scattering factors can become rather large owing to the tunability of the radiation; (*b*) small molecules are investigated.

A better approximation of the $|F''|^2$ coefficients may be obtained by probabilistic methods. The conditional probability distribution of Φ given R^+ and R^- has been recently secured by Hauptman (1982) and Giacovazzo (1983):

$$P(\Phi|R^+, R^-) \simeq [2\pi I_0(Q)]^{-1} \exp\{Q \cos(\Phi - q)\}, \quad (4)$$

where

$$Q = \frac{2R^+R^-}{\sqrt{c}}[c_1^2 + c_2^2]^{1/2},$$

$$\cos q = c_1/(c_1^2 + c_2^2)^{1/2}, \quad \sin q = c_2/(c_1^2 + c_2^2)^{1/2}.$$

By standard techniques, (5) follows from (4):

$$\langle \cos \Phi | R^+, R^- \rangle = \cos q D_1(Q), \quad (5)$$

where $D_1(Q) = I_1(Q)/I_0(Q)$ is the ratio of the modified Bessel functions of order 1 and 0.

Since (see Fig. 1)

$$|F^+|^2 + |F^-|^2 - 2|F^+||F^-| \cos \Phi = 4|F''|^2,$$

the expected value of $|F''|^2$ given $|F^+|$and $|F^-|$ is

$$\langle |F''|^2 | |F^+|, |F^-| \rangle \simeq \tfrac{1}{4}[|F^+|^2 + |F^-|^2 - 2|F^+||F^-| D_1(Q) \cos q]. \quad (6)$$

If (6) is compared with (3) we see that Rossmann's coefficients always assume $Q \simeq \infty$ and $q \simeq 2\pi$. The first approximation may be rough if R^+R^- is small enough; the second if c_2 is not negligible with respect to $(c_1^2 + c_2^2)^{1/2}$.

Relation (6) may find useful application even in two-wavelength techniques applied to crystal structures with one type of anomalous scatterers (Singh & Ramaseshan, 1968; Cascarano, Giacovazzo, Peerdeman & Kroon, 1982). There the analysis of experimental data leads to two possible values for $|F''|$, the most probable of which may be chosen in accordance with (6).

It may finally be noted that the distribution $P(|F''||F^+|, |F^-|)$ is implicitly defined by our approach and may be found by applying the well known formula

$$P_2(y) = P_1[x(y)] \frac{d[x(y)]}{dy},$$

where x is a function of the random variable y. In our case

$$x = \cos \Phi = (|F^+|^2 + |F^-|^2 - 4|F''|^2)/2|F^+F^-|, \quad y = |F''|,$$

$$P_1(x) \simeq [\pi I_0(Q)]^{-1}(1 - x^2)^{-1/2} \exp(Qx).$$

We only note here that the larger Q is, the more reliable is the estimation for $|F''|$ provided by the (6).

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Aufbau **algorithms and the structure of small molecular clusters.*** By B. W. VAN DE WAAL, *Chemical Physics Laboratory, Twente University of Technology, PO Box* 217, 7500 *AE Enschede, The Netherlands*

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Abstract

In a comment [van de Waal (1981). *Acta Cryst.* A**37**, 762–764] on a paper by D. E. Williams [*Acta Cryst.* (1980), A**36**, 715–723] on the conformation of small clusters of benzene molecules, it was understood that Williams's results had been obtained from the application of an aufbau algorithm. Subsequently, it was made clear by Williams (private communication) that his results were actually derived from the reversed procedure. In the present note a comparison is made between the two approaches.

In our comment on Williams's (1980) paper, it was understood that the equilibrium conformations of clusters of benzene molecules, as reported by Williams, had been obtained from the application of an *aufbau* algorithm (van de Waal, 1981). Professor Williams has made clear, however, (Williams, 1981) that the conformation of each N-molecule cluster was actually derived by removing two molecules (related by a centre of symmetry) from an optimized $(N+2)$ cluster, rather than by adding two molecules to an optimized $(N-2)$ cluster. The process was started with a crystal-structure fragment.

Since this latter approach is not equivalent to the former, our comment needs some correction. It is the purpose of the present note to discuss briefly the relative merits of both methods (to which we shall refer as the *aufbau* algorithm and the reversed *aufbau* algorithm, respectively), and to amend our comment accordingly.

The *aufbau* algorithm has been used by several authors (McGinty, 1971; Hoare & Pal, 1971; Pan & Etters, 1980) to calculate equilibrium conformations of clusters of atoms, interacting through a pair potential, usually a Lennard-Jones (LJ) potential. Essentially, it consists of adding individual atoms to a selected seed structure of small

* *Editorial note*: This paper suffered undue delay because the co-editor handling it inadvertently mislaid it.

