Analytical reconstruction of momentum density from directional Compton profiles

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An alternative method for reconstruction of three-dimensional momentum density from directional Compton profiles is proposed and successfully applied to theoretical data on magnesium oxide (with a random noise added). The method consists of obtaining a compact analytical model for the reconstructed $n(\mathbf{p})$ from the least-squares fit directly on the directional profiles. The result is compared, together with a standard numerical-based reconstruction, to the theoretical momentum density from which the profiles were calculated. [S0163-1829(99)07827-3]

I. INTRODUCTION

The refinement of a multipolar model of electron density from measured structure factors is now widely used and very successful in providing accurate electron-density maps that can be analyzed in chemical terms and to which electron-density calculations can be compared with high reliability.[1] In momentum space there is no straightforward method to measure the density $n(\mathbf{p})$. Two experimental techniques are currently popular: positron annihilation and Compton scattering. It has been shown[2–4] that Compton profiles, within the impulse approximation, give representations of the electron density in momentum space projected onto the scattering vector directions. If $\mathbf{u}_i$ is a unit vector in this direction, the directional Compton profile (DCP) is then

$$J(q,\mathbf{u}_i)=\int\int\int n(\mathbf{p})\,\delta(q-\mathbf{p}\cdot\mathbf{u}_i)\,d\mathbf{p}. \tag{1}$$

The fact that the measurement is always a mere projection of the desired quantity $n(\mathbf{p})$ has long been considered as a major obstacle to the optimal use of the information provided by the Compton measurements: an accurate reconstruction of the momentum density would imply the measurement of Compton profiles in an infinite number of directions $\{\mathbf{u}_i\}$.

The most popular method of reconstruction of the three-dimensional (3D) momentum density from a finite set of Compton profiles is probably the method based on Bessel-Fourier transformations.[4] Its success greatly relies on the existence of the program RECONST written by Hansen.[4,5] This program has been able to provide the community with a reliable, fast, and efficient reconstruction based on a numerical approach of the problem. The reconstructed 3D momentum density from programs like RECONST has been shown to be efficient in a simple comparison with calculated densities[6] and also as a basis for the refinement of model crystal wave functions.[7]

Since this pioneer work by Hansen, other methods have been suggested either based on radon transform (RT) or the maximum entropy principle (MEM).[8–10] Reconstructions based on the MEM are still under development, with very encouraging first results, but suffer from an important computational cost.

The aim of the present work is to give an analytical alternative to the previous reconstruction programs with the following considerations. (i) avoiding artifacts generated by numerical derivatives (the RT approach) or integrations (RECONST); (ii) Reconstructing the momentum density as a simple and compact analytical function, easy to calculate at any point in reciprocal space; (iii) Taking full account of experimental statistics in the reconstruction procedure; (iv) Using a more useful quantity, $p^2n(p)$, to check the quality of the reconstruction for the isotropic part.

II. FRAMEWORK OF THE ANALYTICAL RECONSTRUCTION

A. Equations of the Bessel-Fourrier method

Our approach is based on the properties of the Fourier-Bessel transform. Let us summarize a few basic relations used throughout the reconstruction process.

From Ref. 5 we write the autocorrelation function as

$$\begin{aligned}B(t,\mathbf{u})&=\int\int\int n(\mathbf{p})e^{-it\mathbf{u}\cdot\mathbf{p}}d\mathbf{p}\\&=\int dqe^{-iqt}\int\int\int n(\mathbf{p})\,\delta(q-\mathbf{p}\cdot\mathbf{u})d\mathbf{p}\\&=\int e^{-iqt}J(q,\mathbf{u})dq.\end{aligned} \tag{2}$$

