

from the same excited states of their respective molecular ions.

The $C_{10}H_6^+$ ions at onset do not arise from the $C_{10}H_7^+$ ions; however, the $C_{10}H_6^+$ ions from both compounds do have the same heat of formation. The $C_{10}H_7^+$ ions also have the same heat of formation independent of their origin. Therefore it is probable that the excited molecular ion from which these ions are formed is common to both azulene and naphthalene. This possibility is shown schematically in Fig. 1. Isomerization to a structure similar to a cyclopentadienyl radical ion with two hydrogens missing, i.e., removal of the ring-bridging carbon-carbon bond, appears to be a possible rearrangement which would result in a structure accessible to the molecular ions of both compounds. This bond is predominantly of a σ nature and therefore its cleavage requires ionization to one or more excited electronic states with the resultant ion having sufficient additional vibrational energy to break the ring-bridging carbon-carbon bond.

SUMMARY AND CONCLUSION

The ionization-dissociation processes in azulene and naphthalene indicate that these isomers behave as do other sets of isomers such as those studied by Meyerson and co-workers⁹ which break down under electron impact largely via common paths involving common ionic intermediates. The occurrence of a set of common ionic intermediates for azulene and naphthalene is qualitatively demonstrated by the similarity of their mass spectra and by the metastable transitions. Comparison of the difference of the appearance potentials for the same secondary ions in both compounds with the difference in the heats of formation for these molecules in the vapor state indicated that for each of several fragment ions appearing in the spectra of naphthalene and azulene, the lowest ionized state through which the two isomers pass has energies equal within the limits of the experimental uncertainty. These common ionic intermediates appear to be states of the $C_{10}H_8^+$ ions.

Atomic Radii in Crystals

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A set of empirical atomic radii has been set up, such that the sum of the radii of two atoms forming a bond in a crystal or molecule gives an approximate value of the internuclear distance. These radii give fair agreement with experiment in over 1200 cases of bonds in all types of crystals and molecules, with an average deviation of about 0.12 Å. The radii are similar to a set suggested by W. L. Bragg in 1920, but refined by consideration of many more crystals. They hold for covalent, metallic, and ionic binding equally well. These radii agree remarkably well with calculated radii of maximum radial charge density in the outermost shells of the atoms, as taken from previously unpublished calculations of D. Liberman, J. T. Waber, and D. T. Cromer, of the Los Alamos Laboratory, by relativistic self-consistent field calculation, using the exchange correction suggested in 1951 by the present author. There is discussion of the probable reason for this agreement, and discussion of the relation of these radii to the ionic radii of Pauling, Zachariasen, and others, and the tetrahedral and metallic radii of Pauling.

1. EMPIRICAL ATOMIC AND IONIC RADII

THE derivation of empirical atomic and ionic radii has a history stretching back at least to 1920.¹ In that year, Bragg pointed out that atomic distances in crystals could be approximately regarded as sums of radii. He derived a set of radii, whose sums reproduced the observed interatomic spacings in several hundred crystals with an average deviation of about 0.06 Å. The distances were not only between ions of opposite charge in ionic crystals, but also between metallic

atoms in metallic crystals. The purpose of the present note is to revive and extend this idea of Bragg's. In Table I we give a proposed set of atomic radii, similar to Bragg's. In Appendix 1 of the author's forthcoming work, Ref. 2, we compare the sums of these atomic radii with observed interatomic distances in over 1200 cases of bonds in all types of crystals and molecules. Our average deviation is about 0.12 Å, larger than Bragg's, but this is a result of including many types of compounds in which perfect additivity cannot be

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¹ W. L. Bragg, *Phil. Mag.* **40**, 169 (1920). For a general account of different types of atomic and ionic radii, see L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1960), 3rd ed. See particularly Chaps. 7, 11, 13.

² J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill Book Company, Inc., New York, to be published), Vol. 2. The same information is contained in the contribution of the author entitled Empirical Atomic Radii from Crystal Structures, in Quarterly Progress Report No. 46, Solid-State and Molecular Theory Group, MIT, October 1962, p. 6 (unpublished).

