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Rigid-Link Constraints and Rigid-Body Molecules

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Abstract

The rigid-bond condition for harmonic thermal parameters states that the difference of the mean-square displacements of atoms *A* and *B* along the covalent bond *A–B* is negligible. In this paper, the corresponding condition for non-bonded intramolecular distances is called a rigid link. Rigid-body motion according to the TLS formalism requires *all* intramolecular links to be rigid. Conversely, a complete set of rigid links is not necessarily equivalent to rigid-body motion. An algorithm is presented for the determination of the maximum number Q_N of independent rigid links of an *N*-atom molecule. In general for site symmetry 1, $Q_N = N - 1$ for linear and $3N - 6$ for planar molecules. For three-dimensional molecules, $Q_N = N(N - 1)/2$, $N \leq 8$ and $6N - 20$, $N \geq 8$. For particular geometries, Q_N may be smaller. For many molecules, Q_N rigid links are equivalent to rigid-body motion. Notable exceptions are most linear and planar molecules, and all

molecules with six or seven atoms. Higher site symmetries reduce and often eliminate these differences between rigid links and rigid-body motion. The use of rigid-link restraints in crystallographic least squares is recommended. They provide a computationally simple means of relaxing the constraints imposed on the displacement parameters by the TLS model for any molecular site symmetry.

Introduction

For many chemical bonds, the contribution of bond-stretching vibrations to the atomic thermal displacement parameters can be expected to be relatively small in comparison with angle bending, torsional and intermolecular vibrations. This is the basis of the *rigid-bond criterion* for the physical soundness of independently refined anisotropic displacement parameters (Hirshfeld, 1976). If we define the coordinate system by the unit translations of the crystal lattice

\mathbf{a}_i , the harmonic-temperature-factor expression is given by

$$T = \exp(-2\pi^2 \sum U^{ij} h_i h_j) = \exp(-2\pi^2 \mathbf{h}^T \mathbf{U} \mathbf{h}), \quad (1)$$

and the mean-square displacement (m.s.d.), i.e. the second moment of the probability density function (p.d.f.), along the unit vector $\mathbf{s} = \sum s^i \mathbf{a}_i$ is

$$z^2(\mathbf{s}) = \mathbf{s}^T \mathbf{M} \mathbf{U} \mathbf{M} \mathbf{s} = \mathbf{s}^{*T} \mathbf{U} \mathbf{s}^*, \quad \mathbf{s}^* = \mathbf{M} \mathbf{s} = \sum s^i \mathbf{a}^{*i}, \quad (2)$$

\mathbf{M} being the metric tensor $M_{ij} = \mathbf{a}_i \cdot \mathbf{a}_j$ and \mathbf{a}^{*i} the reciprocal coordinate system. In a unitary system, $M_{ij} = \delta_{ij}$. The rigid-bond criterion stipulates that the m.s.d.'s of atoms A and B along a covalent bond $A-B$ should be approximately equal,

$$z^2(A \rightarrow B) \approx z^2(B \rightarrow A). \quad (3)$$

This is a necessary but not a sufficient condition for a bond to be undeformable. It has been found to hold for numerous structures (Trueblood & Dunitz, 1983), and may apply also to non-bonded atoms within a molecule (Rosenfield, Trueblood & Dunitz, 1978). This observation leads naturally to the idea, already proposed by Rollett (1970), of introducing rigid bonds as constraints or restraints in the least-squares refinement. Related to this is the concept of riding motion where the difference of the m.s.d.'s is kept finite (Konnert & Hendrickson, 1980). The generalization for anharmonic displacement parameters results in conditions analogous to (3) for the higher moments of the p.d.f.'s. For a Gram-Charlier series expansion (Johnson & Levy, 1974), these are

$$\begin{aligned} z^3(\mathbf{s}) &= \sum c^{ijk} s_i^* s_j^* s_k^*, \\ z^4(\mathbf{s}) &= \sum c^{ijkl} s_i^* s_j^* s_k^* s_l^* + 3[z^2(\mathbf{s})]^2. \end{aligned} \quad (4)$$

The advantages of constrained refinements are well-known (Pawley, 1972). Since we may want to impose the rigid-bond condition (3) between two atoms which are not covalently bonded, we refer in the following to *rigid-link constraints*. We prefer not to refer to distances in this context because such constraints involve only displacement parameters, and not atomic positions. Conditions imposed on the length of interatomic vectors and on angles are called *shape constraints*. These are completely independent of rigid-link constraints.