It then follows that

$$n(\mathbf{p})=\frac{1}{(2\pi)^3}\int e^{-iqt}e^{it\mathbf{u}\cdot\mathbf{p}}J(q,\mathbf{u})t^2dt\,d\Omega_{\mathbf{u}}dq, \tag{3}$$

where $d\Omega_{\mathbf{u}}$ is the element solid angle in the direction pointed by $\mathbf{u}$. However, this last expression cannot be used in practice since one can only measure a limited number of directional Compton profiles. Nevertheless, making use of the crystal symmetry, it is always possible to expand $J(q,\mathbf{u})$ in lattice harmonics,[11]

$$J(q,\mathbf{u})=\sum_L g_L(q)h_L(\mathbf{u}). \tag{4}$$

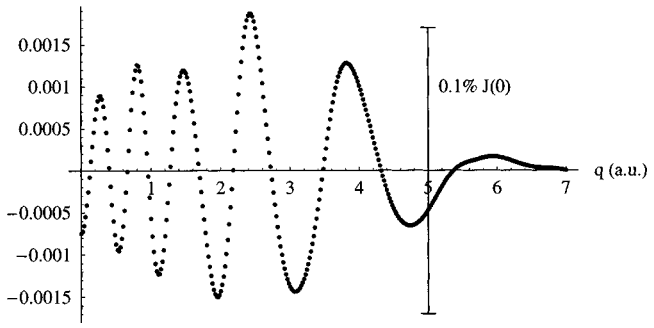

FIG. 1. Difference between the fitted Gaussians contraction and the Hartree-Fock isotropic profile. The value 0.1% of $J(0)$ is also reported for comparison.

If a limited number of directional profiles is available, this expansion is expected to be reasonably approximated by a truncated sum, with $g_L(q)$ being fitted functions. Then using the well-known expansion of plane waves in spherical harmonics, one gets

$$n(\mathbf{p}) = \frac{4\pi}{(2\pi)^3} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} i^l \int j_l(pt) Y_{lm}(\Omega_{\mathbf{p}}) e^{-iqt} \times \int J(q,\mathbf{u}) Y_{lm}(\Omega_{\mathbf{u}}) d\Omega_{\mathbf{u}} t^2 dt\, dq = \frac{4\pi}{(2\pi)^3} \sum_{l=0}^{\infty} i^l h_l(\Omega_{\mathbf{p}}) \int j_l(pt) g_l(q) e^{-iqt} t^2\, dt\, dq. \tag{5}$$

B. Choice of the functions $g_l(q)$

Our main concern is here to retrieve a compact analytical form for the momentum density. This can easily be done if an appropriate expression of the functions $g_l(q)$ is chosen so that the above double integral [Eq. (5)] yields a simple, analytical form. We start by assuming that most Compton profiles have a rather similar shape. One common feature is especially obvious for metals in which the spectrum at very low momentum is expected to resemble the inverse parabola of free electrons. For insulators, the Compton profiles are known to follow a smooth, continuous, and ''*well-behaving*'' curve. For isolated atoms, if the electronic wave function is expanded in terms of Slater-type orbitals, one expects to obtain modified Lorentzian-like momentum densities. This similarity of behavior with the well known, and tabulated, atomic form factors[12] pushes toward the expansion of the radial parts $g_l(q)$ as Gaussian or Lorentzian contractions. The validity of these considerations is obviously restricted to monotonically decreasing profiles and a particular attention should be paid if other profiles with subsidiary peaks are studied.

In the following examples, we choose a fit of the directional Compton profiles using Gaussian contractions of the radial functions. This choice was conditioned by the following considerations: the isotropic part of the reconstructed momentum density is expected to be used in further calculations involving integrals in which Gaussian functions are known to be very convenient. For all the directional profiles

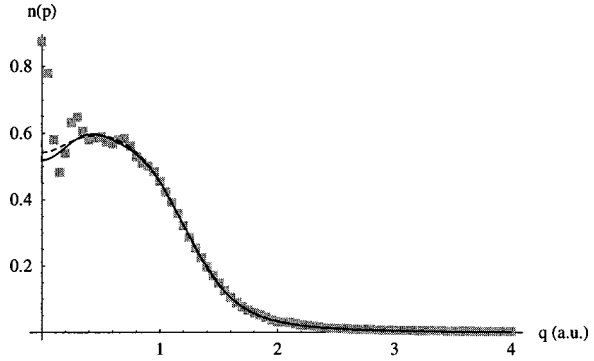

FIG. 2. Reconstructed isotropic momentum density. The dotted line is our reference from the calculated wave function by CRYSTAL. The squares represent the reconstruction using RECONST by Hansen. The reconstructed density from our fitted isotropic profile is shown by the solid line. (See text for comments.)

