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Can random structures refine? A comment on proposals by Booth and Lenstra. By A. J. C. WILSON, *Department of Physics, University of Birmingham, Birmingham B15 2TT, England*

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The proposal by Booth [*Nature, Lond.* (1947), **160**, 196] of shuffling the atoms of a random structure seems somewhat likelier to lead to a solution than that by Lenstra [*Acta Cryst.* (1974), A **30**, 363–369] of adding atoms one or a few at a time to a null structure.

In brief, the method proposed by Booth (1947, 1949) consisted in imagining a residual R plotted as a contour map in m dimensions, where m is the number of parameters to be determined, and allowing the atoms to roll down the hills of R until each settles into the valley bottom corresponding to its true position. The actual mathematical process proposed by Booth was shown by Qurashi (1949) to be equivalent to the diagonal approximation in least-squares refinement, but this is only a detail conditioned by the primitive computing facilities of the 1940's, not an essential part of the idea. Booth believed, or was understood to have claimed, that the process would converge to the true structure, whatever the initial atomic coordinates. This, obviously, would be claiming too much; the process will cease when each atom is in a valley bottom, whether the true one or not. If, say, an S atom ends up where a C atom should be, and *vice versa*, existing refinement programs will not interchange them. Further, the hills and valleys of R drift about as the atoms move, in a way not fully investigated theoretically, and it is possible that R can have self-consistent minima not associated with atomic positions. The probability of false minima, obviously, will increase with the systematic errors and with the size of the statistical fluctuations in the values of F or I on which R is based. Lipson & Cochran (1953, p. 250) sum up the general verdict in these words: '... it may be concluded that unless one begins with parameters which place all atoms within a distance about equal to an atomic diameter from their correct positions ... [the method of Booth] cannot lead from arbitrary parameters to the correct ones'. With the then available computing facilities and knowledge of the properties of R it was a fair summary. In the ensuing twenty years the accuracy of routine intensity measurement has greatly improved (something approaching a factor of 10), computing facilities have improved even more, and the properties of the varieties of R are better, though not fully, understood (*e.g.* Lenstra, 1974; Parthasarathy & Parthasarathi, 1972 and numerous later papers; Wilson, 1969, 1976). One wonders, therefore, if Booth's basic idea should be reconsidered, particularly for organic compounds containing (aside from H) only atoms near C in scattering power. Lenstra (1974) has envisaged a converse of the Booth proposal: starting with an R based on the observed F 's or I 's only, which obviously has the value unity, and assessing the decreases in it as atoms are included in the calculated F 's or I 's one or a few at a time and their positions are adjusted so that R is minimized at each step.

Lenstra considered the residual

$$R_2 = \sum_{hkl} (I_o - I_c)^2 / \sum_{hkl} I_o^2, \quad (1)$$

and showed that in the space group $P1$ it decreased linearly with each atom correctly placed. He showed also that in certain circumstances, not explored in detail, it would decrease also even if the added atom(s) were incorrectly placed. He

treated very briefly the corresponding process in $P\bar{1}$, but made practical applications only to non-centrosymmetric space groups. It is a considerable simplification to use intensities normalized in the sense of Bertaut (1955), as the variation with $(\sin \theta)/\lambda$ is then eliminated. Wilson's (1976) treatment of R_2 is more general, in that it is applicable to any space group, and it permits the assessment of the changes in R_2 by both proposed processes. It makes provision for the effects of dispersion, but for simplicity this will be neglected here and it will be assumed that all atoms have the Wyckoff position. In the form appropriate for the present application Wilson's equation (24) may be written

$$R_2 = 1 - \frac{2\Sigma_o(\Sigma_{cc} + \Sigma_{cw})}{(k+1)\Sigma_o^2 - QT_o} + \frac{(k+1)(\Sigma_{cc} + \Sigma_{cw})^2}{(k+1)\Sigma_o^2 - QT_o} - \frac{2k\Sigma_{cc}^2}{(k+1)\Sigma_o^2 - QT_o} + \frac{QT_{cc}}{(k+1)\Sigma_o^2 - QT_o} - \frac{QT_{cw}}{(k+1)\Sigma_o^2 - QT_o}, \quad (2)$$

