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Derivation of van der Waals Radii from Known Crystal Structures

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Methods which can be used for determining the van der Waals diameter constant in interatomic interaction potentials by using known structures of molecular crystals are discussed. It is shown that the usual lattice energy minimization procedure is invalid due to the presence of molecular strain energy. A method based on the equilibration of nearest-neighbour interactions and the internal pressure is developed. Calculations using all available methods have been made for the three crystalline phases of selenium and results are given.

Introduction

Accurate prior knowledge of the interactions between non-bonded atoms is essential if calculations relating to such matters as the magnitude of packing forces in molecular crystals and the relationship between conformation and energy in sterically hindered molecules are to be meaningful. A further important use for non-bonded interactions has been found (Coulson, 1960) in the field of molecular physics where it has been realized that their influence on the length of chemical bonds may be highly significant. Another consequence of the availability of satisfactory interaction potentials would be that trial structure determinations from packing considerations, such as described by Milledge (1962), could be put on a more quantitative (energy) basis for molecular crystals containing molecules of known geometry.

The purpose of this paper is to investigate various methods which might be used for determining the van der Waals diameter constant in an assumed mathematical form of interaction potential from a knowledge of the geometrical arrangement of atoms in a molecular crystal. We will show that lattice energy calculations cannot be handled exactly as the molecular strain energy contribution cannot be calculated. A method based on internal pressure is developed to circumvent the difficulty.

Methods which have been used for estimating interaction potentials

Two basically different approaches have been used by other workers in attempting to derive interatomic interaction potentials for non-bonded atoms. The first approach involves the deduction from first principles of the attractive term in the interaction expression. Examples of this are due to Slater & Kirkwood (1931), Kirkwood (1932) and London (1930). These have been applied to hexachloroethane by Sasada & Atoji (1953) and result in attractive energies with a spread of some 12% about the mean value. All these interactions involve the reciprocal sixth power of the interatomic distance. The repulsive part of the interaction has been derived by Born & Mayer (1932) using a quantum-mechanical treatment. This, however, was not used by Sasada & Atoji (1953) due to the unavailability of certain constants needed in the expression.

Theory thus indicates that a reasonable general expression for non-bonded interactions would have an exponential repulsive part and an inverse sixth power attractive part (considering only dipole–dipole interactions). This is the basis for the existence of various heuristic expressions for the interatomic interaction: the 6-exp deriving directly from theory and the 6–12 interaction of Lennard-Jones (1937) differing from this in the repulsive part alone. Of these two, the latter has the advantage of containing only two constants and as its ability to describe non-bonded interactions is

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remarkably good, bearing in mind its simplicity, it will be used in the present work.

Existing methods for the derivation of optimum constants in interactions of assumed form from solid-state data

Corner (1939) has used the 6-*n* intermolecular potential of Lennard-Jones (1937) and an energy minimization method to optimize the two constants in each of the interactions for neon and argon in terms of the value of the exponential *n*. Only after zero-point motion is taken into account do the values of the constants, derived from the spectrum of interatomic distances and the vaporization energies of the crystals, agree with those derived from gas-phase properties. The optimum values of *n* range from 10·5 to 12·6 with a mean of 11·5 and taking *n* as 12 is thus a good approximation.

Strel'tsova & Struchkov (1961) have used the 6-exp interaction to determine the values of r_0, the separation at equilibrium, for Cl–Cl, Cl–C and C–C approaches. Their calculations are based on the hexachlorobenzene structure which they determined themselves. They assume values for the three other constants in each interaction and then establish the value of r_0 such that the calculated energy for all interactions of one type is a minimum. On this basis three values of r_0, for the three types of interaction under consideration, are obtained. These are probably reasonably accurate but are undoubtedly liable to error resulting from (1) independent minimization of the energies due to the three types of interaction instead of minimizing their sum alone, and (2) neglect of the molecular strain energy.

Derivation of optimum constants from energy considerations

The manner in which the energy of an array of molecules can be used to establish the optimum values of the constants in an assumed expression for the form of the interaction potential can best be seen from considering the crystallization process. Consider thus a large number of perfectly rigid (*i.e.* non-deformable) molecules, possessing the gas-phase conformation and containing only one electronic form of one element, crystallizing at 0°K into a zero-point-motion-free crystal in which the interactions are additive and exclusively according to a specified form of interaction potential. The arrangement adopted will be such that the potential energy of the system is a minimum. At this stage the external force on each atom in a centrally situated molecule will not, in general, be zero owing to molecular shape irregularities and the fact that the whole crystal is in a state of compression resulting from the operation of long-range attractive interactions within the crystal.

If the temporarily assumed rigidity of the molecule is now relaxed, it will deform in concord with the forces acting upon its constituent atoms and a simultaneous diminution in the lattice energy and (smaller) increase in the molecular strain energy occurs. Equilibrium is reached when the sum of these two energies is a minimum.