(in the specific examples), and for a fixed number of contracted functions, a reasonable quality of the fit was better achieved with Gaussian-based functions. Owing to the unique definition of $n(\vec{0})$, the anisotropic components of the reconstructed density should go to 0 at the origin of momentum space. Hence, we found it more judicious to multiply the Gaussian contractions by a power of p for all radial parts associated with a nonzero angular momentum. It then turns out that if $g_l(q)$ is written as

$$g_l(q) = \frac{i^{-l}}{2\pi} \sum_j a_{lj} \sqrt{\pi/\alpha_{lj}}\, \frac{\partial}{\partial q^l} \{e^{-q^2/4\alpha_{lj}}\}, \tag{6}$$

where the contraction coefficients a_{lj} and extensions α_{lj} are adjustable parameters, then the reconstructed density takes the simple form

$$n(\mathbf{p}) = \frac{1}{(2\pi)^{3/2}} \sum_{l=0}^{\infty} i^l h_l(\mathbf{u}_p) p^l \sum_j \frac{a_{lj}}{(2\alpha_{lj})^{l+3/2}} e^{-p^2/4\alpha_{lj}}. \tag{7}$$

Besides being compact and easy to evaluate at any point in momentum space, this procedure avoids a fitting in direct space on the autocorrelation function. As we will see in the next section, this last point allows for a total weighting throughout the fitting process.

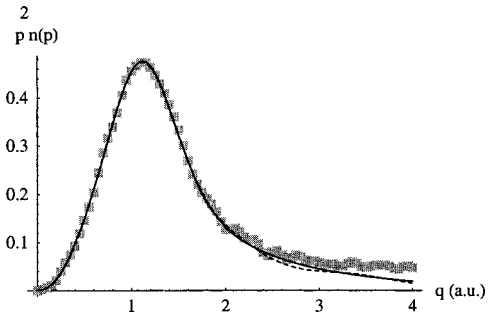

FIG. 3. Reconstructed radial momentum densities compared to the Hartree-Fock result. This work is the solid line; the Hansen reconstruction is represented by the squares. Our reference is the CRYSTAL output given by the dashed line.

III. APPLICATION AND TEST OF THE METHOD

Though this method is obviously aimed at applications to experimental data, it must first be calibrated: this procedure implies a comparison with theoretical data. In that respect we have conducted a calculation for the cubic crystal of magnesium oxide using the CRYSTAL code[13,14] based on the self-consistent Hartree-Fock procedure. This calculation made use of the same basis set as previous publications on this compound.[15] The reason for using the CRYSTAL code is that the calculations of momentum density and Compton profiles are standard features of the output of this program. It then allows for a direct check of the quality of the reconstruction. Eight directional profiles were calculated with points separated by 0.02 a.u., which is approximately what the actual experimental apparatus can routinely provide.

We have also computed an isotropic Compton profile for this cubic compound as

$$\langle J(q)\rangle = \{6J_{100}(q) + 12J_{110}(q) + 8J_{111}(q) + 24J_{210}(q) + 24J_{211}(q) + 24J_{221}(q) + 24J_{310}(q) + 24J_{320}(q)\}/146.$$

