that the transition between the two ordered phases $\varepsilon$ and $\varepsilon'$ also appears to be connected with atomic displacements (Andersson *et al.*, 1978) which thus seem to play a significant part in the structural behaviour of the system.

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# Calculation of Coulombic Energy for Molecular Crystals

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## Abstract

The first Bertaut series has been examined for practical application to evaluating coulombic contribution to lattice energy in molecular crystals; especially with Templeton's correction, its use seems to be quite advantageous because of its simplicity and does not seem to involve a longer computing time than other methods. For rigid molecules, a scheme of obtaining first and second derivatives of coulombic energy with respect to molecular rotation or translation is shown; this scheme can be easily applied to packing energy minimization and also to constrained refinement of crystal structures.

## Introduction

Calculation of various properties in molecular crystals by packing analysis seems nowadays to be a quite well-established routine, which affords promising applications in obtaining, for instance, vibrational data, temperature factors and even thermodynamic functions connected with the second law, such as entropy, free energy, *etc.*, or in the field of surfaces.

In our treatment of several 'rigid' molecules (Filippini, Gramaccioli, Simonetta & Suffritti, 1973, 1974*a*,*b*, 1975*a*,*b*, 1976, 1978), we have excluded coulombic interactions so far; however, in many cases they cannot be neglected, especially when polar molecules are dealt with, and even for 'ordinary' hydrocarbons the introduction of charge effects seems to lead to a definite improvement (Warshel & Lifson, 1970; Williams, 1974).

For molecular crystals, three points are particularly important. The first is connected with the possibility of easy minimization of packing energy by some automatic routine, so that comparison between the packing conformations calculated from different potential functions becomes possible, and also a starting point for lattice-dynamical calculations is obtained (Pawley, 1967); for this reason, if the calculation of derivatives with respect to molecular coordinates (positional and orientational) in the unit cell is easy and fast, this may become an essential advantage. The second point is

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connected with the almost ubiquitous presence of hydrogen, which involves the existence of charged points which are close to each other. For instance, a satisfactory description of a hydrocarbon may be obtained by imagining opposite charges (of the order of 0·1–0·2 electrons) to be present on neighbouring C and H atoms, their distance being consequently of the order of the C—H bond lengths, *i.e.* about 1 Å. Hydrogen-containing ionic crystals are common, but they are not the greatest majority of substances as they are for molecular crystals. It follows that for many 'classic' ionic examples the shortest distances between charged atoms fall between 1·3 and 1·7 Å and, for a considerable number of them, including, for instance, sodium chloride, distances are still longer (beyond 2 Å). As we shall see, the presence of short distances between charged points involves a considerably greater difficulty in reaching convergence.

The last important point is connected with the necessary accuracy of our results. This is a delicate question indeed, since on the one hand considerable errors can be made if no particular precaution is taken in checking for series termination, whereas on the other molecular charges are known with comparatively less accuracy than for ions, such as $Na^+$, $Cl^-$, *etc.* For this reason, a real need of evaluating the electrostatic lattice energy in molecular crystals with an accuracy better than 1% is practically never encountered, and an accuracy of the order of 10–20% is generally sufficient for most cases. As is well known, the advantages of one procedure with respect to another may be quite different at various accuracy levels (Jones & Templeton, 1956), and this is also a reason for determining the proper choice.

For molecular crystals, coulombic effects have so far been calculated by multipole expansion (Pople, 1954; Pawley & Leech, 1977; Schnepp, 1975; Neto, Righini, Califano & Walmsley, 1978), or by representing the charge distribution by arrangements of discrete charges (Luty, 1977; Pawley & Leech, 1977) or discrete multipoles (Rae, 1972; Reynolds, 1973). For the general problem of calculating the coulombic energy in crystals with localized discrete charges, there are substantially two 'classic' procedures, one of which is due to Ewald (1921) and the other to Bertaut (1952); for a detailed discussion about various improvements and routines, see Catti (1978). A convergence acceleration procedure due to Williams (1971, 1972, 1974) is also used; this procedure has the advantage of simultaneously accounting for coulombic and van der Waals energy (if the latter is given as 'Lennard-Jones 12-6' or similar functions). However, it requires that the geometric-mean combining law holds, and the presence of empirical convergence constants; moreover, the derivatives of energy, as calculated by these methods appear to be somewhat elaborate, and this – as we have seen – is an important point to be considered when automatic procedures for energy minimization are taken into account.