We thus proceed to attempt the application of this principle to the determination of one constant in the interaction potential expression using a known crystal structure.

When the asymmetric unit is one molecule or less and this is composed of one element, the lattice energy per molecule can readily be calculated for a static structure if the intermolecular interactions are satisfactorily described by the sum of atom-to-atom interactions. The potential energy (E) of two non-bonded atoms is, according to the 6–12 interaction, given by

$$E=E_m(R^2/r^{12}-2R/r^6) \qquad (1)$$

where $R=r_0^6$ and r_0 is the equilibrium separation.

The sum of the interactions between the atoms of the parent molecule and those in the rest of the crystal follows the calculation of the sums of the reciprocal sixth and twelfth powers of the parent-atom to environmental-atom distances.

$$\text{Let} \sum_{i=1}^{a}\sum_{j=1}^{e} r_{ij}^{-12}=A \quad \text{and} \quad \sum_{i=1}^{a}\sum_{j=1}^{e} r_{ij}^{-6}=B$$

where a and e are respectively the numbers of atoms in the parent molecule and the significant (10 Å) environment.

The lattice energy is thus given by

$$E_L=E_m\,(AR^2-2BR)\,. \qquad (2)$$

The force (F) between two atoms which are a distance r apart is given by $-\mathrm{d}E/\mathrm{d}r$, *i.e.* from (1) by

$$F=12E_m(R^2/r^{13}-R/r^7)\,. \qquad (3)$$

Using this equation we can calculate the sum of the resolved forces in a specific direction on an atom in the parent molecule by carrying out a summation over all environmental atoms. For the force on atom i in the x direction for example we get

$$F_{ix}=12E_m(C_{ix}R^2-D_{ix}R) \qquad (4)$$

where

$$C_{ix}=\sum_{j=1}^{e}(r_{ij}^{-13})\,(x_j-x_i)/r_{ij}$$

and

$$D_{ix}=\sum_{j=1}^{e}(r_{ij}^{-7})\,(x_j-x_i)/r_{ij}\,.$$

Analogous expressions exist for the sum of the resolved forces acting on atom i in the y and z directions. When the squares of these are added to the square of equation (4) above, an equation for the square of the resultant force acting on atom i is obtained. This equation will have the form

$$(F_i)^2=144\,E_m^2(G_iR^4-2H_iR^3+I_iR^2)\,. \qquad (5)$$

We now make the reasonable assumption that the mechanism whereby the crystal forces displace an atom (i) from its gas-phase position in the molecule is an elastic process. The strain energy (E_s) involved in the displacement of an atom i through a distance d_i from its position in the free molecule is given by

$$(E_s)_i = \tfrac{1}{2}k_i d_i^2 \qquad (6)$$

where k_i is the force constant which is directionally appropriate to the displacement d_i.
As

$$F_i = k_i d_i \qquad (7)$$

we can calculate the molecular strain energy (E_{ms}), using (7) in (6).

$$\sum_{i=1}^{a} (E_s)_i = E_{ms} = \sum_{i=1}^{a} (F_i)^2/2k_i \qquad (8)$$

where $(F_i)^2$ is defined from (5) and (4).

If the k_i are known, the molecular strain energy can be calculated. As this is usually not so, we introduce a further simplifying assumption and put $k_i = k$, *i.e.* we assume all k_i to be equal. The molecular strain energy thus becomes

$$E_{ms} = \sum_{i=1}^{a} (F_i)^2/2k\,. \qquad (9)$$

The constant R (*i.e.* r_0^6) should now be chosen to minimize the sum of the lattice and molecular strain energies. It is obvious that this cannot be done unless both E_m and k are known. As neither are known in general, the method cannot be applied to molecular crystals. If, however, the values of r_0 which minimize these two energy terms independently happen to be equal to close approximation, the mean value of r_0 is in effect consistent with a minimum in the sum of the lattice and molecular strain energies. If, as is found in practice, the values of r_0 from the lattice and molecular strain energies differ, the former is nearer the correct value as substitution of reasonable values into (2) and (9) shows that this represents at least 90% of the total energy.

Minimization of the lattice energy E, as given by (2) with respect to R, gives

$$R_l = r_0^6 = B/A = \sum\sum r_{ij}^{-6} / \sum\sum r_{ij}^{-12}. \qquad (10)$$

Minimization of the molecular strain energy E_{ms} from (9) and (5) with respect to R gives

$$R_{ms} = r_{0ms}^6 = \{3\sum_{i=1}^{a} H_i + [9(\sum_{i=1}^{a} H_i)^2 - 8\sum_{i=1}^{a} G_i \sum_{i=1}^{a} I_i]^{1/2}\}/4\sum_{i=1}^{a} G_i\,. \qquad (11)$$

Derivation of constants from mechanical considerations

The preceding work has indicated that energy considerations cannot be used to compute optimum values of the interaction constants without prior knowledge of inaccessible force constants. We thus turn our attention to the derivation of constants from considerations concerning various properties of the forces operating in a crystal in equilibrium.

