

Crystallographic Symmetry

Crystallographic Symmetry in Real and Reciprocal Space.

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Sienna/Crystal Symmetry

Crystallographic symmetry

Crystallographic symmetry in Real Space

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Sienna/Crystal Symmetry

Crystallographic symmetry:

Overview:

- Brief review of concepts.
- Spacegroups and settings.
 - Spacegroup symbols.
- Symmetry operators.
- Symmetry in reciprocal space.
- Symmetry in real space.
- Ideas and implementations.

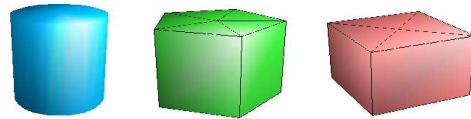
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Crystallographic symmetry:

Concepts:

- Point group – symmetries about a point.
 - e.g. n-fold rotation (any n), mirror, inversion.



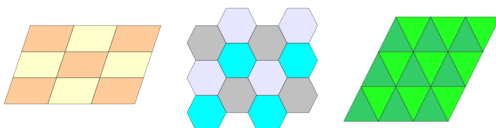
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Sienna/Crystal Symmetry

Crystallographic symmetry:

Concepts:

- Lattice group – symmetries of a lattice.
 - Lattice can be made of any shape which tessellates.
 - 2D: square, rectangle, rhombus, parallelogram, triangle, hexagon.
 - 3D: prisms of above, tetrahedron, parallelepiped.
 - Lattice symmetries restricted by those shapes.



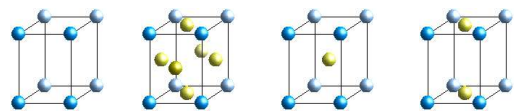
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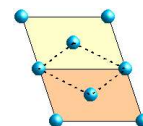
Crystallographic symmetry:

Concepts:

- Bravais lattice – parallelepiped cell with lattice **centerings** to represent the other shapes. (P/F/I/C/R).



- Primitive cell – Un-centered cell chosen from within a centered lattice.



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Crystallographic symmetry:

Space group:

- Combines symmetry of lattice, lattice centering, and symmetry within the primitive cell.
- 230 distinct space groups (i.e. combinations of symmetries consistent with 3D lattice).
 - Tabulated and numbered in International Tables for Crystallography.
 - Also described by Hermann-Mauguin symbols.
 - e.g. Spacegroup 19 = P2₁2₁2₁

Crystallographic symmetry:

- Which is great, but what we really want to know is where the atoms are. Which means knowing the cell and the symmetry operators.
 - e.g. If there is an atom at $x = (13, 17, 24)$, then $u = (0.3, 0.2, 0.4)$, and the symop is $(-u, v+1/2, -w)$, so there is an atom at $u = (-0.3, 0.7, -0.4)$ or $x = (-13, 45, -24)$
- **PROBLEM:** The space group number (or H-M symbol) do not uniquely determine the symmetry operators.
 - Several space groups have multiple *tabulated* settings.
 - And there are a huge number of possible non-standard settings.

Crystallographic symmetry:

- Solutions:
 - Only allow certain settings.
 - Inconvenient for users and hard to spot. More user support.
 - Use a symbol which includes a precise definition of the setting: Hall symbol from **CCTBX** (also in **Clipper**).
 - Hall & Grosse-Kunstleve (2001) Int Tab B, 201.
 - Ignore the space-group symbols, use the symmetry operators.
 - No ambiguity.
 - Symmetry operators present in CCP4 MTZ/map files, and deposited PDB files.
 - Determining other space-group info from operators complex, but already implemented in **CCTBX**, **Clipper**, **CCP4**.

Crystallographic symmetry: Symops

Symmetry operators (Symops):

- Express the symmetry relationships in the unit cell (and therefore in the diffraction pattern).
- Fractional rotation-translation operators.
- For any spacegroup, let there be N_{sym} symops, numbered $0 \dots N_{sym}-1$

$$S_i(\underline{u}) = \mathbf{S}_i \underline{u} + \underline{S}_i$$
- Operator 0 is the identity.