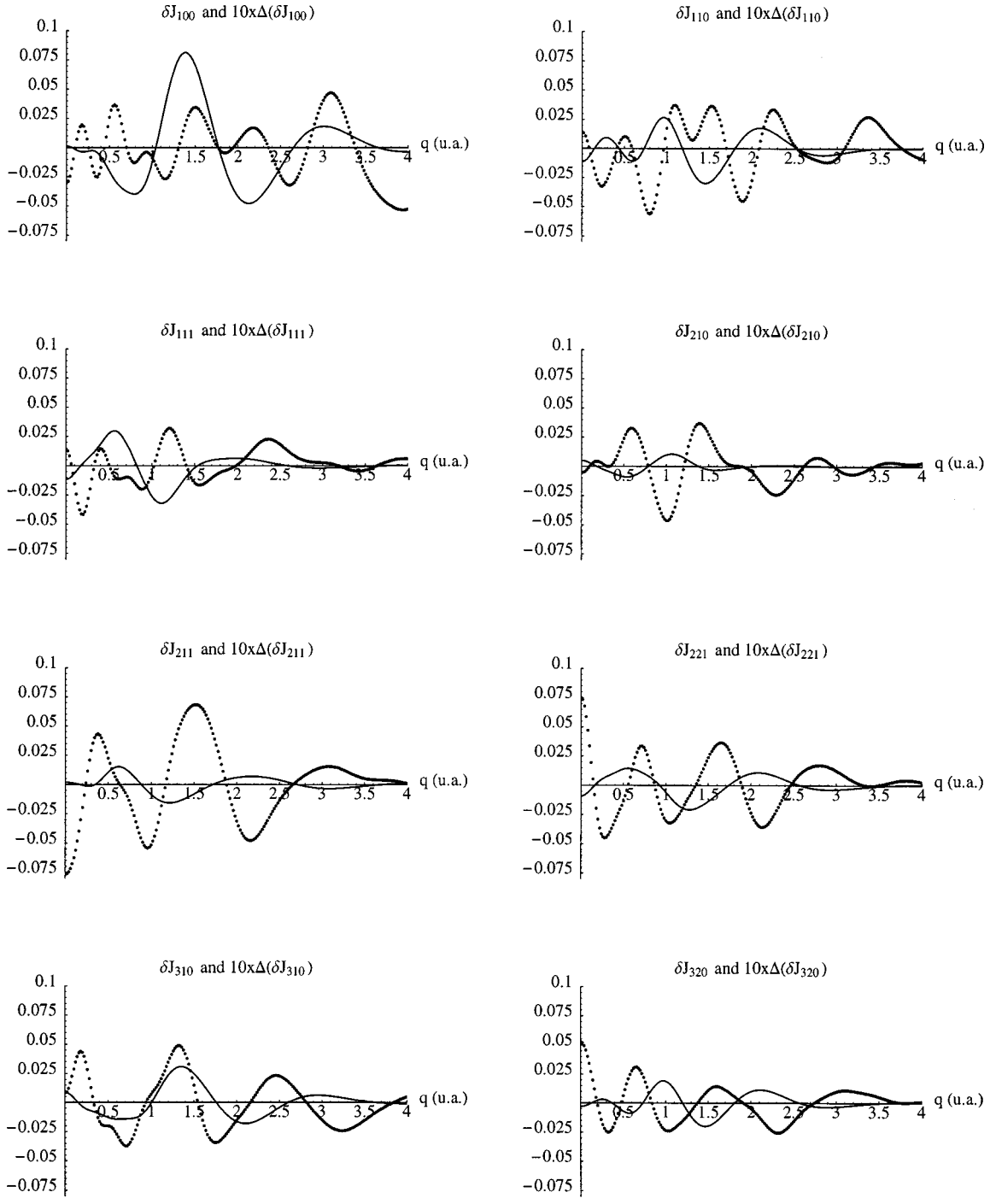

FIG. 4. Fitted Compton anisotropies using Eq. (9) are shown by the solid line. The differences with the calculated anisotropies from the CRYSTAL output are magnified by a factor of 10 and plotted on the dotted lines.

In the case of actual experimental profiles, it would be advisable that one always measures a crystal powder profile. The quality of the reconstructed momentum density is greatly conditioned by what one assumes to be the isotropic profile. In order to simulate a situation close to reconstruction from actual experimental data, a random noise was added to each of the computed Compton profiles. It was calculated, for each point of a given profile, using a pseudo-random number generator in the range $\pm\sqrt{J(q)/N_{\max}}$, $N_{\max}$ being the maximum expected number of counts in the $q=0$ channel. To reproduce the estimated noise from actual experimental data, a $N_{\max}=10\,000$ value was chosen. Assuming that one isotropic profile and a set of eight directional profiles are thus available, our reconstruction is a two step procedure.

