bonded lattices

We start with the bonds lengths/covalent radii of some p block elements. These are obtained from average observed internuclear distances of homonuclear covalent bonds of the particular elements in compounds containing these (and other mainly p block non-metallic elements). All other covalent radii are derived from the averaged (heteronuclear) bond lengths between those elements and the other elements concerned. The covalent radii of elements indirectly derived are then refined/fitted (manually) to give best agreement with observed

internuclear distances in covalent compounds. Values of observed covalent radii in the solid state are shown in Column two, with the exception of the value for nitrogen, which is not directly observed. We have assumed that it is slightly bigger than that of the gaseous state and have multiplied its (gas phase) covalent radius (of 0.759) by 1.02. Indirectly derived covalent radii are listed in Column four of Table 5. All covalent radii are shown in Angstrom units to three decimal places. Experimental uncertainties are in all cases less than $\pm 0.01\text{\AA}$ (or less than 1.0%) all bond lengths and radii in this work are shown/rounded to three decimal places (of an Angstrom).

Table 5. Averaged observed and derived covalent radii.

Observed radii		Indirectly derived radii	
Symbol	Covalent radius (in Angstrom)	Symbol	Covalent Radius (in Angstrom)
B	0.890	Be	1.220
C(sp ³)	0.765	V	1.610
C(carbonyl)	0.754	Mn	1.550
N	0.774	Fe	1.620
O	0.741	Ni	1.510
P	1.128	Cu	1.390
Si	1.180	Zn	1.462
S	1.026	Ga	1.420
Cl	1.134	Ag	1.833
As	1.229	Cd	1.632
Se	1.170	In	1.600
Br	1.271	Hg	1.630
Sb	1.455	Pb	2.110
Te	1.364		
I	1.459		

A comparison of observed and calculated internuclear distance of inorganic covalent solids is listed in Table 6. The specific compounds are shown in column one of Table 6, with the particular bond indicated (M-X, where M

is the metal and X the non-metal forming the bond). Column two shows the reported structure of the covalent lattice. Columns three and four show the observed and calculated values. Following the above described definitions relating to differences in electronegativities, column five shows the particular form of the equation used for the calculation. Equation [1c] is used for covalent solids with ionic character (as defined above) and the exponent k is 1.067. The exponent k is equal to one when equation [1b] is used for covalent solids with little or no ionic character. Column six shows the absolute percentage difference between calculated and observed. We have previously shown a comparison of observed and calculated internuclear separations of bonding involving carbon⁸ in both the gaseous and solid states. There is good agreement in all cases and they are not reproduced here.

Table 6. Comparison of observed and calculated internuclear distances of inorganic covalent lattices.

Compound	Structure	Internuclear distance (in Angstrom)		Equation	Abs% difference
		Observed	Calculated		
B-As	ZnS	2.069	2.083	1b	0.7
B-N	ZnS	1.568	1.564	1b	0.2
B-P	ZnS	1.966	1.969	1b	0.2
Si-P	ZnS	2.269	2.245	1b	1.1
OSi-O	Rutile	1.790	1.790	1b	0.0
V-S	NiAs	2.411	2.435	1c	1.0
V-Se	NiAs	2.608	2.582	1c	1.0
IV-I	CdI ₂	2.849	2.856	1c	0.2
CrI ₂	Rutile	2.907	2.878	1c	1.0
Mn-S	ZnS	2.427	2.382	1c	1.9
Mn-Se	ZnS	2.524	2.530	1c	0.2
Mn-As	NiAs	2.572	2.614	1c	1.6
BrFe-Br	CdI ₂	2.674	2.675	1c	0.0
IFe-I	CdI ₂	2.879	2.875	1c	0.2
Ni-S	NiAs	2.387	2.346	1c	1.7
TeNi-Te	CdI ₂	2.598	2.702	1c	4.0
CuCl ₂	CdI ₂	2.517	2.322	1c	7.7

Cu-Cl	ZnS	2.345	2.321	1c	1.0
Cu-Br	ZnS	2.464	2.468	1c	0.1
Cu-I	ZnS	2.624	2.674	1c	1.9
Zn-S	ZnS	2.341	2.326	1c	0.6
Zn-Se	ZnS	2.456	2.483	1c	1.1
Zn-Te	ZnS	2.641	2.666	1c	1.0
Ga-As	ZnS	2.448	2.457	1c	0.4
Ga-Sb	ZnS	2.657	2.689	1c	1.2
Ga-P	ZnS	2.359	2.355	1c	0.2
Ag-Cl	NaCl	2.778	2.745	1c	1.2
Ag-Br	NaCl	2.888	2.889	1c	0.0
Cd-S	ZnS	2.519	2.484	1c	1.4
Cd-Se	ZnS	2.620	2.638	1c	0.7
Cd-Te	ZnS	2.805	2.846	1c	1.4
In-As	ZnS	2.614	2.628	1c	0.6
In-Sb	ZnS	2.803	2.858	1c	1.9
In-P	ZnS	2.541	2.526	1c	0.6
Hg-S	ZnS	2.537	2.517	1c	0.8
Hg-Se	ZnS	2.633	2.652	1c	0.7
Hg-Te	ZnS	2.758	2.805	1c	1.7
Pb-S	NaCl	2.970	2.916	1c	1.8
Pb-Se	NaCl	3.061	3.062	1c	0.0
Pb-Te	NaCl	3.180	3.260	1c	2.5

The above table shows that all the calculated results agree with the observed to 95% or better and, with the exception of two (NiTe₂ and PbTe) of the values, all agree to 98% or better and just 60% of the values agree to 99% or better.

Calculation of internuclear distances of ionic lattices

Ionic radii of metals are derived from our proposed alternative model³¹ of metallic bonding and structure which accounts for many metallic properties (such as the Hall effect³², work functions of metals and behaviour of

metals under pressure) that cannot be accounted for by the popular “ions in a sea of free electrons or free electron” model. It is also sometimes thought that metals are malleable and ductile due to the defects in the solid state. However, defects in the solid state also occur in non-metallic solids such as sulphur and phosphorus as well as ionic and covalent crystals and these solids do not show similar qualities.