The TLS formalism of Schomaker & Trueblood (1968) is widely used to describe the rigid-body motions of molecules. It is easily shown that in a rigid-body molecule satisfying the TLS equations all bonded and non-bonded interatomic links are rigid. In the following only unitary coordinate systems and a matrix notation as in Johnson & Levy (1974) are used. The anisotropic displacement tensor of an atom at position \mathbf{r}_m is

$$\mathbf{U}(m) = \mathbf{T} + \mathbf{R}_m \mathbf{L} \mathbf{R}_m^T + \mathbf{R}_m \mathbf{S} + \mathbf{S}^T \mathbf{R}_m^T. \quad (5)$$

The antisymmetric matrix \mathbf{R}_m is used to express the vector product in matrix notation, i.e. $\mathbf{R}_m \mathbf{r} = \mathbf{r} \times \mathbf{r}_m$. The m.s.d. of atom A along the link $\mathbf{d} = \mathbf{r}_B - \mathbf{r}_A$ is

$$z^2(A \rightarrow B) = (\mathbf{d}^T \mathbf{d})^{-1} [\mathbf{d}^T \mathbf{T} \mathbf{d} + \mathbf{v}^T \mathbf{L} \mathbf{v} + \mathbf{v}^T \mathbf{S} \mathbf{d} + \mathbf{d}^T \mathbf{S}^T \mathbf{v}], \quad (6)$$

where $\mathbf{v} = \mathbf{R}_A^T \mathbf{d} = \mathbf{R}_B^T \mathbf{d} = \mathbf{r}_A \times \mathbf{r}_B$. This is invariant when A and B are interchanged and the link is thus rigid. Note that surfaces representing the root-m.s.d. are not identical with surfaces of constant probability (Nelmes, 1969). The radius vectors of the thermal ellipsoids of two atoms along a rigid link are in general not of equal length.

Rigid-link and TLS constraints

The appropriateness of the TLS model is often discussed in terms of rigid bonds and rigid angles, i.e. by rigid links in general (Rosenfield, Trueblood & Dunitz, 1978). In the following, we address therefore the question whether rigid-body molecules can be defined by rigid-link constraints. We will clarify the differences between the two concepts by showing that in general the rigid-link conditions are not linearly independent, and that the TLS model may include additional constraints which cannot be expressed in terms of rigid links. These constraints may be difficult to interpret or justify with physical arguments. The problem will first be solved for molecules with site symmetry 1. The \mathbf{T} , \mathbf{L} and \mathbf{S} tensors are usually obtained by a least-squares fit from the individual atomic harmonic displacement tensors using (5). Alternatively, they may be refined directly with respect to the X-ray diffraction data (Pawley, 1972). The latter procedure is equivalent to introducing a set of linear constraints between the $U^{ij}(m)$. In particular, if there are t independent TLS parameters for a molecule comprising N atoms, the number of these linear TLS constraints is $q_N = 6N - t$. It is well known that the trace of \mathbf{S} is indeterminate, and that a singularity will occur if all atoms of a rigid body lie on a conic section (Schomaker & Trueblood, 1968). Apart from this, there appears to exist no general method for the determination of t . The values reported in Table 1 have been obtained by explicit and tedious analyses of (5) for particular geometries. Results have been checked with numerical examples. By virtue of (6), a rigid-body molecule necessarily has $N(N-1)/2$ rigid links, each of which represents a linear relation between the $U^{ij}(m)$. These relations form a $6N$ times $N(N-1)/2$ constraint matrix. Let Q_N be its rank. Since all rigid-link conditions must be equivalent to TLS constraints, but the reverse is not implied by (6), it follows that

$$Q_N \leq q_N, \quad (7)$$

i.e. a full set of rigid links represents a constraint equivalent to, or weaker than, the TLS model.

