

## THE OTHER PHILOSOPHY OF CHARGE DENSITY

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### Résumé

L'article discute les idées de base d'une approche optionnelle pour la densité de charge, qui a été le thème principal de la contribution de l'auteur dans la coopération scientifique Franco-Finlandaise. Elle est caractérisée comme une approche empirique\* ou Fourier en comparaison avec les études conventionnelles de la densité de charge décrites comme l'approche théorique ou d'ajustement. Le pour et le contre des deux approches sont discutés en principe et à la lumière des exemples en soulignant les possibilités complémentaires offertes par l'approche empirique.

\* Au sense de l'adjectif: qui s'appuie exclusivement sur l'expérience et l'observation.

### Abstract

The article discusses the basic ideas of an alternative approach to charge density, which has been the main theme of the author's contribution to the French-Finnish scientific co-operation. It is characterized as the empirical or Fourier approach in comparison with the conventional charge density studies described as the theoretical or fitting approach. The pros and cons of both approaches are discussed in principle and in light of examples emphasizing the complementary possibilities offered by the empirical approach.

### The two approaches

*The interaction of theory and experiment* is the driving force of all science. Their relation is the core of the scientific method and the basic problem of the working philosophy of the scientist. His ways of doing research reflects his attitude on this problem.

The two counterparts are obvious in the macroscopic division of science into theoretical and experimental research, but it is important to realize that both are present in every element of science. Their relation can be traced back to the basic *interaction of observation and human mind*. Therefore they are inseparably interwoven; every concept or process is at the same time both empirical and theoretical. There are neither any purely experimental experiments nor purely theoretical theories. Each experiment, observation, even sensation, is based on a structuring principle or background theory. All theories, models and concepts, even mental pictures, arise from their empirical meanings.

In spite of this inseparability of theory and experiment there are two directions of inference, named here the *empirical approach* and the *theoretical approach*. The question is not about doing experimental or theoretical work, nor about the amount of theory or experimental

data involved. The distinction comes from the direction of the logical processes dominating the thinking or method applied, whether the mental arrow is pointing from theory towards observation or the other way. The direction can be recognized in the treatment of any single problem, small or large.

*The empirical approach is based on perception of Gestalts, recognition of relevant structural features of the observations or measurements. The empirical Gestalts are conceptualized as characteristic properties of entities or phenomena of Nature and quantified into quantities, quantitative measures of the qualities. The empirical approach starts from the simple and specific and proceeds to the structural and general. It proceeds from representation of phenomena towards interpretation and understanding.*

*The theoretical approach starts from theory, from the interpretation of the phenomenon in terms of a theoretical model. It proceeds from the general towards the specific. The model yields predictions which can be tested through experimental investigation of the phenomenon. To meet the experimental test it may be necessary to allow flexibility of the model e.g. through parametrization. The test then leads to fitting of parameters. A good fit is understood to confirm the original theoretical interpretation and to yield "experimental values" for the parameters. Further, the great physical theories give the understanding of phenomena in principle but exact predictions can be calculated for trivial cases only. For any realistic systems simplifying approximations are needed and the experiment gets the extra task to check the validity of the approximation.*

In the development of science empirical approach is the primary process. It is building the Giant of theoretical understanding from conceptual representations of observations through successive steps of generalization. Deeper understanding is reached through more general concepts representing wider structural features of the observations. The great achievements of science are unifying ideas combining different classes of phenomena into one structural whole. Theoretical approach is the process of the Giant. Still, it is a secondary process made possible by this understanding.

### **Existence of atoms**

The game called charge density was initiated about 80 years ago. Both approaches were present right from the beginning.

LAUE's approach was theoretical. On the basis of the well established theoretical model of a crystal as a 3-dimensional periodic array of atoms and the recently confirmed idea of X-rays as short-wavelength electromagnetic radiation he predicted the phenomenon of X-ray diffraction from crystals. The prediction was immediately verified.

The BRAGGS, father and son, started the empirical approach. They attacked the problem, how to determine the structure on the basis of the measured positions and intensities of the diffraction peaks.

Both deserved their Nobel. LAUE standing on the shoulders of the Giant saw the promised land with its immense potentialities. The BRAGGS found the beginning of a path leading to that land and prepared the first tools to cut their way through its unexplored jungles.

The *theoretical approach* found the basic connection between diffraction and structure,

1. the representation of crystal charge density as a Fourier series

$$\rho = \frac{1}{V} \sum_j F_j \exp\{-2\pi \mathbf{S}_j \cdot \mathbf{r}\} \quad (1)$$

2. the relation between the lattice dimensions and the scattering vectors  $\mathbf{S}_j$  of the diffraction peaks
3. the relation between structure factors  $F_j$  of the crystal and the peak intensities .

These relations made possible experimental determination of the lattice and the charge density. Since then *the empirical approach* to charge density would aim at finding and characterization of significant features of the experimental charge density or of its deviations from the theoretical model and at their quantification in terms of quantities which are functionals of the charge density and can, thus, be calculated from the experimental structure factors.

The first great finding was that the constituent atoms were visible as peaks in the charge density. For the first time in the history of science, the atoms appeared as observable entities of nature. The ancient hypothesis had received its first direct verification.

