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Ab initio determination of incommensurately modulated structures by charge flipping in superspace

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The charge flipping algorithm proposed by Oszlányi & Sütő [*Acta Cryst.* (2004), A**60**, 134–141] for *ab initio* reconstruction of crystal structures is generalized towards superspace. Its efficiency is demonstrated by successful reconstruction of eight known incommensurately modulated structures from experimental data. The output of the charge flipping algorithm is an electron density with symmetry $P1$. The symmetry of the structure is recovered by locating the positions of symmetry operators and averaging the density over the symmetry-related pixels. The reconstruction of a modulated structure by the charge flipping algorithm and the accuracy of the result is demonstrated in detail on the modulated structure of tetraphenylphosphonium hexabromotellurate(IV) bis{dibromoselenate(I)}.

1. Introduction

Ab initio structure solution of ordinary periodic crystals from single-crystal X-ray diffraction data has become a routine job during the last few decades, mainly due to the development and continuous improvement of direct methods. Contemporary advanced techniques allow one to solve structures with more than a thousand atoms in the asymmetric unit of the structure. This contrasts with the situation in the crystallography of incommensurately modulated crystals. Their structures are usually solved by embedding in superspace (de Wolff *et al.*, 1981; Janssen *et al.*, 1992; van Smaalen, 1995). In this technique, a structure with d modulation vectors is described in a $(3+d)$-dimensional $[(3+d)\mathrm{D}]$ superspace and its atoms are represented by d-dimensional domains that are continuous along the additional dimensions. For this reason, the methods used for periodic crystals and in particular direct methods cannot be simply generalized to allow for a structure solution directly in superspace because the discrete nature of the atoms (their 'atomicity') is a key property used by most of the *ab initio* structure-determination methods.

The structure solution of a modulated structure is usually done in two steps. In the first step, the average structure is determined, which can be understood as the three-dimensional periodic structure with atoms at the positions obtained by averaging all their positions in the modulated structure. Once the average structure is known, the modulation can often be determined by refinement with arbitrary small starting values of the modulation parameters. If this approach fails, another method can be applied, which uses the known phases of the main reflections and a modified Sayre's equation to determine the phases of the satellite reflections (Hao *et al.*, 1987; Fan *et al.*, 1993). In this method, the phases of the main reflections are determined first by conventional direct methods, and the phases of the satellite reflections are estimated from a modified Sayre's equation with the assumption that the phases of the main reflections are known. Alternatively, Patterson methods in superspace can be used to estimate the modulation phase and amplitude of heavy atoms (Steurer, 1987).

The common feature of all contemporary methods for structure solution of incommensurately modulated crystals is the necessity to determine the average structure. However, in some cases this can be a very difficult task. Complex organic molecular compounds have been discovered that exhibit large modulations with amplitudes exceeding 1 Å (Gaillard *et al.*, 1998; Pinheiro *et al.*, 2004; Schönleber & Chapuis, 2004). With such a huge modulation, the determination of the average structure can be extremely difficult and the structure must be solved in an approximate supercell to obtain an initial structure model. This can be a non-trivial task if the nearest suitable supercell is too large.

This paper presents a method for *ab initio* solution of modulated structures from X-ray diffraction data directly in superspace, without the intermediate step of determining the average structure. It is a generalization of the method dubbed *charge flipping*, which was presented recently by Oszlányi & Sütő (2004). This method was successfully tested with periodic molecular structures having more than 200 non-H atoms in the unit cell. The method does not make use of the point-like character of the atoms ('atomicity') of the underlying structure. Instead it uses the property of the crystal structures that most of the volume is filled by very low electron density and high-density regions fill only a very small part of the space. This property is common to both ordinary and superspace electron densities, making the charge flipping algorithm an

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ideal tool for *ab initio* structure determination of electron densities of modulated structures.

In the first part of the paper, the algorithm is briefly described and generalized towards superspace. In the next section, the determination of the origin of the symmetry in the reconstructed densities is discussed. §§4 and 5 present examples of structures solved by charge flipping in superspace and the presented method is illustrated with the solution of the modulated structure of tetraphenylphosphonium hexabromotellurate(IV) bis{dibromoselenate(I)}.