(a) *Linear molecules*

Without loss of generality, we may align the molecule along the x axis. The atomic-displacement tensors comprise then N terms $U^{11}(m)$ describing the in-line movements along x , and $5N$ out-of-line terms. Likewise, TLS has one in-line term T^{11} and 13 out-of-line terms (ten for $N = 2$). Obviously, $Q_N = N - 1$, since $U^{11}(m) = U^{11}(n)$ and $U^{11}(n) = U^{11}(p)$ implies $U^{11}(m) = U^{11}(p)$. With respect to the in-line terms, the rigid links are therefore equivalent to TLS. This is not the case for the molecule imbedded in three-dimensional space. There are $5N - 13$ TLS constraints between out-of-plane U^{ij} terms which do not represent rigid links (Table 1). These are related to bending modes. Only for the dumbbell $N = 2$ are TLS and the rigid link equivalent.

(b) *Planar molecules*

We may place the molecule in the xy plane. The atomic-displacement tensors then comprise $3N$ in-plane terms $U^{11}(m)$, $U^{22}(m)$ and $U^{12}(m)$, and $3N$ out-of-plane terms $U^{13}(m)$, $U^{23}(m)$ and $U^{33}(m)$. Likewise, TLS for $N \geq 3$ has six in-plane terms T^{11} , T^{22} , T^{12} , L^{33} , S^{31} and S^{32} , and $t - 6$ out-of-plane terms. Rigid-link conditions exist only between in-plane terms, and therefore $Q_N \leq 3N - 6$ in analogy to (7). Suppose that we have identified an N -atom molecular fragment where a complete set of rigid links is equivalent to the TLS constraints, i.e. $Q_N = 3N - 6$. If we add an $(N + 1)$ th atom to this fragment, the number of in-plane displacement parameters is increased by the three in-plane $U^{ij}(N + 1)$, and the total number of links by N . These new links are represented by N linear equations, calculated by using (2) and (3), between the new $U^{ij}(N + 1)$ and the $U^{ij}(1)$ to $U^{ij}(N)$ of the original fragment:

$$\sum_{i=1}^2 \sum_{j=1}^2 s_i^*(N + 1, m) s_j^*(N + 1, m)$$

$$[U^{ij}(N + 1) - U^{ij}(m)] = 0, \quad 1 \leq m \leq N. \quad (3')$$

The equations of any three non-collinear links are linearly independent. If three such links can be found, the $U^{ij}(N + 1)$ can be eliminated from the remaining $N - 3$ equations which are thus transformed into $N - 3$ new equations between the $U^{ij}(1)$ to $U^{ij}(N)$. Since they have been derived from rigid-link equations, they must be equivalent to a combination of TLS constraints. But Q_N is already at its maximal value. The $N - 3$ new equations are therefore redundant and $Q_{N+1} = 3(N + 1) - 6$. The three rigid links in a triangle are linearly independent, thus $Q_3 = q_3 = 3$ (Table 1), and the rigid links are equivalent to TLS. By successively adding atoms with three non-collinear links, molecules of increasing complexity can be constructed possessing in-plane displacement parameters of a rigid body. For $N \geq 5$, TLS gives additional rela-

Table 1. *Comparison of TLS and rigid-link constraints*

Definitions: t = number of independent TLS terms; $q = 6N - t$ = number of TLS constraints between the $B^{ij}(k)$; Q = maximum number of independent rigid-link constraints, $p = q - Q$ = number of TLS-only constraints. The molecule occupies a site with symmetry 1.