Quantum mechanics and the band theory of metallic conduction state that electrons in a metal occupy different energy bands. Some of the energy bands may be partly empty and the highest energy band is only partly filled. Our alternative model considers that in a metallic crystal, the outermost electron(s) in each atom is/are not exactly “free” nor completely delocalised. The outermost electron(s) is/are separated/detached from the atom which forms a positive ion with one or more of the “detached” electron(s) behaving like negative ions. The detached outermost electron(s) can occupy certain equivalent positions that are at the midpoints between the nearest neighbours of the positive ions (similar to ionic crystals, where positive ions occupy positions between negative ions) but can move within these midpoint positions in a unit cell. For the remainder of this work, these midpoint positions will be called “midpoint sites”. Depending on the Group, metallic structure (hexagonal close packed, cubic closed packed or body centred cubic) and electronic configuration, the most likely number of outermost electrons detached from each individual metal atom range from one to a maximum of five. In our model, the “detached” electrons are the electrons that occupy the highest energy band and since only some of the midpoint sites are occupied this description fits in with the principle of the band theory and it is the “detached” electrons that can be promoted into the conduction band and allows current flow. Hence, we consider our physical description of the structure of metal complementary to the band theory.

Consider any crystal with a hexagonal (hcp) or cubic closed pack (fcc) structure of identical atoms, each atom has twelve co-ordination or twelve closest neighbours and in a body centred cubic (bcc) each atom has eight closest neighbours. There are two atoms in each unit cell in a body centred cubic³³, six atoms in each unit in a hexagonal closed pack and four atoms per unit cell in a face centred cubic crystal. The structure of Group 1 metals is discussed here to illustrate our alternative model. At room temperature, all alkali metals have a bcc structure and each atom has one outermost electron. In the alternative model of metallic structure/bonding, each atom has a single outermost electron which it loses to form a unipositive (1+) ion. Each positive ion has eight nearest identical neighbours of positive ions. Hence there are 8 equivalent sites that are midpoint between the internuclear distance of a positive ion and its eight neighbouring positive ions. The outermost electron which is detached from the atom can occupy and move around any one of these eight midpoint sites in a unit cell at any one time. Since there are two positive ions in each unit cell, there are only two detached electrons in each cell

and, therefore, at any one time only two of the eight (or a quarter of) midpoint sites are occupied and the rest are vacant and under certain conditions can be occupied by other detached electrons moving in from other unit cells. The two detached electrons move at random within the unit cell and each spend a quarter of the time at each site. With Group 2 metals, the two outermost electrons are detached from the atom and for transition metals up to five of the outermost electrons may be detached depending on the electronic configuration and the number of sites available. Other details of the proposed alternative model are given elsewhere³¹ in previous work. The atomic/metallic radius of a metal atom (which is half the internuclear distance between the nearest neighbours) or distance between the centres of the positive ion and the detached outermost electron(s), just as in the case of an ionic crystal, can be calculated from the relationship:

$$L[M] = \{[M_i]^k + [e]^k\}^{1/k} \dots\dots\dots[1d]$$

$L[M]$ is half the internuclear distance between any two nearest neighbours in the metallic lattice (i.e. the radius of the metal atom) $[M_i]$ is the ionic radius of the metal ion, $[e]$ is the “orbital radius” of the midpoint site containing the detached electron and the exponent k is defined as above.

Just as with metallic ions or the hydrogen atom, when metal atoms bond the atoms are compressed together to form a solid and the size of the atoms in the solid is smaller than individual isolated metal atoms. Each kind of metallic atom may have a different percentage of compression in the solid state and obviously there may be many different values of the exponent k in terms of expression [1d]. We performed some calculations and found that the values of k vary in the range of 1.3 to 1.5. To simplify the calculation, we have used a single value of k to be equal to 1.4 for all three types (ccp, bcc, hcp) of structures for transition metals.

De Broglie proposed that the same dualism of wave and corpuscle as is present in light may also occur in matter³⁴, where the wavelength of a particle $\lambda = h/mv$, h being Planck’s constant, m is the mass of the particle and v it’s velocity. For a particle moving in an orbit, it was also proposed that $n\lambda = 2\pi r$, where r is the radius of the orbit. For example, in a hydrogen atom with an electron orbital radius of 0.529 Å, λ is approximately 3.3Å. According to the de Broglie relationship the electron wave length is directly proportional to its speed and classical physics shows that the speed v is a function of the coulombic attraction and distance from the nucleus. By making appropriate estimates³⁵ of screening constants the coulombic attraction and hence approximate values of v can be obtained. Since the “detached” electron/s in the mid-point sites are attracted equally by two positive ions and we assume that each one moves in orbital motion or radius r (equal to $[e]$) around the site. Based on the estimated values of v and by trial and error, we obtain rough “orbital radius” $[e]$ values of the sites containing the detached electron for some d and p block metals. As our main aim is to calculate internuclear

separations and the calculations of the “orbital radius” [e] are simple approximations (values of [e] are not absolutely accurate), it is logical to limit the number of values. We grouped them to three values of 0.41, 0.33, and 0.23 respectively for hcp, bcc and ccp structures. The internuclear distances of metals (which we consider as twice the metallic radii) were calculated from the unit cell constants provided in *The Structures of the Elements*¹¹. The relevant ionic radii were then calculated from these metallic radii with equation [1d]. Column one of Table 7 lists the metals, columns two, three and four shows the structure, metallic radii and ionic radii respectively. The ionic radii calculated by this method are used in this work (a) to calculate internuclear distances in ionic crystals, (b) to calculate the lattice energies of ionic crystals, and (c) to show that the function of these metals are simple inverse functions of the calculated ionic radii.

Table 7. Radii (metallic and ionic) of metallic elements.

