

U_{equiv} : its past, present and future¹

David Watkin

Chemical Crystallography Laboratory, 9
Parks Road, Oxford OX1 3PD, EnglandCorrespondence e-mail:
david.watkin@chem.ox.ac.uk

The reporting of U_{equiv} and its standard uncertainty has a chequered history. In spite of the recommendation of the IUCr Commission on Journals that authors use the definition of U_{equiv} of their own choice, possibly without standard uncertainties, there still seems to be some confusion amongst referees and editors about the status of this derived parameter. It is shown that neither of the common definitions are very useful, and that the standard uncertainty computed from the refinement normal matrix is almost worthless. A potential alternative derived parameter is proposed.

Received 2 May 2000
Accepted 14 June 2000**1. Introduction**

As coordinator for the *CRYSTALS* crystallographic program (Watkin *et al.*, 2000), I am frequently asked why *CRYSTALS* does not tabulate the standard uncertainties on U_{equiv} . It seems that there is still some confusion amongst referees and editors about the role and status of U_{equiv} . Perhaps it would be useful to recount its history, and speculate upon a future role.

2. U_{equiv} – its past

By 1959, determination of anisotropic temperature factors (as they were then called) was becoming routine, which led W. C. Hamilton (1959) to believe that ‘it seems worthwhile to define an isotropic temperature factor which we shall call *equivalent* to the anisotropic components. There are a number of situations where such a definition may be convenient. If anisotropic temperature factors have been determined and the deviations from isotropy do not appear to be significant, it would seem wise to include in the report ... the values of the equivalent *B*’s’. Hamilton (1959) did not explain why this was wise, though perhaps the then-common practice of refining *B* or β made it difficult to identify high ellipticity. He went on to write, ‘given an anisotropic thermal motion, we define the *equivalent* isotropic motion as that which gives

rise to the same value ... of the energy in the first vibrational state’, and showed how this might be calculated. Willis & Prior (1975) came to an equivalent expression, and attempts to compute B_{equiv} or U_{equiv} became routine.

Towards the end of the 1970s, the IUCr Commission on Journals recognized that it was unscientific to publish results without some indication of confidence limits – ‘formal estimated standard deviations (e.s.d.’s) should be quoted and their basis defined’ (IUCr Notes for Authors, 1978). This is the proper attitude when reasonably applied, but unfortunately unreasonable applications crept in. One of these was the requirement for e.s.d.’s (as they were then called) to be computed for U_{equiv} – ‘all measured or derived quantities which are of importance ... are required to be accompanied by their standard deviations. The value of such quantities without estimated standard deviations is regarded as being sufficiently ill-defined as not to warrant publication’ (IUCr Commission on Journals, 1979). This led to much discussion and lively debate. For a start, many people did not realize that there were at least two definitions of U_{equiv} – the geometric (U_{geom}) and the arithmetic (U_{arith}) means of the principal components (U^i) of the anisotropic temperature factor (U^j). These two figures are the same for a spherical ellipse, but show quite different properties as the ellipse becomes more eccentric. For example, the arithmetic mean may not reveal that one component has refined to a negative value. They also have different physical interpretations. Hamilton (1959) had given an interpretation of the arithmetic mean, and the geometric mean is just the radius of a sphere

¹ Editorial note: The editors welcome input by e-mail (john.helliwell@man.ac.uk or allen@ccdc.cam.ac.uk) on these points raised by David Watkin, which will then be included in a discussion at the next meeting of the IUCr Journals’ Commission.

with the same volume as the ellipsoid (Ahmed, 1979). It turns out that the arithmetic mean can be computed without diagonalizing the tensor, which might account for its early popularity. In either case, the information in the inverse normal matrix can be propagated through to give an s.u. on U_{equiv} , and some programs do this (with more or less disregard of the off-diagonal terms). Schomaker & Marsh (1983) showed how to compute correctly the s.u. on U_{arith} , and how to come to a fair estimate given only the s.u. on the principal components. The large correlation coefficient ($-\frac{1}{4}$) had been implied but gone unnoticed in a much earlier paper (Cruickshank, 1956). However, even as late as 1988 the U_{equiv} were still being miscalculated (Fischer & Tillmanns, 1988), and one can only speculate on where the s.u.'s were coming from.

At the Ottawa IUCr Computing School in 1981, Donald Sands (1982) gave a talk on errors and error propagation. After his talk, he was asked from the floor about the computation of the s.u. on U_{equiv} . His response must certainly be remembered by all who were there. In essence, he said that just because one can compute a number, that is no indication that it has any scientific or statistical value. In his opinion, computing U_{equiv} could be seen as analogous to trying to compute the 'average fruit' in a fruit bowl. It makes no sense for a bowl containing apples, oranges and bananas, and computing an s.u. makes even less sense. We all had a good laugh. Sadly, questions from the floor and their replies had ceased to be reported in Computing School proceedings by 1982.

