Ab initio structure solution of decagonal quasicrystals by iterative dual space methods: performance tests on synthetic and experimental data

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Abstract. Iterative ab initio structure solution algorithms were tested on their performance power in phasing diffraction data. Statistical investigations on the reproducibility of the recovered phases allow an estimate about the reliability of the results. The working principle is demonstrated on synthetic structures and on experimental diffraction data of decagonal AlCuCo, AlFeNi and AlCoNi quasicrystals.

1. Introduction
The extension of Fourier recycling techniques to arbitrary dimensions [1,2] provides an easy access to quasiperiodic structures. The structure solution of quasicrystals in higher dimensions leads to the reconstruction of geometrical objects – the occupation domains (ODs) – in position, shape and electron density (ED). The reconstruction of non-point-like EDs for quasicrystals is therefore more demanding than structure solutions of ordinary periodic structures. Algorithms, like low-density elimination (LDE) and charge flipping (CF) overcome this problem and were successfully applied for solving quasiperiodic structures [e.g. 1,3,4], however, their working principle is not yet fully understood.

In this paper we present a comprehensive study on the basic CF and LDE algorithms applied on quasicrystals. Systematic performance tests of iterative phase retrieval algorithms – reported in detail for a broad range of simulated diffraction data [5] – are extended to experimental quasicrystal data.

2. The charge flipping and low-density elimination algorithms
The CF and LDE algorithms are Fourier recycling techniques, where the iteration process alternates between reciprocal and physical space. In the first iteration step the experimental form factor amplitudes are combined with random phases. Then, the corresponding ED is calculated by Fourier transformation and modified as follow: a threshold value $\delta$ is set to define the charges that will be manipulated. CF flips the sign of all charges smaller than $\delta$, i.e. positive charges become negative and vice versa. LDE sets all negative charges to zero. Then, a new set of structure factors is calculated by

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Fourier transformation of the perturbed ED. In a final step the resulting phase of each structure factor is combined with the measured intensity and serves as an input for the next iteration cycle. The iteration process is continued until convergence is reached.

All calculations were done with the program package SUPERFLIP [6], which allows performing CF and LDE calculations in arbitrary dimensions. Each data set is first extended to a complete data set corresponding to its Laue symmetry. In the following, data sets are handled in space group $P1$. The result of a typical CF and LDE run is a set of phased structure factors with the constraint $|F_{\text{refined}}(H)|^2 = |F_{\text{obs}}(H)|^2$. All calculations were performed on an ED grid with a resolution of about 0.25 Å along each direction. The number of iteration steps was restricted to 1000, which was found to be adequate to reach convergence. Since the origin of the resulting ED is not defined, the resulting EDs were shifted to a reference ED and inverted if required. The following investigations use the basic algorithms without any performance enhancements to study the \textit{ab initio} abilities of CF and LDE.

3. Test structures

The first part of our investigations is based on synthetic data what allows a direct comparison of resulting phases with the correct ones. In the second part experimental diffraction data from decagonal quasicrystals are used.

3.1. Synthetic diffraction data

The artificial decagonal quasiperiodic structure corresponds to the structure reported in [7] with the modification that all ODs are fully occupied with Al only. An overall atomic displacement parameter $U_{\text{iso}} = 0.02$ Å$^2$ and a phasonic Debye-Waller factor $U_{\text{phason}} = 0.02$ Å$^2$ was used for the calculation of the structure factors. All structure factors of the reciprocal asymmetric unit were calculated within $|Q_{\text{par}}| < 1.4$ Å$^{-1}$ and $|Q_{\text{perp}}| < 1.2$ Å$^{-1}$. The reflections were scaled such that the strongest reflection except $F(0)$ corresponds to $I = 10000$ counts. We added a normally distributed random number with variance $\sigma^2 = I_{\text{calc}}$ to the intensities to simulate more realistic experimental data. To test the influence of incomplete data, test data sets were restricted to the 600 and 150 strongest reflections. We performed 50 CF and LDE runs for each model structure.

3.2. Experimental diffraction data

Bragg data sets of the decagonal phases AlCoNi, AlCuCo and AlNiFe were used as a basis for the experimental test structures. The single crystal X-ray diffraction data of AlCuCo were taken from [8]. The single crystal X-ray diffraction data of AlNiFe were collected with an Oxford Diffraction diffractometer (“Onyx”-CCD detector, graphite monochromator, Mo $K\alpha$ radiation) from a single crystal with composition Al$_{73}$Ni$_{22}$Fe$_{5}$, which was annealed at 920°C and quenched afterwards. The data set for AlCoNi was measured at the Swiss-Norwegian beam line at the European Synchrotron Radiation Facility ESRF, Grenoble, France on a crystal with composition Al$_{71}$Co$_{13}$Ni$_{16}$, which was quenched from 730°C. This phase was identified as the type-I structure. For our studies, only main reflections, i.e. Bragg reflections corresponding to the basic structure, were used.