TABLE III. Ionic radii of Wasastjerne, Goldschmidt, Pauling, and Zachariasen, compared with atomic radii of Table I. Numbers in parentheses are atomic minus ionic radii.

	Atomic	Wasastjerne	Goldschmidt	Pauling	Zachariasen
Li ⁺	1.45		0.78(0.67)	0.60(0.85)	0.68(0.77)
Na ⁺	1.80	1.01(0.79)	0.98(0.82)	0.95(0.85)	0.98(0.82)
K ⁺	2.20	1.30(0.90)	1.33(0.87)	1.33(0.87)	1.33(0.87)
Rb ⁺	2.35	1.50(0.85)	1.49(0.86)	1.48(0.87)	1.48(0.87)
Cs ⁺	2.60	1.75(0.85)	1.65(0.95)	1.69(0.91)	1.67(0.93)
Be ²⁺	1.05		0.34(0.71)	0.31(0.74)	0.39(0.66)
Mg ²⁺	1.50	0.75(0.75)	0.78(0.72)	0.65(0.85)	0.71(0.79)
Ca ²⁺	1.80	1.02(0.78)	1.06(0.74)	0.99(0.81)	0.98(0.82)
Sr ²⁺	2.00	1.20(0.80)	1.27(0.73)	1.13(0.87)	1.15(0.85)
Ba ²⁺	2.15	1.40(0.75)	1.43(0.72)	1.35(0.80)	1.31(0.84)
F ⁻	0.50	1.33(-0.83)	1.33(-0.83)	1.36(-0.86)	1.33(-0.83)
Cl ⁻	1.00	1.72(-0.72)	1.81(-0.81)	1.81(-0.81)	1.81(-0.81)
Br ⁻	1.15	1.92(-0.77)	1.96(-0.81)	1.95(-0.80)	1.96(-0.81)
I ⁻	1.40	2.19(-0.79)	2.20(-0.80)	2.16(-0.76)	2.19(-0.79)
O ²⁻	0.60	1.32(-0.72)	1.32(-0.72)	1.40(-0.80)	1.40(-0.80)
S ²⁻	1.00	1.69(-0.69)	1.74(-0.74)	1.84(-0.84)	1.85(-0.85)
Se ²⁻	1.15	1.77(-0.62)	1.91(-0.76)	1.98(-0.83)	1.96(-0.81)
Te ²⁻	1.40	1.91(-0.51)	2.11(-0.71)	2.21(-0.81)	2.18(-0.78)

electropositive elements are about 0.85 Å smaller than the atomic radii, and those for the electronegative elements are about 0.85 Å larger than the atomic radii. This fact is illustrated in Table III, where we compare our atomic radii of Table I with the ionic radii just described, and give the differences between them. While the differences are not exactly constant, they are close enough to ± 0.85 Å so that we can understand how the sum of ionic radii for an electropositive and electronegative element is able to lead to almost exactly the same result as the sum of the atomic radii of the same elements. In other words, we understand how the agreement between the sum of atomic radii and the observed distances, from Ref. 2, for the ionic crystals, can have approximately the same accuracy as for the sum of ionic radii.

In the development of the empirical radii, an entirely different approach to a set of radii arose, not from the study of ionic crystals, but from sets of crystals such as GaAs, ZnSe, and CuBr, having the zinc-blende or wurtzite structures, with tetrahedral coordination. It was obvious very early that if we set up atomic radii by using half the interatomic distances in the elements and added them for the compounds, the result would give a good agreement with experiment. In this way, by modifying the radii so derived to fit a maximum number of compounds, Huggins and Pauling⁶ derived a set of so-called tetrahedral covalent radii, which would give by their sums the interatomic distances in a large number of tetrahedrally coordinated compounds. These principles are similar to those which we have used in setting up the radii of Table I, and as a matter of fact almost all of the tetrahedral covalent radii of Pauling and Huggins agree within a few hundredths of an angstrom with the radii given in Table I. These

⁶ M. L. Huggins, Ref. 3; L. Pauling and M. L. Huggins, *Z. Krist.* **87**, 205 (1934).

writers have also extended similar radii to other coordinations, and Pauling in his book (Ref. 1) lists metallic radii for many metals, which give good sums when used for intermetallic compounds. These radii have close resemblance to our values of Table I.