Geometry of N -atom molecule	N	t	q	Q	p
Linear	2	11	1	1	0
Linear	≥ 3	14	$6N - 14$	$N - 1$	$5N - 13$
Triangle	3	15	3	3	0
Quadrangle	4	18	6	6	0
Planar N -gon*	≥ 5	19	$6N - 19$	$3N - 6$	$3N - 13$
Planar N -gon†	≥ 6	20	$6N - 20$	$3N - 6$	$3N - 14$
$N - 1$ atoms collinear	≥ 4	17	$6N - 17$	$2N - 3$	$4N - 14$
Tetrahedron	4	18	6	6	0
Three-dimensional‡	5	20	10	10	0
Three-dimensional‡	6	20	16	15	1
Three-dimensional‡	7	20	22	21	1
Three-dimensional‡	8	20	28	28	0
Three-dimensional‡	≥ 8	20	$6N - 20$	$6N - 20$	0
Centred octahedron	7	20	22	18	4
Centred cube	9	20	34	32	2
Pyramid on $(N - 1)$ gon	≥ 5	20	$6N - 20$	$4N - 10$	$2N - 10$
Bipyramid on $(N - 2)$ gon	≥ 5	20	$6N - 20$	$5N - 15$	$N - 5$
Two non-intersecting lines	≥ 5	19	$6N - 19$	$4N - 11$	$2N - 8$

* Atoms lie on a conic section, e.g. regular N -gon.

† Atoms do not lie on a conic section.

‡ Except some particular geometries.

tions between out-of-plane U^{ij} terms which eliminate bending movements. Thus, the following recipe can be used to determine the number Q_N of independent rigid links of a planar molecule:

(i) choose three non-collinear atoms ($Q_3 = 3$), or four atoms forming a quadrangle ($Q_4 = 6$);

(ii) add consecutively atoms having three non-collinear links to the previously chosen atoms, thus $Q_N = Q_{N-1} + 3$;

(iii) if there are no more atoms as in (ii), add the remaining atoms in less-general positions, increasing Q_N by 2.

These rules always give a set of Q_N independent links, but they do not permit one to enumerate all possible such sets (see examples below).

For all but one types of planar molecules, $Q_N = 3N - 6$ (Table 1). This is also the number of independent distances to be specified for the rigid-body *shape* constraint of a two- or three-dimensional N -atom molecule imbedded in three-dimensional space, or the number of its internal degrees of freedom. In this case, however, the constraint equations are quadratic and this introduces some complications not to be discussed here. The above rules (i) and (ii) can nevertheless also be used to construct shape-constrained three-dimensional molecules, starting with the six distances of a four-atom fragment. Again, the rules do not permit one to enumerate all possible sets of distances. In particular, the rigidity of triangulated *convex* polyhedra (Loeb, 1976), e.g. an octahe-

dron defined by its 12 edges, cannot be demonstrated in this way.

(c) *Three-dimensional molecules*

Much of the procedure described for planar molecules is also valid in three dimensions. In general, there are 20 determinable independent TLS terms, resulting in $q_N = 6N - 20$. Suppose that $Q_N = q_N$ for an N -atom fragment with $N \geq 6$. An additional $(N + 1)$ th atom adds six new $U^{ij}(N + 1)$ terms and N new links. If the atom is in a general enough position, we may choose six independent ones among them in such a way that no more than three are coplanar and none are collinear. These can be used to eliminate all $U^{ij}(N + 1)$ from the remaining $N - 6$ equations. The new equations between the $U^{ij}(1)$ to $U^{ij}(N)$ thus created must be redundant because the N -atom rigid body is completely characterized by the Q_N equations. It is also evident by analogous reasoning that all links are in general independent for $N = 3$ to 7, i.e. $Q_N = N(N - 1)/2$. For $N = 4$ and 5, we obtain $Q_N = q_N$ (Table 1). For $N = 6$ and 7, however, there are not enough links to specify completely a rigid body, and TLS implies an additional constraint. Taking as an example a regular octahedron with atoms at $\pm(x00, 0x0, 00x)$, this constraint has been identified from (5) with the rigid-link conditions. It reads $U^{23}(x00) + U^{13}(0x0) + U^{12}(00x) = U^{23}(\bar{x}00) + U^{13}(0\bar{x}0) + U^{12}(00\bar{x})$. Therefore, we cannot predict Q_8 from Q_7 using the previous arguments. Numerical calculation shows, however, that by adding an eighth atom to a seven-atom molecule in the same way as discussed above, all seven new links are independent, and in fact $Q_8 = q_8$. This is true, for example, for all kinds of distorted cubes, for all configurations of ethane-like molecules and for coordinates obtained with a random-number generator. The anomaly for $N = 6$ and 7 appears to be connected with the indeterminate trace of S of the TLS model. If there were in general 21, and not just 20, determinable TLS terms, the number of TLS constraints would be $q'_N = 6N - 21$. The procedure to find Q_N would then be identical with that to be used for shape constraints of five- and six-dimensional molecules imbedded in six-dimensional space.