This paper deals exclusively with the class of incommensurately modulated structures, including composite structures. It does not consider quasicrystals, which can be described in superspace too, but the method is different (Janot, 1995). However, it is very likely that charge flipping in superspace can be applied to the structure solution of quasicrystals too. Another algorithm based on the modification of superspace density has already been applied to quasicrystals by Takakura *et al.* (2001).

2. The algorithm

The algorithm is discussed in detail in the paper by Oszlányi & Sütő (2004) together with its mathematical aspects. The description and analysis of the algorithm given there applies almost completely also to charge flipping in superspace. Therefore only a basic description of the algorithm will be given here. The algorithm is described in the original version for periodic structures and then it is generalized to modulated structures.

The electron density ρ is sampled on a grid with $N_{\rm pix} = N_1 \times N_2 \times N_3$ pixels. The density values ρ_i are evaluated in each pixel $i = 1, \ldots, N_{\rm pix}$ of the grid. $|F^{\rm obs}(\mathbf{H})|$ are the experimental amplitudes of the structure factors. The algorithm is initiated in the zeroth cycle by assigning random starting phases $\varphi_{\rm rand}(\mathbf{H})$ to all experimental amplitudes and making all unobserved amplitudes equal to zero:

$$F^{(0)}(\mathbf{H}) = \begin{cases} |F^{\rm obs}(\mathbf{H})| \exp[i\varphi_{\rm rand}(\mathbf{H})] & \text{if } |F^{\rm obs}(\mathbf{H})| \text{ is known} \\ 0 & \text{otherwise.} \end{cases} \tag{1}$$

The iteration cycle then proceeds as follows:

1. The density $\rho^{(n)}$ is calculated by inverse Fourier transform of $F^{(n)}$.

2. The modified density $g^{(n)}$ is obtained by flipping the density of all pixels with density values below a certain positive threshold δ and keeping the rest of the pixels unchanged:

$$g_i^{(n)} = \begin{cases} \rho_i^{(n)} & \text{if } \rho_i^{(n)} > \delta \\ -\rho_i^{(n)} & \text{if } \rho_i^{(n)} \le \delta. \end{cases} \tag{2}$$

3. Temporary structure factors $G^{(n)}(\mathbf{H}) = |G^{(n)}(\mathbf{H})| \exp[i\varphi_G(\mathbf{H})]$ are calculated by Fourier transform of $g^{(n)}$.

4. New structure factors $F^{(n+1)}$ are obtained by combining the experimental amplitudes with the phases φ_G and setting all non-measured structure factors to zero:

$$F^{(n+1)}(\mathbf{H}) = \begin{cases} |F^{\rm obs}(\mathbf{H})| \exp[i\varphi_G(\mathbf{H})] & \text{if } |F^{\rm obs}(\mathbf{H})| \text{ is known} \\ 0 & \text{otherwise.} \end{cases} \tag{3}$$

These structure factors then enter the next cycle of iteration.

The $F(\mathbf{0})$ structure factor needs special treatment. In the original version of the algorithm presented by Oszlányi & Sütő (2004), the $F(\mathbf{0})$ structure factor is set to zero in the zeroth cycle of the iteration and allowed to change freely in the subsequent cycles. In this work, a different method of handling the $F(\mathbf{0})$ value has been adopted. $F(\mathbf{0})$ is set to zero not only at the beginning of the iteration but also at the beginning of each cycle, before the density $\rho^{(n)}$ is calculated from $F^{(n)}(\mathbf{H})$. This modification made it possible to use lower values of δ, which in turn produced considerably clearer density maps with lower noise level. The interval of acceptable values of δ was broader and the speed of convergence was comparable to or better than the convergence of the original version. However, thorough tests are necessary to assess the applicability of the modified version of the algorithm to large 3D structures. Preliminary results indicate that this modification performs worse than the original version in the case of very complex structures (Oszlányi, private communication).