We may summarize this discussion by pointing out the relation between our atomic radii of Table I which were set up simply to get as good agreement as possible with the empirical material, and these various sets of radii. For the positive and negative ions, our radii differ from the ionic radii by approximately ± 0.85 Å, the sign being that of the ion, so that the sums of either atomic or ionic radii for an electropositive and an electronegative element are approximately the same. For compounds with tetrahedral coordination, we essentially duplicate Pauling's tetrahedral covalent radii. Our radii differ from the existing sets, however, aside from Bragg's radii, in that we can use the single set of radii with tolerable accuracy for the elements, intermetallic compounds, and other non-ionic compounds, as well as for ionic compounds. It is this convenience of having a single set of radii for all purposes, eliminating the necessity of making a preliminary judgment as to whether a crystal is ionic or not, in order to decide which set of radii to use, which is the main advantage of the present set of radii.

Since we are not including corrections for coordination number and other effects considered by Pauling and Zachariasen, we are subject to larger errors in some cases, and cannot hope to reproduce all the distances as accurately as they do. For this reason, we have not tried to give radii more accurately than 0.05 Å. It is worth while to point out, however, that the worst errors in our agreement between experimental distance and the sum of radii in Ref. 2 come for compounds involving a few elements, among which are Ag and Tl, which seem to be peculiar in their behavior as far as

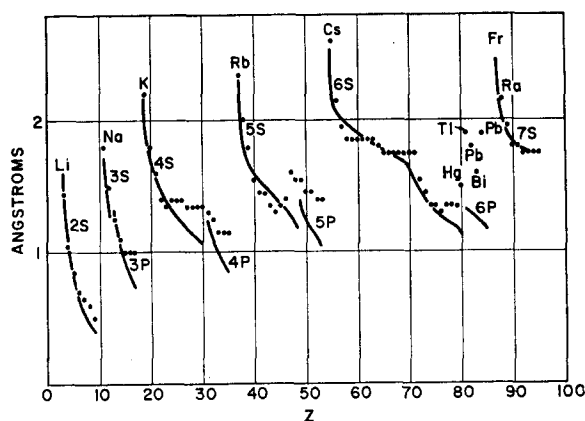


FIG. 1. Empirical atomic radii (round dots) and calculated radii of maximum radial charge density of largest shell in atoms, by self-consistent-field method of Liberman, Waber, and Cromer (full lines), as function of atomic number. Quantum numbers of outermost shell are given. Certain small departures from the smooth curves of Liberman, Waber, and Cromer are not shown in the figure; they arise on account of the different multiplets and configurations forming the ground states of the various atoms, leading to small apparently erratic fluctuations of radii from atom to atom. Calculated radii of Liberman, Waber, and Cromer are given in Ref. 2, and will be presented in a paper shortly to be submitted for publication by the authors just named.

interatomic distances are concerned, and which Pauling and Zachariasen are not able to handle significantly better than we are.

2. PHYSICAL SIGNIFICANCE OF ATOMIC AND IONIC RADII

In the preceding section we have discussed the various sets of atomic and ionic radii from the purely empirical point of view of their success in reproducing the observed interatomic distances. Let us now ask the broader question as to what these radii mean, why the atomic and ionic radii differ as they do, and what connection they have with the wavefunctions of the atoms and ions, which in the last analysis must determine the radii.