### Atomic definition – partitioning

*The existence of atoms* as identifiable structural entities within the crystals justified the idea of treating matter as a system of interacting atoms. This divides the problem into two largely independent phases: 1. *the structure* and 2. *the charge density*. The interactions of atoms would (1) determine the structure, *i.e.* the lattice, mutual positions and motions of the atoms and (2) modify the atoms. It became obvious to represent both the crystal charge density and the structure factors as sums of atomic contributions

$$\begin{array}{ccccccc} \Leftarrow & \Leftarrow & \text{Th. appr.} & \Leftarrow & \Leftarrow & & \\ \rho = \sum_{\text{at}} \rho_{\text{at}}(\mathbf{r} - \mathbf{r}_j) & & & F_j = \sum_{\text{at}} f_{\text{at}} \exp\{2\pi i \mathbf{S}_j \cdot \mathbf{r}_{\text{at}}\} & & & (2) \\ \Rightarrow & \Rightarrow & \text{E. appr.} & \Rightarrow & \Rightarrow & & \end{array}$$

where the first sum runs through all atoms of the crystal and the second through the atoms of the unit cell.

The *theoretical approach* applies the eqs. (2) from right to left. It proceeds from theoretical evaluation of atomic charge densities and atomic factors to prediction of the composite charge density and the structure factors, while the *empirical approach* proceeds from left to right, from the experimental structure factors and crystal charge density towards evaluation and characterization of the atomic contributions and their comparison with theory.

Quantum mechanics is the present starting point of the theoretical approach. The work of the HARTREES – again father and son – gave the theoretical means for treating the atomic

contributions in eqs. (2). In principle, quantum mechanics offers the basis for predicting both the structure and the charge density on the basis of the known composition of the crystal – at least we believe so. In practice, it gives solutions for trivially simple systems only and has led us to an endless succession of tedious small steps towards the treatment of less simple systems and less crude approximations. Even today, we are still not very good in predicting structures or – knowing the structure – the charge density.

The theoretical approach becomes, thus, reduced to a *fitting approach*. The background theory is restricted to the basic structural idea of LAUE and that behind the theoretical atomic contributions, plus – particularly for the charge density – various general principles guiding the parametrization. And the fit of the theoretical structure factors with the experimental ones acts as the main criterion for the validity of results.

Atomic superposition model built of theoretical free atoms in harmonic motion with free parameters determined by the symmetry turned out to be sufficient for structure determination. This has become routine, except for extreme cases. At present the number of new structures reported is of the order of 10000 a year. Charge density has then become a matter of refinement. Parameters representing modifications of atoms and, when relevant, anharmonicity of their motions are added to the model. Such models are crudely approximate as compared with the quantum mechanical basic ideas of the problem. Therefore the theoretical approach to charge density aims as much at improvement of the approximations as at determination of the charge density.

The *empirical approach* has to work with the crystal charge density corresponding to the experimental structure factors and represented by the Fourier series (1). It becomes, thus, reduced to a *Fourier approach* aiming at characterization of modifications of the atoms in terms of empirical features to represent in proper way "what has happened to the atoms when forming the crystal".

Here we meet the problem of *partitioning*. It is clear that no unique division of the composite charge distribution into individual atomic contributions is possible. Any result, qualitative or quantitative, concerning a crystal atom includes an uncertainty, which is not an experimental inaccuracy but a result in its own value, since it reflects the basic conceptual inaccuracy of the atom itself. Therefore, any empirical statement concerning atomic properties must consist of two parts: 1. the statement itself plus 2. uncertainty of the statement due to the conceptual inaccuracy. Both parts include their own experimental inaccuracies.

The view of the theoretical approach on this problem is different. A superposition model in itself defines the atoms. Its parameters define the limits within which the atoms are allowed to be modified. It seems controversial that on one hand the theoretical approach thus neglects the partitioning problem completely, but on the other hand it has led to crude overestimations of the problem.

### **Atomic size – locality**

The first quantification problem in atomic charge densities was determination of the ionic state. This problem has been discussed repeatedly since the first propositions by DEBYE and SCHERRER in 1918 [7] and by COMPTON in 1926 [5], *cf.* [21, 15].

DEBYE and SCHERRER [7] were the first to apply *reciprocal-space partitioning*. In the case of some simple structures it seemed possible to derive "experimental atomic factors" from the structure factors by an experimental approach which required only straight-forward interpolation and simple algebra and to obtain "experimental atomic charges" by subsequent extrapolation to  $\sin \theta/\lambda = 0$ . The partitioning problem is evident in the apparent arbitrariness of the interpolation and extrapolation. The conventional *theoretical approach* inverts this procedure. It starts from theoretical atomic factors representing the atoms in different ionic states and compares the resulting structure factors with the experimental ones. The problem of partitioning is hidden in the assumed theoretical atomic shapes and becomes, thus, easily neglected. At worst the reciprocal-space partitioning – independent of the direction of approach – has led to the completely negative conclusion, that the ionic state cannot be determined at all by X-ray diffraction, as first argued by BIJVOET and LONSDALE [2].

The alkali halides offer a good example. The structure factors derived from neutral atoms and those corresponding to atoms in different ionic states differ so little that it is far beyond the most optimistic experimental accuracy. This is discouraging. If X-ray diffraction cannot tell the obvious, that sodium chloride is ionic, is it worth anything?