δ is the only adjustable parameter of the algorithm. Its value should be selected small relative to the maximum density, but larger than the typical amplitude of the Fourier artifacts induced by the series-termination error. In practice, the value of δ is determined by trial and error.

An important aspect of the algorithm is that all operations are performed in the whole unit cell with symmetry $P1$. The origin of the structure is thus not fixed and the structure can emerge anywhere in the unit cell. If the electron density is forced to obey the symmetry in each cycle, the convergence is much slower and the results are considerably worse. It will be shown in the next section that the symmetry of the electron density can be recovered by locating the symmetry elements in the output of the charge flipping algorithm instead of forcing the symmetry to be obeyed during the iteration.

The progress of the iteration can be monitored for example by observing the R value of amplitudes $|G^{(n)}(\mathbf{H})|$ with respect to $|F^{\rm obs}(\mathbf{H})|$. It is large in the initial cycles of the iteration and the onset of the convergence is signalled by a sharp decrease of the R value. The iteration is converged if the R value stops decreasing and oscillates around a constant value. The final R values are larger than the values typical for successful structure refinement, typically 20–30%. However, the R value is not used as a measure of the quality of the reconstruction, but merely as an indicator of convergence. For more information see Oszlányi & Sütő (2004).

The generalization of the algorithm for reconstructions of incommensurately modulated and composite crystal structures is straightforward. Following the method of embedding of aperiodic crystal structures in superspace (de Wolff *et al.*, 1981; Janssen *et al.*, 1992; van Smaalen, 1995), the 3D density is replaced by a $(3+d)$D superspace density sampled using a $(3+d)$D grid with $N_{\rm pix} = N_1 \times N_2 \times \ldots \times N_{3+d}$ pixels, where d is the number of independent modulation vectors. The structure factors are indexed by $(3 + d)$ integer indices. They represent the coefficients of the Fourier transform of the superspace density. With these modifications, the algorithm described at the beginning of this section can be applied directly to incommensurate structures. The analysis of the output superspace density yields positions of the atoms and their modulation functions (§5).

The algorithm described in this and next sections was implemented in a computer program *BayMEM*, whose main purpose is the reconstruction of the electron densities by the maximum-entropy method in arbitrary dimensions (van Smaalen *et al.*, 2003). *BayMEM* was used for all tests presented in this work.[1]

3. Reconstruction of the symmetry

The output of the charge flipping algorithm is a density with symmetry $P1$. However, the symmetry of the structure is present in the density with good accuracy and it is desirable to locate the symmetry elements and to shift the origin of the density to the origin of the (super)space group. If the positions of the symmetry elements are located, then averaging over symmetry-related pixels of the unit cell is possible reducing the random noise present in the density and enhancing the significant features of the density.

The positions of the symmetry elements can be located by a method proposed by Hendrixson & Jacobson (1997) for locating symmetry elements in Patterson superposition maps. Every symmetry element $\hat{S}$ is characterized by its rotational component $\mathbf{R}$ and translational component $\boldsymbol{\tau}$. If the symmetry element is shifted from its position by an additional vector $\mathbf{t}$, then the operation of such an operator on a point $\mathbf{r}$ is given by

$$\{\hat{S}, \mathbf{t}\}\mathbf{r} = \mathbf{R}\mathbf{r} + (\mathbf{I} - \mathbf{R}) \cdot \mathbf{t} + \boldsymbol{\tau}, \tag{4}$$

where $\mathbf{I}$ is the identity matrix. The proper value of $\mathbf{t}$ must be found in order to locate the position of the symmetry element. If a symmetry element with incorrect $\mathbf{t}$ operates on the ideal symmetric density, it will produce an identical image of the density, which is however shifted with respect to the original density. Only if the shift vector $\mathbf{t}$ is correct will both densities be identical. The coincidence of the original density $\rho(\mathbf{r})$ and the density $\rho(\{\hat{S}, \mathbf{t}\}\mathbf{r})$ obtained by applying the symmetry operator $\hat{S}$ with shift $\mathbf{t}$ can be quantified by evaluating the product function $Q(\hat{S}, \mathbf{t})$ [equation (5) in Hendrixson & Jacobson (1997)]:

$$Q(\hat{S}, \mathbf{t}) = \int\limits_{V_{\text{cell}}} \rho(\mathbf{r})\rho(\{\hat{S}, \mathbf{t}\}\mathbf{r})\,\mathrm{d}\mathbf{r}. \tag{5}$$

This function has a maximum for the correct shift vector $\mathbf{t}$. It can be evaluated in direct space, where it transforms into a summation over all pixels in the discrete density, or in reciprocal space using the structure factors calculated from the electron density [equations (8) and (10) in Hendrixson & Jacobson (1997)].

