Charge density study with the Maximum Entropy Method on model data of silicon.
A search for non-nuclear attractors

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Abstract: In 1990 Sakata and Sato applied the maximum entropy method (MEM) to a set of structure factors measured earlier by Saka and Kato with the Pendellosung method. They found the presence of non-nuclear attractors, i.e., maxima in the density between two bonded atoms. We applied the MEM to a limited set of Fourier data calculated from a known electron density distribution (EDD) of silicon. The EDD of silicon was calculated with the program ADF-BAND. This program performs electronic structure calculations, including periodicity, based on the density functional theory of Hohenberg and Kohn. No non-nuclear attractor between two bonded silicon atoms was observed in this density. Structure factors were calculated from this density and the same set of structure factors that was measured by Saka and Kato was used in the MEM analysis. The EDD obtained with the MEM shows the same non-nuclear attractors that were later obtained by Sakata and Sato. This means that the non-nuclear attractors in silicon are really an artefact of the MEM.

Key words: Maximum Entropy Method, non-nuclear attractors, charge density, X-ray diffraction.

Résumé : Sakata et Sato (1990) ont appliqué la méthode d'entropie maximale (MEM) sur un ensemble de facteurs de structures mesurés par Saka et Kato à l'aide de la méthode Pendellosung. Ils ont trouvé la présence d'attracteurs non nucléaires, c'est-à-dire de maxima dans la densité entre deux atomes liés. On a appliqué la MEM à un ensemble limité de données de Fourier calculées à partir d'une distribution de densité électronique connue (DDE) du silicium. On a calculé la DDE du silicium à l'aide du programme ADF-BAND. Ce programme effectue des calculs de structures électroniques, y compris la périodicité, repose sur la théorie de la densité fonctionnelle de Hohenberg et Kohn. Aucun attracteur non nucléaire entre deux atomes de silicium non liés n'a été observé dans cette densité. On a calculé les facteurs de structure à partir de cette densité et, pour l'analyse MEM, on a utilisé l'ensemble de facteurs de structure qui avait été mesuré par Saka et Kato. Les DDE obtenues avec l'analyse MEM montrent la présence des mêmes attracteurs non nucléaires que ceux obtenus par Sakata et Sato. On peut en déduire que les attracteurs non nucléaires dans le silicium sont en réalité des artefacts de l'analyse MEM.

Mots clés : méthode d'entropie maximale, attracteurs non nucléaires, densité de charge, diffraction par rayons X.

[Traduit par la réduction]

1. Introduction

In the study of the electron density distribution (EDD) with the help of X-ray diffraction, experiment yields a set of intensities. In most, if not all, centrosymmetric crystals, structure factors can be derived from these intensities without any ambiguity in the phases. The most common method of extracting the EDD from an incomplete and noisy set of structure factors is to fit the data to a multipole model (e.g., POP (1), MOLLY (2), and LSEXP (3, 4)). The advantages of a multipole fit over a direct Fourier synthesis are that a multipole fit allows one to overcome the series termination effect, to filter out the noise from the data that were measured, and to extract the static density from the thermally smeared density. A drawback to a multipole fit is the fact that bias is introduced, and random errors are traded for systematic errors (5).

In the past few years, the maximum entropy method (MEM) has been used to obtain the EDD from an incomplete and noisy set of structure factors (e.g., Sakata and Sato (6), Sakata et al. (7), and Takata et al. (8)). The MEM is capable of handling the series termination effect by estimating missing data. The MEM selects the EDD that is closest to an a priori EDD or, in its absence, closest to a uniform distribution. It is believed that all the features that show up in the EDD are supported by the data and that the MEM gives least biased results.

It has been pointed out by Jauch (9) that the EDDs produced with the MEM have to be interpreted with great care. Our MEM study on a hypothetical water crystal (10) confirmed these reservations with respect to the method. In particular we showed that the MEM results yield an unrealistic $\chi^2$-distribution. In case the data is very accurate the
ture factors are forced to be nearly equal to their measured values and the obtained EDD is independent of the distribution. Therefore, Sakata and Sato (6) did not have similar problems in their MEM study on silicon data since their work was based on highly accurate data. They found a local maximum in the middle of the Si-Si bond. Although this (3, -3) critical point (Bader, ref. 11) was unexpected, no doubt about this non-nuclear attractor was expressed. Recently, a MEM study by Iversen et al. (12) revealed non-nuclear attractors in beryllium. The phenomenon, however, is small and the MEM has not been tested on this level of accuracy by means of model studies. Thus we decided to create a set of structure factors corresponding with a known EDD and to apply the MEM.