COMPTON [5] was the first to propose *direct-space partitioning*, *i. e.* simple counting of electrons from the atomic charge density peaks of the experimental charge density. This procedure corresponds to the idea of the *empirical Fourier approach*. It yields a definite outcome within certain conceptual inaccuracy. In this way also the ionicity of the alkali halides becomes obvious, *cf.* [14, 15, 21, 27].

The apparent contradiction between the two methods calls for conceptual clarity as was emphasized already by COCHRAN [3, 4, 5]. The idea of atoms as constituents requires a certain degree of *locality*. The definition of an atom should involve the charge density peak at the atomic position as its main part and it should not engage distant parts of the charge distribution. Several proposals have been made to define more exactly the nature of this requirement to reduce the conceptual inaccuracy of the results, either in terms of strict spatial partitioning or through principles governing the overlapping of neighbouring atoms. In this context just the general principle is important.

The nature of the direct-space partitioning problem is clearly reflected by fig. 1. While the degree of conceptual uncertainty of the atom is different in different cases, the nature of bonding as well as the ionic state can be discussed in terms of such curves.

The requirement of locality limits correspondingly the nature of the reciprocal-space partitioning, but it is difficult to define it in terms of the interpolation-extrapolation procedure. However, it should be obvious that use of the theoretical free atoms in different ionic states involves an invalid principle of extrapolation since any bonding effects as well as the requirement of locality affect the atomic factors most strongly in the region of small  $\sin\theta/\lambda$ . The impossibility to determine the state of ionization through such an approach is a consequence of violation of locality. Any conclusions on the ionic state obtained in this way are questionable. In a study of bonding the free-atom superposition model assumes what should be determined experimentally and makes a wrong assumption.

