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Use of the Consistency Check in the Vector Verification Method

Alan D. Mighell* and R. A. Jacobson [1]

Institute for Materials Research, National Bureau of Standards, Washington, D.C.

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The consistency check is a type of frequency check in which full use is made of the space group symmetry. It is designed for application to a symmetry map, to a tentative atom map, to the results of superpositions, or to any pseudoelectron-density map. Like the frequency check, its purpose is to aid in the analysis of one of the above maps by assigning a relative weight (relative weight equals the number of other peaks that the given peak is consistent with) to the peaks in these maps. To determine the relative weight, each peak in the map is compared with each of the others to see if it is consistent. Two peaks are considered consistent with each other, if and only if, the set of unique vectors between the two is present in the Patterson map. The method is equivalent to doing a full set of symmetry superpositions at each peak in a symmetry map or a tentative atom map; counting the number of points in the resulting map; and outputting this number at the initial peak position. No assumptions other than that for space group symmetry are required to apply the consistency check to a symmetry map. The resulting map, which has been calculated in a routine fashion directly from the Patterson map, may then be conveniently used as the starting point for the structure analysis of an unknown compound.

Key Words: Crystal, structure, Patterson, vector, symmetry, consistency, frequency, superposition.

1. Introduction

Vector methods based on analysis of the Patterson function are extremely useful in solving crystal structures. Since these methods can be adapted to high speed digital computers, it has been possible to derive both centric and acentric crystal structures from complex Patterson functions.

Vector verification is one type of vector method which has been adapted to the computer. This method has been shown to be a valuable approach to the analysis of the Patterson function [Mighell and Jacobson, 1963, 1964]. The procedures involved in this method are

1. The formation of a map, referred to as a symmetry map, containing only the electron-density space positions consistent with both the Patterson map and the space group of the crystal. The frequency or consistency check is then applied to part or all of the symmetry map.
2. The choice of a trial atomic position, called a tentative atom position, from the symmetry map prepared in step 1.
3. The formation of a new map, referred to as a tentative atom map, containing only the electron-density space positions consistent with the tentative atom position, in addition to the restrictions in step one above. The frequency check or consistency check is then applied to part or all of the tentative atom map.
4. Repetition of steps 2 and 3 until a refinable trial model results.

In the frequency check method [Gorres and Jacobson, 1964], the Patterson map is superimposed on each location in the symmetry, in the tentative atom, or in any similar pseudoelectron-density map. After each superposition, a frequency corresponding to the number of peak coincidences is assigned to the superposition point, resulting in a frequency map indicative of the probable atomic locations.

The consistency check is a type of frequency check in which full use is made of space group symmetry. Closely related methods were reported by Gorres and Gaertner [1965] and Corfield and Rosenstein [1965] at the American Crystallographic Association Meeting in Gatlinburg, Tenn. The consistency check is designed to aid in the analysis of a symmetry map, a tentative atom map, the results of superpositions, or of similar pseudoelectron-density maps. Like the frequency check, the method extends the information present in one of the above maps by assigning a weight to each peak in the map. The procedure may be carried out in a routine fashion as it requires no assumptions about the final structure other than that of space group symmetry.

After the consistency check has been applied to the peaks in a symmetry map or in a tentative atom map, one is in a much better position to distinguish real from

*National Research Council-National Bureau of Standards Postdoctoral Research Associate, 1964–1966.

[1] Present Address: Department of Chemistry, Iowa State University, Ames, Iowa.

spurious peaks. It is then possible to choose in a systematic way the best peaks to use in the tentative atom procedure, the most suitable vectors to use in the superposition procedure, or the most likely peaks to use in the final structure.

2. The Method of the Consistency Check

The consistency check may be run on a symmetry map, on a tentative atom map [Mighell and Jacobson, 1964] or on any pseudoelectron-density map. Before initiating the consistency check, a three-dimensional sharpened Patterson map [Jacobson, Wunderlich, and Lipscomb, 1961] is stored in the memory of the computer. For programming convenience all grid positions having a value above a given value are stored as a 1 and those below as a 0. However, in a later version it is planned to use the actual peak heights. Also all of the peaks in the symmetry or tentative atom map (i.e., grid coordinates that survived the symmetry or tentative atom procedure) are stored in memory as a list.