When multipole moments can be adequately described by figuring out localized charges on the atoms, the first series proposed by Bertaut is, however, so simple to deal with that a discussion about its practical application also to molecular crystals has seemed to us to be quite useful. This is in line with a very recent article by Bertaut (1978), who replaces dipoles, and – more generally – multipoles, with equivalent charges.

## Method of calculation

In his paper, Bertaut (1952) gives the following series as equation (41):

$$W_c = 18\pi R^2/V \sum_{\mathbf{h}} |F(\mathbf{h})|^2 (\sin\alpha - \alpha\cos\alpha)^2/\alpha^8 - 3/(5R) \sum_j q_j^2. \qquad (1)$$

Here $W_c$ is the electrostatic energy of the unit cell, $R$ is a distance not exceeding one-half of the shortest distance between the atoms, $q_j$ is the charge on the $j$th atom, $V$ is the cell volume, $\alpha = 2\pi|\mathbf{h}|R$, and $F(\mathbf{h})$ are the Fourier transforms of the charge density, which for the point-charge crystal are obtained just as crystallographic structure factors, where the atomic scattering factors are replaced with atomic charges (see Appendix).

According to Templeton (1954), the accuracy of the results from (1) is substantially improved if a further term $\Delta W_c = Q/R \sum_j q_j^2$ is added, which accounts for the error of series termination. Here $Q$ is the value of a relatively elaborate function, which is tabulated in Table 1 of Templeton's work *versus* various values of $\beta/\pi = 4R(\sin\theta/\lambda)_{\max}$ (the third column in the same table gives the percentage error in the Madelung constant; the assumptions on which this error has been evaluated are valid only for ionic crystals, and do not apply to our

Table 1. *A comparison between the values of the $Q$ function as calculated by Templeton* (1954) *in his Table* 1 (*first column*) *and by our approximation* $Q = 0{\cdot}016161\,x^{-3{\cdot}0381}$

| $x = \beta/\pi$ | $Q_{\text{Templeton}}$ | $Q_{\text{approx}}$ |
|---|---|---|
| 1·0 | 0·015992 | 0·016161 |
| 1·5 | 0·004715 | 0·004715 |
| 2·0 | 0·001950 | 0·001967 |
| 2·5 | 0·000996 | 0·000999 |
| 3·0 | 0·000574 | 0·000574 |
| 3·5 | 0·000362 | 0·000359 |
| 4·0 | 0·000242 | 0·000240 |
| 4·5 | 0·000170 | 0·000167 |
| 5·0 | 0·000123 | 0·000121 |

case). We have seen that the dependence of $Q$ upon $\beta/\pi$ can be approximated quite well by a relatively simple expression $Q = 0{\cdot}016161(\beta/\pi)^{-3{\cdot}0381}$; this expression holds quite satisfactorily for any value in the table, except for $\beta/\pi < 1$, a region where the approximation itself is, however, poor (see Table 1). More recently, Bertaut (1978) has given new corrections for series termination errors, in particular for dipolar interaction energy.