The procedure for choosing independent links closely follows that proposed for planar molecules. It starts by choosing four atoms of which no more than two are collinear ($Q_4 = 6$). Adding a fifth, sixth, seventh and eighth atom in general positions as described above adds four, five, six and seven independent links respectively. From there on, every additional atom in a general position adds six independent links. Atoms in less-general positions increasing Q_N by less than six are added at the end of the procedure.

(d) *Molecules with site symmetry higher than 1*

Let the positions and displacement tensors of two atoms related by a point-symmetry operation A be (r, U) and (Ar, AUA^T) respectively. The rigid-link condition along $Ar - r = (A - I)r$ is then

$$r^T[(A^T - I)U(A - I) - (A - I)U(A^T - I)]r = 0, \quad (8)$$

I being the identity matrix, and $A^{-1} = A^T$. Introducing for A an n -fold rotation axis n or rotoinversion axis \bar{n} along z gives

$$n: \sin \varphi (\cos \varphi - 1) \{ \} = 0, \quad (9a)$$

$$\bar{n}: \sin \varphi [(\cos \varphi + 1) \{ \} + 2r_3(r_2 U^{13} - r_1 U^{23})] = 0, \quad (9b)$$

$$\{ \} = \{ (U^{11} - U^{22})r_1 r_2 - U^{12}(r_1^2 - r_2^2) \}, \quad \varphi = 2\pi/n.$$

From this, the following implications of symmetry are derived:

(i) $A^T = A$ is a solution of (8) and (9), independently of U . Thus, links between two atoms related by $\bar{1}$, 2 or m are always rigid. This is also the case for atoms related through the centre of a rotoinversion axis, specifically for atoms located on a $\bar{4}$ axis ($r_1 = r_2 = 0$).

(ii) For $\varphi \neq 0$ or π , and $r_3 = 0$ in (9b), a φ -independent relation between the U^{ij} is obtained. Thus, all links of a regular planar n -gon generated by an n or \bar{n} axis are rigid if one of the edges is specified to be rigid. This is obvious for triangles and squares. In a hexagon, a rigid link between nearest-neighbour atoms related by a sixfold rotation implies rigid links between next-nearest neighbours related by a threefold rotation. The eigenvectors of the displacement tensor U^{ij} ($i, j = 1, 2$) in the plane of the n -gon are then parallel and perpendicular to the radius vector $(r_1 r_2 0)$.

(iii) If (9a) is satisfied, the part containing $\{ \}$ in (9b) is also zero independently of φ . Therefore, only two rigid-link conditions of a set of equivalent atoms (general orbit) generated by a rotation axis n parallel to a rotoinversion axis \bar{m} ($n, m \geq 3$) are independent. This is obvious for the groups $\bar{3}$, $\bar{6}$ and $4/m$, but non-trivial for $6/m$ where rigid links between nearest-neighbour atoms generated by operations 6 and $\bar{3}$ imply rigid links also between next-nearest neighbours generated by 3 and $\bar{6}$. One of the eigenvectors of the displacement tensor U is then perpendicular to the plane formed by the n, \bar{m} axes and the atomic position vector r .

(iv) It can be shown by tedious algebra that only four rigid-link conditions of a set of equivalent atoms (general orbit) generated by any of the cubic point groups are independent. These may be chosen between atoms generated by the four threefold axes, namely from $r_1 r_2 r_3$ to $r_3 r_1 r_2$, $r_3 \bar{r}_1 \bar{r}_2$, $\bar{r}_3 \bar{r}_1 r_2$ and $\bar{r}_3 r_1 \bar{r}_2$, respectively. The displacement tensor U is then

cylindrically symmetric, represented by an ellipsoid of revolution with axis r .