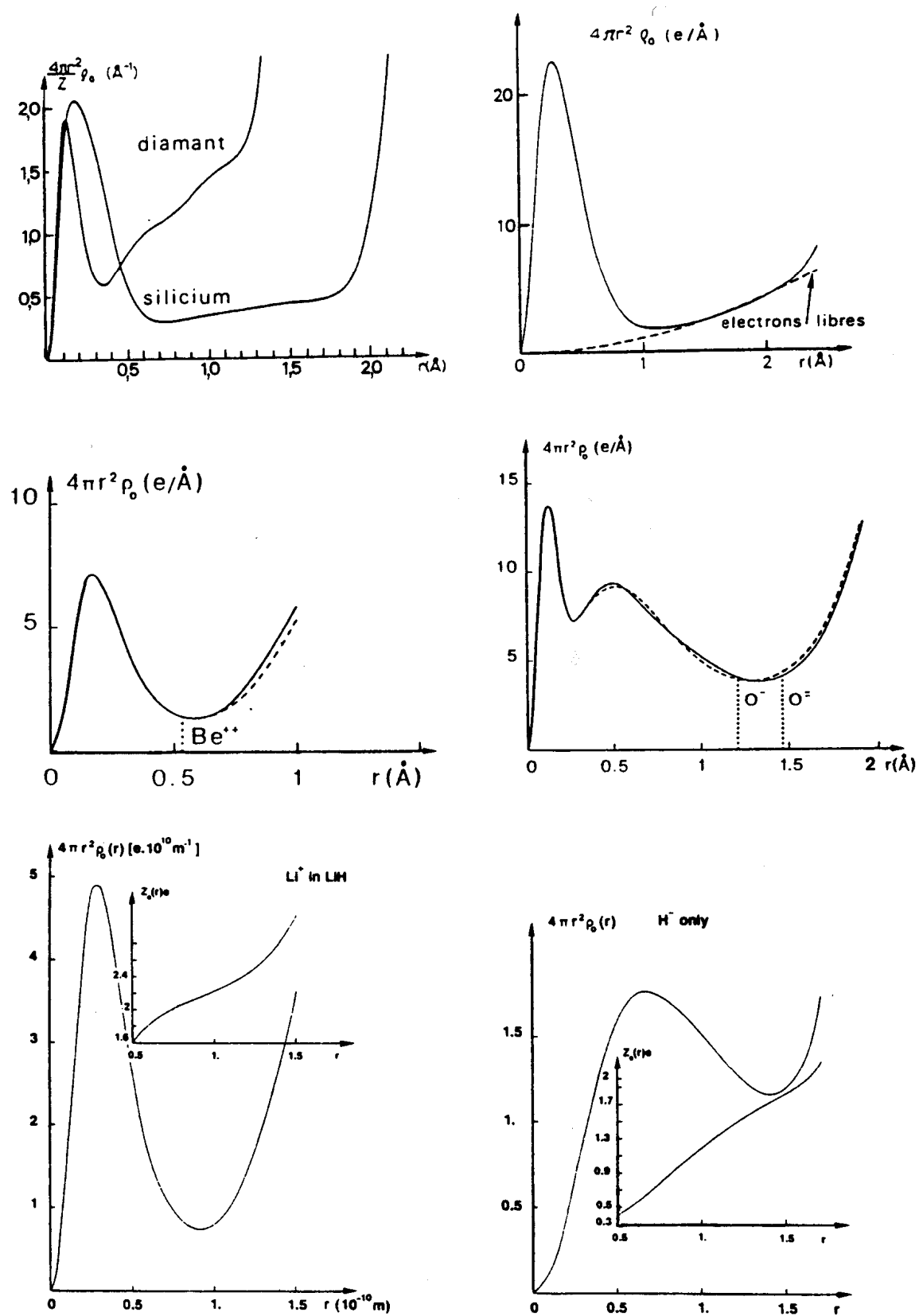


Figure 1: Radial charge density  $4\pi r^2 \rho_0(r)$  of C in Diamond and Si in Silicon [20], Mg in metallic Magnesium [23], Be in BeO after subtraction of  $\text{Be}^{++}$  [26], Li in LiH and H in LiH after subtraction of  $\text{Li}^+$  [29].

### Atomic shape - multipoles

Bonding is expected to affect in the first place the shape of the atomic charge distributions. The changes as compared to the free atoms are however not arbitrary. There are both physical and mathematical grounds to believe that they can be represented reasonably well by functions with low-order harmonic angular behaviour. This leads to the idea of representing the crystal charge density in terms of site-symmetric harmonic expansions

$$\rho_n = \sum_j \rho_{nj}(\mathbf{r}) K_j(\theta, \phi) \quad (3)$$

around each atomic center, first proposed by ATOJI in 1958 [1]. The idea was adopted by DAWSON in 1967 [6] as the guiding principle of the theoretical approach, which has then been expanded into multipole analysis of charge densities through fitting. The first formulations of an empirical approach in terms of multipole expansions were presented in the same year [12, 18]. Development of these principles has been a central theme in the French-Finnish co-operation on charge density [25 – 29]. The principles of symmetrization were discussed in detail by the present author [16]. The most complete tables of the resulting site-symmetric harmonics have been presented in the context of the extension to the treatment of rigid molecular motions [10].

Representation of crystal charge density by the series (3) requires very many terms already at the distance of nearest neighbours. However, for representation of the central atom itself low-order terms are sufficient. This is a qualitative requirement supported by quantum mechanical considerations and by the empirical fact that crystal charge density is closely represented by the free atom superposition model.

The argument is enhanced by the requirement of locality. Because of a mathematical reciprocity principle higher order terms of local objects become unobservable unless they are immensely strong, *cf.* fig. 2.

Representation of charge density by eq. (3) differs essentially from the conventional map representations in that each multipole shows a full three-dimensional feature of the atomic charge distribution. Some imagination is needed to form a clear mental picture of their shapes. Otherwise this is ideal, because just few one-dimensional radial densities are required, each coupled to a definite well known angular behaviour, to form a full picture of the shape of the atom, *cf.* fig. 3.

The multipole representation by eq. (3) guides interpretation of the charge density features in several ways.

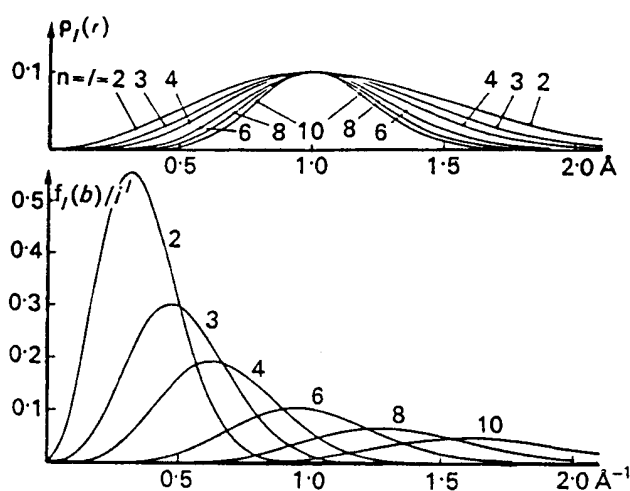


Figure 2. Radial charge densities of different orders and the corresponding scattering factors [13].