To illustrate this we have applied the MEM to data calculated from a known EDD of silicon. This EDD was obtained by means of an electronic structure calculation, including periodicity, with the Amsterdam density functional BAND (ADF-BAND) program (13). The results were compared with those obtained by Sakata and Sato (6) who applied the MEM to experimental data on silicon.

2. Method

The maximum entropy principle states that out of all EDDs that satisfy certain constraints one should chose the EDD that maximizes the entropy $S$ (because this is the least biased), defined by Jaynes (14) as:

$$ S = - \int p(x, y, z) \ln \left( \frac{p(x, y, z)}{m(x, y, z)} \right) \, dx \, dy \, dz $$

where

$$ p(x, y, z) = \frac{\rho(x, y, z)}{\int \rho(x, y, z) \, dx \, dy \, dz} $$

and

$$ m(x, y, z) = m'(x, y, z) \int m'(x, y, z) \, dx \, dy \, dz $$

$m'$ is a prior density for the EDD $p(x, y, z)$, i.e., some estimate before the present set of data was used. To calculate the integral in eq. [1] the density is usually represented on a grid $(N_1 \times N_2 \times N_3)$, to give:

$$ S = - \sum_{j=1}^{N_1} \sum_{k=1}^{N_2} \sum_{l=1}^{N_3} p_{ijm} \ln \left( \frac{p_{ijm}}{m_{ijm}} \right) $$

In case the prior density $m'$ is not specified, a uniform distribution is assumed and eq. [4] reduces to

$$ S = - \sum_{j=1}^{N_1} \sum_{k=1}^{N_2} \sum_{l=1}^{N_3} p_{ijm} \ln p_{ijm} + \text{constant} $$

The second term in eq. [5] can be dropped in the maximization process. This is the form we will use since we do not assume any prior information.

The constraints are provided by the experiment and involve the structure factors that were measured. We also constrain the total number of electrons per unit cell to the correct value $N$:

$$ \left( \frac{V_{\text{cell}}}{N_1 N_2 N_3} \right) \sum_{i,j,m} p_{ijm} = N $$

The most common way to incorporate the reflections that were measured is by maximizing the entropy subject to

$$ \chi^2 = \sum_{h,k,l} \left( \frac{|F_{hkl} - D_{hkl}|}{\sigma_{hkl}} \right)^2 = M $$

where $D_{hkl}$ is the measured structure factor, $F_{hkl}$ is the structure factor calculated from the resulting density, $\sigma_{hkl}$ is the standard deviation of the measurement, and $M$ is the total number of (unique) reflections that were measured. Of course the EDD has to be positive everywhere. This is automatically satisfied since the logarithm of a negative number does not exist.

It has been shown (10) that maximizing the entropy subject to this constraint does not necessarily lead to a proper frequency histogram of reduced differences $(|F_{hkl} - D_{hkl}|/\sigma_{hkl})$ between calculated and observed structure factors. In particular, a few strong low-order structure factors calculated from the EDD obtained by MEM show large deviations (up to 19σ in the model study presented) from the measured values. The value of $\chi^2$ is dominated by these structure factors. This causes the remaining structure factors to be exactly equal to their measured values with disastrous effects on the resulting EDD. The same effect was also observed by Jauch and Palmer (15). The introduction of a weighting scheme as proposed by Feil and co-workers (10) partially solves this problem.

Structure factors can be measured very accurately with the Penodessung method. In case the error in the measurements is very small the resulting EDD is insensitive to the distribution. The structure factors calculated from the maximum entropy EDD are then forced to have the same value as the measured structure factors. In this case only the series termination effect is dealt with by the MEM.

In the present study we focus on the series termination effect. We have calculated structure factors from a known density and want to apply the MEM with $\sigma_{hkl} = 0$. The program that was used to perform the optimization was based on the algorithm that was presented by Skilling and Bryan (16). A detailed description of this algorithm was given by de Vries, Briels, and Feil (10). Since the use of $\sigma = 0$ leads to calculational problems in applying constraint [7] we have chosen the error to be very small ($\sigma_{hkl} = 0.0005$). The iterations were stopped when $\chi^2 = M$ and $\delta < 5 \times 10^{-4}$ where $\delta$ is defined as

$$ \delta = \frac{1}{2} \left( \frac{\nabla S}{\nabla \chi^2} - \frac{\nabla \chi^2}{\nabla S} \right)^2 $$

3. Calculation of the EDD and the structure factors

The EDD of silicon was calculated with the program ADF-BAND (13). This program performs an electronic structure calculation based on density functional theory (17) taking
Fig. 1. Fourier synthesis of the structure factors for which
\( \sin(\theta)/\lambda < 5.5 \ \text{Å}^{-1} \). The (static) structure factors were
calculated with the program ADF-BAND. Thermal motion was
introduced with the program FITTER. Contour intervals are at
0.1 e/Å³.

into account the periodicity of the system. For the present
purpose it is not important that \( p(x, y, z) \) be very accurate. It
should be a reasonable, but accurately known, density. Once
the EDD is known from this calculation, the structure fac-
tors can be calculated in a straightforward way by taking
the Fourier transformation of the EDD. This will give us the
structure factors of the static density. In principle this is very
simple. One can calculate the density in the unit cell on a
regular, 3-dimensional grid. From this, the structure factors
be calculated using Fast Fourier Transform (FFT) rou-
tines. However, the grid that has to be used in this case has
to be very dense to make sure that aliasing does not occur
in Fourier space. The calculation of the density on all these
grid points would simply take too long.