As a first step, we must presumably expect a correlation between the atomic radius, and the radius of maximum charge density in the outermost electron shell of the atom. Huggins³ investigated such a correlation between his atomic radii, which approximate ours, and the information regarding dimensions of atomic wavefunctions available when he wrote in 1926, which naturally was very inadequate, and found evidence of correlation. To get up-to-date information regarding such correlation, we give in Fig. 1 a comparison of the atomic radii of Table I, and the radii of the maximum radial charge density in the outermost shells of the atoms, the latter coming from unpublished calculations of Liberman, Waber, and Cromer⁷ of the Los Alamos Scientific Laboratory, who have computed self-

consistent wavefunctions for all the atoms, with relativistic corrections according to the Dirac equations, using the approximate treatment of exchange suggested by the present writer.⁸ The writer is greatly indebted to Waber for the use of this unpublished information, which for the first time has made it possible to study the dimensions of the heavier elements. Similar very recent calculations of Herman and Skillman⁹ also make such study possible, and agree well with those of Liberman *et al.*

From Fig. 1, we see that there is in fact a very good correlation, and in many cases practically an equality, between the atomic radii of Table I, which were found purely from study of the empirical interatomic distances, before the results of the calculations of Liberman, Waber, and Cromer were available, and the calculated radius of maximum radial charge density in the outermost shell of the atom. This correlation is particularly striking through the series of elements from cesium to platinum, in which the 6s electron is the outer electron. The only set of elements in which there is particularly bad correlation is the group from mercury to polonium, in which the 6p orbital is coming in as the outermost orbital. It is perhaps significant that some of these elements are among those to which it is very difficult on the basis of empirical evidence to assign a unique radius from the crystal structure.

Next we may consider the ionic radii from Table III. Here we naturally compare these with the radii of the outermost shell of the ion, lacking the outer electrons (for a positive ion). When we make this comparison,

TABLE IV. Pauling's ionic radii, from Table III, compared with radius of maximum radial charge density in outermost shell of electrons in ions, and ratio of ionic radius to radius of shell. Radii in angstroms.

Ion	Ionic radius	Radius of shell	Ratio
Li ⁺	0.60	0.186 (1s)	3.2
Na ⁺	0.95	0.316 (2s)	3.0
K ⁺	1.33	0.59 (3p)	2.2
Rb ⁺	1.48	0.74 (4p)	2.0
Cs ⁺	1.90	0.92 (5p)	2.1
Be ²⁺	0.31	0.138 (1s)	2.2
Mg ²⁺	0.65	0.285 (2s)	2.3
Ca ²⁺	0.99	0.54 (3p)	1.8
Sr ²⁺	1.13	0.69 (4p)	1.6
Ba ²⁺	1.35	0.87 (5p)	1.6
F ⁻	1.36	0.40 (2s)	3.4
Cl ⁻	1.81	0.74 (3p)	2.4
Br ⁻	1.95	0.87 (4p)	2.3
I ⁻	2.16	1.06 (5p)	2.0
O ²⁻	1.40	0.46 (2s)	3.0
S ²⁻	1.84	0.83 (3p)	2.2
Se ²⁻	1.98	0.92 (4p)	2.2
Te ²⁻	2.21	1.12 (5p)	2.0

⁸ J. C. Slater, *Phys. Rev.* **81**, 385 (1951).

⁹ F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall Inc., Englewood Cliffs, New Jersey, 1963).

⁷ D. Liberman, J. T. Waber, and D. T. Cromer, 1964 (unpublished).

we find that the ionic radii are of the order of magnitude of twice to three times the radii of the outermost shell of the ion. This comparison is given in Table IV. The fact that the ratio of ionic radius to the radius of the electronic shell is approximately the same for such a sequence as S^{2-} , Cl^{-} , K^{+} , and Ca^{2+} is to be expected, since Pauling derived the radii of these ions from an argument based on screening constants, which amounts to making their radii proportional to the radii of the shells.