Crystallographic symmetry: Symops

Symmetry operators (Symops):

- We can extract from the N_{sym} symops, two subgroups of operators: the centering operators and the primitive operators, such that:

$$N_{sym} = N_{primitive} \times N_{centering}$$
- The centering operators have $\mathbf{S} = \mathbf{I}$.
- The primitive operators may have translation parts, but all have $\mathbf{S} \neq \mathbf{I}$.
 - These are the operators from the corresponding “P” space-group.
 - In reciprocal space we generally ignore the centering operators.

Crystallographic symmetry: Symops

Symmetry operators (Symops):

- e.g. **P 2₁ 1** (P 1 2₁ 1, spacegroup 4)
- Equivalent posns: $u.v.w: -u.v+1/2,-w;$

$$\mathbf{S}_0 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \underline{S}_0 = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

$$\mathbf{S}_1 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \underline{S}_1 = \begin{pmatrix} 0 \\ 1/2 \\ 0 \end{pmatrix}$$

Crystallographic symmetry: Symops

Symmetry operators (Symops):

- e.g. **P 31** ($P 3_1$, spacegroup 144)
- Equivalent posns: $u, v, w; -v, u-v, w+1/3; -u+v, -u, w+2/3;$

$$S_0 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \underline{S}_0 = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

$$S_1 = \begin{pmatrix} 0 & -1 & 0 \\ 1 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \underline{S}_1 = \begin{pmatrix} 0 \\ 0 \\ 1/3 \end{pmatrix}$$

$$S_2 = \begin{pmatrix} -1 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \underline{S}_2 = \begin{pmatrix} 0 \\ 0 \\ 2/3 \end{pmatrix}$$

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Crystallographic symmetry: Symops

Symmetry operators (Symops):

- e.g. **C 2 2 2** ($C 2 2 2$, spacegroup 21)
- Equivalent posns:
 - $u, v, w;$
 - $-u, -v, w;$
 - $-u, v, -w;$
 - $u, -v, -w;$
 - $u+1/2, v+1/2, w;$
 - $-u+1/2, -v+1/2, w;$
 - $-u+1/2, v+1/2, -w;$
 - $u+1/2, -v+1/2, -w;$
- Primitive:
 - $u, v, w;$
 - $-u, -v, w;$
 - $-u, v, -w;$
 - $u, -v, -w;$
- Centering:
 - $u, v, w;$
 - $u+1/2, v+1/2, w;$

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Crystallographic symmetry: Symops

Symmetry operators (Symops):

- Remember: symops are **fractional**, and therefore the matrix is not a true rotation.
- Convert the symop to **orthogonal** form, and it may be used to transform orthogonal coordinates.
 - If the cell is consistent, the matrix part should become a true rotation.
- We can also convert symops to **grid coordinates** by scaling the translations (assuming grid is consistent with symmetry). Useful optimization when handling maps.

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Crystallographic symmetry: Symops

Symmetry operators (Symops):

- Related symmetry groups:
 - Point group: (symmetry of anomalous data)
 - Just take the unique rotation parts of the symmetry operators.
 - Laue group: (symmetry of non-anomalous data)
 - Point group + inversion operator.
 - Patterson group: (symmetry of the Patterson map)
 - Laue group + centering operators.

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Crystallographic symmetry:

Dealing with symmetry in mathematics:

- In our Likelihood functions we often treat different reflections as independent. But symmetry related reflections (and Friedel opposites) are not independent – these must be handled explicitly.

Dealing with symmetry in software:

- Symmetry related values should never be inconsistent. When we change a structure factor or density, every related value should change immediately.
 - Only store a unique set of values (asymmetric unit), and generate related values on-the-fly.

