

Identification, display, and use of symmetry elements in atomic and electronic structure models

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Crystallographic symmetry plays an important role in structure determination from diffraction or scattering data, in spectroscopy and in simulations. It is convenient and insightful to integrate the display and use of such symmetry data with data analysis and modeling methods. We outline the integration of a suite of crystallographic algorithms, closely coupled with interactive graphical displays. These include techniques for identifying the unit cell of a solid, for automatically determining space and point group symmetries, for generalized displays of symmetry elements overlaid on structural models, and for construction, editing, and transformation of models subject to symmetry constraints. In addition, electron densities derived from periodic density functional calculations can be symmetrized and displayed with the corresponding symmetry elements. Applications of these various capabilities in crystallographic research are illustrated by topical examples. © 2000 by Elsevier Science Inc.

Keywords: space group, symmetry displays, crystallographic algorithm, plane group, point group

1. INTRODUCTION

In applying molecular graphics and simulation techniques to solid state materials, it is vital that the principles of translational periodicity and space group symmetry be applied and exploited in an efficient fashion. The derivation and use of these attributes facilitate the development and interpretation of crystal structure models, the simulation of a variety of analyt-

ical data, and structural characterization. They can also enable large savings in computational costs.

Previous papers¹⁻⁹ have described specific developments, algorithms, or applications of various components within a crystallographic modeling repertoire. Some of these components are available in existing software. For instance, a variety of software is available for building crystals and specifying or manipulating symmetry elements,¹⁰ others are available for calculating diffraction patterns¹¹ and powder indexing,^{12,13} but all of these components exist in separate environments. This article illustrates the integration of symmetry and crystallographic modeling techniques, through various examples, obtained when these techniques are accessed in a common environment.¹⁴ The components permit, for example, simultaneous symmetry-constrained model adjustment, visualization of calculated or observed electron density, and interactive diffraction calculation.

2. CRYSTALLOGRAPHIC CONSTRUCTION AND DISPLAYS

2.1. Periodicity and symmetry

For a wide range of applications, we have found it convenient to apply periodicity and symmetry at three levels; nonperiodic systems with point group symmetry, two-dimensionally periodic systems with plane group symmetry, and three-dimensionally periodic systems with space group symmetry.^{15,16} As an example of a two-dimensionally periodic model, we show in Color Plate 1 a slab extracted from a zeolite with the EMT framework,¹⁷ which, when interconnected with similar slabs related by inversion or mirror symmetry, generates families of intergrowth structures.¹⁸

Color Plate 2 shows an exemplary display of symmetry elements in space group *Pbca*, and Color Plate 3¹⁹ illustrates the application of symmetry element displays in a point group symmetry case.

The major effort needed to implement an analogous treatment of one-dimensional periodicity with rod group symmetry

Color Plates for this article are on pages 325–328.

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has not yet proven justified, although special cases such as the construction of frameworks from chain units, and of crystalline polymers from packing of helical chains, have warranted specialized treatment. Noncrystallographic point group symmetry, occasionally useful to exploit in protein crystallography, is another special case.

The description of a structure that has 0-D, 2-D, or 3-D periodicity comprises the contents of the asymmetric unit, the group of zero, two, or three translation vectors, respectively, and a general set of coordinate triplets capturing the symmetry interrelationships. The coordinate triplets relate to orthogonal angstrom units for 3, 1, or 0 of the axes. In the molecular modeling case in which neither symmetry nor periodicity is present the asymmetric unit would be the set of all atoms in the molecule. For the space group symmetry (3-D) case, the standard settings listed in *International Tables for Crystallography*¹ are a convenient reference point, but a general treatment proves more flexible and convenient in practice, particularly when referring to historical crystallographic data or working with super- and subgroup descriptions.