First and second derivatives of coulombic energy with respect to molecular coordinates in the unit cell are quite useful for minimization of packing energy. This minimization can be carried out by a Newton–Raphson routine (Filippini, Gramaccioli, Simonetta & Suffritti, 1973), which involves a linear system of the following kind: $\mathbf{M}\Delta\mathbf{u} = \mathbf{d}$, where $M_{ij} = \partial W/\partial u_i \partial u_j$, $W$ is the packing energy (coulombic and van der Waals), $\Delta\mathbf{u}$ is the vector whose components are atomic or molecular shifts, and $d_i = -\partial W/\partial u_i$. Following this procedure, iteration can be performed until no significant change is observed in coordinates and first derivatives of the energy are close to zero. If the unit-cell parameters are kept constant and no variation in charge distribution due to inductive effects is considered, as for small molecular shifts, the derivatives of $W_c$ only involve derivatives of structure factors, which have the advantage of being just in the line of ordinary crystallographic routine.

Table 2. *Results for* NaCl *with various values of R and sin $\theta/\lambda$*

No corrections for series termination have been applied.

| sin $\theta/\lambda$ | No. of reflexions | Coulombic lattice energy (kJ/mol) $R = 1{\cdot}4$ | $R = 1{\cdot}0$ | $R = 0{\cdot}8$ |
|---|---|---|---|---|
| 0·5 | 4 | −863·32 | −867·71 | |
| 0·7 | 12 | −861·98 | −863·32 | −864·99 |
| 0·9 | 24 | −861·64 | −862·44 | −863·90 |
| 1·2 | 58 | −861·56 | −861·81 | −862·48 |
| 1·5 | 110 | −861·48 | −861·64 | −861·98 |

In order to see a practical way of using formula (1) in computer calculations relative to rigid molecules, let us rewrite it:

$$W_c = K \sum_{\mathbf{h}'} p_{\mathbf{h}} |F(\mathbf{h})|^2 - k', \qquad (2)$$

where

$$K = 18\pi R^2/V$$

and

$$k' = (3/5 - Q) \sum_j q_j^2/R + \sum_{ij} q_i q_j / r_{ij}.$$

The last summation in $k'$ corresponds to coulombic interactions within the molecule (here $r_{ij}$ is the distance between the atoms $i$ and $j$) which must be subtracted, since (1) includes all contributions in the unit cell; with our assumption of rigidity and constancy of charge distribution in the various molecules and of unit-cell parameters, the constants $K$ and $k'$ can be evaluated once for all.

The summation in (2) is extended only to symmetrically independent $F$'s, and the prime in $\mathbf{h}'$ is just a reminder of this point. Consequently,

$$p_{\mathbf{h}} = m(\sin\alpha - \alpha\cos\alpha)^2/\alpha^8,$$

where $m$ is the multiplicity of the reflexion; all these factors $p_{\mathbf{h}}$ can be evaluated once for all for each reflexion.

In practice, a table is prepared by generating all combinations of indices for which $1/d$ is below a certain pre-set value of sin $\theta/\lambda$, a parameter which somehow

Table 3. *Coulombic lattice energy* (kJ/mol) *as a function of maximum sin θ/λ for acetylene, benzene and naphthalene*

For each substance, columns (1), (2) and (3) report values uncorrected for series termination, corrected according to Templeton (1954), and number of independent reflexions, respectively.