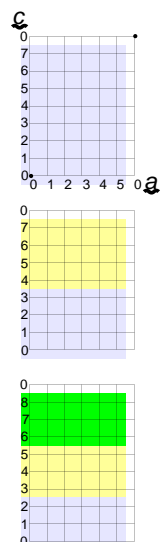
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Crystallographic symmetry:

Map asymmetric units (ASUs):

- In **P 1**, the ASU is the whole cell.
- In **P 2yb** ($P 1 2_1 1$, spacegroup 4),
 - Symops are: $u, v, w; -u, v+1/2, -w;$
 - Use $v+1/2$ to generate half the cell along the b axis.
- For any screw axis, divide the cell length by the screw translation.
 - e.g. **P 31**



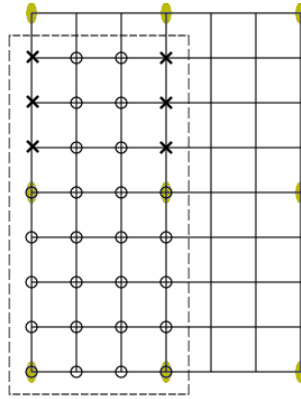
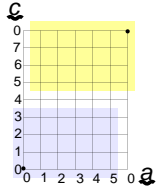
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Crystallographic symmetry: Maps

Map asymmetric units (ASUs):

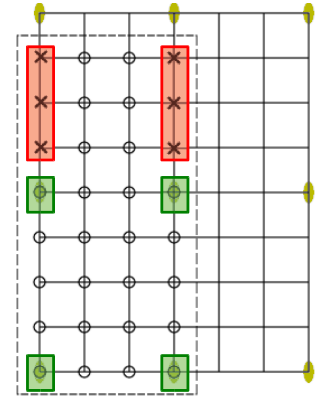
- In **P 2₁b** (P 1 2 1),
 - Symops are: $u, v, w; -u, v, -w;$
 - Several sensible ASUs



Crystallographic symmetry: Maps

Map asymmetric units (ASUs):

- We can define a box which roughly encloses the ASU.
- Some points may still be duplicates.
- Other points may be related to themselves:
 - 'symmetry enhanced'
 - in atom density calculation, they may require special treatment.



Crystallographic symmetry

Crystallographic symmetry in Reciprocal Space

Crystallographic symmetry: hkl

- Relationships between reflections:

$$E(\mathbf{h}) = \sum_j f_j(\mathbf{h}) \exp(2\pi i \mathbf{h}^T \mathbf{u}_j)$$

$$= \sum_j f_j(\mathbf{h}) \exp(2\pi i \mathbf{h}^T [\mathbf{S}_k \mathbf{u}_j + \mathbf{S}_k])$$

$$= \sum_j f_j(\mathbf{h}) \exp(2\pi i [\mathbf{h}^T \mathbf{S}_k \mathbf{u}_j + \mathbf{h}^T \mathbf{S}_k])$$

$$= \sum_j f_j(\mathbf{h}) \exp(2\pi i [(\mathbf{S}_k^T \mathbf{h})^T \mathbf{u}_j + \mathbf{h}^T \mathbf{S}_k])$$

but:

$$E(\mathbf{S}_k^T \mathbf{h}) = \sum_j f_j(\mathbf{h}) \exp(2\pi i (\mathbf{S}_k^T \mathbf{h})^T \mathbf{u}_j)$$

therefore:

$$E(\mathbf{h}) = E(\mathbf{S}_k^T \mathbf{h}) \exp(2\pi i \mathbf{h}^T \mathbf{S}_k)$$

$$E(\mathbf{S}_k^T \mathbf{h}) = E(\mathbf{h}) \exp(-2\pi i \mathbf{h}^T \mathbf{S}_k)$$

Crystallographic symmetry: hkl

- Example: **P 31**

$$\mathbf{S}_0 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \mathbf{S}_0 = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

$$\mathbf{S}_1 = \begin{pmatrix} 0 & -1 & 0 \\ 1 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \mathbf{S}_1 = \begin{pmatrix} 0 \\ 0 \\ 1/3 \end{pmatrix}$$

$$\mathbf{S}_2 = \begin{pmatrix} -1 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \mathbf{S}_2 = \begin{pmatrix} 0 \\ 0 \\ 2/3 \end{pmatrix}$$

