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A new verification of Kovalev's tables of irreducible representations of the space groups

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Abstract

In the application of representation theory to physical and crystallographic problems, Kovalev's tables provide a uniquely reliable and complete source for the required irreducible representations of the space groups. A number of programs based on these tables, designed to automate the lengthy calculations involved, generate non-physical or incorrect solutions to some problems, raising questions over the validity of Kovalev's work. In this work the tables are verified to the point of homomorphism with the groups and subgroups that they represent through the use of the digitized versions of the tables used in SARA*h*. The results support the correctness of Kovalev's definitions, highlighting difficulties in interpreting the tables themselves and some general failings of the programs used in the application of representation theory to physical problems.

1. Introduction

Symmetry is integral to our theoretical and experimental understanding of molecular and solid state properties. In spectroscopy and crystallography, it allows us to derive selection and coupling rules that characterize structures, and to understand systematic absences in diffraction patterns or optical spectra. Symmetry adapted functions provide the basis for descriptions of electronic bonding, vibrations, magnetic ordering and related physical properties, as well as drastically simplifying calculations in fields as diverse as density functional theory [1] and x-ray diffraction [2].

The symmetry of simple R^3 Euclidean spaces under affine transformations is well developed, and its application to crystallography comprehensively covered in the International Tables for Crystallography—A (IT-A) [3]. More general symmetries in terms of vector spaces are used to describe physical properties such as lattice vibrations, distortions, and magnetic structures, and could be applied to problems in incommensurate crystallography. The symmetry of these spaces is best described using representation theory, in which the subgroup symmetries of the space group are projected onto symmetry adapted basis vectors (BVs); in vibrational spectroscopy these are termed the fundamental modes. This area has been extensively explored by Bertaut [4–6], Wigner [7], and Russian authors such as Kovalev [8], and Izyumov [9], but representation theory, and the more complete co-representation theory, has not been as widely or readily accepted. This is largely due to the fact that, unlike crystallographic space groups (SGs), the number of possible vector fields is infinite and therefore some calculation must always be involved in their use. Further, there are as yet no agreed conventions on the definition of crystal settings, the irreducible representations (IRs), or the labels of the IRs that form the basis of representation theory. The tables provided by Kovalev contain all the prerequisite information for the application of representation theory to crystallographic problems; this is the most comprehensive work on the subject.

A number of programs (SARA*h* [10], MODY [11], Isotropy [12]) have been developed to automate the

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use of Kovalev's tables and the calculations involved in applying representation theory to physical systems; they have precipitated an increase in the use of representation theory, specifically for work on phonons [13] and magnetic orderings [14]. However, for all of these programs, difficulties have arisen in their application; particularly in the low symmetry triclinic and monoclinic lattices or when the definition of Kovalev's space group differs from that used in the IT-A. These have fuelled a general controversy over the validity of the different alternative sources of irreducible representations and confusion over the translational parts of the symmetry that are appropriate for Kovalev's space groups as these were not defined in the first version of his tables. The tables in the English translation of the second edition of Kovalev's book were validated by its editors and over 500 mistakes in the Russian version corrected. However, the details of the validation are unclear [15], therefore it was decided to validate independently the tables fully in order to clarify the problems encountered in some calculations and when differences appear between irreducible representations provided by different sources. This process is important for the use of Kovalev's irreducible representations, as without confidence in the contents any results derived from calculations based upon it are of indeterminable value.

We will briefly cover the relevant group theory before describing, in section 3, which properties of Kovalev's tables were validated and how this was done.

2. Space groups and representation theory

In crystallography the starting symmetry of interest is the space group of the crystal, $\mathbb{G}$, whose elements are affine transformations of the R^3 Euclidean space which leave the crystal unchanged: rotations and roto-inversions, combined with translations. In the following discussion, we use Kovalev's notation $g_i = (\vec{\alpha}_i|h_i)$ for an operator $g_i \in \mathbb{G}$, where h_i is the rotation/roto-inversion and $\vec{\alpha}_i$ is the translation (this notation follows the mathematical convention that operations should be applied from right to left).