Symbol	Structure	Metallic Radius(in Angstrom)	Ionic Radius(in Angstrom)
Li	bcc	1.519	1.094
Be	hcp	1.127	0.744
Na	bcc	1.858	1.497
Mg	hcp	1.602	1.282
K	bcc	2.304	1.971
Ca	ccp	1.973	1.657
Sc	hcp	1.640	1.467
Ti	hcp	1.460	1.280
V	bcc	1.309	1.170
Cr	bcc	1.249	1.108
Mn	bcc	1.328	1.189
Fe	bcc	1.241	1.100
Co	ccp	1.253	1.168
Ni	hcp	1.313	1.124
Cu	ccp	1.278	1.195
Zn	hcp	1.394	1.210

Rb	bcc	2.469	2.160
Sr	ccp	2.152	1.861
Zr	hcp	1.603	1.429
Nb	bcc	1.429	1.295
Mo	bcc	1.363	1.225
Ru	hcp	1.339	1.151
Rh	ccp	1.346	1.263
Ag	ccp	1.445	1.364
Cd	hcp	1.568	1.392
Cs	bcc	2.674	2.370
Ba	bcc	2.175	2.084
Ta	bcc	1.430	1.296
W	bcc	1.370	1.235
Te*	bcc	1.417	1.282
Hg	hcp	1.842	1.678
Tl	hcp	1.716	1.549
Pb	ccp	1.750	1.677

We have only worked out the ionic radii of metals that are used in this work to calculate internuclear distances of ionic lattices. The metallic radii of those metals used to calculate internuclear distances of intermetallic compounds are also shown above. *Tellurium is included above because the ionic radius was worked out the same way as any metal, although it is not usually regarded as a metal. Ionic radii of non-metallic elements which have been mainly derived previously²⁶ and radii derived in this work (OH⁻, N³⁻ and CN⁻) are shown in Table 8. For the ionic radius of OH⁻, we assumed that the radius of the oxygen atom to be approximately 10% bigger than its covalent radius and added on the radius of H⁻ which was derived in earlier work to obtain a figure of 1.515. This value was refined to 1.550 to give a better result. The ionic radius of N³⁻ was estimated by subtracting the radius of H⁻ from the radius of NH₄⁺ to give a figure of 1.408 and refined to a valued of 1.420 for a better fit. The radius of CN⁻ was estimated by adding the radius of N³⁻ (1.420) to the radius of a carbon atom (which we assume to be about 10% bigger than its covalent radius) to obtain a figure of 2.282 which was then refined to 2.345.

Table 8. Radii of Anions (derived in earlier work or this work).

Symbol	Radius (in Angstrom)	Symbol	Radius (in Angstrom)
N ³⁻	1.420	O ²⁻	1.458
F ⁻	1.547	Cl ⁻	2.181
Br ⁻	2.372	I ⁻	2.668
S ²⁻	2.035	Se ²⁻	2.179
Te ²⁻	2.440	CN ⁻	2.345
OH ⁻	1.550		

Internuclear distances between ions in ionic crystals are calculated by expressions [1a] or [1c] depending on the electronegativity difference and bond type as defined above and using the ionic radii listed in Tables 7 and 8. A comparison between observed and calculated internuclear distances of these ionic lattices are listed in Table 9. Columns one to six of the Table show respectively the compound, structure, observed and calculated internuclear distance, equation used and absolute percentage difference between observed and calculated.

Table 9. Comparison of observed and calculated internuclear distances of inorganic ionic lattices.

Compound	Structure	Internuclear distance (in Angstrom)		Equation	Abs% difference
		Observed	Calculated		
BeS	ZnS	2.108	2.171	1c	3.0
BeSe	ZnS	2.226	2.309	1c	3.7
BeTe	ZnS	2.437	2.560	1c	5.0
NaCN	NaCl	2.940	2.959	1a	0.7
KCN	NaCl	3.264	3.280	1a	0.5
RbCN	NaCl	3.417	3.417	1a	0.0
CsCN	CsCl	3.715	3.692	1a	0.6
Mg(OH) ₂	CdI ₂	2.173	2.153	1a	0.9

Ca(OH) ₂	CdI ₂	2.411	2.432	1a	0.9
VN	NaCl	2.065	2.101	1c	1.7
CrN	NaCl	2.074	2.051	1c	1.1
ZrN	NaCl	2.305	2.316	1c	0.5
TiO	NaCl*	2.090	2.200	1c	5.3
TiO ₂	Rutile	1.960	1.944	1c	0.8
VO	NaCl	2.060	2.111	1c	2.5
VO ₂	Rutile*	1.953	1.901	1c	2.7
CrO ₂	Rutile	1.884	1.858	1c	1.4
MnO	NaCl	2.223	2.130	1c	4.2
MnO ₂	Rutile*	1.880	1.918	1c	2.0
FeO	NaCl*	2.145	2.059	1c	4.0
CoO	NaCl	2.129	2.117	1c	0.5
NiO	NaCl	2.088	2.085	1c	0.2
ZnO	NaCl	2.140	2.166	1c	1.2
ZrO ₂	CaF ₂ *	2.200	2.126	1c	3.4
NbO	NaCl*	2.105	2.214	1c	5.2
RuO ₂	Rutile	1.944	1.893	1c	2.6
RhO ₂	Rutile	1.910	1.977	1c	3.5
CdO	NaCl	2.348	2.314	1c	1.4
TaO	NaCl	2.211	2.219	1c	0.4
TaO ₂	Rutile	2.014	1.997	1c	0.8
PbO ₂	CaF ₂	2.316	2.321	1c	0.2
CrF ₂	Rutile*	2.143	2.031	1a	5.2
MnF ₂	Rutile	2.062	2.086	1a	1.1
FeF ₂	Rutile	1.990	2.025	1a	1.8
CoF ₂	CaF ₂	2.126	2.137	1a	0.5
NiF ₂	Rutile*	2.000	2.041	1a	2.1
CuF ₂	Rutile	2.100	2.090	1a	0.5
ZnF ₂	Rutile	1.980	1.964	1c	0.8