2.2. Model construction

The above descriptions allow substantial flexibility in creating models, by applying various combinations of the translation and symmetry operations to all or subsets of the contents of the asymmetric unit. Redundancies that occur when atoms reside on special positions, i.e., symmetry elements (Color Plate 4²⁰), must be managed suitably in this construction operation.²¹ Appropriate transforms are applied if anisotropic information, such as thermal ellipsoid data, is stored with each atom. It may be convenient to display a full cluster that has point group symmetry by applying all of the point group symmetry operations to the asymmetric atom set, or to generate replicates of full unit cells by applying the full set of space group symmetry operations and the appropriate set of translation vectors. However, it may be more revealing or convenient to apply subsets of the translation and symmetry operations. For example, appropriate choice of the construction criteria allows a "single shot" construction of the supercage in zeolite X (Color Plate 5), or filling of volumes defined by successive picks in space allows construction of chain units in polyethylene. By retaining the operations used to create any given atom within the periodic model, these operations can be applied subsequently in any form of editing mode. Individual atoms, groups, or molecules can be repositioned, with all translation- or symmetry-related atoms being moved in consort. This feature proves useful in exploring structural possibilities when motifs and symmetries are known.

Flexibility in construction and editing requires the availability of other tools, particularly "regularization,"²¹ in which atom positions are automatically adjusted within user-defined tolerances so as to rigorously obey a defined symmetry (Color Plate 6), and "snap-to-special,"²¹ in which atoms within a defined distance of a symmetry element are moved so as to reside exactly on that element.

2.3. Display modes

The slate of now standard display modes for molecular models applies directly to periodic systems, but with the added advantage that subsetting can be applied also to groups defined by

translation or symmetry interrelationships. Thus it is simple to highlight atoms related by given translation vectors or symmetry elements.

Several additional display modes, however, are particularly useful for periodic models. As with molecular systems, the bonding topology may be revealing, particularly for molecular solids or framework structures with predominantly covalent bonding. However, for metallic and ionic solids other topologies might be convenient to display. For example, anion close contacts, or interconnects that form polygons or polyhedra can be highlighted. Particularly in framework structures, it is useful to be able to highlight automatically rings of a defined size, coordination shells, or coordination sequences.²¹ For example, certain structures are conveniently regarded as being constructed from two-dimensionally periodic sheets (Color Plate 1) or, in the aluminophosphate case illustrated in Color Plate 7, from interlinked chains of four rings sharing edges.

Many inorganic solids are conveniently viewed as being constructed from discrete polyhedra. Thus, zeolites are composed of tetrahedral silicate and aluminate groups, and perovskites and pyrochlores are composed of octahedral MO₃ groups. Cubes, square pyramids, trigonal prisms, and higher polyhedra are useful in interpreting the features of other inorganic systems. By automating the identification of polygons and polyhedra in a given system and providing flexibility in graphical display modes, even complex inorganic systems can be viewed and analyzed in terms of simpler construction principles.²²

Other polygons or polyhedra that are usefully displayed in crystal structure models include plane cells or unit cells, asymmetric areas or volumes, and Wigner-Seitz cells (Color Plate 8). As with the symmetry operations themselves, the asymmetric volume for a given space group might have various locations, orientations and even, in some cases, shapes, depending on which bounding symmetry elements are chosen.¹

3. ANALYTICAL DATA SIMULATIONS

A wide variety of analytical fingerprints can be computed, with some confidence, on the basis of molecular or crystal structure models. Even in cases in which simulations of quantitative reliability are not yet possible, analyses of bonding or symmetry at the atomic level can often yield insight sufficient to enable spectral assignment and partial interpretation.

Perhaps most useful for crystal structure models is the dynamic calculation of diffraction data, be it for the single crystal, fiber, or powder diffraction case.²³ For a defined crystal structure model of up to modest size, such calculations are fast and can be performed interactively. Thus, simulated diffraction data can be dynamically updated (Color Plate 9) as a model is edited, and direct comparison with experimental data can also be performed dynamically as the elements of the crystal structure model are adjusted, so as to best reproduce the features in the experimental pattern.

