Momentum density is quite insensitive to some features of the wave function, such as polarization and atomic differentiation, and it is proposed to generalize the method to a simultaneous refinement of the wave function based on several independent experiments (Compton, Bragg diffraction, spectroscopy, magnetic diffraction *etc.*).

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Bravais Lattice Invariants

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Abstract

Invariants are those properties by which objects (in chemistry, physics, mathematics *etc.*) are commonly identified. They remove sensitivity to presentation and allow the intrinsic properties of the object to be seen. Invariants used for unit-cell comparison and for Bravais-lattice identification are reviewed, and proposals are made for possible directions of future research. The results of an exhaustive search for polynomial invariants of the components of the metric tensor through degree 12 are that polynomials in the volume squared are the only non-trivial such invariants.

Introduction

If some infinitesimal changes in an object cause discontinuous change in an invariant, then that invariant

may be useful for identifying a particular object, but it will be useless for examining a neighborhood of that object. We shall call such invariants (those that under some conditions have discontinuous change) unstable. For the identification of crystallographic lattices, stable invariants are needed (Andrews, Bernstein & Pelletier, 1980; Andrews & Bernstein, 1988). In this paper, we review some stable invariants of Bravais lattices. The results of an exhaustive search for polynomial invariants of the components of the metric tensor through degree 12 are that polynomials in the volume squared are the only non-trivial such invariants.

It is important to realize that there is a difference between the symmetry of the lattice and the symmetry of the contents of the unit cell. In this paper (and in reduced-cell studies in general), one considers only the symmetry of the lattice (the so-called metric symmetry). Such a

focus can prevent the erroneous assignment of less-symmetrical Bravais lattices in many cases. While this can then cause difficulties in refinement, no better alternative is known than first to correctly identify the possible symmetries of the lattice and then to consider the contents of the cell later as described by Stout & Jensen (1989, p. 141). For a recent review of these methods, see Andrews & Bernstein (1988).

Although there is a great deal of implicit use of invariants in lattice studies, little discussion of the merits of particular invariants exists in the literature since the early work of Seeber (1831; cited by Engel, 1989). In fact, much of the confusion in the literature concerning the determination of correct Bravais lattices is due to the treatment of unstable invariants and non-invariants as if they were stable invariants (see the review by Andrews, Bernstein & Pelletier, 1980). In this paper, we have concentrated on numerical invariants. Another class of invariants is the non-numerical invariants (often called labels). An example of this class is the names of the Bravais lattices. A triclinic lattice might well be nearly cubic but still it would be triclinic.

Earlier invariants

It is widely understood that the volume of any primitive unit cell of a lattice is a stable invariant of that lattice. The volume, being the square root of the determinant of the metric tensor (a positive-definite symmetric matrix), is inherently stable. Other commonly cited invariants are those derived from the properties of the edge vectors of reduced cells. In the Niggli formalism (Burzlaff, Zimmermann & de Wolff, 1983), the lengths of the edges of the reduced cell ($\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$) and the angles between them are encoded as the vector inner products $\mathbf{a} \cdot \mathbf{a}$, $\mathbf{b} \cdot \mathbf{b}$, $\mathbf{c} \cdot \mathbf{c}$, $\mathbf{b} \cdot \mathbf{c}$, $\mathbf{a} \cdot \mathbf{c}$ and $\mathbf{a} \cdot \mathbf{b}$, which are also the elements of the metric tensor:

$$\begin{pmatrix} \mathbf{a} \cdot \mathbf{a} & \mathbf{a} \cdot \mathbf{b} & \mathbf{a} \cdot \mathbf{c} \\ \mathbf{a} \cdot \mathbf{b} & \mathbf{b} \cdot \mathbf{b} & \mathbf{b} \cdot \mathbf{c} \\ \mathbf{c} \cdot \mathbf{c} & \mathbf{b} \cdot \mathbf{c} & \mathbf{c} \cdot \mathbf{c} \end{pmatrix}.$$