The components of the vector $\mathbf{t}$ of a particular symmetry operator are arbitrary in all lines of the matrix $(\mathbf{I} - \mathbf{R})$, which contain only zeros. The origin shift along the coordinates corresponding to those lines cannot be determined from that operator. Thus, the shift of origin of the density must be sometimes determined from several symmetry operators, each of which allows determination of different components of the origin shift.

In principle, this method of locating symmetry could be used to check for the presence or absence of symmetry operators in the structure. This could help in distinguishing (super)space-group symmetries that cannot be uniquely determined solely from the symmetry and systematic extinctions in the diffraction pattern (the space groups with the same diffraction symmetry). However, tests on various 3D and 4D structures have shown that the symmetry elements can be located, but the agreement is not quantitative. In other words, the function $Q(\hat{S}, \mathbf{t})$ [equation (5)] has a maximum for the best shift $\mathbf{t}$, but the height of the maximum can vary strongly for different symmetry operators in the same structure. Thus, no hard limit can be set to decide whether a particular symmetry operator is present or absent and the inferences about the symmetry based upon the results of the charge flipping algorithm must be made with great care. The behavior of the symmetry in the results of the charge flipping algorithm will be a topic of future research.

4. Applications

The algorithm was tested with several modulated structures, ranging from a simple displacively modulated structure of ammonium tetrafluoroberyllate and composite structure of $(\mathrm{LaS})_{1.14}\mathrm{NbS}_2$ to complex strongly modulated organic compounds. An overview of all tested structures is given in Table 1. All structures were successfully reconstructed by charge flipping in superspace except for the structure of quininium (*R*)-mandelate. This exception will be discussed separately at the end of this section. In the successfully solved structures, all non-H atoms of the average structure could be located.

The tests were performed with experimental data. The tests with simulated data (noiseless structure factors computed from the structure model) provided results very similar to the experimental data and the latter are therefore used throughout this paper to emphasize the immediate applicability of the method to real problems.

Oszlányi & Sütő (2004) point out the necessity of correction for the overall isotropic thermal parameter $\mathbf{B}$. In the examples presented here, no such correction was necessary. The structures could be reconstructed from uncorrected data and the correction has only a little impact on the speed of convergence and quality of reconstructions. This is actually an expected result, since the values of $\mathbf{B}$ in the tested structures are relatively small – about 4.5 Å^2 or less.

The only free parameter of the algorithm is the parameter δ. Its proper value can usually be found very quickly by trial and error. For amplitudes scaled to the absolute scale, the values

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[1] This program is available free of charge for non-commercial use. Requests for copies of the software should be addressed to Professor Sander van Smaalen, University of Bayreuth, Germany, e-mail: smash@uni-bayreuth.de.

Table 1
Basic characteristics of structures tested with charge flipping in superspace.

The number of atoms corresponds to the primitive cell. R denotes the converged R value of the iteration of charge flipping.