Now we must correlate the results of these two tables, and find the interpretation of the difference between atomic and ionic radii. Naturally, the atomic radii are used in cases where two atoms are held to each other by a covalent bond, or a metallic bond, which is essentially of the same nature. Such a bond depends on the overlapping of charge in the outer shells of the two atoms being bonded together. We expect this overlapping to be a maximum when the maximum charge densities of the outer shells of the two atoms coincide; that is, when the atoms approach to such a distance that the atomic radii, which as we see from Fig. 1 are approximately the distances out to the radius of maximum radial charge density, add to give an interatomic distance. This is the general significance of the atomic radii.

The conventional ionic picture of an ionic compound is very different from this. We start, in such a case as KCl, by removing the outer electron from the electropositive element, in this case by removing the 4s electron from the potassium atom, and using it to fill in the gap in the outer shell of the electronegative element, in this case the chlorine. The 4s electron in potassium, as we see from Fig. 1, has a radius of maximum radial charge density of 2.16 Å, whereas the outer shell of the positive ion, which is all that is left when the 4s electron is removed, has a radius of only 0.59 Å, as we see from Table IV. In other words, the potassium positive ion is a very much smaller structure than the neutral potassium atom. On the other hand, the addition of the single electron to the 3p shell of chlorine, to complete this shell and convert this to the Cl^{-} ion, makes only a small increase in the radius of this shell, of the order of 0.01 Å.

Once we have made these ions, we then allow them to be bonded together in a crystal by the Coulomb attractions between the oppositely charged ions. It is this attraction that was discussed by Born and others in the early development of the theory of ionic crystals. The ions, consisting of closed shells, have a repulsion for each other at small distances, just like inert gas atoms, in this case argon atoms. The equilibrium in the crystal is a result of the Coulomb attraction working against this repulsion.

With the amount of attraction produced by the Coulomb forces, the inert gas shells are quite far apart when the repulsion is great enough to balance the

attraction. We see this from Table IV, where in the sequence we are considering, the interatomic distance at equilibrium is something more than twice the sum of the radii of maximum radial charge density in the two ions. In other words, it is necessary only for the tails of the wavefunctions of the outer electrons to overlap, in order to produce enough repulsion of the inert gas shells to balance the Coulomb attractions. This is very much less overlapping than would be found in the case of a covalent bond, where, as we have seen previously, the radii of maximum radial charge density in the two atoms approximately coincide. The difference between the two cases, of course, is that in the case of the covalent bond, there are vacancies in the outer shells of the bonding atoms, and the possibility of electrons shared between the two atoms, while with the inert gas shells the outer shells are filled, and the exclusion principle prevents their overlapping.

We can now understand the difference between the two sorts of radii, the atomic and ionic, in such cases as the sequence of atoms from sulfur to calcium. For the electropositive elements, the atomic radius is approximately the actual radius of the valence electron shell. The ionic radius is something like twice the radius of the next inner shell, the outermost one in the inner core of the ion. At the same time it is about 0.85 Å smaller than the radius of the valence electron wavefunction. For the electronegative element, the added electron or electrons in the outer shell, required to produce the negative ion, cause a slight increase in the size of the shell, but this is a minor effect. The main reason why the ionic radius of the electronegative element is about 0.85 Å larger than the atomic radius is the factor of approximately 2 found in Table IV: the ionic radius extends out into the tail of the wavefunction of the outer electrons, whereas the atomic radius extends out only to the maximum charge density in the shell. We see, in other words, that the atomic and ionic radii measure quite different things, but there is no conflict between them.

There remains the question as to the physical meaning of using the atomic radii in discussing ionic crystals, which as we see from Ref. 2 is possible. Here we gain a rather new insight into the nature of ionic bonds, if we consider the case of such a crystal as KCl from an atomic point of view. Instead of starting with ions, as we did in an earlier paragraph, we can start with the separated neutral atoms at infinite separation, which, of course, has a much lower energy than the separated ions. We bring them together, and the energy does not begin to decrease until the charge distributions begin to overlap. We start to build up overlap charge between the atoms, as in any case of covalent binding. This charge appears where the outer wavefunctions of both atoms are large; that is, in the region between the atoms, but near the Cl.