Shortly after this, the requirement for s.u.'s on U_{equiv} was dropped by *Acta Crystallographica*. Schomaker & Marsh (1983), having shown how to compute the s.u. on U_{arith} , concluded by saying, 'who really cares about U_{equiv} or $\sigma(U_{\text{equiv}})$, which are next to meaningless, if he has full information about the U^i 's'. The IUCr Notes for Authors (1983) the same year states that 'estimated standard deviations on such equivalent values are not required'. The IUCr Commission on Journals (1986) noted the two commonly used definitions of U_{equiv} and 'encouraged (authors) to use their definition of choice' (with a warning about the problem of non-orthogonal crystal systems), provided the source was referenced, and still without mention of the re-introduction of standard uncertainties. Ten years later, Trueblood *et al.* (1996) repeated Hamilton's (1959) caution that an equivalent temperature factor should only be computed for cases with minor departures from isotropic motion but, curiously, misreported the IUCr

Commission on Journals (1986) recommendations, plumping for U_{arith} as the 'recommended' definition, and adding (erroneously) that *Acta Crystallographica* required that published values of U_{equiv} be accompanied by an evaluation of the standard deviation (now standard uncertainty).

What Sands (1982) was saying is subtle and needs careful analysis. An average fruit is nonsense, but if the bowl contained only apples, the characteristics of an average apple might have a use, and so might its standard uncertainty. This situation had been foreseen by Hamilton (1959) – 'if anisotropic temperature factors have been determined and the deviations from isotropy do not appear to be significant or be physically unrealistic...'. This is the crux of the problem. Hamilton (1959) recognized that it only makes sense to compute an average of items purporting to be measures of the same thing. For example, all the carbon-carbon bond lengths in the Cambridge Structural Database could be added together and their mean value computed, but such a mean has no physical interpretation. More simply, one could take the mean values for sp^3-sp^3 , sp^2-sp^2 and sp^1-sp^1 carbon-carbon bond lengths and their σ values (*International Tables of Crystallography*, 1998), and compute the weighted mean (Taylor & Kennard, 1985). Typical values might be: 1.53 (01), 1.31 (01) and 1.19 (01) Å, respectively, with a weighted mean of 1.34 (006) Å. Apparently, we have a more precise estimate of a physically meaningless parameter.

Over the years, the condition that the a.d.p.'s be approximately isotropic for U_{arith} to have a physical meaning has become forgotten, and computer programs evaluate it for all anisotropic atoms, often with an accompanying s.u. Curiously, as shown by Schomaker & Marsh (1983), this s.u. can be less than that obtained by proper refinement of U_{iso} . U_{equiv} might be useful as a summary of the a.d.p. of an almost isotropic atom, but for eccentric cases it does not warrant the honour of an s.u. propagated through from the normal matrix. However, since the computation is only valid for approximately isotropic displacement parameters, one might just as well not bother with U_{equiv} and simply quote any of the U^{ii} and their s.u.'s.

3. U_{equiv} – its future

It seems that some of the contention about what definition of U_{equiv} should be used in publications derives from the potentially different uses which can be made of the quantity. For a well defined, well refined

structure, in which Hamilton's condition is met, variations in U_{equiv} from atom to atom provide a convenient approximation to the a.d.p.'s, with anomalously large or small U_{equiv} drawing the readers attention to potentially interesting areas of the structure. An alternative use is as a flag to draw the readers' (or referees') eye to a potentially poorly refined area.

Table 1 shows how these differing U_{equiv} values look for differing degrees of eccentricity of the a.d.p.'s. U^i are the principal components with the 0.01 as their (invented) s.u.'s from the least squares. The s.u. on the U_{equiv} are derived analytically (falsely) assuming no correlation between the standard uncertainties of the U^i . These numbers convince me that U_{arith} is not a particularly sensitive flag for highlighting anomalous atoms, even though poorly defined/refined atoms are often associated with highly anisotropic displacement parameters. U_{geom} is just a little more useful, since it is sensitive to small or negative principal components. In neither case do the s.u.'s serve any useful purpose. More useful might be the r.m.s. deviations of the principal components (U^i) from U_{equiv} , since they would be measures of the eccentricity of the ellipsoid, or the reporting of $U_{\text{max}} - U_{\text{min}}$. Here the s.u. (of the difference) computed from the normal matrix serves to indicate how significant the eccentricity is, and so is a statistically useful quantity.