From an educational perspective, the combination of analytical data simulation and graphical displays can be particularly valuable. Thus, displaying the families of Miller planes contributing to a particular diffraction event (Color Plate 9) and the disposition of the atoms in the structure relative to these planes helps a student appreciate, in a physical sense, the principles of diffraction.

Extended X-ray absorption fine structure (EXAFS) spectra are computed from discrete clusters or cluster models selected

from a periodic environment, with appropriate averaging over the differing local configurations of the absorbing elements. Nuclear magnetic resonance (NMR) spectra can also be simulated on the basis of a crystal structure model where contributors to isotropic chemical shifts can be estimated from local composition and geometry. Through implementing such analytical data calculations in an augmentative fashion,⁶ these various types of spectra can be simulated simultaneously for a given model, with each of the fingerprints being dynamically updated as the model is adjusted to best match the features in the set of analytical spectra. The model might thus be edited to match, simultaneously, data sensitive to both long- and short-range ordering phenomena.

Vibrational spectra, while calculable for organic molecules with good accuracy by both molecular and quantum methods, prove more difficult in the solid state given the requirement of suitably capturing or computing the various interatomic force constants. Periodic quantum methods and third generation forcefield^{24–26} technology do allow such calculations in select cases, but the majority of today's inorganic force fields permit no more than reproduction of the overall features in, for example, the infrared spectrum; this may, nonetheless, be sufficient for partial spectral assignment.²⁷ The frequencies of modes in Raman spectra can be computed with the same accuracy, and symmetry analyses allow identification of those modes that are expected to be Raman active, although intensity calculations are more challenging in the Raman case, being governed by differential polarizabilities.

4. CRYSTAL STRUCTURE DETERMINATIONS

4.1. Manual model development using the crystallographic workbench

An integrated crystallographic workbench proves particularly helpful in crystal structure determination, when dealing with structures for which sample or structural complexities prevent the straightforward application of single crystal diffraction methods. The display and analysis tools help highlight structural features or motifs in materials classes. These might be a sensible basis on which to explore structural possibilities for a synthesized, but as yet structurally uncharacterized, material, or to enumerate viable structures in a design or virtual library enumeration project (Color Plates 10 and 11).

At the simplest level, molecular fragments or polyhedra can be combined within the crystallographic environment in direct analogy to the manipulation of physical models. Once a sensible cluster has been developed, a putative repeating volume can be defined graphically, or determined automatically by the corresponding tool, "Find—Cell," in the crystallographic workbench. Similarly, from this triclinic, P1 description, the most likely space group symmetry can be determined automatically ("Find—Symmetry"),^{28,29} subject to the user-defined catchment radius for coordinate equivalencies.

4.2. Automated routes to crystal structure models

Monte Carlo methods can be used to automatically develop crystal structure models. The polymorph predictor,³⁰ for example, explores possible periodic packing arrangements of dis-

crete molecular systems within the confines of the stipulated space group symmetry.³¹

Similarly, in analogy to the manual editing of a structure while monitoring changes in the simulated powder X-ray diffraction pattern, Monte Carlo-based simulated annealing has been developed as an effective route to the solution of inorganic and molecular crystal structures.^{5,32–38} The initial motif, be it a collection of discrete atoms or one or more clusters, is repositioned and reoriented within the defined unit cell so as to best match the target powder diffraction pattern.

4.3. Crystal structure refinement and completion

The initial structure solution step, whether or not it takes benefit from molecular simulation, will generally reveal the overall structural features. The following stage of structure refinement can also be facilitated, via, for example,⁶ monitoring of the instantaneous structure and diffraction data match, cycle by cycle through the least-squares Rietveld refinement procedure.