Due to the relatively homogeneous distribution of atoms in crystals, the usual mechanical laws do not lead to a satisfactory method for determining optimum constants. For example, the resultant force on a molecule is inevitably calculated to be zero when the molecule is centred on a crystallographic centre of symmetry. The magnitude of the resultant force is thus independent of the interaction used in this case. When the molecule is not at a centre of symmetry, the resultant force is small and the vectorial sums involved consist mainly of accumulated errors and are thus unsuited to use in constant-determining procedures. Analogous argument is valid for the moments of these forces but in this case zero sums are induced by *mmm* symmetry.

Mechanical equilibrium involves more than simply the equality of the resultant forces (or moments) acting on each side of the molecule. There is an internal pressure operating within the crystal, resulting from attractions which bridge each molecule, and this pressure can be calculated in the same way that the other forces within the crystal can be calculated. This internal pressure results in the forces between atoms in the parent molecule and the nearest neighbour environment being repulsive in total in such a way that they exactly oppose the effect of the internal pressure. The manner in which this principle can be used in practice is best illustrated by the following example.

Consider Fig. 1. Let (i) RE and LE represent all the atoms in the environmental molecules to the right and left of the stippled line respectively, excluding those in the parent (P) molecule: and (ii) RS and LS represent all the atoms in a line sequence of molecules to the right and left of the stippled line respectively, *e.g.* those in molecules A, B and C and A', B' and C' respectively. The x components of the forces between the parent molecule atoms and the RE must equilibrate

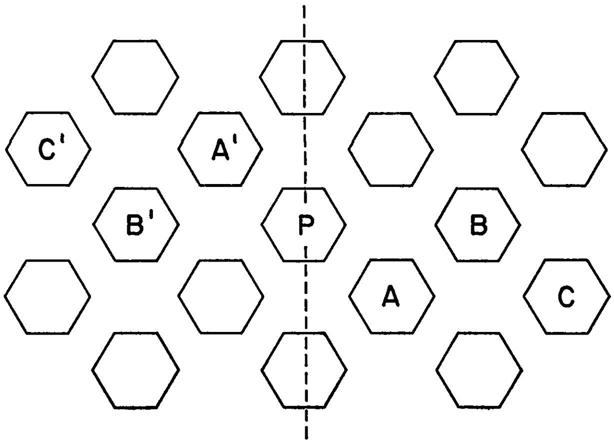

Fig. 1. The environment of the parent molecule.

those between one LS and the RE. Likewise those between the parent molecule and the LE must balance those between one RS and the LE. When this is so, the repulsions between nearest-neighbour molecules exactly compensate the internal pressure resulting from long range attractions. When there is a single or a fraction of a molecule in the asymmetric unit, this condition can be expressed as follows, making errors in only third and more remote neighbour interactions:

$$\sum_{P} \sum_{\mathrm{TE}} |F_{ij}|x + \sum_{P} \sum_{\mathrm{SNE}} |F_{ij}|x = 0$$

in which P represents summation over the parent molecule,

TE $=$ RE $+$ LE and represents summation over the total environment,

SNE $=$ summation over all non-nearest-neighbour molecules in the total environment.

The modulus signs in the equations above imply the ignoring of the directions of the interatomic vectors. Some of the forces will be repulsive and others attractive, depending on the magnitude of R, and this will not be affected by taking moduli as indicated.

Carrying out these summations results in equations of the form

$$12E_m[(R_x^2 J_x - R_x K_x) + (R_x^2 J'_x - R_x K'_x)] = 0$$

and thus

$$r_{0x}^6 = R_x = (K_x + K'_x)/(J_x + J'_x) \, . \qquad (14)$$

Three values are thus obtained for r_0, and these are deduced from the requirement that the repulsions between nearest neighbours compensate the internal pressure forces in the crystal in each direction.

Programming of the calculations

A FORTRAN program has been written to perform the calculations. Input data consist of the cell constants, the number of molecules per cell, the number of atoms per molecule, the coordinates of each atom in the cell, the range in cells of the computer-generated parent molecule environment, the maximum interatomic distance to be taken into account in the calculations and an interatomic distance which when found indicates that the molecules containing the atoms in question are nearest neighbours. A feature which allows elimination of thermal expansion effects by contracting the cell without contracting the molecules has also been incorporated into the program.

The program calculates all interatomic distances r_{ij} from the parent molecule to those in the environment and generates the sums needed to determine r_0 from equations (10), (11) and (14).