A. Reconstruction of the isotropic density

The isotropic profile is fitted by seven Gaussians. In our example a χ^2 of 2×10^{-4} was reached. The difference $J_{\rm iso}^{\rm fit}(q)-\langle J(q)\rangle$, after convergence, is plotted in Fig. 1. (Note that since the contraction coefficients and exponents are highly correlated, each additional Gaussian has to be introduced with extreme care.) The isotropic part of the momentum density is then readily derived [setting $l=0$ in Eq. (6)] and can immediately be compared to the isotropic momentum density calculated with CRYSTAL (Fig. 2). In this particular case, one can observe the discrepancies at low momentum for the two reported reconstructions. It is now a well-known fact that reconstruction at low momentum is difficult in any case. Indeed, for the isotropic part, the standard reconstruction formula is

$$n_{\rm iso}^{\rm rec}(p)=\frac{-1}{2\pi p}\,\frac{\partial J_{\rm iso}(p)}{\partial p}. \tag{8}$$

Hence a small uncertainty in the calculation of the derivative can be tremendously amplified in the low momentum region. In that respect, we have checked that with such small steps (0.02 a.u.) reducing the noise improves the quality of the reconstructed density with a particularly large effect on the RECONST results. However, one should not focus too much on this particular region of the spectrum. The isotropic momentum density is seldom used on its own, a more useful and relevant quantity being the radial distribution $p^2n(p)$, i.e., $p^2n(p)dp$ is the number of electrons with the modulus of its momentum between p and $p+dp$. We have reported this last quantity in Fig. 3. The result of our reconstruction shows no significant discrepancy and appears much more reliable than the numerical method at higher momentum. This last point, together with the Gaussian-contraction expression of the reconstructed isotropic density, should prove to be of great utility in the calculations of properties like the kinetic energy.

B. Reconstruction of the anisotropic part of the density

The set of eight Compton anisotropies, defined as $\Delta J(q,\mathbf{u}_j)=J(q,\mathbf{u}_j)-\langle J(q)\rangle$, are fitted with the following expression:

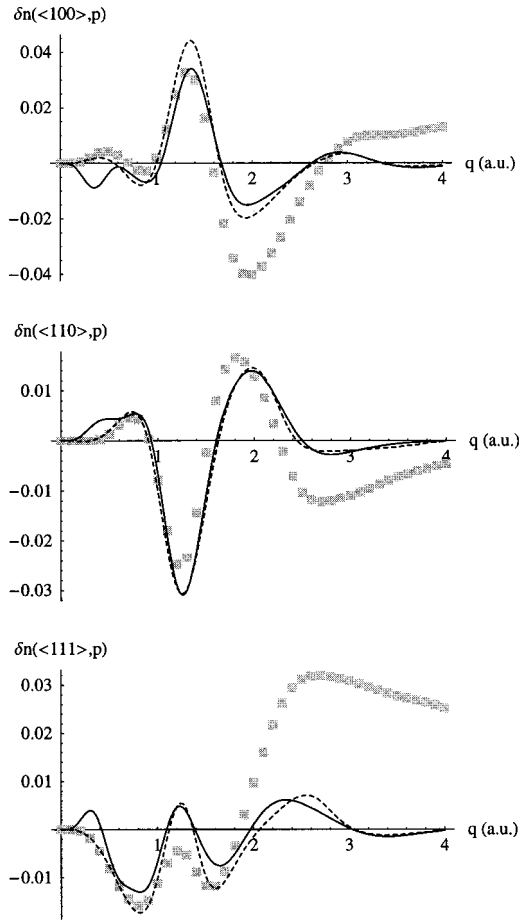

FIG. 5. Reconstructed anisotropic part of the momentum density in the three principal directions. The dotted square is the result from RECONST. The Hartree-Fock reference is given by the dotted line and our reconstruction is shown by the solid line.