When considering a vector space, e.g. a magnetic structure, phonon or crystallographic distortion, with translational properties defied by the propagation vector $\vec{k}$, the space group symmetry is reduced to those symmetry elements in $\mathbb{G}$ that leave $\vec{k}$ invariant within a reciprocal lattice vector $\vec{b}$:

$$\vec{k}g = \vec{k} + \vec{b} \qquad \forall g \in \mathbb{G}_{\vec{k}}. \tag{1}$$

For clarity we have explicitly stated that this operation is of the complete rotation–translation operation $g \in \mathbb{G}_{\vec{k}}$ in order to emphasize the use of the little group $\mathbb{G}_{\vec{k}}$. However, it should be remembered that only the rotational part of a symmetry operation, h, has any effect on a reciprocal space vector, as real space translations α leave it invariant. Consequentially, the subgroup of point symmetry operations that leave $\vec{k}$ invariant is also the point group $\mathbb{H}_{\vec{k}}$.

2.1. Composition of SIRs and LIRs

Rather than the small IRs (SIRs), τ_i, of the group $\mathbb{G}_{\vec{k}}$, for succinctness Kovalev's tables list the loaded IRs (LIRs), $\hat{\tau}_i$, of each group $\mathbb{H}_{\vec{k}}$. For a given symmetry operation g_i in $\mathbb{G}_{\vec{k}}$ these are related according to:

$$\tau_i = \hat{\tau}_i \cdot \mathrm{e}^{-2\pi \mathrm{i}\vec{k}\cdot\vec{\alpha}_i}, \tag{2}$$

where $\vec{\alpha}_i$ is the translational part of the symmetry operation $g_i = (\vec{\alpha}_i|h_i)$.

The irreducible representations (IRs) of $\mathbb{G}$, and the Small IRs (SIRs) of the subgroups $\mathbb{G}_{\vec{k}}$ must have the same structure as the space group that they are a homomorphic map of; in particular they must obey the law of composition. For symmetry operations, this is simply that the successive application of each transformation as:

$$(\vec{\alpha}_i|h_i) \circ (\vec{\alpha}_j|h_j) = (\vec{\alpha}_i + h_i \circ \vec{\alpha}_j|h_i h_j). \tag{3}$$

If τ_i is a representation of the operation $(\vec{\alpha}_i|h_i)$ then by homomorphism:

$$\tau_i \times \tau_j = \tau_{i\circ j}. \tag{4}$$

Here the $\times$ symbol indicates matrix multiplication. For the small irreducible representations the law of composition then becomes:

$$\begin{aligned}
&\hat{\tau}_i \cdot \mathrm{e}^{-2\pi \mathrm{i}\vec{k}\cdot\vec{\alpha}_i} \times \hat{\tau}_j \cdot \mathrm{e}^{-2\pi \mathrm{i}\vec{k}\cdot\vec{\alpha}_j} = \hat{\tau}_{i\circ j} \cdot \mathrm{e}^{-2\pi \mathrm{i}\vec{k}\cdot(\vec{\alpha}_i + h_i\times\vec{\alpha}_j)} \\
&\hat{\tau}_i \times \hat{\tau}_j = \hat{\tau}_{i\circ j} \cdot \mathrm{e}^{-2\pi \mathrm{i}\vec{k}\cdot(\vec{\alpha}_i + h_i\times\vec{\alpha}_j)} \cdot \mathrm{e}^{2\pi \mathrm{i}\vec{k}\cdot\vec{\alpha}_i} \cdot \mathrm{e}^{2\pi \mathrm{i}\vec{k}\cdot\vec{\alpha}_j} \\
&\quad = \hat{\tau}_{i\circ j} \cdot \mathrm{e}^{-2\pi \mathrm{i}\vec{k}\cdot(\vec{\alpha}_i - \vec{\alpha}_j - \vec{\alpha}_i + h_i\times\vec{\alpha}_j)} \\
&\quad = \hat{\tau}_{i\circ j} \cdot \mathrm{e}^{2\pi \mathrm{i}\vec{k}\cdot(\vec{\alpha}_j - h_i\times\vec{\alpha}_j)}.
\end{aligned} \tag{5}$$

The exponent in the last line of equation (5) is the 'load', $\mathbb{W}$. It is the last relationship we have used to validate Kovalev's tables.

3. Method

The method of validation follows from the relationship derived in equation (5); two separate methods of generating the 'load' were compared to determine any inconsistencies between the tables and the law of composition. Calculations were performed for each of the distinct points, lines and planes of the Brillouin zone that define the k-types used by Kovalev. For the lines and planes, several arbitrary values of any variables in the k-vector were used.