Application of the method to selenium

Selenium is an ideal material on which to test the methods given here for the determination of van der Waals diameters. This results from its existence in three crystalline forms whose structures have been determined. These are α-monoclinic: Burbank (1951); β-monoclinic: Marsh, Pauling & McCullough (1953); and hexagonal: Straumanis (1940). The thermal constants needed to establish approximate 0°K structures are available for the α (Newton & Colby, 1951), and hexagonal (Straumanis, 1940) phases. The former have also been used for the β-phase extrapolation to 0°K as, after suitably interchanging axes, these two structures are very similar.

The results of the calculations for selenium are given in Table 1. The spread in the results obtained for the three orthogonal directions using the internal pressure method is about 1% for each phase. Partial elimination of the anisotropic thermal motion effects by contracting the structure to an extrapolated 0°K arrangement leads to no improvement in the agreement between the results for the three directions. The two monoclinic phases should give similar results as they are both molecular crystals containing eight-membered selenium rings. This is found to be the case to within the experimental errors (~1%) of the structure determinations. The calculations for the hexagonal structure were done by excluding from the summations all interactions between adjacent atoms in the same spiral chain. The resulting values are some 5% lower than those for the monoclinic structures. This is in keeping with the metallic nature of the hexagonal phase.

The van der Waals diameters which stem from independent lattice and molecular strain energy minimization are, respectively, slightly higher and substantially lower than those deduced from internal pressure considerations. This is what is expected qualitatively as the *sum* of the two energies should be minimized. The weighted mean of the two results should thus be correct and this would be far closer to that deduced from lattice energy minimization as the molecular strain energy is by far the smaller of the two types.

It must be emphasized that the constants derived are probably applicable only to the situation on which their derivation is based. Thus constants derived from lattice-energy or equilibrium considerations may be seriously in error when applied to the much closer approaches found between non-bonded atoms within molecules.

This situation cannot be rectified until an interaction potential is available which has been shown to be valid over a large range of atomic separations.

Derivation of the second constant E_m is straightforward when compressibilities are known. As these are not known for the three phases of selenium, full specification of the Se–Se interaction potential cannot be made at this stage.

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Table 1. *Results of calculations for selenium*

Phase	Temperature °K	Van der Waals diameter in Å from: Internal pressure x	y	z	Lattice energy	Molecular strain energy
α-Selenium	300	3·96	3·99	4·00	4·04	3·67
	0	3·92	3·94	3·96	3·99	3·63
β-Selenium	300	3·95	3·91	3·99	4·00	3·57
	0	3·92	3·89	3·91	3·95	3·56
Hexagonal selenium	300	3·78	3·77	3·74	3·82	3·49
	0	3·68	3·68	3·65	3·73	3·41

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Discrepancy Factors for Use in Crystal Structure Analysis*

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Theoretical expressions for two types of discrepancy factors have been obtained for crystals containing both heavy and light atoms in the unit cell. One of the discrepancy factors is defined in terms of the structure amplitude and is called the Booth's reliability index (R_B). The other discrepancy factor (denoted by R_2) is based on intensities. While the expressions for R_2 can be used for crystals of any space group and for crystals containing any number and type of atoms in the unit cell, those for R_B can be used only for crystals in the triclinic and a few monoclinic space groups.

1. Introduction

In this paper we shall obtain theoretical expressions for the discrepancy factors R_B and R_2 [suggested by Booth (1945) and Wilson (1969) respectively] for crystals containing both heavy and light atoms in the unit cell. In the standard notation, these reliability indices can be defined as

$$R_B=\sum_{hkl}(|F_o|-|F_c|)^2/\sum_{hkl}|F_o|^2 \quad (1)$$

$$R_2=\sum_{hkl}(I_o-I_c)^2/\sum_{hkl}I_o^2\,. \quad (2)$$

The interest in R_B lies in the fact that it is closely related to the quantity being minimized in the usual least-squares method (Buerger, 1967). The theoretical expressions for R_2 can be obtained under more general conditions than for any other R indices (Wilson, 1969). Owing to the difficulties in the theory, we shall obtain different expressions for the R indices which are applicable under different circumstances.

When the atoms in the model structure† are completely correct we shall call it the *related case* and when all the atoms in the model are completely wrong we shall call it the *unrelated case*. When the model consists of some completely wrong atoms and the rest completely correct, we shall call it the *semi-related case*. When the coordinates of all the atoms in the model suffer finite errors, we shall call it the *imperfectly related case*. For simplicity of notation, we shall use *R*, *UR*, *SR* and *IR* to denote the related, unrelated, semi-related and imperfectly related cases respectively. It is obvious that the *R* and *UR* cases are limiting cases of the *IR* case. We can also think of the *R* and *UR* cases as limiting cases of the *SR* case.

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† The model structure need not include all the atoms in the unit cell.