Another presentation of the same information is the G^6 formalism introduced by Andrews & Bernstein (1988):

$$\mathbf{g} = \begin{pmatrix} \mathbf{a} \cdot \mathbf{a} \\ \mathbf{b} \cdot \mathbf{b} \\ \mathbf{c} \cdot \mathbf{c} \\ 2\mathbf{b} \cdot \mathbf{c} \\ 2\mathbf{a} \cdot \mathbf{c} \\ 2\mathbf{a} \cdot \mathbf{b} \end{pmatrix}.$$

Apparently, the first reference in the crystallographic literature to these invariants is by Seeber (1831), who demonstrated that the three shortest non-coplanar lattice vectors formed a basis for a lattice. The lengths of these vectors are, of course, invariants of the lattice; however, only those quantities not dependent on angles (that is,

$\mathbf{a} \cdot \mathbf{a}$, $\mathbf{b} \cdot \mathbf{b}$ and $\mathbf{c} \cdot \mathbf{c}$) are stable. Those inner products between different vectors are unstable invariants (Andrews, Bernstein & Pelletier, 1980). Similar work by Patterson & Love (1957) on the Delaunay reduction has shown unstable behavior for it.

Seeber's (1831) analysis included the presentation of what is now termed the reciprocal lattice. Since this lattice and the real lattice are derivable from one another, the invariants of one are effectively invariants of the other. Andrews, Bernstein & Pelletier (1980) cite the edge lengths of the reduced reciprocal cell as three additional stable invariants useful in some applications. Their use is equivalent to using the areas of linearly independent cell faces in real space. The recent rediscovery by Rodgers & Le Page (1992) of these additional invariants demonstrates both their utility and the importance of investigating invariants themselves.

Although not obviously useful for identification of particular lattices, the recent work of Paciorek & Bonin (1992) describes the invariant projectors of the various subspaces (in G^6) of the Niggli-reduced cells of the Bravais lattices.

New stable invariants

A productive method of searching for new stable invariants is to explore various extremal measures of lattices. Owing to the infinite extent of lattices, minimization is usually most productive. It is tempting to avoid the combinatorial nature of computations of minima. Therefore, one also considers polynomial and other closed-form algebraic invariants, such as rational invariants. The stable invariants cited above are all such minimal measures. The volume is additionally a polynomial invariant. The length of $\mathbf{a}$ is the shortest non-zero length in a lattice. We list here several suggestions for useful stable invariants.

(1) An invariant related to some invariants already in use is the surface area of the primitive cell with minimal surface area. This cell is the cell reciprocal to the reduced reciprocal cell. This choice of cell is somewhat related to the proposal of Gruber (1978), who distinguished ambiguous reduced cells by choosing the one with minimal area as the reference one.

(2) The length of the shortest G^6 vector among the cells of a lattice is a new invariant that derives from new investigations of representations of lattices (Andrews & Bernstein, 1988). In many cases, but not all, the shortest G^6 vector corresponds to that of the reduced cell.

(3) The eigenvalues of the metric tensor (for primitive cells) provide another place to search for stable invariants. Because the product of the three eigenvalues is always the square of the volume of the cell, there are strong bounds on these values. Two appropriate candidates are the largest minimal eigenvalue and the smallest maximal eigenvalue that can be found by searching among the cells of a lattice.

(4) A stable invariant actually in use for a different purpose is the quantity that is minimized during the Delaunay reduction. For any basis set of vectors and the negative of their vector sum, the sum of the six inner product of these four vectors is minimized. Although the Delaunay reduced cell is not stable to perturbation, the 'Delaunay sum' is stable.

(5) A more difficult, but possibly fruitful, area of research is among various physical analyses of inferred physical properties such as the areas of minimal surfaces [analogous to soap films; see, for example, the work of Hyde (1989)], maximal or minimal areas and volumes of inscribed spheres and polyhedra, and possibly elastic properties and the corresponding normal modes (that is, eigenvalues and eigenfunctions of vibrations) of lattices.