where Σ_o is the observed mean intensity, equal to the sum of the squares of the atomic scattering factors (Wilson, 1942), Σ_{cc} is the sum of the squares of atomic scattering factors of the correctly placed atoms, Σ_{cw} is the sum for the wrongly placed atoms, T_o , T_{cc} and T_{cw} are the corresponding sums of the fourth powers of the atomic scattering factors, k is 1 for non-centrosymmetric structures and 2 for centrosymmetric, and

$$Q \equiv (1+k)p - q/p \quad (3)$$

is a number determinate for any space group; in fact p is the multiplicity of the Wyckoff position and q is the mean value of the fourth power of the geometric structure factor (Foster & Hargreaves, 1963; Wilson, 1976). From (2) we see, first, that R_2 decreases linearly with number of correctly added quasi-equal atoms (both Σ_{cc} and T_{cc} are proportional to this number) only if the third and fourth terms cancel. This requires either (i) that there be no wrongly added atoms and that the structure be non-centrosymmetric, which is reasonable, or (ii) that wrongly added atoms should be provided in a ratio so that $\Sigma_{cw} = [(2/3) - 1]\Sigma_{cc}$ and the structure be centrosymmetric, which is hardly reasonable. In general, then, Lenstra's result of linearity will hold only in the determination of non-centrosymmetric structures. Secondly, the first-order second term and the second-order third term are exactly the same, whether the atoms are added correctly or wrongly, so the process is likely to be insensitive. Thirdly, and perhaps most importantly, a large number of atoms can be added wrongly before R_2 ceases to decrease. The limit is, in fact, if the terms in T are neglected,

$$\Sigma_{cw} = \Sigma_o/(k+1), \quad (4)$$

corresponding to an incorrect placing of one-half or one-third of the scattering power, and a value of R_2 of 0.75 or 0.89. The same amounts of scattering power correctly placed

would give $R_2 = 0.50$ or 0.74 , which are not overwhelmingly smaller.

The situation is perhaps a little more favourable on starting from an entirely wrong structure, and moving the atoms so as to reduce R_2 – the Booth approach. With all atoms wrongly placed $\Sigma_{cw} = \Sigma_o$. If some atoms (one atom and its symmetry-related equivalents, or perhaps a structural fragment and its equivalents) are now moved to their correct positions,

$$\Sigma_{cw} = \Sigma_o - \Sigma_{cc}, \quad (5)$$

$$T_{cw} = T_o - T_{cc}, \quad (6)$$

and (2) becomes

$$R_2 = 2 - \frac{2\Sigma_o^2}{(k+1)\Sigma_o^2 - QT_o} - 2 \frac{k\Sigma_{cc}^2 - QT_{cc}}{(k+1)\Sigma_o^2 - QT_o}. \quad (7)$$

This reduces to the expected values (Wilson, 1974) for no atoms correct and for all atoms correct. The first two terms are constants, and the third term represents a genuine reduction in R_2 as the atoms reach their correct positions.

One can compare the Booth and Lenstra approaches qualitatively by writing approximate equations for the case of equal atoms and terms in T neglected. If the total number of atoms is N , and the number of correctly placed atoms is n , the Lenstra approach gives

$$R_2 = 1 - 2n/(k+1)N - (k-1)n^2/(k+1)N^2, \quad (8)$$

(equation 2), whereas the Booth approach gives

$$R_2 = 2k/(k+1) - 2kn^2/(k+1)N^2 \quad (9)$$

(equation 7). If the atoms in the Lenstra approach are all wrongly placed,

$$R_2 = 1 - 2n/(k+1)N + n^2/N^2. \quad (10)$$

The discriminatory part of the reduction in R_2 is of the second order in n/N in both approaches, but in the Booth approach it is the only reduction, not confused by the larger first-order reduction that occurs in the Lenstra approach, whether the atoms are correctly placed or not. It would seem, therefore, that the Booth approach has a somewhat higher chance of being successful.

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