| | Acetylene | | | Benzene | | | Naphthalene | | |
|---|---|---|---|---|---|---|---|---|---|
| sin $\theta/\lambda$ | (1) | (2) | (3) | (1) | (2) | (3) | (1) | (2) | (3) |
| 0·5 | 9·404 | 4·241 | 62 | 26·775 | 11·283 | 247 | 34·026 | 13·377 | 401 |
| 0·6 | 6·636 | 3·663 | 104 | 20·339 | 11·438 | 427 | 23·220 | 11·355 | 690 |
| 0·7 | 6·397 | 4·543 | 167 | 19·611 | 14·038 | 684 | 22·278 | 14·851 | 1094 |
| 0·8 | 6·268 | 5·028 | 241 | 19·243 | 15·529 | 1008 | 21·759 | 16·806 | 1616 |
| 0·9 | 5·702 | 4·832 | 343 | 17·589 | 14·993 | 1447 | 19·544 | 16·077 | 2294 |
| 1·0 | 5·300 | 4·430 | 461 | 16·253 | 14·365 | 1989 | 17·853 | 15·336 | 3127 |
| 1·1 | 5·091 | 4·622 | 611 | 15·751 | 14·340 | 2643 | 17·124 | 15·240 | 4154 |
| 1·2 | 5·070 | 4·786 | 790 | 15·659 | 14·574 | 3430 | 17·011 | 15·567 | 5380 |
| 1·4 | 4·974 | 4·744 | 1249 | 15·491 | 14·683 | 5452 | 16·630 | 15·638 | 8509 |
| 1·6 | 4·857 | 4·706 | 1843 | 15·018 | 14·566 | 8124 | 16·161 | 15·558 | 12667 |
| 1·8 | 4·844 | 4·735 | 2613 | 14·988 | 14·671 | 11582 | 16·119 | 15·692 | 17952 |
| 2·0 | 4·798 | 4·723 | 3570 | 14·842 | 14·612 | 15882 | | | |
| 2·4 | 4·773 | 4·727 | 6149 | | | | | | |
| 2·8 | 4·756 | 4·727 | 9714 | | | | | | |
| 3·2 | 4·748 | 4·731 | 14446 | | | | | | |

corresponds to the maximum considered packing distance in summations over the direct lattice; examples of convergence as a function of $\sin\theta/\lambda$ are given in Tables 2 and 3. For a certain combination of indices **h**, possible extinctions are checked for each space group, for instance by following the routine proposed by Gavezzotti & Gramaccioli (1973); for evaluation of *m*, the simple method proposed by Brown (1971) seems to be the most adequate for complex cases, whereas a first pre-selection according to the Laue group might be used in order to save computing time and space in the computer memory (for instance, by generating only positive indices for the orthorhombic system, *etc.*). From this table containing the necessary data for all the reflexions to be considered (in general about 1000 for relatively complex cases, see below) the calculation of coulombic packing energy and derivatives is straightforward (see the Appendix).

## Results and discussion

Results from calculations for acetylene (orthorhombic phase), benzene and naphthalene are given in Table 3. For these substances, experimental unit cell and atomic coordinates have been taken from Koski (1975), Bacon, Curry & Wilson (1964) and Cruickshank (1957), respectively. All the C—H distances have been 'normalized' to 1·027 Å, and opposite charges of 0·177 electrons have been assigned to adjacent carbon and hydrogen atoms; percentage errors in evaluating lattice coulombic energy are reported in Table 4.

From these tables, the advantage of applying Templeton's (1954) correction is quite evident, especially for structures like benzene and naphthalene, where the unit cell is not too small, just in agreement with this criterion of approximation. An important question is the choice of maximum $\sin\theta/\lambda$; for instance, accuracy of the order of 1% is obtained only for $\sin\theta/\lambda \geq 1\cdot2$. Consequently, for a structure like naphthalene we should consider more than 5000 independent reflexions. In practice, however, such an accuracy is actually not needed, because of the uncertainty about the charge distribution, which is considerable. The percentage error in coulombic energy can be shown to be about twice as great as the percentage error in the charge. Since in only a few cases the charge distribution in the isolated molecule is claimed to be known at 1% accuracy, whereas for most substances accuracy of 10% is considered to be 'good', we see that this already implies an error of at least 20% in lattice coulombic energy and of 2% only in the most favourable cases; all this, of course, is apart from considering variations in charge from the isolated molecule to the crystal state due to inductive effects.