- The operators of the SG were combined pairwise to generate a product operator; then the LIRs were from Kovalev's tables for those two operators were multiplied together to generate a product matrix, $\mathbb{M}$. $\mathbb{M}$ was then expressed as the LIR matrix for the product operator multiplied by a coefficient: the load.

$$\hat{\tau}_i \times \hat{\tau}_j = \mathbb{M} = \mathbb{W}\hat{\tau}_{\text{product}}. \tag{6}$$

- The load is calculated according to equation (5).

$$\mathbb{W} = \mathrm{e}^{2\pi \mathrm{i}\vec{k}\cdot(\vec{\alpha}_j - h_i\times\vec{\alpha}_j)}. \tag{7}$$

An example of the calculations performed is given in equation (8). In this example the SG is $P2_12_12_1$, the operators are g_2 and g_4 (following Kovalev's notation) and $\vec{k}_{26} : (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$:

$$g_2\text{: } (\tfrac{1}{2}, \tfrac{1}{2}, 0|x, -y, -z)$$

$$g_4\text{: } (\tfrac{1}{2}, 0, \tfrac{1}{2}| -x, -y, z)$$

$$\begin{aligned}\hat{\tau}_2 \times \hat{\tau}_4 &= \begin{pmatrix} \mathrm{i} & 0 \\ 0 & -\mathrm{i} \end{pmatrix} \begin{pmatrix} 0 & \mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} \qquad \hat{\tau}_{2\circ 4} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \\ &= \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \\ &= -1 \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}\end{aligned} \tag{8}$$

$$\begin{aligned}\mathrm{e}^{2\pi \mathrm{i} \vec{k} \cdot (\vec{\alpha}_4 - h_2 \times \vec{\alpha}_4)} &= \mathrm{e}^{2\pi \mathrm{i} (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \cdot ((\frac{1}{2}, 0, \frac{1}{2}) - (\frac{1}{2}, 0, -\frac{1}{2}))} \\ &= \mathrm{e}^{\pi \mathrm{i}} \\ &= -1.\end{aligned}$$

Most of the input files were taken from SARA*h*. All the inherited files underwent corrections, for both the *K* and *I* settings, and these corrections have been incorporated into a new release of SARA*h*.

4. Results

For the finalized program and input files, there were no inconsistencies found within the tables of Kovalev, provided his definitions of the axis systems and symmetry operators were used.

5. Discussion

In validating the Kovalev's collected set of irreducible representations of the space groups, to resolve problems in previous calculations and doubts over their accuracy, we have found that without exception errors arise from the applications performing the calculations and misunderstanding of the precise definitions that he used. Our work indicates that the tables are entirely consistent within those definitions, however, most users prefer to work within the definitions of the space groups laid out by the IT-A. Great care must be taken to ensure that the transformation between the IT-A space groups and that used by Kovalev's must retain the homomorphism on which representation theory is based.

The fundamental obstacle to correctly moving between the various axis systems is a lack of clarity in Kovalev's tables as to which information is given in which setting. This thorough review of his work leads to the following conclusions:

- Kovalev's fundamental periods define his primitive lattice, and are listed in the Kovalev defined cubic/hexagonal axis system.
- The operators of the triclinic and monoclinic SGs have their translational parts defined in the Kovalev primitive axis systems that differs from that used to define the rotational parts of the symmetry operators. They are tabulated as linear combinations of the fundamental reciprocal periods to indicate this. Operators for all other SGs are in the cubic/hexagonal axis system.
- Where the Kovalev centred setting differs from the IT setting, Kovalev list transformations between them. However, *Kovalev always refers to settings defined in the International Tables for X-Ray Crystallography* (IT-X) [16] which was the accepted reference when Kovalev first calculated his tables.
- Due to the International Union of Crystallography redefining some space groups between IT-X and IT-A, many of the current software programs contain associated errors, particularly in the transformation of coordinates, symmetry operations, and *k*-vectors. An additional transformation from the IT-A setting to the IT-X setting is required *before* the transformations listed in Kovalev's work can be performed to bring the problem into his defined primitive settings.
- The tables of Kovalev are intolerant to redefinitions of the axes or the operators that do not preserve the homomorphism.

6. Conclusions

This work reinforces the earlier, indeterminate validation of Kovalev's tables; the loaded irreducible representations and small irreducible representations tabulated are homomorphic to the point and space groups they represent. The latter are therefore consistent with the translations elements defined for each space group operator in the second version of the tables. Questions concerning the accuracy of the representations arise from ambiguity regarding the axis system that various information is presented in, and from the difference in space group definitions that has arisen between the International Tables for X-ray Crystallography and the current version of the International Tables for Crystallography-A.

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