Each K atom, with its one outer electron, will form

overlap charge near each of its six neighboring Cl's. Since the total charge arising from the K valence electron cannot be greater than one unit, the overlap can contribute a maximum of one-sixth of an electron to each of the six neighboring Cl's. Each of the Cl's can acquire up to one-sixth of an electron from each of its six neighbors, however, so that the net result is that enough charge can build up on each Cl, arising from the 4s electrons of its neighboring K's, to give the Cl one extra negative charge, or produce a Cl⁻ ion. According to this covalent view of the process of binding, no charge need actually move from the K to the Cl atom to produce the ions: the radius of the outer shell of the K atom is such that the charge will automatically have moved over to the Cl, merely by the fact that the atoms have moved to the observed equilibrium distance.

The true wavefunction, of course, can be built up as a linear combination of many different types of functions, including the ionic and covalent types we have just indicated. By the process of configuration interaction, we combine initial wavefunctions of different types to produce the final wavefunction. We may expect that in the particular case of KCl the final result will be close to the ionic case. This is shown by the calculation of Löwdin¹⁰ on the binding energy of the KCl crystal, in which he has started with an ionic model of the crystal, has calculated its energy by proper wave-mechanical methods, and gets very acceptable values for the binding energy.

Nevertheless, we see by this example that even in a typically ionic compound we can make a very plausible interpretation of a covalent sort, indicating that such components enter into the description of the wavefunction by means of configuration interaction. There are many other cases in which an ionic picture could be given, but in which presumably the covalent parts of the wavefunctions are much more important. For instance, we may consider the sequence CuBr, ZnSe, GaAs, and the element Ge. We could interpret these in an ionic way, as made from Cu⁺ and Br⁻, Zn²⁺ and Se²⁻, Ga³⁺ and As³⁻, and presumably this interpretation is not unreasonable for CuBr, which is not entirely unlike an alkali halide. With the others, however, all experimental indications tell us that there is very little ionic character. By the time we get to GaAs,

¹⁰ P.-O. Löwdin, *Arkiv Mat. Astron. Fysik* **A35**, Nos. 9, 30 (1947); *Advan. Phys.* **5**, 1 (1956).

its properties are very similar to those of germanium. Both are semiconductors, with almost identical energy band structures, and a bonding mechanism like diamond, definitely covalent. In other words, as we go along such a series, the covalent part of the wavefunction gets more and more important.

The significance of the fact that we can get the interatomic distances by adding atomic radii, as in Ref. 2, seems then to be that even in the typical ionic compounds, the covalent contribution to the wavefunction is large enough to be determining in fixing the interatomic distances. This does not mean at all that ionic elements do not enter into the wavefunction, but they are a comparatively small part of the whole. Atoms, in other words, tend to be much more nearly neutral in a crystal than a straight ionic interpretation would indicate.

Our emphasis in the preceding discussion has been on atoms, or ions, which were forming bonds with each other. A very important feature of the structure of crystals, however, is the interaction between ions which are presumably repelling each other. The most striking examples of this are seen in crystals containing oxygen. In almost no cases are the oxygens bonded together, and yet their interactions are a feature of fundamental importance in the crystal structure.

In many such cases, the distance between oxygen atoms is found to be approximately 2.80 Å, twice the ionic radius of 1.40 Å, as compared to the distance 1.20 Å, twice the atomic radius of 0.60 Å, if they were forming a bond. In all such cases, where we are studying the packing of negative ions, we must use the ionic radii. They come in, for instance, in the familiar problem of establishing how many negative ions can be packed around a positive ion of a given size, subject to the fact that two negative ions will not approach to a smaller distance than approximately the sum of their ionic radii. It is for atoms definitely held together by bonds, either covalent or ionic, that the atomic radii are appropriate, and all the bonds listed in Ref. 2 are of this sort. This suggests an interesting type of application of the atomic radii. If, in studying the structure of a given crystal, two atoms are found to approach to a distance approximately equal to the sum of their atomic radii, we may consider that there is a definite bonding action between them. If their distance is much greater than this, no bond is formed.