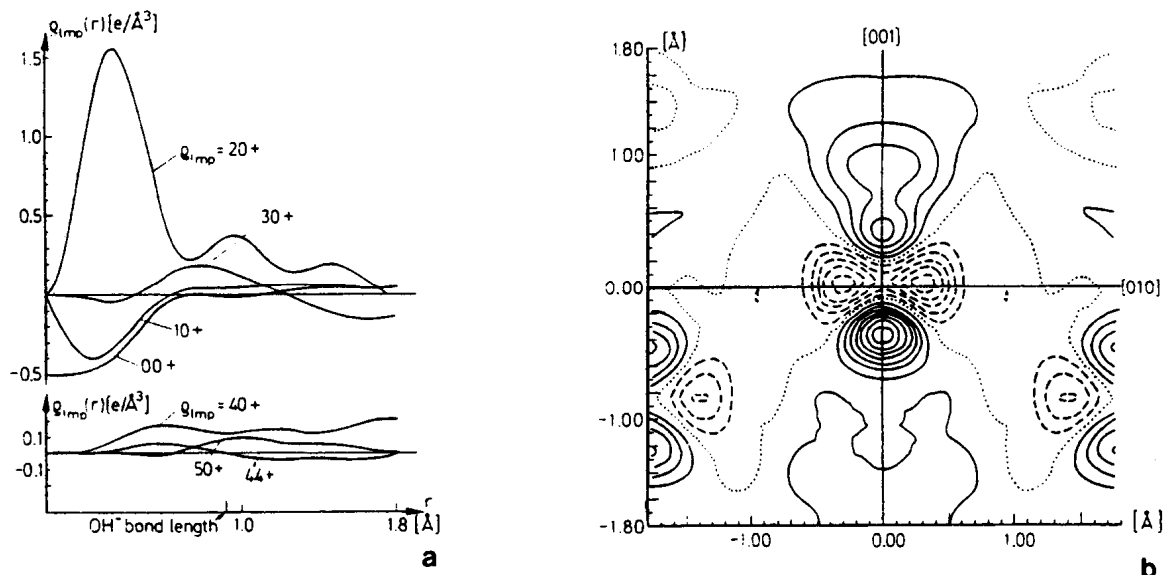


Figure 3. Difference density at the Oxygen position in LiOH in the multipole and the Fourier representations [22].

Different multipoles refer to different parameters and to different physical properties of the atom. Any need to correct the atomic positions or motions in the reference model is clearly seen, each parameter corresponding to its own multipolar component [17] as is demonstrated by comparison of figs. 4 and 3a.

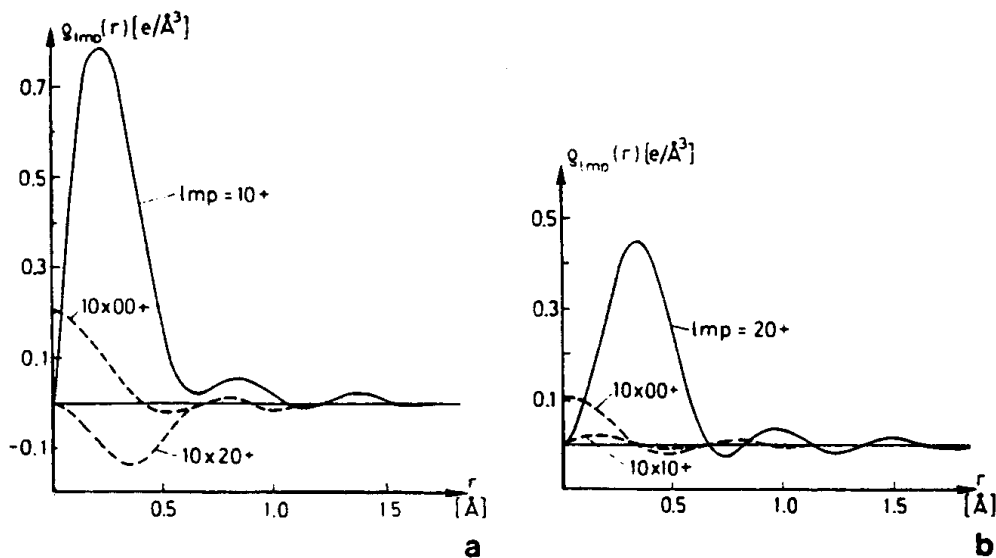


Figure 4. The effect on the radial densities at the Oxygen position in LiOH a) of the change  $\{D\}z = 0,01 \text{ \AA}$  of the Oxygen position b) of introducing prolateness  $\langle u_z^2 \rangle - \langle u^2 \rangle = 0,002 \text{ \AA}^2$  of the Oxygen thermal motion [22].

If some feature observed in the map is seen to be a part of a consistent three-dimensional behaviour of a neighbouring atom it is much more likely to be real and can be immediately assigned to that atom. It may happen that such a detail between two atoms arises from the low-order multipolar behaviour by just one of the atoms. One can then conclude that this detail also is due to the electrons belonging to that atom. The opposite may occur. A feature may be shared by two atoms in the sense that it is composed by contributions due to low order multipoles of both. This certainly hints to interpretation of the feature as a bonding effect between the atoms, *cf.* fig. 5.