These symmetry implications permit one to identify for *all* sets of equivalent atoms, *i.e.* for general as well as for special orbits, the links which may be independently specified as rigid. For general orbits the number of such links is 0 for the groups 1, $\bar{1}$, 2, m , $2/m$, 222 , $mm2$, mmm ; one for the groups 4, $\bar{4}$, 422 , $4mm$, $\bar{4}2m$, 3, 32, $3m$, 6, 622 , $6mm$; two for the groups $4/m$, $4/mmm$, $\bar{3}$, $\bar{3}m$, $\bar{6}$, $6/m$, $\bar{6}m2$, $6/mmm$; four for the cubic groups. These numbers are smaller for special orbits. Orbits situated on the diagonal mirror planes of $\bar{4}3m$ and $m3m$, for example, have only the two independent links from $r_1 r_1 r_3$ to $r_3 \bar{r}_1 \bar{r}_1$ and $\bar{r}_3 \bar{r}_1 r_1$, respectively, the other two links of (iv) being perpendicular to mirror planes.

In addition, molecular site symmetry may result in (v) symmetrically equivalent links $r_m - r_n$ and $A(r_m - r_n)$, where m and n are inequivalent atoms, and

(vi) a reduction of the number of TLS-only constraints.

The maximum number and possible choice of independent rigid links for molecules containing inequivalent atoms is easily obtained with the rules given in (b) and (c), and taking into account the implications of symmetry. The number of independent TLS terms can be obtained from Schomaker & Trueblood (1968), except for special geometries which require an explicit analysis of (5). The number of independent U^i terms is obtained in the usual way from the site symmetries of the individual atoms. From this, the number of TLS-only constraints is determined.

(e) Examples (Table 1)

In the following the molecular site symmetry is assumed to be 1 unless specified otherwise. The interested reader is invited to verify the examples by marking the links to be rigid in a sketch of the molecule. We do not publish such figures because they are constantly evolving during the assignment of links.

Planar hexagon, $N = 6$. There are 15 links, *viz* six edges, six short diagonals spanning one corner and three long diagonals spanning two corners. Three of them are redundant since $Q_6 = 12$. There are $\binom{15}{3}$ ways of choosing 12 links out of 15, 50 of which cannot be transformed into each other by a permutation of the corners. Of these, 39 can be constructed by the procedure given above. Numerical calculation shows that the links of three others are also linearly independent. The remaining eight combinations of 12 links each only represent 11 independent equations. Included among these eight cases is the most symmetrical choice of links, namely the six edges

and the six short diagonals. For a discussion of the effects of molecular site symmetry, a coordinate system is chosen with x through a corner, y through an edge and z perpendicular to the plane of the hexagon. Since the atoms lie on a conic section, out-of-plane TLS terms from Table 4 of Schomaker & Trueblood (1968) must be reduced by 1. Site symmetry $1m1$ makes two short diagonals parallel to y rigid, and $Q_6 = 6$. In plane, there are indeed four TLS and ten U^i terms. Out of plane, there are seven TLS and ten U^i terms, and thus three TLS-only constraints as compared with five for symmetry 1. For $m11$ and $11m$ two and one TLS-only constraints are obtained respectively. Finally, for the symmetries $112/m$, $m2m$, 6 and their supergroups, there remain no TLS-only constraints. The groups $\bar{3}m$, 622 , $6mm$ and $6/mmm$ imply all links to be rigid since every one of them is perpendicular to a mirror plane or a twofold axis.