The problem is to devise a single parameter which satisfies both the need to show the properties of well behaved atoms and at the same time draw attention to ill-behaved atoms. One possible candidate (with an evident weakness) would be

$$U' = U_{\text{med}}(U_{\text{max}}/U_{\text{min}}). \quad (1)$$

For an atom meeting Hamilton's criteria, this will be more or less the same as U_{arith} or U_{geom} , but it will take on increasingly large values for both prolate and oblate ellipsoids.

4. On the reporting of standard uncertainties

It would lead to less correspondence for us if *CRYSTALS* reported a standard uncertainty on U_{equiv} using Schomaker & Marsh's formulation and ignoring the sphericity criterion. However, my feeling is that if standard uncertainties cannot be computed in a meaningful way, they are best left out of papers. We appreciate the warning about 'Chi-by-eye' given by Press *et al.* (1992), but somehow publication of a numerical figure for a standard uncertainty seems to give it an authority it may not merit. In any case,

Table 1

Comparison of U_{arith} , U_{geom} and U' for ellipsoids of increasing eccentricity.

U_1 , U_2 and U_3 are the principal axes with their uncorrelated standard uncertainties.

U_1	U_2	U_3	U'	U_{equiv}	σ	r.m.s.d.	
0.050 0.010	0.050 0.010	0.050 0.010	0.050				
				0.050 0.050	0.017 0.006	0.000 0.000	Arithmetic mean Geometric mean
0.070 0.010	0.050 0.010	0.030 0.010	0.117				
				0.050 0.047	0.017 0.007	0.016 0.017	Arithmetic mean Geometric mean
0.090 0.010	0.050 0.010	0.010 0.010	0.450				
				0.050 0.036	0.017 0.012	0.033 0.036	Arithmetic mean Geometric mean
0.095 0.010	0.050 0.010	0.005 0.010	0.950				
				0.050 0.029	0.017 0.019	0.037 0.042	Arithmetic mean Geometric mean
0.099 0.010	0.050 0.010	0.001 0.010	4.950				
				0.050 0.017	0.017 0.057	0.040 0.052	Arithmetic mean Geometric mean

science has moved on since the IUCr Commission on Journals (1979) insisted that a quantity without a standard deviation did not warrant publication, and the ranking of observations has become respectable. In the annual Oxford and Cambridge Boat Race, the crew wearing light blue can generally be distinguished from that in dark blue, without any attempt at establishing standard uncer-

tainties. In a publication, if no standard uncertainty is given, the reader is forced to make up their own mind. An a.d.p. plot can be viewed and, if necessary, the U^i can be retrieved. The highest quality work requires the highest quality data, the highest quality mathematics and the highest quality scrutiny, but such work is not the focus of this contribution.

References

Ahmed, F. R. (1979). Summary Sheet, IUCr Commission on Journals.
 Cruickshank, D. W. J. (1956). *Acta Cryst.* **9**, 747–753.
 Fischer, R. X. & Tillmanns, E. (1988). *Acta Cryst.* **C44**, 775–776.
 Hamilton, W. C. (1959). *Acta Cryst.* **12**, 609–610.
 IUCr Commission on Journals (1979). *Acta Cryst.* **A35**, 508.
 IUCr Commission on Journals (1986). *Acta Cryst.* **C42**, 1100.
 IUCr Notes for Authors (1978). *Acta Cryst.* **A34**, 143–157.
 IUCr Notes for Authors (1983). *Acta Cryst.* **A39**, 174–186.
 Press, W. H., Teukolsky, S. A., Vetterling, W. T. & Flannery, B. P. (1992). *Numerical Recipes*. Cambridge University Press.
 Sands, D. E. (1982). *Computational Crystallography*, edited by D. Sayre, pp. 421–429. Oxford: Clarendon Press.
 Schomaker, V. & Marsh, R. E. (1983). *Acta Cryst.* **A39**, 819–820.
 Taylor, R. & Kennard, O. (1985). *Acta Cryst.* **A41**, 85–89.
 Trueblood, K. N., Burgi, H.-B., Burzlaff, H., Dunitz, J. D., Gramaccioli, C. M., Schulz, H. H., Shmueli, U. & Abrahams, C. (1996). *Acta Cryst.* **A52**, 770–781.
 Watkin, D. J., Prout, C. K., Carruthers, J. R., Betteridge, P. W. & Cooper, R. I. (2000). *CRYSTALS*. Issue 11. Chemical Crystallography Laboratory, University of Oxford, England.
 Willis, B. T. M. & Prior, A. W. (1975). *Thermal Vibrations in Crystallography*, pp. 101–102. Cambridge University Press.