Table 4. *Percentage errors in evaluating coulombic lattice energy*

For each substance, reference is made to uncorrected and corrected values for series termination.

| | Acetylene | | Benzene | | Naphthalene | |
|---|---|---|---|---|---|---|
| $\sin\theta/\lambda$ | uncorr. | corr. | uncorr. | corr. | uncorr. | corr. |
| 0·6 | 40·2 | 22·5 | 40·0 | 21·8 | 48·2 | 27·5 |
| 0·7 | 35·2 | 4·0 | 34·0 | 4·1 | 42·3 | 5·2 |
| 0·8 | 32·4 | 6·3 | 31·5 | 6·1 | 39·0 | 7·3 |
| 0·9 | 20·5 | 2·1 | 20·2 | 2·5 | 24·8 | 2·7 |
| 1·0 | 12·0 | 6·3 | 11·1 | 1·8 | 14·0 | 2·0 |
| 1·2 | 7·2 | 1·1 | 7·0 | 0·4 | 8·6 | 0·6 |
| 1·4 | 5·1 | 0·3 | 5·9 | ~0·3 | 6·2 | ~0·1 |

For these reasons, a maximum value of 0·9 for $\sin\theta/\lambda$ in benzene and naphthalene is already more than satisfactory, and a reasonable value for an average case may be about 0·6–0·7. For acetylene, since the unit cell is smaller, the correction for series termination becomes effective at a higher value of $\sin\theta/\lambda$; on the other hand, however, just because the unit cell is smaller, extending this parameter does not involve a considerable amount of terms, and we see that also in this case about 1000 independent reflexions are more than sufficient.

In their work, Jones & Templeton (1956) have discussed the advantages of various functions for evaluating the coulombic energy in crystals; these authors show that the Bertaut series with a uniform charge distribution within a sphere, which is just the procedure we have followed, gives the best approximation if accuracy down to 1% is needed, whereas the advantage of other series is clear only when higher accuracy is necessary. A comparison of the convergence with the corresponding one of other procedures, such as Ewald's or Williams' would indeed be interesting; however, the only data of this kind reported in the literature for molecular crystals are given by Williams (1971), who shows the relative error only for the faster converging $r^{-6}$ crystal lattice potential sum in benzene.

On these grounds, and especially when derivatives are needed, the first Bertaut series seems indeed to be the most recommendable for evaluation of coulombic energy in molecular crystals. In practice the procedure is quite fast, because, for instance, we have seen that for naphthalene with $(\sin\theta/\lambda)_{\max} = 1\cdot2$ (and nine atoms in the asymmetric unit), the evaluation of coulombic lattice energy requires about 4 s of execution time on a computer such as Univac 1108, which is a comparable time with other fast procedures such as the one described by Catti (1978); for energy minimization procedures, a run on naphthalene at 5% accuracy, including evaluation of van der Waals interactions up to distances of 15 Å, reached convergence in three steps of a Newton–Raphson routine, employing 3 min on the same computer.

## APPENDIX

The structure factor $F(\mathbf{h})$, for the point-charge crystal, is obtained by replacing the atomic scattering factors with atomic charges $q_n$:

$$F(\mathbf{h}) = \sum_s \exp(2\pi i \mathbf{h}^T \mathbf{t}_s) \sum_n (A_{ns} + iB_{ns}) = A_{\mathbf{h}} + iB_{\mathbf{h}}, \quad (3)$$

where

$$A_{ns} = q_n \cos 2\pi \mathbf{h}_s^T \mathbf{x}_n \quad \text{and} \quad B_{ns} = q_n \sin 2\pi \mathbf{h}_s^T \mathbf{x}_n,$$

the indices $s$ and $n$ range over the space group operations and the atoms in the asymmetric unit, respectively; $\mathbf{h}_s^T = \mathbf{h}^T \mathbf{P}_s$, where $(\mathbf{P}_s|\mathbf{t}_s)$ is a space group operation and

$$\mathbf{h}_s^T \mathbf{x}_n = \sum_{l=1}^{3} h_{sl} x_{nl},$$

where the symmetry transformed reciprocal lattice vector $\mathbf{h}_s$ and the atomic position vector $\mathbf{x}_n$ are referred to the working (preferably cartesian) system.