- Symmetry related reflections are: $\mathbf{S}_k^T \mathbf{h}$

$$\begin{pmatrix} h \\ k \\ l \end{pmatrix}, \begin{pmatrix} k \\ -h-k \\ l \end{pmatrix}, \begin{pmatrix} -h-k \\ h \\ l \end{pmatrix}$$

Crystallographic symmetry: hkl

- Relationships between reflections:

$$E(\mathbf{S}_k^T \mathbf{h}) = E(\mathbf{h}) \exp(-2\pi i \mathbf{h}^T \mathbf{S}_k)$$
- But: Sometimes the symmetry operation relates a reflection to itself or its Friedel opposite.
 - e.g. (1,0,0) under (u,-v,-w) or (-u,-v,w)
- We know:

$$E(\mathbf{h}) = E(\mathbf{h}) \quad (\text{by definition})$$

$$E(\mathbf{h}) = E(-\mathbf{h})^* \quad (\text{Hermitian symmetry})$$

Crystallographic symmetry: hkl

- Suppose:

$$\mathbf{S}_k^T \underline{h} = \underline{h}$$
- Then:

$$E(\underline{h}) = E(\underline{h}) \exp(-2\pi i \underline{h}^T \underline{S}_k)$$
- This can only be true if $\underline{h}^T \underline{S}_k$ is an integer.
 - If $\underline{h}^T \underline{S}_k$ is an integer, $E(\underline{h})$ is an enhanced reflection, i.e. its intensity $I(\underline{h})$ is increased by a factor of ϵ , where ϵ is the number of operators relating \underline{h} to itself.
 - If $\underline{h}^T \underline{S}_k$ is not an integer, $E(\underline{h})$ is a systematic absence.

Crystallographic symmetry: hkl

- Suppose:

$$\mathbf{S}_k^T \underline{h} = -\underline{h}$$
- Then:

$$E(\underline{h})^* = E(\underline{h}) \exp(-2\pi i \underline{h}^T \underline{S}_k)$$

$$-\phi(\underline{h}) = \phi(\underline{h}) - 2\pi \underline{h}^T \underline{S}_k + 2n\pi$$

$$\phi(\underline{h}) = \pi \underline{h}^T \underline{S}_k + n\pi$$
 i.e. one of two values separated by π .
 e.g. $0, \pi$; $+\pi/2, -\pi/2$; $-\pi/3, +2\pi/3$;
- The reflection is centric.
 - It may also be enhanced.

Crystallographic symmetry: hkl

- Determining the class of a reflection: (clipper::HKL_class)
 - Loop over all (primitive) symmetry operators.
 - If $\mathbf{S}_k^T \underline{h} = -\underline{h}$, the reflection is centric.
 - Calculate its allowed phases.
 - If $\mathbf{S}_k^T \underline{h} = \underline{h}$:
 - If $\underline{h}^T \underline{S}_k$ is an integer, increase the enhancement by 1, otherwise the reflection is a systematic absence.
 - Enhancement is increased by the number of centerings.

Crystallographic symmetry: hkl

- Transforming a reflection about reciprocal space:

$$|E(\mathbf{S}_k^T \underline{h})| = |E(\underline{h})|$$

$$\phi(\mathbf{S}_k^T \underline{h}) = \phi(\underline{h}) - 2\pi \underline{h}^T \underline{S}_k$$
- From these, calculate the transformations for other types of data, e.g. A,B, Hendrickson-Lattmann coefficients.
 - Clipper: when a reflection data type is defined, its behavior under phase shift or Friedel inversion is also defined. With these the reflection can be transformed about reciprocal space by 'magic'.

Crystallographic symmetry: hkl

Reciprocal space asymmetric units (ASUs).

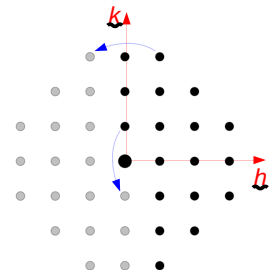
- P1:
 - For the most common calculations, we don't need to store both a reflection and its Friedel opposite (since $E(-\underline{h}) = E(\underline{h})^*$). Even for anomalous data, we usually store $E(\underline{h})$ and $E(-\underline{h})$ together.
 - Therefore, we only need to store a hemisphere of data.