Instead, a different approach is followed that was imple-
mented by Bruning and Feil (18) in the program FITTER.
This
program contains the following steps:
1. Partition the density according to the stockholder prin-
ciple (19) to obtain “atomic” densities.
2. Subtract “free” atoms (calculated with the same basis
set) from these atomic densities. Since these free atoms
are spherically symmetric, their Fourier transform can
be easily calculated. The remaining density is referred
to as the (atomic) deformation density. It no longer has
the problem of “near singularities.”
3. Fit the (atomic) deformation densities with suitable
functions that can be Fourier transformed analytically.
4. Calculate the Fourier transform of these functions.
5. Add the Fourier transform of the free atoms.
6. Introduce individual atomic thermal motion.
7. Calculate the structure factors by summing the struc-
ture factors of all atoms.

In the present study the atomic thermal motion is introduced
by multiplying the structure factors with an isotropic temper-
ature factor: \( \exp (-B(\sin(\theta)/\lambda)^2) \) with \( B = 0.4632 \ \text{Å}^2 \). This
value of \( B \) was taken from Spackman (20). Structure factors
with \( \sin(\theta)/\lambda < 5.5 \ \text{Å}^{-1} \) were calculated. A Fourier transform
of these structure factors was made to obtain the thermally smeared density, the dynamic density. This is shown in Fig.

1 where the density in the 110 plane of silicon is plotted.
Non-nuclear attractors are seen to be absent. We have con-
"vered this by calculating the electron density along the Si—
Si bond: along this line a minimum in the electron density is
found. Extension of the set of structure factors by increasing
the value of \( \sin(\theta)/\lambda \) did not change the EDD. It is easily
shown that thermal motion obliterates all information beyond
\( \sin(\theta)/\lambda = 5.5 \ \text{Å}^{-1} \).

4. Results
A number of MEM calculations was performed using a 64 x
64 x 64 grid to describe the density. The first calculation
only involved structure factors with the same \( h, k, \) and \( l \)
values as those measured by Saka and Kato (21). A direct
Fourier transformation of these structure factors is shown in
Fig. 2. The result of the MEM calculation is shown in Fig.
3. The similarity between the latter density and the density
obtained by Sakata and Sato (6), who used experimental data,
is striking. To our surprise the same non-nuclear attractors
between the silicon atoms appear. However, from Fig. 1, the
dynamic density, we know that the midpoint between two
bonded atoms is a saddle point.

All structure factors of the dynamic density are known.
We can compare them with the values that were “predicted”
by the MEM. For a number of structure factors this is shown
in Table 1. As can be seen from Table 1, the absolute values
of the structure factors predicted by the MEM are, in most
cases, smaller than the exact values. Furthermore, the sign
of the 622 structure factor is opposite to the sign of the
622 structure factor of the exact density. This is also found
when the experimental data are used (comparing the phase of
the 622 structure factor with the experimentally determined
phase (22)). Sakata and Sato (6) suggested that the 622 struc-
ture factor might be affected significantly when the number
of pixels is increased. We have done the calculation using
a 128 x 128 x 128 grid and found that the value of the 622
reflection hardly changes: \( F(622) = -0.0070 \).
Fig. 3. The EDD calculated with the MEM from the same structure factors that were used to calculate the EDD of Fig. 2. The contours are at intervals of 0.1 e/Å³.

**Table 1.** The exact values of some structure factors (calculated from the dynamic density) compared with the values that were predicted by the MEM.