Structure [ref.]	Symmetry	Composition	Cell volume (Å^3)	Atoms	R (%)
Ammonium tetrafluoroberyllate [1]	$Pnma(\alpha 00)0ss$	$(NH_4)_2BeF_4$	462.35	28	19
Tantalum germanium telluride [2]	$Pnma(00\gamma)s00$	$TaGe_{0.354}Te_2$	347.3	16	32
Lanthanum niobium sulfide† [3]	$F'm2m(\alpha 00)00s$	$(LaS)_{1.14}NbS_2$	439.9	5.32	19
4,4′-Azoxyphenetole [4]	$I2(\alpha 0\gamma)0$	$C_{16}H_{18}N_2O_3$	1457.0	42	32
Quininium (R)-mandelate [5]	$P2_1(\alpha 0\gamma)0$	$C_{20}H_{25}N_2O_2{}^+ \cdot C_8H_7O_3{}^-$	1214.6	70	–
Tetraphenylphosphonium hexabromotellurate(IV) bis{dibromoselenate(I)} [6]	$C2/m(\alpha 0\gamma)0s$	$[(C_6H_5)_4P]_2\,[TeBr_6(Se_2Br_2)_2]$	2913.9	130	32
Hexamethylenetetramine sebacate [7]	$P2_1(\alpha 0\gamma)0$	$N_4(CH_2)_6 \cdot (CH_2)_8(COOH)_2$	942.05	48	31
Hexamethylenetetramine resorcinol [8]	$I'mcm(0\beta 0)s0s$	$N_4(CH_2)_6 \cdot C_6H_4(OH)_2$	1232.47	32	30

References: [1] Palatinus *et al.* (2004); [2] Boucher *et al.* (1996); [3] Jobst & van Smaalen (2002); [4] Pinheiro *et al.* (2004); [5] Schönleber & Chapuis (2004); [6] Janickis *et al.* (2002); [7] Gaillard *et al.* (1998); [8] Rodriguez & Chapuis (2004). † The unit-cell volume and the number of atoms of this composite crystal structure are related to the first (NbS_2) subsystem.

$\delta = 0.1 - 1.0$ were applied for the structures listed in Table 1. The exact value of δ was not critical and it only marginally influenced the speed of convergence, final R value and the amount of noise in the resulting density.

The iteration started to converge almost immediately, after five or ten cycles in all cases. The R value decreased steadily until it reached the level of convergence (Table 1), where it oscillated typically within 0.5%.

For practical purposes, it is advisable to include only reflections with observed intensities in the input data set (usually $I > 3\sigma$). Omitting the weak reflections reduces the computation time and the overall amount of noise in the resulting density. No negative influence on the performance of the algorithm could be observed. The results presented in Table 1 and in the following section were obtained with only observed reflections in the data sets. This also led to significantly lower R values in all test cases, contrary to the preliminary results mentioned in Oszlányi & Sütő (2004).

The only structure that could not be solved by the charge flipping algorithm is quininium (R)-mandelate [Schönleber & Chapuis (2004), see Table 1]. The volume of the primitive basic unit cell is the second largest among the tested structures and the number of atoms in the primitive cell is the largest of all tested structures. These facts and the large number of H atoms make this structure probably the most complex among the structures listed in Table 1. In order to find the reason for the failure of the algorithm, a number of simulated data sets were generated using the published structure model. In addition to the unmodified simulated data with experimental resolution, data sets were calculated with the resolution increased from the experimental $(\sin\theta/\lambda)_{\max}$ = 0.5 to $(\sin\theta/\lambda)_{\max}$ = 0.7 Å^{-1}. A data set with maximal index of satellites limited from 4 to 2 was also created as well as one data set generated from a structure model with zero displacement parameters. None of the calculations on these modified data sets have led to reconstruction of the structure, despite several dozens of runs with different random starting phases. The behavior of all runs was quite similar. The R value started decreasing after a few cycles but the decrease stopped at about 45% and oscillated at this value. The dominating feature of the density at this stage was one large positive peak. The rest of the density was filled with many smaller randomly scattered peaks without any relationship to the true structure. The presence of the large positive peak might be an explanation for the failure of the algorithm. The density in the peak is larger than δ, it thus cannot be eliminated by flipping of charge. As the peak is structured and large enough to fix the phases of many reflections, the iteration converges to a false stable configuration of phases. However, the reason for the repeated occurrence of the large positive peak in all reconstructions of many different data sets still remains to be clarified. Understanding this feature might shed more light on the basic properties of the algorithm.