AgF	NaCl	2.465	2.482	1a	0.7
HgF ₂	CaF ₂	2.403	2.400	1c	0.1
PbF ₂	CaF ₂	2.572	2.526	1a	1.8
TiCl ₂	CdI ₂	2.527	2.565	1c	1.5
CrCl ₂	Rutile	2.563	2.503	1c	2.3
CuCl	ZnS	2.345	2.468	1c	5.1
CuCl ₂	CdI ₂	2.517	2.535	1c	0.7
TlCl	NaCl	3.150	3.065	1c	2.7
BaCl ₂	CaF ₂	3.171	3.135	1c	1.1
VBr ₂	CdI ₂	2.669	2.685	1c	0.6
CrBr ₂	Rutile	2.693	2.688	1c	0.2
TlBr	NaCl	3.290	3.248	1c	1.3
TlI	NaCl	3.470	3.533	1c	1.8
TeO ₂	Rutile	2.005	1.998	1c	0.3

In certain ionic lattices such as the hcp structure and the rutile structure the internuclear distances between the cation and the nearest neighbouring anions may not be equidistant²⁵ although the bonds are usually considered to be equivalent. Hence, where there are two different bond lengths we have calculated and shown an averaged value of the two distances in the Table. For lattices with a distorted structure, they are marked with an “*”. As shown in the Table, there is good agreement between calculated and observed values of internuclear separations. All calculated values (with the exception of TiO, NbO, CrF₂, all of which possess distorted structures and CuCl which is borderline between covalent and ionic) agree with the observed to 95% or better and 70% of the values agree with the observed to 98% or better.

Intermetallic compounds and transition metal carbonyls

Intermetallic compounds, as far as internuclear distances is concerned, can be roughly divided into two groups, one group can be considered as simple interstitial compounds where the smaller metal atoms simply occupy the holes in between the larger metal atoms and the internuclear distance between the smaller and larger atoms is the sum of the two metallic radii or bigger. In the second group the internuclear distances between the atoms are reduced by a certain amount and can be calculated. Equation [1b] is used for the calculation because the

electronegativity differences between the metals are usually less than one and we assume the metals spheres overlap slightly as in covalent bonds. Three simple transition carbonyls are solids at room temperature and again the internuclear distance between the carbon and the central metal atom can be calculated using [1b] since the carbon and metal bond can be treated as a covalent bond. To complete the calculation of the internuclear distances we have used the observed carbon covalent radius of 0.754 (half the internuclear distance of the bond -C-C=). Table 10 shows a comparison of observed and calculated internuclear distances of some intermetallic compounds and three transition metal carbonyls.

Table 10. Internuclear distances of intermetallic lattices and transition metal carbonyls.

Internuclear distance (in Angstrom)					
Compound	Structure	Observed	Calculated	Equation	Abs% difference
BeCo	CsCl	2.261	2.323	1b	2.7
BeCu	CsCl	2.347	2.370	1b	1.0
MnV	CsCl	2.515	2.578	1b	2.5
FeTi	CsCl	2.577	2.657	1b	3.1
FeV	CsCl	2.520	2.511	1b	0.3
FeNi	CsCl	2.512	2.495	1b	.07
CoTi	CsCl	2.587	2.660	1b	2.8
NiTi	CsCl	2.596	2.647	1b	2.0
CuSc	CsCl	2.820	2.846	1b	0.9
ZnZr	CsCl	2.889	2.921	1b	1.1
BeCu	CsCl	2.347	2.370	1b	1.0
Cr-(CO) ₆	octahedral	1.916	1.923	1b	0.4
Mo-(CO) ₆	octahedral	2.063	2.037	1b	1.3
W-(CO) ₆ octahedral	2.058	2.054	1b	0.2	

Lattice energies

Lattice energies of ionic compounds can normally obtained from the Born-Haber cycle or similar procedure. Alternatively, they can be calculated by the Born-Lande/ Born-Mayer or Kapustinskii equations. It has been

shown that lattice energies can be calculated by the Born/Kapustinskii type equations for alkali metal halides give a fair degree of accuracy and agree to within a few % of the experimental results³⁶ but for transition metal compounds the agreement is often very poor and can have discrepancies of 20% or more. As discussed elsewhere, the two or more ions of a compound in a crystal lattice are deformed and overlap each other. Therefore, the lattice energy is the energy required to overcome this deformation or interpenetration of the ions, which can be approximated as the energy required to remove the electron(s) bonding the ions in the overlap space. The lattice energy can be calculated if the relative sizes and degree of deformation of the ions are known, provided the energy to remove an electron (dissociate) from a standard species is known. With the model discussed above, the degree of compression/overlap is a function of k , where k is an appropriate constant for each type of structure/co-ordination as defined above. For example, k is 1.6667 for alkali metal halides with sodium chloride structures. The simplest species is hydrogen with only one electron and the Rydberg constant is known accurately. The lattice energy can then be calculated by the following:

$$\text{(Lattice energy)} E_L = R(H_0/M)(M^{k-1})/(X^{k-1.333})(\frac{1}{2})^{0.333}(\Sigma Q_i^2) \dots\dots\dots[4]$$

R is the Rydberg constant for infinite mass converted to kilo Joules per mole, H_0 is the classical Bohr radius, M is the size of the cation, X is the size of the anion and Q_i is the charge on the ions. Hence, for sodium chloride $\Sigma Q_i^2 = 1 + 1 = 2$ and for calcium fluoride it is $4 + 1 + 1 = 6$ etc. R is the amount of energy needed to remove an electron from a species the size of a hydrogen atom, (H_0/M) provides a ratio of the distance of the electron from the nucleus, since the greater the size the less is the energy needed to remove the electron. $(M^{k-1})/(X^{k-1.333})$ gives an approximation of the overlap, this is multiplied by a factor which is approximated to $(\frac{1}{2})^{0.333}$ because the electron is not removed to infinity away from both ions (but rather removed from the deformed/overlap region). ΣQ_i^2 is the sum of all the squares of the charges on the ions, since the higher the charge on the ions the more the more energy is required to separate them. Lattice energies are calculated by equation [4]. In Table 11, we show only values of lattice energies (in kilo Joules per mole) where there is a counterpart available in the *CRC Handbook of Chemistry and Physics* for comparison.

Table 11. Comparison of lattice energies published by the CRC and calculated by equation [4].