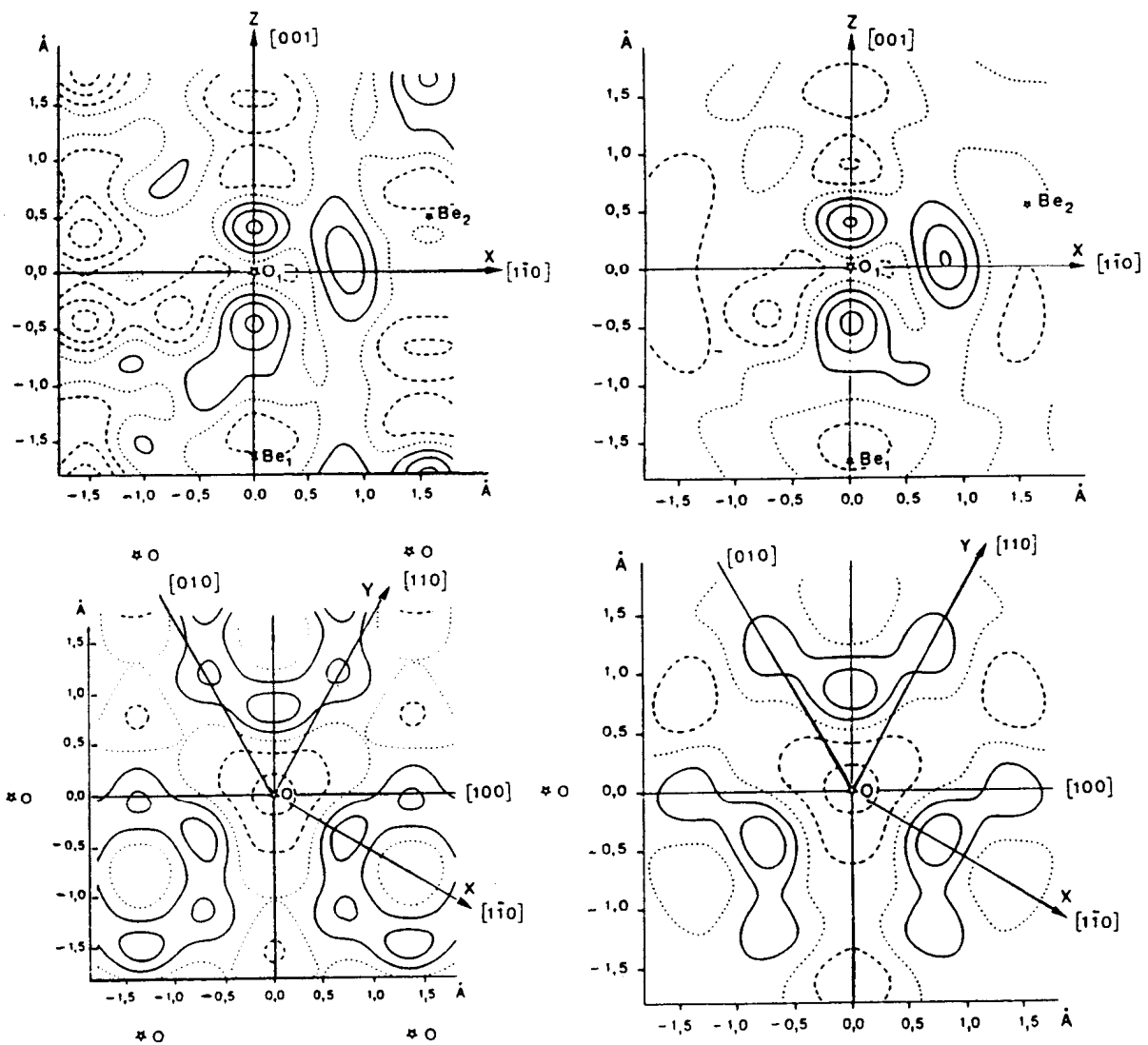


Figure 5. Difference density at O in BeO and the corresponding low-order multipole expansion [26].

It is also clear that interpretation will depend on the radial nature of the multipoles, whether they represent features at small or large  $\sin \theta/\lambda$  in reciprocal space. Any possible additional information like thermal dependence and complementary results from other types of experiments will help.

### Quantification – integral quantities

In the *theoretical approach* the problem of quantification does not occur. The "experimental information" is expressed in terms of parameters which have predefined physical meanings given by the theory or model. Parameters attached to the atoms represent properties of the atoms. Fitting is understood to yield their quantitative values. Here some care is required since, as indicated by the example of the ionic state, this is not always justified. The nature of the model parameter or its value may contradict the principles to be taken into account in the partitioning.

In the *empirical approach* perception of significant features is followed by the problem of quantification, representation of the features in terms of quantities, which are functionals of the charge density, reflect properly the nature of the features and yield, thus, empirical measures for their "strengths". This process must be guided by the requirements of physicality and reliability. The quantities should offer the opportunity to proceed towards a physically reasonable interpretation, and it must be possible to derive them reliably from the data. Considerations of the size and shape of the atoms serve the first purpose and indicate that the multipole expansion eq. (3) is a proper tool to guide the perception.

The second requirement can be discussed in terms of the general class of *linear functionals* of the charge density [14, 15]. Such quantities have similar representations in the real space and in the reciprocal space defined by its real and reciprocal distribution function  $\gamma_X(\mathbf{r})$  and  $q_X(\mathbf{S})$

$$X = \int \gamma_X(\mathbf{r})\gamma_X(\mathbf{r})d^3r = \int q_X(\mathbf{S})f(\mathbf{S})d^3S . \quad (4)$$

Charge density  $\rho(\mathbf{r})$  at any point  $\mathbf{r}$ , multipolar radial charge densities  $\rho_j(r)$  at any distance  $r$  from the center of the expansion (3), electron count  $Z_V$  of any volume  $V$ , multipolar electron counts  $Z_j(R) = B_j \int_0^R \rho_{nj}(r)r^2 d^3r$ , within any distance  $R$  from the center, where  $B_j$  is the angular normalization coefficient, more generally, any moment  $Z_{pj}(R) = B_j \int_0^R \rho_j(r)r^{2+p} dr$ ,

scattering factor  $f_V(\mathbf{S})$  of any volume  $V$  partitioned from the charge distribution and radial scattering factors  $f_j(\mathbf{S}; R)$  corresponding to the multipolar radial charge densities up to some radius  $R$ , are different relevant examples of linear functionals with evident real distributions.