5. Example of structure solution using charge flipping in superspace

The process of structure solution with charge flipping in superspace and the analysis of the resulting density will be demonstrated with the structure of tetraphenylphosphonium hexabromotellurate(IV) bis{dibromoselenate(I)} (see Table 1). This structure contains heavy atoms (Te, Se, Br) in combination with very light atoms (C). Large positional and occupational (crenel-like) modulations occur in the structure, making it an ideal example for testing the quality of the reconstruction by the charge flipping algorithm. The structure was solved and published by Janickis *et al.* (2002). The lattice parameters are $a = 11.261$, $b = 24.543$, $c = 10.814$ Å, $\beta = 102.84°$, modulation vector $\mathbf{q} = 0.736\mathbf{a}^* + 0.545\mathbf{c}^*$. The data set comprises 4247 observed reflections (main reflections + first-order satellites) with maximum resolution $(\sin\theta/\lambda)_{\max} = 0.67$ Å^{-1}.

As a first and crucial step, the density map in four dimensions was determined by the charge flipping algorithm on a grid $48 \times 128 \times 48 \times 16$ points, which corresponds approximately to a pixel size of 0.2 Å in all real-space dimensions. The resulting map with symmetry $P1$ was analyzed for positions of symmetry elements (§3). The origin of the density was shifted to the position of the inversion center of the superspace group $C2/m(\alpha 0\gamma)0s$ and the density was averaged over symmetrically equivalent pixels.

Table 2
Atomic coordinates and integrated charges found for the average structure of tetraphenylphosphonium hexabromotellurate(IV) bis{dibromoselenate(I)} from charge flipping and from the structure model.

The integrated charges were normalized to 52 electrons for the Te atom. The last column contains the number of electrons of each atom multiplied by the atom's occupancy in the structure.

	Charge flipping			Structure model			Integrated charge	Electrons × occupancy
Atom	*x*	*y*	*z*	*x*	*y*	*z*		
Te	0.5000	0.5000	0.5000	0.5000	0.5000	0.5000	52.0	52
Br1	0.5503	0.5000	0.2679	0.5490	0.5000	0.2680	32.6	35
Br2	0.6739	0.5772	0.5784	0.6730	0.5770	0.5738	31.1	35
Se1	0.8521	0.4479	0.4125	0.8525	0.4486	0.4141	13.6	17
Br4	0.9546	0.4788	0.2531	0.9563	0.4801	0.2556	18.0	17.5
Se2	1.0060	0.4086	0.5604	1.0054	0.4091	0.5582	13.7	17
Br5	1.0202	0.3212	0.4683	1.0214	0.3210	0.4712	13.5	17.5
P	0.0000	0.6904	0.0000	0.0000	0.6908	0.0000	10.1	15
C1	0.8708	0.6476	0.0145	0.8747	0.6465	0.0149	2.6	6
C2	0.8157	0.6523	0.1091	0.8195	0.6503	0.1200	2.6	6
C3	0.7175	0.6198	0.0986	0.7225	0.6151	0.1244	3.5	6
C4	0.6877	0.5796	0.0199	0.6835	0.5775	0.0303	4.7	6
C5	0.7244	0.5808	0.9447	0.7386	0.5736	0.9296	3.4	6
C6	0.8279	0.6071	0.9440	0.8348	0.6079	0.9202	3.9	6

The averaged density was then analyzed by the program *EDMA* for analysis of discrete electron densities in arbitrary dimensions (Palatinus, 2003). At the first stage, the density was projected along the fourth dimension to obtain an average 3D density. This was then searched for positions of maxima. All non-H atoms of the average structure could be located, while only three spurious maxima had a peak density larger than the weakest of the atoms. These false maxima were located in the vicinity of the heavy atoms and were easy to identify and remove. The noise could be probably further reduced by averaging several electron densities obtained from different starting phases, as proposed recently by Wu *et al.* (2004).