(6) Returning to polynomial invariants, one can do an exhaustive search by defining an invariant with variable coefficients and requiring it to remain unchanged under the operations of the modular group (that is, operations that convert one cell of a lattice into another). We have performed that exhaustive numerical search through degree 12. Only polynomials in the square of the volume remained. It is the nature of the G^6 representation for the square of the volume (rather than the volume) to appear. We conjecture that going to higher-degree polynomials will not produce additional types of invariants. It remains a topic for additional research to see whether the more computationally intensive search for rational invariants will be productive.

Future directions

Another source of invariants in mathematics is fixed points under some set of transformations. An example is the set of Bravais lattices, which are fixed subspaces within the space of unit cells. For example, exchange of edges does not change the fact that a cell is cubic. The extremal invariants mentioned above are also fixed points. The advantage of looking beyond extremal solutions to other fixed-point solutions that cannot be approached continuously is that we can find isolated solutions that appear useful only as labels. However, we will now consider ways to combine transformations with unstable invariants in order to achieve effectively stable invariants. As a simple example, we will consider a pair of primitive monoclinic cells:

(10, 10.1, 10, 90, 95, 90) and (10, 9.9, 10, 90, 95, 90).

The Niggli reduced cells are:

(10, 10, 10.1, 90, 90, 95) and (9.9, 10, 10, 95, 90, 90), respectively.

Although the two lattices are obviously similar, the reduced cells do not easily show the relationship (remember that this is only a simple example). If we carried along all versions of the reduced cells with permuted axes, then among the permutations we would find nearly identical cells (including the original pair). In this way, an effective stability can be achieved in a case where simpler rules lead to an apparent instability. Other examples of this approach applied to the study of lattices are in Andrews & Bernstein (1988).

It is, however, unsatisfactory to have to replace simple vectors of parameters with entire families of vectors derived under applications of families of transformations. The computational complexity of working with these families is very large, making simple distance calculations into complex combinatorial problems. A highly desirable goal is the realization of a 'toroidal' representation of these families of vectors, which would allow a single point in some space to represent all members of the family. A trivial example of a toroidal solution is the location of a point on a circle. A point can be represented by an angle or that angle plus $2p$, plus $4p$,..., giving an infinite family of points. However, the common toroidal solution is as the vector $(\cos Q, \sin Q)$, which is smooth, continuous and single-valued. Such a single-valued description of lattices would be highly desirable. Embedding theorems from topology (Hurewicz & Wallman, 1948) demonstrate that such toroidal descriptions exist (and that they are, in many desirable ways, linear). The embedding theorems tell us that it is possible to embed a space of dimensionality (n) within another higher space of dimensionality $(2n + 1)$. How to derive such spaces is not clear, but they would be a considerable advance in the study of experimental lattices.

Invariants are often grouped into vectors that are spectra of some invariant properties. An example in common use is the spectrum of the eigenvalues of matrices. An example of such invariants in crystallography would be the lengths of the reduced-cell edges. Other intermediate lengths could be added for finer discrimination. Properly composed invariant vectors can by themselves be diagnostic. By sorting the vector carefully and allowing properly for multiplicities, e.g. making the first element the minimal value of some instance of a property, the second element the minimal value of instances excluding the first, but listing it even if it assumes the scalar value that is already in the list, and continuing in this fashion through the list, the vector itself can be an invariant. Since it is unlikely that a single scalar value could distinguish among the Bravais lattices, some spectrum-like set of numbers is obviously necessary. The Niggli matrix could be thought of as a nested spectrum in which the first three values $(\mathbf{a} \cdot \mathbf{a}, \mathbf{b} \cdot \mathbf{b},$ and $\mathbf{c} \cdot \mathbf{c})$ are a spectrum and the following three values ($\mathbf{b} \cdot \mathbf{c}, \mathbf{a} \cdot \mathbf{c}$ and $\mathbf{a} \cdot \mathbf{b}$) are subspectra, the ordering of which is subordinate to the sort order of the first three.