Crystallographic symmetry: hkl

Reciprocal space asymmetric units (ASUs).

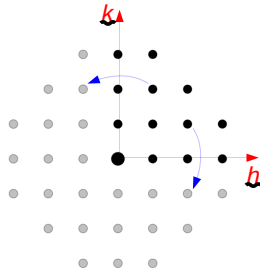
- P1: Hemisphere of data.
 - But even that isn't simple.
 - Use for example:
 - ($l > 0$) or
 - ($l = 0$ and $h > 0$) or
 - ($l = 0$ and $h = 0$ and $k > 0$)



Crystallographic symmetry: hkl

Reciprocal space asymmetric units (ASUs).

- **P 2 2:** (P 2 2 2)
 - $h \geq 0$ and $k \geq 0$ and $l \geq 0$
- **P 3:** (P 3)
 - $(h \geq 0 \text{ and } k \geq 0)$ or
 - $(h = 0 \text{ and } k = 0 \text{ and } l \geq 0)$
- **P 4 3 2:** (P 4 3 2)
 - $k \geq l$ and $l \geq h$ and $h \geq 0$



Crystallographic symmetry: hkl

Implementation:

- Calculate point-group, and 'change-of-basis' to get to standard setting, then use ASU for that point-group on transformed hkl . (13 tabulated ASUs).
 - **CCTBX, CCP4**
- Calculate oriented point-group, and then use ASU for that point-group hkl . (51 tabulated ASUs).
 - **Clipper** optimization.
 - Sanity check by using a sample set of reflections.

Crystallographic symmetry:

General implementation points:

- **CCTBX** is fully space-group general, and will handle made-up settings without difficulty.
- **Clipper** is fully space-group general, and will handle made-up settings without difficulty (except it won't name a space-group from the symops unless they match one from a list of common and uncommon settings).
- **CCP4** uses a data file of common and uncommon settings, and won't handle anything else.

Crystallographic symmetry:

Implementation: Maps

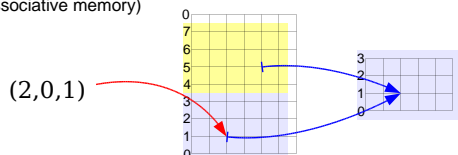
- Typical map access modes...
 - Loop over each unique grid point in turn.
 - Access a grid point, and then one of its neighbors.
 - Access grid points at random.
- Map data objects are ideally specialized to the access pattern required.
 - But useful compromises are possible.

Crystallographic symmetry:

Implementation: Maps

- e.g. for random access, use `mod()` to get grid coordinates into the unit box, and then use a unit cell grid of pointer pointing to the density value in an asymmetric unit list.
 - Cost: an extra memory access.
 - To save memory share lookup tables between maps using the same grid and space-group.

(Associative memory)



Crystallographic symmetry:

Implementation: Maps

- **Clipper approach: random access is rare. Store an ASU grid with pointers round the edge so that when we run out of the grid we know where to get the next density.**
 - No additional lookup.
 - Good for sequential access and neighbor access.
 - Lower overhead.
 - For full-cell random access, a search over symops is required (or expand to P1).

Crystallographic symmetry:

Implementation: Reflections

- Store a list of reflections with h,k,l?
 - Good for sequential access.
 - Efficient storage of ASU.
- Or store a 3D array of reflections?
 - Good for random access.
 - Inefficient storage of ASU.
 - Sequential access may be harder.

Crystallographic symmetry:

Implementation: Reflections

- **Clipper approach: Store a list of h,k,l and reflection data values of arbitrary types. But also provide a ragged 3D index array (ASU only) for when random access is required.**
 - Fairly compact.
 - For full-sphere random access, a search over symops is required.

Crystallographic symmetry:

Summary:

- Symmetry is fundamental to crystallographic calculation in both real and reciprocal space.
- We use space-group symbols, calculations use the symmetry operators.
- Symmetry involves a lot of book-keeping, which may be avoided by good enough class design.
 - General designs are useful for many/most purposes.
 - However, optimal solutions may be problem specific.