All diffraction data were indexed using a 5D decagonal lattice with $a_1^* \ldots a_5^*$ listed in Table 1. We performed 100 CF and LDE runs on all experimental data sets.

4. Quality factors

In previous tests on synthetic structures [5], we defined quality parameters to compare the resulting phases of a CF and LDE run with correct phases. The phase difference between the retrieved and the known correct phase of a reflection averaged over $n$ runs is calculated by

$$\Delta\varphi(H) = \varphi_{\text{true}}(H) - \arg \left( \frac{1}{n} \sum_{i=1}^{n} F_{i\text{refined}}(H) \right)$$ (1)
Table 1. Overview of the quality parameters of the chosen experimental data sets of the decagonal quasicrystals AlCoNi, AlCuCo, AlNiFe

| Laue group   | AlCoNi    | AlCuCo    | AlNiFe    |
|--------------|-----------|-----------|-----------|
| $a_1$ ... $a_4$ | 0.1635(3) Å$^{-1}$ | 0.2656(2) Å$^{-1}$ | 0.2651(3) Å$^{-1}$ |
| $a_5$        | 0.2444(2) Å$^{-1}$ | 0.24107(3) Å$^{-1}$ | 0.2437(4) Å$^{-1}$ |
| Independent reflections | 1355 | 259 | 898 |
| $R_{int}$   | 0.061     | 0.062     | 0.033     |
| $Q_{\text{max}}^{\text{par}}$ | 2.00 Å$^{-1}$ | 1.98 Å$^{-1}$ | 1.50 Å$^{-1}$ |
| $Q_{\text{max}}^{\text{perp}}$ | 0.51 Å$^{-1}$ | 2.14 Å$^{-1}$ | 1.50 Å$^{-1}$ |

In practice it is essential to have a quality parameter that does not require the knowledge of the correct phases. We defined a quality parameter $\kappa(H)$, which quantifies the reproducibility of the phases of each reflection. Since a random number generator is used for initialization, each run has different start conditions and therefore different phases are obtained, even if the structure solution was successful. The definition of the reproducibility parameter is based on the constrain $|F_{\text{refined}}(H)|^2 = |F_{\text{obs}}(H)|^2$ and is defined as the ratio between the average and the experimental structure factor amplitudes.

$$\kappa(H) = \frac{\left| \frac{1}{n} \sum_{i=1}^{n} F_{\text{refined}}(H) \right|^2}{\left| F_{\text{refined}}(H) \right|^2} . \quad (2)$$

The value $\kappa(H)$ may range between 0 and 1. The phase of a reflection was found with a high consistency if $\kappa(H)$ is large, otherwise the phase shows a strong variation in different runs. An overall reproducibility factor for a complete data set is defined by weighting the reliability factor of each reflection with its intensity:

$$K = \frac{\sum_j |F_{\text{obs}}(H_j)|^2 \cdot \kappa_j(H)}{\sum_j |F_{\text{obs}}(H_j)|^2} . \quad (3)$$

$K$ may range between 0 and 1. An overall $K$ of about 1 corresponds to a data set with a high phase reproducibility of most reflections, whereby a small value indicates that the phase retrieval is almost at random.

The averaging of several runs can drastically increase the quality of the phased data set. Averaging leads to an improvement of phases, but intensities of reflections with a low $\kappa(H)$ become smaller compared to experimental intensities. Therefore, re-scaling of the resulting structure factor amplitudes to the observed ones leads to an improvement of the reconstructed ED [5]. From eq 2 follows:

$$F_{\text{scaled}}(H) = \frac{1}{n \cdot \sqrt{\kappa(H)}} \sum_{i=1}^{n} F_{\text{refined}}(H) . \quad (4)$$

Averaging was done using 50 runs for the synthetic data and 100 runs for the experimental data.
Figure 1 Maps of reconstructed occupation domains for a model structure averaged from the results of 50 CF and LDE runs and rescaled to the experimental amplitude. EDs were calculated from data sets restricted to the 150 and 600 strongest symmetry independent reflections. Since the inversion related ODs A/D and B/C were reconstructed without significant differences in shape and ED, only the non-symmetry related ODs A and B are shown. Line scans (blue lines) were taken across the ODs (white dashed line in one inset) to show details of the ED distribution. Strong truncation effects are observed in the centres of the ODs (arrows) especially for small data sets. Typical distributions of the reliability factor $\kappa(H)$ as a function of the phase difference $\Delta\varphi(H)$ and of the intensity of the reflections are shown in the right columns.

5. Results and discussion

5.1. Synthetic diffraction data

All CF and LDE runs converged within 1000 iteration steps and the structures could be solved in all cases. The reconstructed ED maps of the average solutions (Fig. 1) allow a direct comparison between LDE and CF results. Significant truncation errors at the center of the ODs can be observed in
particular in the case of the data set containing only 150 reflections, what could lead to a misinterpretation of the results. This effect was also demonstrated on experimental data by [4].