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New Analytical Scattering-Factor Functions for Free Atoms and Ions

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Abstract

New analytical X-ray scattering-factor representations valid for the full range of $\sin \Theta/\lambda$ from 0.0 to 6.0 Å^{-1} have been developed from fits of a linear combination of five Gaussians to the values of the scattering factors tabulated in *International Tables for Crystallography* (1992) [Vol. C. Dordrecht: Kluwer Academic Publishers]. The resulting functions for both neutral atoms and ions are compared with the existing parametrizations, which are applicable for 0.0–2.0 Å^{-1} and 2.0–6.0 Å^{-1}, respectively. The quality of the new parametrization involving 11 parameters per atom (ion) compares well with the previous work or is even superior. Examples are discussed, some errors in *International Tables for Crystallography*, Vol. C are indicated and a warning is given that most of the previously published four Gaussian expansions for ions are inadequate for calculations involving $\sin \Theta/\lambda \geq 2.0$ Å^{-1}.

Introduction

Isotropic X-ray scattering factors for free atoms and/or ions are required in numerous crystallographic calculations, in particular in structure least-squares refinements. Results for distinct values of $s = \sin \Theta/\lambda$ obtained from atomic wavefunctions are compiled in *International Tables for Crystallography*, Vol. C (Maslen, Fox & O'Keefe, 1992), Tables 6.1.1.1 and 6.1.1.3. With the exception of hydrogen, all scattering-factor values are either derived from the calculations of Doyle & Turner (1968) using the wavefunctions of Coulthard (1967) or from those of Cromer & Waber (1968) using the wavefunctions of Mann (1968). The latter calculations are designated by an asterisk indicating a more exact treatment with respect to the finite size of the nucleus. Scattering factors for ions are either based on non-relativistic or relativistic Hartree–Fock calculations

(Cromer & Mann, 1968) using the wavefunctions of Mann (1968) or on relativistic Dirac–Slater wavefunctions (Cromer & Waber, 1968).

While the calculations of Doyle & Turner were made for 76 elements up to $s = 6.0$ Å^{-1}, Cromer & Waber filled in the missing elements, though only for $0 < s < 2.0$ Å^{-1}, which is sufficient for most applications. Owing to an increasing number of applications requiring high-angle X-ray or electron scattering factors, *e.g.* high-resolution electron microscopy or experiments with γ-radiation or synchrotron radiation, extended scattering-factor calculations for the range $2.0 < s < 6.0$ Å^{-1} were provided by Fox, O'Keefe & Tabbernor (1989) and have been included into Table 6.1.1.1, which is the basis for the interpretation of almost any X-ray or electron scattering experiment.

For a given atom and scattering-vector length, the corresponding scattering-factor value $f(s)$ must be calculated from the nearest entries of the appropriate table. In order to circumvent interpolation and to facilitate computational handling, several authors have presented analytical scattering-factor functions for the data available, *e.g.* Onken & Fischer (1968) who also reviewed earlier studies. The most frequently used representations to date are those developed by Doyle & Turner (1968) who used linear combinations of four Gaussians:

$$f(s) = \sum_{i=1}^{4} a_i \exp(-b_i s^2) + c. \tag{1}$$

These have been found to give close fits to the tabulated values up to $s_{\max} = 2.0$ Å^{-1}. Equation (1) and the parameters a_i, b_i and c compiled in Table 6.1.1.4 of *International Tables for Crystallography* (1992), Vol. C can be easily implemented in programs, *e.g.* the recently released *SHELXL*-93. One interesting application of the analytical scattering functions is given by Sasaki, Fujino,