Crystal	Structure	CRC	Equation[4]	Abs % difference
(A)	(B)	(C)	(D)	(E)
BeSe	ZnS	3431	3252	5.2

BeTe	ZnS	3319	3085	7.1
NaCN	NaCl	766	725	5.4
Mg(OH) ₂	CdI ₂	2870	2631	8.3
KCN	NaCl	692	662	4.4
Ca(OH) ₂	CdI ₂	2506	2415	3.7
TiO	NaCl	3832	3756	2.0
TiO ₂	Rutile	12150	10837	10.8
TiCl ₂	CdI ₂	2439	2349	3.7
VN	NaCl	8283	8992	8.5
VO	NaCl	3932	3999	1.7
VBr ₂	CdI ₂	2534	2354	7.1
VI ₂ *	CdI ₂	2470	2345	5.1
CrN	NaCl	8358	9341	11.8
CrF ₂	Rutile	2778	2763	0.5
MnF ₂	Rutile	2644	2699	2.1
MnO	NaCl	3745	3955	5.6
MnO ₂	Rutile	12970	11161	13.9
MnSe*	ZnS	3176	3054	3.8
FeF ₂	Rutile	2849	2770	2.8
FeO	NaCl	3865	4176	8.1
FeBr ₂ *	CdI ₂	2515	2247	10.7
FeI ₂ *	CdI ₂	2439	2329	4.5
CoF ₂	CaF ₂	3004	2809	6.5
CoO	NaCl	3930	4004	1.9
NiF ₂	Rutile	3098	2751	11.0
NiO	NaCl	4010	4113	2.6
ZnF ₂	Rutile	3021	2684	11.2
RbCN	NaCl	638	641	0.6
CuF ₂	Rutile	3046	2699	11.4
CuCl*	ZnS	992	844	15.0

CuBr*	ZnS	969	870	10.2
CuI*	ZnS	948	903	4.8
ZrN	NaCl	7723	7817	1.2
ZrO ₂	CaF ₂	11188	10381	7.2
AgF	NaCl	953	890	5.6
CdF ₂	CaF ₂	2809	2594	7.7
CdO	NaCl	3806	3542	7.0
CsCN	CsCl	601	621	3.4
BaCl ₂	CaF ₂	2046	1984	3.0
HgF ₂	CaF ₂	2757	2382	13.6
PbF ₂	CaF ₂	2535	2383	6.0

*In accordance with the definition in this work, these are considered to be covalent lattices (more covalent than ionic)

In a few cases two marginally different values obtained from slightly different methods are given in the *CRC*, we have chosen one that seems more appropriate. As shown in the above table, agreement between those calculated by [4] and the published values are reasonable. Agreement is best when the solid is mainly ionic as with a Group 1 or Group 2 metal salt. Mercury at room temperature is a liquid and the ionic radius used in the calculation assumed it to be a solid so it is not surprising that agreement between the calculated and published value is poor.

Work function of metals

In our model of metallic structure, unlike the “ions in an electron sea/electron gas” model, the separated/detached outermost electrons can only occupy midpoint sites between two positive ions inside a unit cell, which means that there is almost no detached outermost electron(s) on the surface of the metal. Hence, energy has to be expended to draw those electrons onto the surface of the metal. The work function is an inverse function of the soft-sphere radius since the further the outermost electron(s) is/are from the nucleus of the positive metal ion the less energy is required to draw it/them to the surface. The work functions of the transition and *p* block metals can be approximated by the following simple expression:

$$W = C_w / [(R)^{1/2}] \dots \dots \dots [5]$$

W is the work function, R is the soft-sphere ionic radius and the constant C_w is 4.75 for metals with bcc structures, 5.05 for hcp and 5.4 for ccp respectively. Column two of Table 12 lists the type of structure, Column three shows the work functions (in eV) calculated by expression [5], Column four shows the observed work functions in eV and the absolute percentage differences are shown in Column five. With the exception of mercury, which is a liquid at room temperature and not a solid, all values agree to better than 90%.

Table 12. Observed and calculated work functions.

Element	Structure	Calculated work function(eV)	Observed work function (eV)	Abs % difference
(A)	(B)	(C)	(D)	(E)
Ti	hcp	4.46	4.33	3.1
V	bcc	4.39	4.30	2.1
Cr	bcc	4.51	4.50	0.3
Mn	bcc	4.36	4.10	6.2
Fe	bcc	4.53	4.74	4.4
Co	ccp	5.00	5.00	0.0
Ni	hcp	4.76	5.20	8.4
Cu	ccp	4.94	4.76	3.7
Zn	hcp	4.59	4.27	7.6
Nb	bcc	4.17	4.33	3.6
Zr	hcp	4.22	4.05	4.3
Mo	bcc	4.29	4.57	6.2
Ru	hcp	4.71	4.71	0.0
Rh	ccp	4.80	4.98	3.5
Ag	ccp	4.62	4.63	0.1
Cd	hcp	4.28	4.08	4.9
Ta	bcc	4.17	4.30	2.9
W	bcc	4.27	4.55	6.1
Hg	hcp	3.90	4.47	12.9

Discussion

Our earlier work⁸ also showed that the internuclear distance between two atoms forming a covalent bond may be different between the gaseous and solid states and that in the gaseous state bonds are more likely to be covalent than ionic. In the solid state, the size of the nearby atoms may prevent the bonding atoms from approaching closer to each other (steric effect). Repulsion between positive/negative ions (or atoms in a covalent bond with ionic character) that are neighbours in the solid lattice may also alter the internuclear separation. Hence, the exponent k may be different between solid and gaseous states and radii that have been derived for atoms in the gaseous state may not be appropriate for use to calculate internuclear distances in the solid state.

The energy of an ionic bond may be considered to consist of the ionic contribution to the energy measured by the electrostatic attraction between the ions, any residual covalent bond energy, energy contribution from polarisation of the ions, repulsive forces due to partial overlapping of any adjacent charge clouds and zero point vibrational energy plus any (usually small) relativistic/quantum electrodynamic effects that needs to be applied. The equilibrium internuclear distance can be calculated from the total energy. In theory, all these effects can be modelled. However, with the exception of the simplest systems, it is difficult if not impossible to model the true energy exactly. All models/equations are approximations of reality. Part of our proposed model/equation can be considered as an approximation of a macrostate where the ionic/covalent solid is seen (by the observer) as particles fixed in a firm lattice without any visible movement, vibration or rotation.