The list of the extracted maxima and their comparison with the atomic parameters from the final structure model is given in Table 2. The coordinates of the heavy atoms agree with the refined ones within 0.05 Å, the largest difference occurs for the *z* coordinate of the atom C3, 0.28 Å. This can be considered to be a very good accuracy for an *ab initio* structure solution, particularly for an average structure of a modulated crystal. The chemical types can be assigned to individual maxima on the basis of the integrated charge of each maximum, as illustrated in Table 2. The charges determined from the density were normalized to 52 electrons for the Te atom. The normalized charges then allow an easy distinction

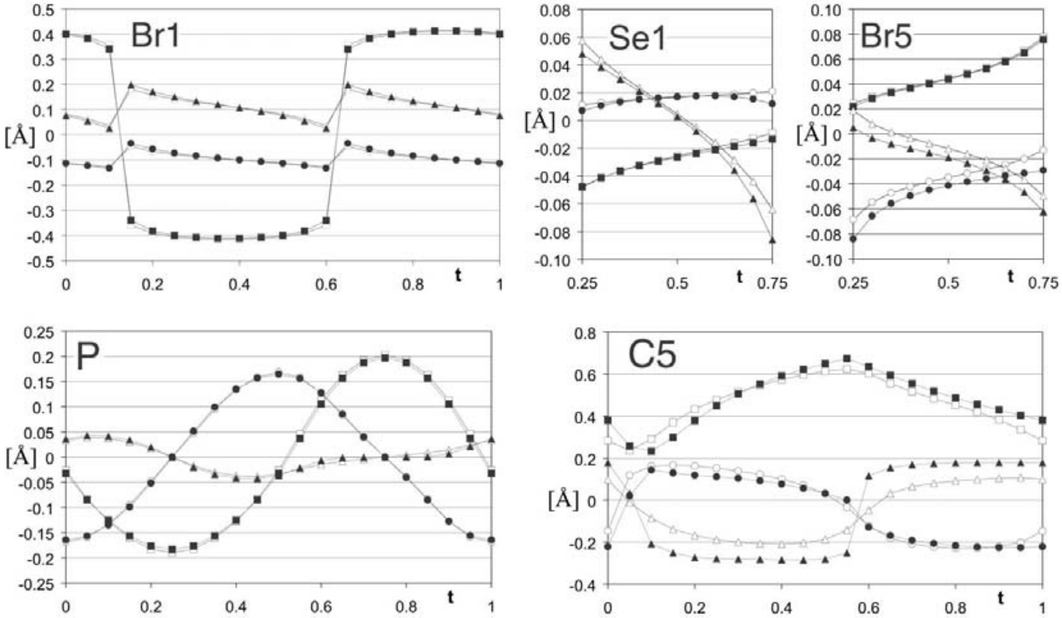

Figure 1
Modulation functions of atoms Br1, Se1, Br5, P and C5 of tetraphenylphosphonium hexabromotellurate(IV) bis{dibromoselenate(I)}. Modulations obtained by the analysis of the density from charge flipping (full symbols) and by the analysis of the Fourier map of model structure factors (empty symbols). Circles, squares and triangles denote modulation along **x**, **y** and **z**, respectively.

between the Te, Se/Br, P and C atoms. The Se and Br atoms cannot be distinguished because of their similar atomic numbers. It can also be observed that the charges of the atoms are systematically underestimated. This is a consequence of the noise present in the map. The low-density regions, which would be assigned to the atomic maxima in the noiseless density, disappear in the noise and they are assigned to small spurious maxima in the noise instead of the atomic maxima. This effect is more pronounced for light atoms.

The low normalized charges in the average structure can also be caused by the presence of an occupational modulation in the modulated structure. In this example, this is the case for atoms Se1, Se2, Br4 and Br5. This can complicate the proper assignment of the chemical type in the average structure. The occupational modulation can be determined by inspecting the four-dimensional density in these cases, or – most easily – the atomic type can be assigned on the basis of chemical knowledge by inspecting the average structure in a crystal-structure viewer.