The two distributions fulfill the normal reciprocity theorem: a narrow real distribution corresponds to a broad real distribution and *vice versa*, and the degree of singularity of the one determines the asymptotic behaviour of the other, as demonstrated by fig. 6.

In case of a crystal the reciprocal representation eq. (4) becomes a series

$$X = \frac{1}{V} \sum_j F_j q_X(\mathbf{S}_j) \quad (5)$$

in terms of crystal structure factors.

In view of the finite number of observed structure factors  $F_j$  it is obvious how the reliability of the empirical values obtained for different quantities depends on their distribution functions. The dependence of conclusions on the unknown structure factors at large  $\sin \theta/\lambda$  becomes minimized when based on integral quantities with wide and smooth real distribu-

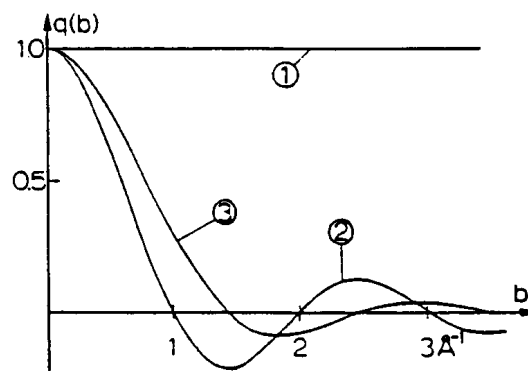


Figure 6. Reciprocal distributions of 1. the charge density at a point, 2. the average charge density on a spherical surface of radius 0,5 Å and 3. the electron count in the same sphere [14].

tions and, hence, narrow reciprocal distributions. The listed examples are, thus, roughly in the order of increasing reliability.

Charge density at a point has the most singular real distribution, a  $\delta$ -function at that point. Correspondingly, its values depend critically on the residual term. This gives rise to the old paradox. On statistical grounds the experimental inaccuracy of charge density at any point increases roughly like  $\sqrt{N}$  with the number  $N$  of the observed structure factors. Thus, in the empirical approach, "the more we know, the less we know".

The radial charge densities have  $\delta$ -function distributions of the form of a spherical shell. Thus, their reliability increases with the distance from the center and they are proper tools for discussion of bonding effects.

Electron counts, moments and scattering factors are integrals over finite volumes. The singularity of their real distributions is not worse than a discontinuity at the boarder. They are therefore the most reliable quantities on the list. Their reliability increases with the volume. However, the reciprocal distributions of the scattering factors  $f_l(S)$  and  $f_l(S; R)$  are peaked at  $S$  and  $S$ , respectively, and their reliability therefore drops steeply at the experimental cut-off in  $\sin \theta/\lambda$  [13, 15].

Further, it should be noted that the "angular smoothness" of the real distributions of all multipolar quantities is reduced and, hence, the reciprocal distributions are broadened, with the increasing multipole order  $j$ .

It has been argued that multipolar information represents such a degree of detail that it is not realistic as compared to conclusions made on the basis of density maps. This turns the basic argumentation upside down. Any charge density values, hills and valleys visible in the maps, are details, local features, which represent the uttermost unreliability as basis of conclusions, while the multipolar radial densities are angular integrals of the charge density over the full  $4\{p\}$  solid angle. They do not represent details but consistent integral or large-scale features.

In this respect the radial scattering factors  $f_l(S; R)$  are still better since they are integrals over spherical volumes. They are therefore the most sensitive measures for the presence and for the significance of different multipole components of the atomic peaks.

For the same reason comparison of the significances and strengths of different multipoles is most conveniently done in terms of contributing electron counts. It follows from the integral nature of such quantities that they can be experimentally significant even when their presence is difficult to realize in the charge density, *cf.* fig. 7.

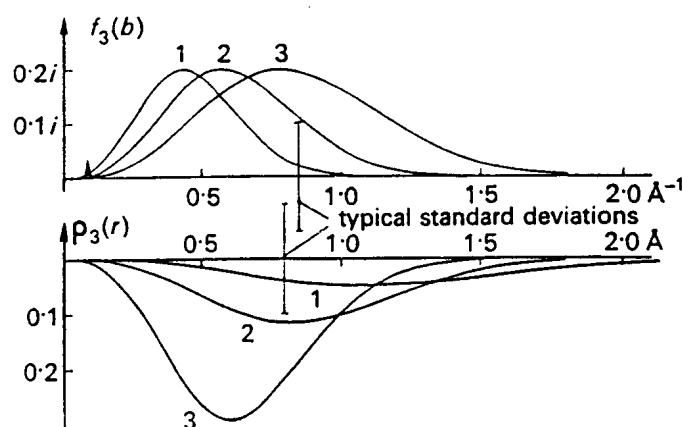


Figure 7. The radial scattering factors and the corresponding radial densities of some third order multipole components of equal observability [13].

In the conventional theoretical approach these questions look different. Due to the definition of atoms in terms of analytic basis functions, the charge distribution corresponding to the fitted theoretical model is bound to such smoothness conditions that there are no special problems in considering the density values at different points. The above arguments become, however, valid when discussing the residual difference maps.