In this work, we have devised 3 slightly different versions of a simple equation. Internuclear separations of mainly ionic or covalent compounds can be calculated by [1a] and [1b] respectively. Examples in Tables 1 and 2 show clearly that Groups 1 and 2 and compounds where the difference in electronegativity is greater than two (mainly fluorides) are mainly ionic and not polarisable. It is also evident from earlier work⁸ on covalent bond distances and from the results above that bonds between non-metals where the electronegativity differences are one or less are mainly covalent. It is also fairly clear that when a metal bonds with a non-metal and the electronegativity between the two is one or less the bond only has some ionic character but more covalent than ionic. The bond type is not so precise when a metal atom bonds with a non-metal atom and the electronegativity difference is somewhere between two and one. It is fairly obvious that although it is common to refer to these bonds as ionic, the bonds are more polarised and the amount of covalent character gradually increases as the

electronegativity difference decrease. When there is some covalent character in the bond, such as in many of the transition metal oxides, the value of the exponent k is much smaller (for the same co-ordination number). This is so because the ions, having covalent character, are less attracted to each other and not packed as tightly as in pure ionic compounds. In addition, to further account for this gradual change from ionic to covalent character we have introduced the last term of [1c] into the expression.

It is important to note that when two atoms join to form a covalent bond, the internuclear separation is equal to the sum of the two individual covalent radii when the electronegativity difference is zero. The difference between the sum of the two individual radii and the internuclear separation increases with increasing electronegativity difference. Hence, with the last term in both [1b] and [1c] the absolute value of the term decreases as the electronegativity difference decreases.

The calculated internuclear distances of mainly ionic solids also show excellent agreement with observed values. Table 9 (and Table 14 in Appendix 2) show that agreement between observed and calculated is best for Group 1 and Group 2 compounds or those with little or no covalent character. Agreement is also good for covalent solids but less good with ionic solids with covalent character and/or with some compounds (with the rutile structure) where four of the six bonds between the metal and non-metal are of one bond length and the other two have a very different bond length. Further more, some inorganic crystals have distorted structures which mean that not all the bonds are equidistant and agreement may be less good.

When the electronegativity difference between the metal atom and non-metal atom approaches the value of one the bond changes from being slightly more ionic to more covalent. This is the major drawback of our methodology because the transition is gradual and may not occur sharply at the value of 1.0, say may be between 0.9 to 1.1, but the transition is defined at the value of 1.0 to allow for the appropriate equation to be used. However, this is preferable to being too subjective in deciding which compound should be considered ionic or covalent when the electronegativity difference falls within a certain range.

Quite some time ago, Slater produced a set of empirical radii which were supposed to be additive³⁷. In his paper, Slater accepted that the empirical values he produced do not hold for covalent, ionic and metallic bonding equally well. The average disagreement between observed and calculated internuclear separation was 0.12 Å. We do not agree that covalent or ionic radii are additive except for a narrow range of purely ionic solids. Values calculated by our proposed equation with our set of radii when compared with the observed showed much better agreement. The average disagreement between observed and calculated values is less than 0.03 Å.

The values shown in Tables 5 and 6 when compared with our earlier work on covalent radii of diatomic gaseous molecules provide good evidence that (a) the covalent radius of an atom is likely to be different between the solid and gaseous state; (b) where the covalent bond is formed between a metal and a non-metal or if the electronegativity difference between two non-metallic atoms forming a covalent bond is one or higher there is ionic character in the bond; (c) where agreement is less good between observed and calculated internuclear distances may be the bond is less covalent/more ionic than expected. For example, it is well known that copper halides show covalent character and the covalent character increases from chloride to iodide. The calculated internuclear separations of CuCl and CuCl₂ are shown in both Table 6 and Table 9. In Table 6 they are considered as covalent (but with ionic character, i.e. more covalent than ionic) and in Table 9 they are treated as ionic (but with covalent character, i.e. more ionic than covalent). The results in the two Tables indicated that the degree of covalency of the two halides are different and that CuCl is more covalent than CuCl₂. Hence, in situations such as the above, bond type can only be determined by checking the agreement of the lattice energy calculated by [4] in comparison with values obtained from the Born-Haber cycle.

We have excluded many compounds in our calculations for a number of reasons, for example in NbI₄ there are three different bond lengths between Nb and I and there is no certainty that the bonds are equivalent or which bond distance is most appropriate to use, MoCl₂ is another example where six atoms of Mo cluster in an octahedron and the bond lengths between Mo and the nearest neighbour Cl ions are again not all the same. We have also discounted compounds where the reported structures are unclear (as in some examples provided in *J. Chem. Phys. Ref. Data*) and hence we cannot work out reliable internuclear separations.

Soft sphere ionic radii are not consistent with the traditional radius ratio rules. The radius ratio rules alone are not reliable. We consider that the rules need to be used with care and they only work in combination with an evaluation of coulombic potential energy and repulsion/compression energy when free ions are “squeezed” into a solid structure. When working out the value of k in a structure such as CaF₂, we have only considered the smaller co-ordination number (co-ordination of F which is four rather than the co-ordination of Ca) because we are interested to find out the maximum amount of compression of an ion in a solid and that the smaller the co-ordination number the bigger the compression.