Charge flipping in superspace can also provide a starting model for the modulation. In the presented example, the program *EDMA* was used to extract the positions of the atoms as a function of the internal coordinate *t*. The atomic positions as a function of *t* can be used to obtain a starting model for the modulation functions. Fig. 1 shows the modulation functions of selected atoms as obtained by the charge flipping algorithm and from the Fourier map of structure factors calculated from the final refined model. The perfect agreement of the two densities is illustrated in Fig. 2. The quality of the reconstruction can be assessed also in reciprocal space by comparing the phases estimated by the charge flipping algorithm with the model phases. Out of 4247 reflections in the input data set, 4086 have phases identical with those obtained from the final structure model.

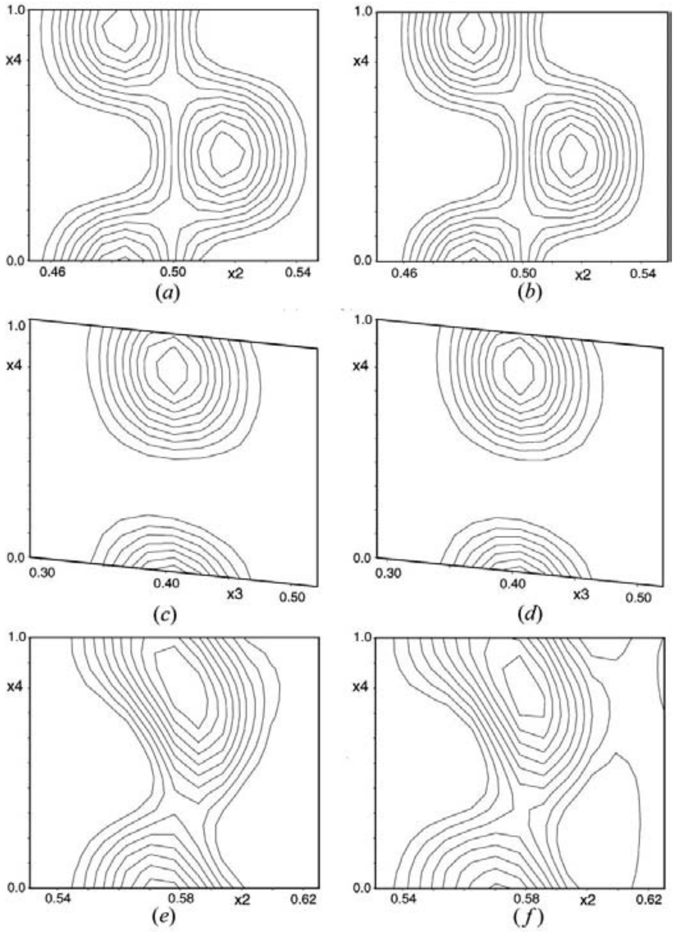

Figure 2
$x_i - x_4$ sections through the electron densities from charge flipping and model Fourier map. (*a*) Br1 charge flipping, (*b*) Br1 Fourier map, (*c*) Se1 charge flipping, (*d*) Se1 Fourier map, (*e*) C5 charge flipping, (*f*) C5 Fourier map. Contour interval is 10% of the maximum density in each section.

6. Conclusions

Charge flipping in superspace proved to be a useful method for *ab initio* structure solution of modulated structures from X-ray diffraction data directly in superspace. The output of the method is an approximate superspace electron density of the structure that can be further analyzed for the positions of the symmetry elements, the positions of the atoms and the shapes of the modulation functions.

From eight modulated structures having up to 130 atoms in the primitive cells, seven structures were successfully reconstructed. Thus, the success is not granted in all cases but the success rate is high. It should be emphasized that some of the presented examples rank among the most complex modulated structures described so far.

The structure analysis of tetraphenylphosphonium hexabromotellurate(IV) bis{dibromoselenate(I)} has shown that the charge flipping algorithm produces a structure model with errors in the atomic positions typically less than 0.1 Å. Such a model represents a good starting point for the structure refinement.

For ordinary 3D structures, the charge flipping algorithm represents only one of several effective methods for *ab initio* structure solution. Its importance for solution of modulated structures is larger than for the 3D structures, as the generalization of the algorithm towards superspace is easily possible, while the usage of other methods for modulated structures is limited. Thus, charge flipping in superspace has a potential to become a leading tool for *ab initio* solution of modulated structures directly in superspace.

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