### **Accuracy and interpretation**

The questions of accuracy and interpretation of results look completely different in the two approaches.

In the *fitting approach* the two problems are coupled indistinguishably together. The model is a set of predefined physical meanings expressed in terms of parameters coupled together. Fitting means always fitting of a model as a whole, not of individual parameters. The goodness of fit measures in the first place the validity of the model, i.e. the validity of the whole set of physical significances involved.

A good model leads to a good fit and to results, which are far more accurate and present much finer details of the charge distribution than can be discussed in the empirical approach. The experimental information becomes expressed in terms of the model parameters. The experimental errors or inaccuracies are transformed into error limits of the parameters. However, in principle, the value obtained for any single parameter is not an independent experimental result concerning some definite physical property of the charge density. Both the value and its error are conditional, they have a meaning only as a part of the model, i. e. on the condition that the whole set of the predefined physical significances is valid. Correlations of the parameters indicate the extent to which the significances overlap within the model.

In careful studies the dependence of results on the model must be discussed. This is understood to give some idea of their genuine experimental reliability. The problem is still present. The physical significances of parameters are defined and coupled together by the model and they vary with the variations of the model.

In the *empirical approach* each quantity is defined and determined separately as a measure of some systematic feature of the experimental charge distribution. Its value and conceptual inaccuracy together with the experimental inaccuracies of both are estimated independently of other quantities considered and can, thus, be understood to be genuine empirical results. Since no model is involved no fits can be presented to support them or to reduce the error limits, which are always very large as compared to what is normal in the fitting approach.

Interpretation of the results or conclusions of their physical meanings is a matter of separate discussion, although expectations on possible interpretations may conduct the choice of quantities to be calculated.

### **Notes on the residual term**

The finite number of observed structure factors causes the residual-term problem, present always when empirical values of any quantities (1), (3), (5) are evaluated.

In the *fitting approach* the problem is apparently avoided, since the fit can be made on the basis of any subset of structure factors. The internal coherence of the model replaces the lacking information on unmeasurable or neglected reflections. The lack of information becomes visible only in the dependence of the accuracies and correlations on the subset applied. The problem is, however, present in the discussion of the residual information possibly contained by the difference density.

In the *empirical approach* the problem requires estimation of the residual term. Use of integral quantities, as discussed above, reduces the uncertainties involved but it does not eliminate the problem. The experimental value of any quantity derived from the data must include the residual term contribution, because any charge density feature depends on all structure factors, except for specific extinction rules which apply on certain multipoles at certain symmetries.

This is quite evident from the problem of ionic state. The residual term is seen to contribute significantly to the empirical values of any integrated charges [14, 21]. Differences of atomic parameters as determined from difference charge densities are not sufficient. It is not clear what they possibly mean, because one cannot add them to values corresponding to the theoretical model atoms just because they correspond to an essentially different definition of the atom. One should apply the same atomic definition on the theoretical composite charge density to derive a model parameter on equal basis.

The only possibility to evaluate the residual terms is the use of a theoretical model. Therefore, a theoretical *reference model* is always necessary as the starting point. It represents the minimum amount of theoretical basis needed in the empirical approach. For this purpose an *asymptotical model* is required, *i.e.* a model which is reliable asymptotically at large  $\sin \theta/\lambda$  [11]. The free atom superposition model with harmonic thermal motion is often sufficient, when fitted to the data at large  $\sin \theta/\lambda$ . Even the correct ionic state of the atoms is not important. This is based on the assumption that the free atom core is not disturbed by the crystal environment and that it is well represented by the theory.

To obtain the experimental value  $X_{\text{obs}}$  for the quantity  $X$  one has to calculate the value  $X_{\text{ref}}$  for the reference charge density and to add the value  $\Delta X$  corresponding to the deviations of observed structure factors from those of the reference model

$$X_{\text{obs}} = \Delta X + X_{\text{ref}} \quad (6)$$

To avoid infinite series it is practicable to use an analytical reference model where the theoretical atomic factors are replaced *e.g.* by Gaussian representations, as suggested already by HOSEMANN and BAGCHI [8, 9]. Again it is essential that the Gaussians are fitted to the theoretical atomic factors asymptotically at large  $\sin \theta/\lambda$  [19, 24].

It should be obvious that the same definition of the quantity  $X$  must be used for both terms of eq. (6). Still this is an old trap as demonstrated by the problem of ionic state. There is a temptation to use the parameter of the model atom, in this case the atomic factor values at  $\sin \theta/\lambda = 0$ , instead of the integrated value. This seems to be an easy way to avoid extra calculation but it leads to a misconception comparable to the "nightingale liver pate" of the well known old story, largely responsible for the frustrating negative conclusions referred to earlier.

This procedure does not solve the problem caused by unmeasured reflections at small  $\sin \theta/\lambda$ . In the fitting approach they need no special treatment but in the empirical approach a separate discussion is necessary. If they are not too many, the locality and the low-order multipolar shape of atoms are sufficient to produce an internal coherence which makes it possible to observe the significant multipoles and to correct the structure factors of the reference model to yield some estimates for the unobserved ones. In principle this leads to an iterative procedure [20]. The same argument applies to the lacking information on the phases in noncentric structures, and it is possible to take it into account through an analogous iterative procedure [26].

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