It is not exactly correct to consider that metals are malleable and ductile because of defects in the solid state. Non-metallic solids such as sulphur and phosphorus as well as ionic/covalent crystals contain solid state defects but are not malleable or ductile. We believe that because not all available midpoint sites are occupied by electrons when a metal is twisted or bent, electrons can move from one site to another within a unit cell,

allowing the shape of the metal to change without any bonds being broken. The detached electrons can move around different midpoint sites inside a unit cell. As discussed above, only some of those sites are occupied at any one time. A “detached” electron is equally attracted by two positive ions in opposite directions and hence move or vibrate within the mid-point site with orbital radius r equal to $[e]$ and where $2\pi r$ is the de Broglie wave length. As there are defects/imperfections in the solid state the metal crystal is divided into “domains” limited by the defects and any electron flow along a particular direction will be limited to flow within the domain. Since all unit cells in a metal are identical and there are vacant sites which facilitate electron movement, a very small potential difference between the ends of a metal strip or wire can generate an electron flow along the wire. It has been shown that when sodium is under very high pressure the resistance of the metal increases drastically and acts more like an insulator³⁸ than a conductor of electricity. One may expect that under pressure with shorter interatomic distances the widths of the valence and conduction bands to increase and lead to more “free electron like behaviour”. However, when the metal is under pressure the resistivity increases significantly. This behaviour cannot be easily explained by the standard “electron sea” model. However, this can be accounted for by the soft-sphere model. When a metal is under pressure, the shape and size of the unit cell changes. This reduces the volume of the site(s) occupied by the detached electron(s) and if the volume is reduced sufficiently it can no longer be occupied. When the shape of the unit cell changes, the distance between some of the “midpoint sites” may increase to such an extent, the detached electrons occupying those sites may no longer be able to move from one site to another. When there are no vacant sites and the space between the ions under pressure become too small to facilitate electron movement or the electrons cannot move between sites in neighbouring unit cells the metal becomes a virtual insulator. We believe that our proposed model of metallic structure resembles reality much closer than the “free electron/electron sea” models. Hence, we derive the ionic radii of metals based on this model. It is of course very probable that the values of k and $[e]$ may be different for different periods or if the elements are in different blocks (s , p or d). However, we believe that any differences in values are small and do not have any significant impact on the proposed concepts or results. Our “soft sphere” radii when compared to any other set of radii produced appear to be always bigger simply because the “soft sphere” covalent/ionic radius of an atom or ion is the “hypothetical radius” of the ion isolated on its own when not bonded to any other atom/ion, once bonded in a solid the radius/size of the ion becomes much smaller and the reduction in size is influenced by the factor k .

The work functions of some metals are much higher than some bond dissociation energies and ionisation energies. For example, the work function of beryllium at 480.5 kJ/mole is greater than the bond dissociation

energy of the of the Cl-Cl bond (242.4 kJ/mole) or the Ca-Ca bond (at only 16.5 kJ/mole). The results in Table 9 show that work functions of metals are simple inverse functions of ionic radii derived from our proposed model of metals. This added confidence to using the ionic radii listed in Table 7 in our calculations.

Electronegativity, size and the ionisation energies (and/or electron affinities) of the atoms can confer greater or lesser ionic character or allow the different atoms to approach each other closer (or not as close).

Lattice energies calculated by the Born-Landé/ Born-Mayer or Kapustinskii equations show good agreement with observed values only for a limited number of binary ionic solids. Factors such as covalent bond character or crystal field stabilization may also have an effect on the lattice energy³⁹. In Table 11, the lattice energies, are calculated from expression [4] using the appropriate k value and derived ionic/covalent radii depending on whether the bond is considered ionic or covalent but with ionic character as described above. As shown in the Table, agreement with values published by the *CRC* is good for mainly ionic lattices and in some cases, even lattices with more covalent than ionic character. It is also fairly obvious that agreement may not be as good when the structures of the lattices are distorted or when it is the rutile structure because the true internuclear distance between the nearest neighbours are different from what is perceived to be. Solid copper (I) halides and some transition metal iodides, sulfides, selenides and tellurides are known to be more covalent than ionic and the calculated results as shown above are good examples to support the bond type criterion.

Lattice energies and work functions calculated by [4] and [5] respectively supply further evidence that the ionic radii calculated from [1d] are reliable and further support the usefulness of the proposed model in this work.

It is of interest to note that for AgCl, the difference in electronegativity between silver and chlorine is one. As such, it is similar to copper (I and II) chloride and is on the border line between ionic and covalent. We have calculated the internuclear distance assuming it is a covalent lattice (with ionic character) and the difference between calculated and observed is only 1.2%. When the soft-sphere covalent radii values of silver and chlorine and a k value of 1.0667 are substituted into equation [4] the calculated result differs from the *CRC* value by 28%. However, when the soft-sphere ionic radii of silver and chlorine and a k value of 1.3 are used in equation [4] to calculate the lattice energy the result is identical to the published *CRC* value.

Although we have obtained our expressions and radii broadly following the principles of physics and quantum mechanics, it is important to note that our assumptions and rationale are mainly based on experimental values of Groups 1 and 2 ions. Our model is best described as based on observed behaviour of ionic/covalent compounds rather than derived from first principles. However, we believe it still adds to the understanding of chemical bonding.

Conclusion

We have shown in this work that for any particular co-ordination number, only Groups 1 and 2 ions behave like fairly hard spheres. Internuclear separations of other ionic/covalent solids calculated from soft sphere radii with the proposed equation produce good agreement with observed values for binary compounds. In addition, lattice energies calculated by equation [4] for mainly solid ionic lattices and ionic compounds with covalent character also agree well with published values in many cases. This suggests that lattice energies calculated by equation [4] are as least as reliable if not even more accurate than the Born-Landé/Born-Mayer type equations. The expressions introduced in this work are based on interpretation of classical physics and principles of quantum mechanics. This work demonstrates that equation [1] works well for calculating internuclear distances of solid covalent, ionic and intermetallic lattices and where there may be uncertainty of bond type, lattice energy calculated by [4] can be used as a guide. The “free electron/electron sea” model, although very elegant and convincing at the time before many sophisticated experiments were made possible to test it and before quantum mechanics was firmly established, is shown to be inadequate. We consider that “band theory” provides a correct “theoretical description” of metallic structure. The good agreement between observed and calculated internuclear separation is very strong evidence that our proposed model of metallic structure and bonding is a realistic “physical description” and complementary to band theory rather than an alternative. Ionic radii derived from our proposed model can be used to calculate internuclear distances and lattice energies with good agreement when compared with observed values. This work also shows that electronegativity is an important factor affecting bond lengths and bond type.

