

Journal of  
**Applied  
Crystallography**  
ISSN 0021-8898  
Editor: **Gernot Kosterz**

## ***SHADE* web server for estimation of hydrogen anisotropic displacement parameters**

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# SHADE web server for estimation of hydrogen anisotropic displacement parameters

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The *SHADE* web server estimates anisotropic displacement parameters for hydrogen atoms by combining a rigid-body analysis of the non-hydrogen-atom anisotropic displacement parameters (ADPs) with a contribution from internal atomic motion. The contributions from internal mean square displacements are based on a previously compiled database derived from analysis of neutron diffraction experiments. The estimated hydrogen-atom ADPs can be used as fixed parameters in advanced applications of high-resolution X-ray diffraction, such as electron density studies using multipole modelling. The resulting electron density models have been shown to be in excellent agreement with reference models based on atomic motion derived from neutron diffraction experiments.

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## 1. Introduction

The low X-ray scattering power of H atoms is a well known problem in crystallography. The sparse and polarized electron density near the H-atom nucleus is barely sufficient to locate the H atom. Only after the introduction of the H form factor of Stewart *et al.* (1965) has it been possible to refine the H-atom position and an isotropic displacement parameter, albeit still leading to errors in the H position of 0.1 to 0.2 Å (see *e.g.* Hope & Ottersen, 1978). A more sophisticated modelling, such as the refinement of anisotropic displacement parameters, has proven to be impossible.

However, as evident from structures based on neutron diffraction experiments (where the scattering length of the H atom is comparable in magnitude with those of heavier elements such as carbon and oxygen), the use of an isotropic displacement parameter is a very crude approximation.

We have demonstrated that the neglect of an anisotropic displacement model for H atoms has severe consequences in advanced applications of high-resolution X-ray crystallography, *i.e.* electron density studies using the multipole formalism (Stewart, 1976). The static model electron density in covalent bonds is severely affected by the isotropic H-atom description. To address this problem, we have described and validated a procedure to estimate the anisotropic motion of H atoms (Madsen *et al.*, 2004).

In brief, the procedure is an analysis of displacement parameters of the non-H-atom framework as a rigid body in terms of a TLS (translation–libration–screw) model (Schomaker & Trueblood, 1968). The resulting rigid-body model is then imposed on the H atoms along with an estimate of the internal mean square displacements of the H atoms:

$$U^{ij} = U_{\text{rigid}}^{ij} + U_{\text{internal}}^{ij} \quad (1)$$

The sum of the contributions from the different internal vibrational modes comprises the total internal motion. If the internal mode  $k$  has a mean square displacement  $\langle u^2 \rangle_k$  in the direction given by the unit vector  $\mathbf{e}_k$ , then the total atomic internal motion is

$$U_{\text{internal}}^{ij} = \sum_k \langle u^2 \rangle_k \mathbf{e}_k \mathbf{e}_k^T, \quad (2)$$

where  $\mathbf{e}_k^T$  is the transpose of  $\mathbf{e}_k$ , expressed in an orthonormal coordinate system.

The resulting estimates have been shown to be in good agreement with models where the atomic motions were derived from neutron diffraction studies. A detailed discussion of the algorithms and physical significance of the resulting model has been given elsewhere (Madsen *et al.*, 2004).

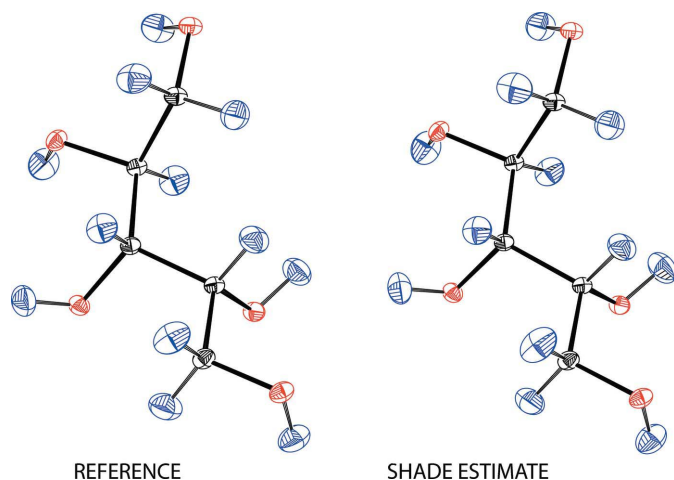
The procedure has now been implemented as a general algorithm called *SHADE* (*Simple Hydrogen Anisotropic Displacement Estimator*) and is available *via* a web server.