Given a set of rigid-body parameters $r_l$, *e.g.* Eulerian angles and coordinates of the centre of mass, we wish to minimize the electrostatic interaction energy with respect to these parameters. Since the only quantity in (2) depending on the molecular orientation and location is $|F(\mathbf{h})|^2$, we can write the required derivatives as:

$$W_{c,l} = 2K \sum_{\mathbf{h}} p_{\mathbf{h}} (A_{\mathbf{h}} A_{\mathbf{h},l} + B_{\mathbf{h}} B_{\mathbf{h},l}), \quad (4)$$

$$W_{c,ml} = 2K \sum_{\mathbf{h}} p_{\mathbf{h}} (A_{\mathbf{h}} A_{\mathbf{h},ml} + A_{\mathbf{h},m} A_{\mathbf{h},l} + B_{\mathbf{h},m} B_{\mathbf{h},l} + B_{\mathbf{h}} B_{\mathbf{h},ml}), \quad (5)$$

where the abbreviated partial derivative notation used in tensor algebra has been employed. Thus, $f_{,l} \equiv \partial f/\partial r_l$ and $f_{,ml} \equiv \partial^2 f/\partial r_m \partial r_l$.

Calculation of the needed derivatives follows the same path as in constrained least-squares refinement algorithms (*e.g.* Pawley, 1969, 1971). Since, however, the second derivatives are also involved, we shall present here the required expressions.

Since:

$$A_{\mathbf{h}} = \sum_s \cos 2\pi \mathbf{h}^T \mathbf{t}_s \sum_n A_{ns} - \sum_s \sin 2\pi \mathbf{h}^T \mathbf{t}_s \sum_n B_{ns}, \quad (6)$$

$$B_{\mathbf{h}} = \sum_s \sin 2\pi \mathbf{h}^T \mathbf{t}_s \sum_n A_{ns} + \sum_s \cos 2\pi \mathbf{h}^T \mathbf{t}_s \sum_n B_{ns}, \quad (7)$$

the necessary derivatives are

$$A_{\mathbf{h},l} = \sum_s \cos 2\pi \mathbf{h}^T \mathbf{t}_s \sum_n A_{ns,l} - \sum_s \sin 2\pi \mathbf{h}^T \mathbf{t}_s \sum_n B_{ns,l}, \quad (8)$$

$$B_{\mathbf{h},l} = \sum_s \sin 2\pi \mathbf{h}^T \mathbf{t}_s \sum_n A_{ns,l} + \sum_s \cos 2\pi \mathbf{h}^T \mathbf{t}_s \sum_n B_{ns,l}, \quad (9)$$

$$A_{\mathbf{h},ml} = \sum_s \cos 2\pi \mathbf{h}^T \mathbf{t}_s \sum_n A_{ns,ml} - \sum_s \sin 2\pi \mathbf{h}^T \mathbf{t}_s \sum_n B_{ns,ml}, \quad (10)$$

$$B_{\mathbf{h},ml} = \sum_s \sin 2\pi \mathbf{h}^T \mathbf{t}_s \sum_n A_{ns,ml} + \sum_s \cos 2\pi \mathbf{h}^T \mathbf{t}_s \sum_n B_{ns,ml}, \quad (11)$$

where

$$A_{ns,l} = -2\pi B_{ns} u_{snl}, \quad (12)$$

$$B_{ns,l} = 2\pi A_{ns} u_{snl}, \quad (13)$$

$$A_{ns,ml} = -4\pi^2 A_{ns} u_{snm} u_{snl} - 2\pi B_{ns} v_{snml}, \quad (14)$$

$$B_{ns,ml} = -4\pi^2 B_{ns} u_{snm} u_{snl} + 2\pi A_{ns} v_{snml}, \quad (15)$$