<table>
<thead>
<tr>
<th>hkl</th>
<th>Exact</th>
<th>MEM</th>
</tr>
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<tbody>
<tr>
<td>2 2 2</td>
<td>1.1547</td>
<td>1.3336</td>
</tr>
<tr>
<td>4 4 2</td>
<td>-0.0376</td>
<td>-0.0243</td>
</tr>
<tr>
<td>6 2 2</td>
<td>0.0040</td>
<td>-0.0065</td>
</tr>
<tr>
<td>9 3 1</td>
<td>-12.9648</td>
<td>-12.8838</td>
</tr>
<tr>
<td>7 5 5</td>
<td>11.8025</td>
<td>11.7844</td>
</tr>
<tr>
<td>9 3 3</td>
<td>11.7940</td>
<td>11.6661</td>
</tr>
<tr>
<td>7 7 1</td>
<td>11.7946</td>
<td>11.8050</td>
</tr>
<tr>
<td>8 6 2</td>
<td>15.7646</td>
<td>15.5886</td>
</tr>
<tr>
<td>10 2 0</td>
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</tr>
<tr>
<td>7 7 3</td>
<td>10.7861</td>
<td>10.6664</td>
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<td>9 5 1</td>
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<td>9 5 3</td>
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</tr>
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</tr>
<tr>
<td>7 7 5</td>
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<td>11 1 1</td>
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<td>9 7 1</td>
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<tr>
<td>9 5 5</td>
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</tr>
<tr>
<td>10 6 0</td>
<td>11.3806</td>
<td>10.7407</td>
</tr>
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</table>

It should be noticed that, although error-free data were used, the contours of the EDD obtained through MEM are still not very smooth. It has been suggested (23) that only a complete sphere of structure factors in reciprocal space should be used in the MEM analysis. This means that the 844 and the 880 structure factors should be omitted from the data set measured by Saka and Kato (21). The result of this calculation is shown in Fig. 4. The contours are indeed much smoother and although it looks like the non-nuclear attractors have disappeared they are still present but do not show on the contour level that was used. One could expect that when all the structure factors (except the forbidden ones) up to the 880 reflection (= sin(θ)/λ = 1.05 Å⁻¹, 42 structure factors in total) are used in the MEM analysis, the density should become even smoother. This is shown in Fig. 5. Contrary to expectation, the contours are less smooth than with the MEM optimization shown in Fig. 4. In general, the information of the EDD is not evenly distributed in reciprocal space but occurs in regions of high density. We believe that it is important to include such a high-density region completely in the analysis.

The EDD that is obtained when all the structure factors (except the forbidden ones) for which sin(θ)/λ < 1.4 Å⁻¹ (92 structure factors) are included in the optimization is shown in Fig. 6. Figure 7 shows the result when the series cutoff level is extended to the structure factors for which sin(θ)/λ < 1.7 Å⁻¹ (152 structure factors). When we calculate the 222 structure factor from the density that is shown in Fig. 7, we find the value \( F(222) = 1.35 \). So, although the densities of Fig. 7 and Fig. 1 look very similar, the value of the 222 structure factor is quite different from the exact value.

Fig. 4. The EDD calculated with the MEM from the same structure factors that were used to calculate the EDD of Fig. 2 except for the 844 and the 880 structure factors. The contours are at intervals of 0.1 e/Å³.

Fig. 5. The EDD calculated with the MEM from all the structure factors up to 880 (sin(θ)/λ < 1.05 Å⁻¹) except the forbidden structure factors. The contours are at intervals of 0.1 e/Å³.
The EDD calculated with the MEM from all the structure factors for which $\sin(\theta)/\lambda < 1.4 \, \text{Å}^{-1}$ except the forbidden structure factors. The contours are at intervals of 0.1 $e/\text{Å}^3$.

Fig. 6.

The EDD calculated with the MEM from all the structure factors for which $\sin(\theta)/\lambda < 1.7 \, \text{Å}^{-1}$ except the forbidden structure factors. The contours are at intervals of 0.1 $e/\text{Å}^3$.

Fig. 7.

5. Discussion and concluding remarks

The MEM calculation on model data of silicon shows that one has to be very careful when interpreting the EDD obtained by MEM. If we compare both the Fourier synthesis (Fig. 2) of the data and the density obtained by the MEM (Fig. 3) with the original density (Fig. 1) we can say that the MEM deals well with the series termination effect. Minor peaks remain, however, which were not present in the theoretically calculated EDD. In a sense we are the victim of our own success when we interpret the remaining structure as being real physical features. One advantage of the direct Fourier transform of the data is that one will never be tempted to give such an overinterpretation of these little features.

Thus, from remaining maxima obtained by the application of MEM on experimental data one cannot draw conclusions about the presence or absence of non-nuclear attractors in the Si bonds.

The use of a complete sphere in reciprocal space still shows the presence of this non-nuclear attractor but the height of this non-nuclear attractor is much smaller. But a complete sphere is no guarantee that the EDD will be smooth. We have seen that this depends on the range in reciprocal space that is used in the analysis. Increasing the size of the sphere in reciprocal space does not automatically mean that the EDD becomes more smooth.

An interesting option for improving the EDDs obtained by MEM might be the use of prior densities. For instance, by using the sum of "free atoms" as a prior density the method can focus on the deformation density itself.

Acknowledgement

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References