## 2. The SHADE web server

The *SHADE* program is accessed through a web interface. The algorithms and web server are implemented as a set of routines in Python (van Rossum, 2006). *PyCifRW* (Hester, 2006*a,b*; McMahon, 2005) is used to parse CIF (Hall *et al.*, 1991) data to and from the *SHADE* routines.

We have created a database of internal mean square displacements, derived from an analysis of a range of high-quality neutron diffraction studies of organic compounds (Madsen *et al.*, 2003). Individual internal mean square displacements are assigned in the bond direction and in two perpendicular directions. The database currently contains data for methylene, methyl, methine, hydroxy, water and ammonium groups. If an H atom does not belong to a chemical fragment present in the database, *SHADE* defaults to mean square displacements of 0.005 Å<sup>2</sup> in the bond direction and 0.020 Å<sup>2</sup> in the directions perpendicular to the X–H bond.

Similar internal mean square displacements can be derived from normal-coordinate analysis of Raman spectra (in the case of simple compounds) or from theoretical *ab initio* calculations; future versions of *SHADE* will allow the user to input such data.



**Figure 1**  
Comparison of reference (neutron diffraction) and *SHADE*-estimated ADPs for H atoms (blue colour). The displacement ellipsoids are shown at the 50% probability level. The crystal structure is the pentitol xylitol, C<sub>5</sub>O<sub>5</sub>H<sub>12</sub> (Madsen *et al.*, 2003), visualized using *PLATON* (Spek, 1990).

## 2.1. Input models

The *SHADE* web interface allows the user to upload a CIF containing a description of the molecule or molecular fragment including ADPs for the non-H atoms. The *SHADE* procedure can be applied to all types of organic and metal organic structures where the H atoms can be considered to be part of a rigid group of non-H atoms.

A generalized Rosenfield *et al.* (1978) 'rigid-bond test' as proposed by Hirshfeld (1976) and a weighted *R* factor are used to ensure that the ADPs in the CIF file input by the user and the resulting rigid-body model are physically reasonable.

The *SHADE* server automates the TLS analysis, which is performed by the *THMAIL* program (Schomaker & Trueblood, 1968). The input CIF file is read by the *PyCifRW* routines and input for the *THMAIL* program is created.

The input model must meet certain criteria in order to perform the analysis and estimations.

(i) The CIF file should contain a description of one rigid fragment. This could be a molecule or a part of a molecule that is considered as rigid. If the crystal contains more than one rigid entity, the CIF file must be split into several files or described in separate data blocks in the CIF.

(ii) Atoms will be recognized by the *THMAIL* program on the basis of their name; therefore all atom names should start with the atomic symbol.

(iii) Only rigid fragments with at least four non-H atoms can be analysed using the TLS formalism. If fewer non-H atoms are encountered, the program will revert to a simpler model, considering the H atoms as 'riding atoms' on the atoms they are bound to.

(iv) The program does not take internal molecular symmetry into account. Thus, a full ADP matrix should be included for all non-H atoms in the rigid entity.

## 2.2. Returned results

The *SHADE* estimations of H-atom ADPs are made available via the web interface as a CIF file. The CIF file contains the original information submitted by the user along with the estimated H-atom ADPs. *SHADE* also produces an output file in *SHELX* (Sheldrick, 1997) style.

Information related to the rigid-body analysis (the *THMAIL* program input and output) is also made available. Apart from the check made by *SHADE*, the user is thus able to go through the detailed analysis in the output to check the quality of the TLS model and the input crystallographic data.

The ADPs estimated by *SHADE* can be visualized as equal-probability ellipsoids by a large range of comprehensive molecular visualization tools. An example is given in Fig. 1. On the left-hand side we show the xylitol structure with H-atom ADPs derived from a neutron diffraction experiment, while on the right-hand side the estimate made by the *SHADE* program is presented.

## 3. Availability

The server can be accessed via <http://shade.ki.ku.dk>.

The source code is available on request to the author. It is released under the GNU General Public License (<http://www.gnu.org/copyleft/gpl.html>).

The author wishes to thank H. O. Sørensen for testing the program and S. Larsen for her interest in the project.

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