Centred octahedron, $N = 7$. The centring atom adds only three independent links to the octahedron with $Q_6 = 15$. Therefore $Q_7 = 18$, and there are no rigid-link conditions for $U^{12}(7)$, $U^{13}(7)$ and $U^{23}(7)$. Displacing the centring atom along z reduces the maximum molecular site symmetry to $4mm$ and gives $Q_7 = 20$ with no rigid-link condition for $U^{12}(7)$. The TLS-only constraint of the simple octahedron mentioned in (c) is obeyed independently of the U^i for the site symmetries $\bar{1}$, m , . . . , 2, 4 . . . and their supergroups [oriented site symmetry symbols are explained in *International Tables for Crystallography* (1983)]. The additional TLS-only constraints of the centred octahedron are obeyed if $U^i(7) = 0$ for $i \neq j$, as is the case *e.g.* for mmm . . . All links of the simple octahedron are rigid for the groups $\bar{3}m$, 432 , $m3m$ and $43m$; for $43m$ there also exists a TLS-only constraint. In the centred octahedron possessing one of these symmetries, one rigid link can be specified from the centre to a summit.

Pentagonal pyramid, $N = 6$. The apical and four of the equatorial atoms form a distorted five-atom pyramid with $Q_5 = 10$. The last equatorial atom adds only four, and not five independent links, namely three in the equator and one to the apical atom; thus $Q_6 = 14$. By adding additional atoms in the equator, the number of independent links for a general pyramid based on an $(N-1)$ gon is easily shown to be $Q_N = 4N - 10$. For site symmetry m , the number of TLS-only constraints is reduced to $N - 5$, independently of the orientation of the mirror plane and the parity of N . The expression for a bipyramid based on an $(N-2)$ gon is obtained by starting with the two apical and four of the equatorial atoms, for which $Q_6 = 15$. A mirror plane parallel to the $(N-2)$ gon eliminates all TLS-only constraints.

Two non-intersecting skew lines, each one occupied by at least three atoms. Starting with four atoms, two on each line, we obtain $Q_4 = 6$. A fifth atom adds three independent links, $Q_5 = 9$. This configuration corresponds to a tetrahedron with one centred edge

($t = 19$). Adding a sixth atom not in line with the fifth gives four more independent links, three of which are coplanar. Every additional atom added to this configuration on either of the lines adds four independent links, resulting in $Q_N = 4N - 11$. For a tetrahedron centred on two opposite edges and possessing site symmetry $42m$, $t = 5$ and $Q_6 = 2$. Adding four symmetry-equivalent atoms on these edges increases Q by 3, and the number of U^j terms by four. The number of TLS-only constraints is thus $n - 1$ for $N = 4n + 2$.

Concluding remarks

It is often useful to impose constraints or restraints on the structural parameters during refinement with respect to structure factors. This is particularly advisable for parameters whose values are more easily obtained from a more sophisticated model than from an unconstrained least-squares refinement. Thus, the rigid-body model might be imposed on the harmonic displacement parameters, but even molecules of only medium complexity are hardly ever rigid, and metal-ligand bonds may be particularly non-rigid (Ammeter, Bürgi, Gamp, Meyer-Sandrin & Jensen, 1979). Rigid links in the form of restraints provide a computationally simpler means to relax the TLS conditions during structure refinement than a segmented-body model or the introduction of some internal molecular vibrations. They may be limited to the covalent bonds only, where they may in fact be well justified. They can, on the other hand, be applied also to links between non-bonded atoms. For many three-dimensional molecules, and particularly for the more complex ones, they can be made equivalent to the full TLS model, and cover thus the whole domain between individual rigid bonds and a rigid body. There are molecules where the rigid-link constraints are always weaker than TLS, but the former are more easily justified by physical arguments than the TLS-only constraints. Thus for planar molecules out-of-plane internal vibrations are probably less negligible than in-plane ones. For small molecules with less than five atoms, the rigid-link constraints can almost always be made equivalent to TLS, and are more easily imposed than the latter. In the case of molecules with site symmetry higher than 1, it is simply necessary to identify the non-trivial and symmetrically inequivalent links, in order not to specify the same condition more than once. This can be done by hand, or accomplished by the program. All other implications of symmetry are taken care of automatically by a standard least-squares program. The results of the restrained refinement may be subsequently expressed in terms of rigid-body TLS or segmented-body parameters.