and

$$u_{snl} = \sum_i h_{sl} x_{nl,l}, \quad (16)$$

$$v_{snml} = \sum_l h_{sl} x_{nl,ml}, \quad (17)$$

with

$$x_{ni,l} \equiv \partial x_{nl}/\partial r_l, \quad (18)$$

$$x_{ni,ml} \equiv \partial^2 x_{nl}/\partial r_m \partial r_l. \quad (19)$$

Therefore, the derivatives of $W_c$ can be computed in a straightforward manner, once the choice of rigid body parameters, $r_l$, has been made, and the derivatives of the atomic coordinates, $x_{ni}$, with respect to these parameters are evaluated. For this purpose, the algorithm proposed by Pawley (1969) can be applied and easily generalized to second derivatives, which can be different from zero only if the parameters $r_i$ are exclusively rotation angles.

Especially for cases involving second derivatives, a different general rotation matrix turns out to be useful:

$$\mathbf{R} = \mathbf{R}_{\theta 3} \mathbf{R}_{\theta 2} \mathbf{R}_{\theta 1} = \begin{pmatrix} C_3 & -S_3 & 0 \\ S_3 & C_3 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} C_2 & 0 & S_2 \\ 0 & 1 & 0 \\ -S_2 & 0 & C_2 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & C_1 & -S_1 \\ 0 & S_1 & C_1 \end{pmatrix}.$$

Here $C_1 = \cos\theta_1$, $S_1 = \sin\theta_1$, $C_2 = \cos\theta_2$, *etc.*, where $\theta_1$, $\theta_2$ and $\theta_3$ are rotation angles around the three cartesian axes. It will be, for instance:

$$\partial\mathbf{R}/\partial\theta_1 = \mathbf{R}_{\theta 3} \mathbf{R}_{\theta 2} \begin{pmatrix} 0 & 0 & 0 \\ 0 & -S_1 & -C_1 \\ 0 & C_1 & -S_1 \end{pmatrix},$$

*etc.* and

$$\partial^2 \mathbf{R}/\partial\theta_1\,\partial\theta_2 = \mathbf{R}_{\theta 3}\begin{pmatrix} -S_2 & 0 & C_2 \\ 0 & 0 & 0 \\ -C_2 & 0 & -S_2 \end{pmatrix}\begin{pmatrix} 0 & 0 & 0 \\ 0 & -S_1 & -C_1 \\ 0 & C_1 & -S_1 \end{pmatrix} = \mathbf{R}_{\theta 3}\begin{pmatrix} 0 & C_1C_2 & -C_2S_1 \\ 0 & 0 & 0 \\ 0 & -S_2C_1 & S_1S_2 \end{pmatrix}.$$

In agreement with these conventions, the atomic coordinates $x_{ni}$ are given by:

$$\mathbf{x}_n = \mathbf{R}\mathbf{X}_n + \mathbf{u}, \tag{20}$$

where $\mathbf{X}_n$ are the atomic coordinates in a rigid molecular model and $\mathbf{u}$ a translation vector. In particular, if the atomic coordinates of the model $\mathbf{X}_n$ are not referred to a general orientation, but they are made to coincide with the $\mathbf{x}_n$ at the starting point (or derived from the preceding cycle), the rotation angles $\theta_1$, $\theta_2$ and $\theta_3$ all become zero, and a considerable simplification occurs. For instance:

$$\partial\mathbf{R}/\partial\theta_1 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix};$$

$$\partial^2 \mathbf{R}/\partial\theta_1\,\partial\theta_2 = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \textit{etc.} \tag{21}$$

This procedure implies that after each cycle the coordinates $\mathbf{X}_n$ are modified, but has also the advantage of avoiding ill conditioning (which in this case does not occur for zero rotation angles), without resorting to more complicated rotation matrices, such as the one proposed by Scheringer (1963).

Since most of the second derivatives, $x_{ni,ml}$, with respect to atomic coordinates are zero, and considering the relative simplicity of these calculations, this shows a possibility of introducing second derivatives in rigid-body constrained least-squares refinement of crystal structures without much effort, a point which might be useful at the initial stage.

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