We calculated the reproducibility factors $\kappa(H)$ and the phase difference $\Delta \phi(H)$ for each reflection, based on 50 averaged runs for each synthetic diffraction data set and found a typical distribution (Fig. 1). Indicated by the strong correlation between high $\kappa(H)$-values and phase differences of $\Delta \phi(H) \approx 0$, it can be concluded that reproducibility of phases is a measure for the quality of the results. The overall quality factor $R_{\text{wp}}$, which is defined as a conventional intensity-weighted $R$-factor of the phase difference $\Delta \phi(H)$, is $R_{\text{wp}} \approx 0.014$ for CF and 0.004 for LDE. The overall reproducibility factor $K$ was obtained as $K \approx 0.90$ for CF and $K \approx 0.97$ for LDE, i.e. phases are found with higher consistency when using LDE. Especially weak reflections were found with higher consistency and smaller phase errors.

5.2. Experimental data

The transfer of the procedure to experimental data and the reconstruction of high quality EDs by averaging is shown for decagonal AlCoNi, AlCuCo and AlNiFe quasicrystals. The higher-dimensional structure solution is represented by the reconstruction of the ODs. Though sizes and positions of ODs can be estimated from single runs, an accurate shape and occupation can be estimated only after averaging and re-scaling on the observed structure factor amplitudes (Fig. 2). Apart from some differences in details CF and LDE could consistently solve all experimental test structures. The space group of all reconstructed structures was determined from the reconstructed EDs as $P10_5/mmc$, which is in agreement with previously reported results [8,9].

After averaging all successful runs, LDE shows well-defined ODs with partially occupied regions (e.g. triangles, parallelograms, see arrows in Fig. 2). This richness in detail is not found in the results obtained with CF, what is due to inconsistent phase retrievals, especially in the case of weak reflections. The significance of the detailed observations, however, is not known. Though we believe that most of the details seen in the averaged LDE maps in Fig. 2 represent true structural information, our limited experience with LDE/CF does currently not allow a reliable separation of artifacts from true structural features. On the one hand truncations errors are always present and corresponding artifacts are expected to be present. On the other hand, our performed tests on synthetic structures suggest that CF and, to a larger extent, LDE deliver reliable EDs. The final proof of presence and absence of observed features can only be done with least-squares refinements. Since quasicrystal refinements are rare, time-consuming and often not in the quality as in the case of periodic structures, a comprehensive comparison of structure models obtained by LDE/CF and by least-squares refinements is currently hardly possible. It can, however, be stated that the structure solution of decagonal AlCuCo shows no significant differences to the refined structure reported in [8].

The observed $I(H)$-$\kappa(H)$ distribution are similar to the ones observed from the simulated model structures. High $\kappa(H)$-values are obtained for strong reflections, while weak reflections tend to show smaller $\kappa(H)$-values. It is reasonable to conclude that phases of reflections with high $\kappa(H)$-values are correct, since performance tests on centrosymmetric model structures have shown that a high reproducibility of phases usually correlate with a high quality of the retrieved phases. A much higher overall reliability factor was observed for structures solved with LDE ($K > 0.97$) than for CF ($K \approx 0.79$).

6. Conclusion

Tests on artificial data show a high reliability for the phase retrieval of reflections with consistently reproduced phases indicating that $\kappa(H)$ may be used as a quality factor for the retrieved phases. Iterative phase retrieval algorithms like LDE and CF are useful to derive reasonable structure models from experimental quasicrystal data and an averaging procedure allows the reconstruction of high quality EDs. This was shown for decagonal AlNiFe, AlCoCu and AlCoNi quasicrystals on experimental data with different quality. The quality of such solved structures as initial starting models for least-square techniques has to be evaluated in further tests.
Figure 2 Maps of reconstructed occupation domains for experimental data sets of AlNiFe, AlCuCo and AlCoNi. The ODs reconstructed from a single LDE run and the averaged structure factors of 100 successful CF and LDE runs for AlNiFe are shown as typical examples. Furthermore, the EDs calculated from 100 LDE runs of the decagonal phases AlCuCo and AlCoNi are shown. The density for the ODs B and C are scaled by a factor of two compared to the ODs A and D, as they are occupied by Al, which has a scattering factor of about two times smaller than the transition metals. Arrows mark some details of the ODs for the averaged results of 100 runs. The calculations were performed without any symmetry averaging in $P1$. ODs A and B are located at $+((i/5, i/5, i/5, i/5, 1/4) (i = 1$, 2) and OD C and D are found at $-(i/5, i/5, i/5, i/5, 3/4) (i = 1$, 2). The $\kappa(H)$-intensity distribution and the overall $K$ are given in the diagrams. The ODs of AlCoNi are $\tau$-inflated ($\tau = (1+\sqrt{5})/2 = 1.61803...$) compare to AlNiFe and AlCuCo, because a different basis was used.
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