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dimensions (typically 2–6 atoms). After each step the potential energy is minimized with respect to all atomic coordinates. It is clear that, with increasing size of the cluster, the number of favourable sites with respect to the accommodation of an additional atom increases as well. Thus, branching occurs, even in the early stages of the *aufbau* algorithm, eventually resulting in a large number of isomers. The total count of distinct isomers of clusters of atoms, interacting through an LJ potential, in the range $N = 6, \ldots, 13$, is reported to be: 2, 4, 8, 18, 57, 145, 366, 988 (McInnes, 1976). In view of the additional rotational coordinates and the more complex nature of the interaction, these numbers will be even larger for molecular clusters, and an exhaustive search seems virtually impossible. Consequently, in practice, the conformation of only a small fraction of a (supposedly) very large number of isomers is known, without any indication of the relative significance of this fraction, in some respect or other. In this situation, the observation that a particular cluster conformation reveals some structural features, not unlike that found in the observed crystal structure, is rather arbitrary, since it cannot be asserted that this conformation is distinguished from its isomers in *other* respects, *e.g.* by its energy, or by the way it was obtained.

Alternatively, in the branched structure that results from the application of an *aufbau* algorithm among all traces that lead from the seed structure to all possible isomers of the largest size considered, one path is unique: the so-called minimal growth sequence or MGS (Hoare, 1979). In this sequence every step is the most favourable with respect to binding energy, as compared to all possible other steps. Although this sequence is not necessarily the same as that which leads to the highest binding energy in the largest cluster considered, it has the advantage that the number of isomers to be dealt with in every stage is drastically reduced, thus opening the possibility of an exhaustive search, at least for atomic clusters.

The *reversed aufbau* algorithm starts at the other end, *i.e.* with a cluster of the largest size that will be considered. After this cluster has been optimized with respect to its potential energy, the algorithm proceeds by removing atoms (or molecules) from the cluster, one at a time, and allowing the remaining cluster to change its conformation in response to each single removal. Since the choice of the atom to be removed is not unique, in general, branching occurs. A notable difference with the *aufbau* algorithm is the dependence of the number of isomers on cluster size. This number must be maximum, not for the largest cluster considered, but for a medium-sized cluster, since the beginning and end of the sequence are marked by a single configuration (the end point is simply a single atom or molecule).

It may be argued that, although the two algorithms are clearly inequivalent, the MGS of the *aufbau* algorithm is equivalent to the reversed MGS of the reversed *aufbau* algorithm. (The reversed MGS is obtained if only those atoms are removed that give minimum loss in binding energy as compared to all other possible removals). For this conjecture to be true, the starting point of the reversed MGS must be identical to the end point of the 'normal' MGS, which is not known. The choice of the starting point of the reversed MGS is thus rather arbitrary and implies a guess with respect to the end point of the MGS, if the conjecture is true. Also, the atom whose addition to a given cluster results in maximum gain in binding energy should always be the same as the atom whose removal results in minimum loss. This latter condition cannot be fulfilled in general, as a consequence of the fact that the $(N+1)$ cluster with highest binding energy is not necessarily an MGS descendant (or a reversed-MGS parent) of the N cluster with highest binding energy. Thus, cluster conformations figuring in a MGS are different from cluster conformations making up a reversed MGS with the same starting and ending point. There seems to be no reason to expect one sequence to be physically more significant than the other. From a computational point of view, calculation of the reversed MGS is far more tractable owing to the limited number of possible steps (at most N steps for each N cluster), whereas in the MGS scheme even the *counting* of possible steps may be prohibitive. Accordingly, the best step can be selected without ambiguity whereas the MGS scheme permits only a guess as to whether the applied step is the best possible. However, since the structure of the largest clusters considered in a reversed growth sequence can hardly be regarded as *resulting* from the calculation, any observation concerning their structure relates strongly to the choice of the initial configuration rather than to the calculation.

It is clear that our suggestion to compare results of cluster calculations with relaxed crystal fragments (van de Waal, 1981) applies only to MGS (or related) calculations. Our observation that the conformation of the iso-tridecamer, as found by Williams, is identical to a relaxed crystal-structure fragment is not surprising, since this conformation was actually *derived* by relaxation of a crystal fragment. (Removal of the two second-shell molecules of a relaxed 15-molecule fragment results in the normal tridecamer configuration, after relaxation.) Since the smaller clusters reported by Williams are less intimately related to the observed crystal structure, it is not to be *expected* that they will be identical to relaxed crystal-structure fragments of the same size. However, if an appropriate trimer is selected from the crystal-structure arrangement and allowed to relax, it readily transforms to the conformation found by Williams.

Finally, we note that the question whether crystalline structures may be constructed from growth sequences (Hoare, 1979) remains unanswered for molecular crystals. Other types of calculation (*viz* Monte Carlo or molecular-dynamics simulations) seem to be more promising to the extent that results can be made virtually independent of starting conditions, albeit that the required number of steps restricts the application to small systems with comparatively simple two-body interaction potentials. Even so, it is very unlikely (if not impossible) that the bulk-like crystal structure will emerge, since this structure is almost invariably mechanically unstable in small fragments of molecular crystals consisting of only a few molecules (van de Waal, 1983).

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