The rules discussed in this paper allow one to determine the number of independent links Q_N , and

thus indicate to what extent a rigid-link model can be made equivalent to TLS. The numerically most advantageous choice of the independent links represents a more difficult problem which depends on the details of the molecular geometry. It is evident that a near-violation of our above rules, e.g. the choice of nearly collinear links, should be avoided. The independent links obtained by our rules are usually not disposed according to the symmetry of the molecule, as has been illustrated by the regular hexagon. If all links, including the redundant ones, are specified to be rigid in a restrained refinement, the numerical problems disappear. The choice of the weights should then also be influenced by the presence of these redundant links.

The introduction of rigid links in the form of restraints in a crystallographic least-squares program is a relatively easy programming task. Coupled with shape constraints, they allow the refinement of groups of atoms, e.g. phenyl rings, on the basis of a reasonable physical model. We prefer this scheme to a group refinement with Euler angles (Doedens, 1970) and TLS parameters. We also recommend it for disordered molecules (Bünzli, Leonard, Plancherel & Chapuis, 1986) where the refinement of split atoms with isotropic displacement parameters is usually not justifiable. The relevant modifications of our local version of the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) have been tested with the 14-atom molecule boratrantrione (2,8,9-trioxa-5-aza-1-borabicycloundecane-3,7,10-trione), $C_6H_6BNO_6$, $Q_{14} = 64$ (Bürgi, Delley, Hauser, Moeckli, Schwarzenbach & Thong, 1987; Bürgi & Hummel, 1987). The displacement parameters obtained with a complete set of rigid-link restraints equivalent to TLS satisfied (5) perfectly.

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Fundamentals for the Description of Hexagonal Lattices in General and in Coincidence Orientation

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Abstract

The connection between the rotation matrix in hexagonal lattice coordinates and an angle-axis quadruple is given. The multiplication law of quadruples is derived. It corresponds to multiplying two matrices and gives the effect of two successive rotations. The relation is given between two quadruples that describe the same relative orientation of two lattices owing to their hexagonal symmetry; a unique standard description of the relative orientation is proposed. The restrictions satisfied by rotations generating coincidence site lattices (CSL's) are derived for any value of the axial ratio $\rho = c/a$. It is shown that the law for cubic lattices, where the multiplicity Σ of the CSL is equal to the lowest common denominator of the elements of the rotation matrix, does not always hold for hexagonal lattices. A generalization of this law to lattices of arbitrary symmetry is given and another, quicker, method of determining Σ for hexagonal lattices is derived. Finally, convenient algorithms are described for determining bases of the CSL and the DSC lattice.

1. Introduction

Consider a boundary between two grains of the same homogeneous phase. The boundary energy per unit area depends on the relative orientation of the two grains. It has often been observed that this energy has a relative minimum if a significant fraction $1/\Sigma$ of symmetry translations of one grain are simul-

taneously symmetry translations of the other. The lattice formed by the common translations is called the coincidence site lattice (CSL), Σ its multiplicity. The relative orientation of the two grains can be described by a rotation mapping one set of symmetry translations onto the other.

Motivated by investigations into the frequency with which different relative orientations of grains occur in hexagonal materials, considerable attention has been given to coincidence rotations, *i.e.* rotations generating CSL's in hexagonal lattices (Warrington, 1975; Fortes & Smith, 1976; Bonnet, Cousineau & Warrington, 1981; Hagège, Nouet & Delavignette, 1980; Bleris, Nouet, Hagège & Delavignette, 1982). This last paper, which will be referred to as BNHD, uses an axis-angle description in lattice coordinates for the rotations, which turns out to be convenient for deriving the coincidence rotations.

BNHD and a recent paper by Hagège & Nouet (1985) have stimulated the present investigation because we have found that the two different rules proposed for determining the multiplicity Σ do not always give the correct result. The main purpose of the present investigation is to derive universally valid methods for determining Σ . At the same time, some gaps are filled in the derivation of the BNHD method to find the coincidence rotations and some arguments are simplified.

Some of the results on coincidence rotations including the first method of determining Σ have already been presented without complete proofs in two pre-