Appendix 1

At the beginning of our work we used different sets of electronegativities, for example the set developed by Allred and Rochow⁴⁰, to calculate internuclear distances of inorganic lattices but find that none of them suit the needs of this work. We first considered that electronegativity values are functions of electron affinities and ionisation energies. We produced many sets of electronegativity values based on generally accepted values of electron affinities²⁴ and ionisation energies but none of them were satisfactory. Finally, we produced a set deduced from the ionisation energies adjusted for pairing and exchange interactions^{41,42}. This set of electronegativity scales as shown in Table 10 improved the agreement between the calculated and the observed internuclear distances. There are some elements such as technetium and polonium, where little observed data on bond lengths or radii or lattice energies are available. In such cases, their electronegativities are estimated by interpolation/extrapolation of electronegativities of neighbouring elements.

Table 13. Electronegativities of the Main Groups and Transition elements.

Atomic Number	Symbol	Electronegativity
1	H	2.00
2	He	N/A
3	Li	1.24
4	Be	2.14
5	B	1.81
6	C	2.30
7	N	2.82
8	O	3.39
9	F	4.00
10	Ne	N/A
11	Na	1.18
12	Mg	1.76
13	Al	1.31
14	Si	1.66
15	P	2.05
16	S	2.49
17	Cl	2.95
18	Ar	N/A
19	K	1.00
20	Ca	1.40
21	Sc	1.51
22	Ti	1.57
23	V	1.62

24	Cr	1.65
25	Mn	1.71
26	Fe	1.77
27	Co	1.84
28	Ni	1.92
29	Cu	2.02
30	Zn	2.16
31	Ga	1.31
32	Ge	1.62
33	As	1.95
34	Se	2.30
35	Br	2.67
36	Kr	N/A
37	Rb	0.96
38	Sr	1.31
39	Y	1.54
40	Zr	1.57
41	Nb	1.61
42	Mo	1.66
43	Tc	1.71
44	Ru	1.76
45	Rh	1.84
46	Pd	1.91
47	Ag	1.92
48	Cd	2.06
49	In	1.26
50	Sn	1.49
51	Sb	1.73
52	Te	2.01
53	I	2.32

54	Xe	N/A
55	Cs	0.89
56	Ba	1.20
57	La	1.28
59	Pr	1.25
60	Nd	1.27
61	Pm	1.28
62	Sm	1.30
63	Eu	1.30
64	Gd	1.41
65	Tb	1.35
66	Dy	1.36
67	Ho	1.38
68	Er	1.40
69	Tm	1.42
70	Yb	1.44
71	Lu	1.25
72	Hf	1.57
73	Ta	1.73
74	W	1.81
75	Re	1.80
76	Os	1.94
77	Ir	2.06
78	Pt	2.06
79	Au	2.12
80	Hg	2.40
81	Tl	1.34
82	Pb	1.51
83	Bi	1.68
84	Po	1.90

Appendix 2

In earlier work we have calculated the internuclear separations of many ionic crystals involving Group 1 and Group 2 metals. Some are reproduced below to illustrate the reliability/accuracy of our equation for calculating internuclear distances of purely ionic solids. The ionic radius of NH_4^+ was previously derived to be 2.107 Å. From the comparisons in the table below it is evident that for mainly ionic compounds our proposed equation produces very accurate results and the ionic radii derived from our soft sphere model are reliable.

Table 14. Comparison of observed and calculated internuclear distances of Groups 1 and 2 ionic lattices.

Compound	Structure	Internuclear distance (in Angstrom)		Equation	Abs% difference
		Observed	Calculated		
LiF	NaCl	2.013	2.021	1a	0.4
LiCl	NaCl	2.570	2.572	1a	0.1
LiBr	NaCl	2.751	2.744	1a	0.2
LiI	NaCl	3.006	3.015	1a	0.3
NaF	NaCl	2.314	2.307	1a	0.3
NaCl	NaCl	2.820	2.819	1a	0.0
NaBr	NaCl	2.987	2.982	1a	0.2
NaI	NaCl	3.238	3.239	1a	0.1
KF	NaCl	2.672	2.679	1a	0.3
KCl	NaCl	3.146	3.149	1a	0.1
KBr	NaCl	3.300	3.300	1a	0.0
KI	NaCl	3.533	3.542	1a	0.3
RbF	NaCl	2.827	2.835	1a	0.3
RbCl	NaCl	3.295	3.290	1a	0.1
RbBr	NaCl	3.434	3.437	1a	0.1
RbI	NaCl	3.670	3.672	1a	0.1

CsF	NaCl	3.001	3.010	1a	0.3
CsCl	CsCl	3.569	3.563	1a	0.2
CsBr	CsCl	3.720	3.711	1a	0.2
CsI	CsCl	3.955	3.947	1a	0.2
NH ₄ Cl	CsCl	3.357	3.358	1a	0.0
NH ₄ Br	CsCl	3.515	3.510	1a	0.1
NH ₄ I	NaCl	3.515	3.510	1a	0.1
MgO	NaCl	2.107	2.115	1a	0.4
MgS	NaCl	2.602	2.597	1a	0.2
MgSe	NaCl	2.731	2.722	1a	0.3
CaO	NaCl	2.406	2.405	1a	0.0
CaS	NaCl	2.851	2.856	1a	0.2
CaSe	NaCl	2.962	2.974	1a	0.4
CaTe	NaCl	3.186	3.194	1a	0.2
SrO	NaCl	2.572	2.571	1a	0.1
SrS	NaCl	3.012	3.006	1a	0.2
SrSe	NaCl	3.123	3.121	1a	0.1
SrTe	NaCl	3.333	3.335	1a	0.1
BaO	NaCl	2.762	2.758	1a	0.2
BaS	NaCl	3.184	3.176	1a	0.2
BaSe	NaCl	3.295	3.288	1a	0.2
BaTe	NaCl	3.500	3.495	1a	0.1
CaF ₂	CaF ₂	2.365	2.356	1a	0.4
SrF ₂	CaF ₂	2.509	2.513	1a	0.2
BaF ₂	CaF ₂	2.683	2.692	1a	0.3
NaH	NaCl	2.441	2.436	1a	0.2
KH	NaCl	2.855	2.847	1a	0.2
RbH	NaCl	3.025	3.016	1a	0.3
CsH	NaCl	3.195	3.203	1c	0.3

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