Structure completion entails the identification of orderings, or of species that are absent from the initial structure solution. Thus, in the case of a crystalline microporous material, the initial stage of structure solution from the powder X-ray diffraction might reveal the overall framework topology. Subsequent stages need to identify the disposition of framework cations,³⁹ the distribution of non-framework cations,^{40–42} and the localization of any template^{43–46} or sorbed species present within the complete structure.⁴⁷ A recently described methodology⁴¹ for rapidly identifying possible locations of extraframework cation takes advantage of framework symmetry. The method relies on calculation of potential energy surfaces for the interaction of cations with a host framework at discrete grid points. Only those points that are symmetrically unique need be calculated, all other points being generated by application of the symmetry operators. A second potential energy grid is calculated for the mutual interaction of cations. By superimposition and addition of these grids, the potential energy surface can be updated as a function of cation addition, without requiring recomputation at each stage (Color Plate 12).

Structure completion is facilitated by dynamical Fourier syntheses of the scattering density or scattering density differences within the unit cell, overlaid on the developing structural model. Manual positioning of missing groups within the electron density map is then possible in direct analogy to the comparable process in protein structure elucidation. Perhaps more powerfully, a variety of docking techniques^{48,49} can be used to automatically place missing features within the overall structural model. Thus protocols have been developed for identifying the appropriate sites for sorbed molecules,^{43,50} solvents of crystallization, and nonframework ions within a host framework.^{40–42}

5. EXPLOITING SPACE GROUP SYMMETRY IN SIMULATIONS

The implementation of an efficient treatment of translational periodicity and symmetry within simulation engines requires reasonable planning. Atom typing, atom charge assignment, structure error checking, and calculation of properties that depend on bonding topologies all require that the links to atoms that are equivalent by symmetry or translation to parents within

the asymmetric unit be appropriately considered. Two- or three-dimensional periodicity complicates the evaluation of nonbonding contributions to a system's internal energy. Techniques, such as the Ewald summation method for 3-D^{51,52} and 2-D⁵³⁻⁵⁵ periodic systems or the periodic cell multiple method, need to be employed for handling the Coulomb interactions.

Symmetry, in reducing the volume or number of unique species for which terms must be evaluated, can also allow substantial speedups in quantum and molecular calculations. Point group symmetry constraints are a standard feature of most first principles molecular quantum chemistry codes and, for periodic density functional codes, such as CASTEP^{56,57} and DMol³⁵⁸⁻⁶¹ or the periodic Hartree-Fock code CRYSTAL,⁶² the computational savings can be substantial. Analogous efficiencies can be gained in, for example, docking calculations for periodic solids in which grids reflecting contributions to system energy (Color Plate 12) or population densities can be accumulated by mapping results for just the unique volume, or by symmetrizing the results of a calculation in triclinic symmetry, P1, to improve the effective map definition. Color Plate 13 shows a slice through the electrostatic potential of the α -polymorph of the glycine crystal structure. Localized basis set periodic density functional theory calculations⁶³ provide a detailed description of the structure and energetics of such systems. As with data derived from diffraction experiments, interpretation is facilitated by the combination of structure visualization and manipulation techniques, with established 3D graphical analysis tools such as the interactive "slide plane" (Color Plate 13).

6. CONCLUSION

A large number of methods for determining, manipulating, displaying, and exploiting symmetry and periodicity is conveniently incorporated within a general utility crystallographic workbook. Such an implementation provides a useful aid in the education of crystallographic concepts. It also offers efficiencies in constructing crystal structure models, determining crystal structures by model building or diffraction-based routes, and exploiting today's capabilities for performing classic and quantum simulations.

ACKNOWLEDGMENTS

MSI's Catalysis and Sorption, Polymer and Pharmaceutical Development projects are supported by consortia of industrial, governmental, and academic groups. We thank the members of these consortia for their ongoing ideas, guidance, and support. We also thank our numerous scientific advisors, consultants, and collaborators, who have played a key role in the research, design, and validation of these various crystallographic techniques.

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