$$\begin{aligned}\Delta J^{\rm fit}(q,\mathbf{u})=\frac{1}{2\pi}\Bigg[&\left\{\tfrac{1}{16}\sum_{j=1}^{10} a_{4j}\sqrt{\pi/\alpha_{4j}^{9}}(q^4+12\alpha_{4j}^2-12q^2\alpha_{4j})e^{-q^2/4\alpha_{4j}}\right\}h_4(\mathbf{u})\\&+\left\{\tfrac{1}{64}\sum_{j=1}^{10} a_{6j}\sqrt{\pi/\alpha_{6j}^{13}}(-q^6+30q^4\alpha_{6j}-180q^2\alpha_{6j}^2+120\alpha_{6j}^3)e^{-q^2/4\alpha_{6j}}\right\}h_6(\mathbf{u})\\&+\left\{\tfrac{1}{256}\sum_{j=1}^{10} a_{8j}\sqrt{\pi/\alpha_{8j}^{17}}(q^8-56q^6\alpha_{8j}+840q^4\alpha_{8j}^2-3360q^2\alpha_{8j}^3+1680\alpha_{8j}^4)e^{-q^2/4\alpha_{8j}}\right\}h_8(\mathbf{u})\Bigg].\end{aligned} \tag{9}$$

Further harmonics could be added but were not found to be essential to our demonstration. The quality of the fit can be checked in Fig. 4 for each direction. The overall χ^2 (including the eight directions) is close to 7.6×10^{-3}.

Using expression (7), the anisotropic part of the reconstructed momentum density is then easy to calculate and is plotted for three main directions on Fig. 5. Once again the low momentum part shows the limited flexibility of our analytical model. However, the overall agreement is satisfactory and does not exhibit the large discrepencies generated by numerical artifacts of the RECONST procedure.

IV. POSSIBLE EXTENSIONS OF THE METHOD

Our reconstruction method is based on the fit of an analytical model for the function $J(q,\mathbf{u})$ from which the momentum density is immediately accessible. It is thus possible to introduce any sort of weights in the least-squares treatment. One obvious possibility is, of course, to use the estimated variance for each data point.[16] This weighting was much more difficult for previous reconstruction procedures based on autocorrelation functions. In the above-mentioned example several weighting schemes were tried. Considering our remarks on the importance of the quantity $p^2n(p)$, we found that a possible choice of weight, leading to satisfactory results, was

$$w_n=\frac{q_n}{2\pi}\,\frac{I(q_{n-1})-I(q_{n+1})}{q_{n+1}-q_{n-1}},$$

where $I(q_n)$ is the total number of counts in the channel q_n. A more classical choice, like $w_n=I(q_n)$, would of course give more importance to data points in the low momentum region but should yield a more direct estimate of the variance of contraction and extension refined parameters.

The above-described example was chosen from our current interest field.[17] The generalization to noncubic systems is straightforward and only necessitates other symmetry-adapted harmonics. The present method is, of course, limited to monotonically decreasing DCP's. In the cases of crystals for which Compton profiles exhibit singularities or for the analysis of magnetic Compton profiles, the fit should be carried out by using other types of functions: in particular, the model should incorporate the physical origin of those singularities. However, we expect the momentum density resulting from such a fit to be not as easy to manipulate as the expression obtained with Eq. (7). In these particular cases, the numerical-based program RECONST by Hansen is probably the most versatile and can still be considered as a reference.

V. CONCLUSION

On the basis of the previous work by Hansen, we have established a new reconstruction procedure yielding a compact and efficient representation of $n(\mathbf{p})$ in the case of monotonically decreasing Compton profiles. Besides the appealing final result, the method has the main advantage of working in the unique reciprocal space with no explicit use of the autocorrelation function. The consequence is the possibility of using the mean variance associated with each data point as a weight in the fitting process.

The results obtained in the particular case of fcc magnesium oxide show the great stability of the reconstruction even when noise is introduced. Numerical artifacts are avoided, yielding a much more reliable result in the high momentum range. Further tests should be carried out on other compounds. Especially, we expect that functions other than Gaussians should be used for metals in order to avoid a smoothing of the Fermi break. A general reconstruction program based on our analytical approach is expected to be available shortly.

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[1] See, for example, *The Application of Charge Density Research to Chemistry and Drug Design*, Vol. 250 of *NATO Advanced Study Institute, Series B, Physics*, edited by G. A. Jeffrey and J. F. Piniella (Plenum, NY, 1991); *Electron and Magnetization Densities in Molecules and Crystals*, Vol. 48 of *NATO Advanced Study Institute, Series B, Physics*, edited by P. J. Becker (Plenum, NY, 1980); or P. Coppens, *Charge Densities and Chemical Bonding* (Oxford, New York, 1998).

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