Each peak in the list is compared against all of the others, one by one, to see if it is consistent. Two points are defined as consistent with each other if, and only if, the set of unique vectors between the two is present in the Patterson map. For example, in the case where there are four equivalent positions in the space group, the unique vectors between atoms located at positions X and Y would be $\mathbf{X}-\mathbf{Y}$, $\mathbf{X}-\mathbf{Y}'$, $\mathbf{X}-\mathbf{Y}''$, $\mathbf{X}-\mathbf{Y}'''$ (the primes indicate atoms related to Y by space group symmetry). For a given peak X (grid coordinates x, y, z) in the list, the total number of peaks in the list that X is consistent with, is recorded and outputted at grid position x, y, z.

Although the entire symmetry map is stored in the computer as a list, it is necessary to execute the consistency check only on the peaks that comprise the asymmetric unit of the symmetry map. The calculations for the entire consistency check are extensive but the method is easy to program and may be successfully carried out in a routine way on a large digital computer. However, if only limited computer time is available or if a small computer is to be used, it is often sufficient to run the consistency check on only a part of the symmetry map or on a part of the tentative atom map.

The symmetry map, or the tentative atom map to which the consistency check has been applied, is outputted in the same format as the input map. In addition, a record is made at every peak of the number of consistencies, that is, the number of other peaks in the map with which it is consistent. Actual peaks tend to be consistent with many more peaks than do spurious peaks.

3. Interpretation of the Results From the Consistency Check

As indicated above, the consistency check may be applied either to a symmetry map or to a tentative atom map. If the check is applied to a symmetry map, the peaks having the highest consistencies are more likely to represent actual atomic positions and are therefore the best possibilities to use as the tentative atom in the tentative atom procedure. Also the peaks, having the highest consistency, may be used to calculate the best vectors to use in the conventional superposition procedure.

The calculation of the symmetry map followed by the applications of the consistency check is based solely on the knowledge of the space group and the Patterson map. No other assumptions as to the arrangement of the atoms in the space group are made. Thus, for a new compound it is possible to calculate in a routine way a Patterson map and a symmetry map to which the consistency check has been applied.

If the consistency check is applied to a tentative atom map or to a similar pseudoelectron-density map, the peaks having the highest consistencies are the best possibilities for final atomic positions, for a second tentative atom, or for a peak on which to base further superpositions.

4. Equivalence of the Consistency Check

The consistency check is exactly equivalent to performing the tentative atom procedure at every peak (grid coordinates that satisfy the symmetry or tentative atom conditions for a given space group) in a symmetry map or in a map resulting from the tentative atom procedure.

For example, take the case in which the consistency check is applied to the results of the symmetry check. Consider a typical peak X in the symmetry map [Mighell and Jacobson, 1963]. Peak X is used as a tentative atom in the tentative atom procedure and the total number of peaks (grid positions that satisfied the conditions of the tentative atom procedure) in the resulting tentative atom map are counted. This number, which tells exactly how many points survive the tentative atom procedure, is placed in the position X in the symmetry map. The same procedure is carried out at all the other peaks in the symmetry map.

The consistency check is also equivalent to doing a series of superpositions (using the set of vectors between the tentative atom and its equivalent positions) at each peak in the symmetry map or in the tentative atom map. If there is only one vector, then the consistency check gives results equivalent to the frequency check [Gorres and Jacobson, 1964]. But in all of the higher space groups, where there is more than one vector, the consistency check is more powerful than the frequency check.

5. Conclusion and Extension

The consistency check, like the frequency check, is a method designed to evaluate the peaks resulting from the symmetry check, the tentative atom procedure, or the standard superposition method. This method can be applied to both centric and acentric

crystals and is especially useful for crystals belonging to space groups of high symmetry. It is useful in distinguishing real peaks form spurious peaks, in ascertaining the centers of peaks, in picking tentative atoms or in selecting vectors for superpositions.

The symmetry map to which the consistency check has been applied can be derived routinely from the Patterson function. This map can then serve as a useful adjunct to other methods of structure solution. For example, it may serve as a starting point for either mathematical or vector phasing methods.

Since the present method has been based entirely on peak positions, a useful extension of the method would be to calculate a symmetry map, a tentative atom map, and a consistency check using the Patterson map with the actual peak heights rather than the bi-valued Patterson. The method would then become considerably more powerful but the computer time and memory requirements would be greatly increased.

6. References

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