VI. Charge Deformation Models

KAARLE KURKI-SUONIO
Department of Physics, University of Helsinki, SF-00170 Helsinki 17, Finland

Abstract. Basic construction principles of charge-density models based on independent deformed atoms are presented. The asymptotic validity of the rigid free-atom model in reciprocal space; mathematical properties of possible radial bases of multipole expansions; requirements put by symmetry, by regularity, by approximate free-atom nature, by approximate harmonicity of motion and by N-representability on the deformation models; and the connection between orthogonality and independence of model parameters are discussed together with consequent conclusions about the analysis of diffraction data in terms of deformation models.

INTRODUCTION

A *deformation model* is an interpretational scheme in charge-density analysis. It involves the basic idea that matter is built of atoms which can be identified with the free atoms performing thermal motion and suffering some *deformation* under their mutual interactions.

It is thus assumed that the total charge density of a crystal can be represented as a superposition of atomic densities. The *model* itself requires a quantitative description of the shape and motion of the atoms. It must also involve some dynamical principle which allows interpretation of the thermally averaged charge density in terms of atomic at-rest charge densities and their motions.

The consequences of symmetry discussed in Chapter IV are general mathematical rules, not bound to any particular model. This chapter is confined to deformation models. It gives a discussion of mathematical and physical conditions, exact or approximate, to be fulfilled by the deformation model, of criteria and arguments which can be applied in construction and further development of such models, and principles concerning the analysis of neutron and X-ray diffraction data in terms of them.

Because the construction principle of the deformation model is simple superposition, it is mostly sufficient to discuss only one atomic contribution.

THE RIGID-BODY MODEL

The simplest dynamical principle which can be assumed to relate an atom at rest to the thermally smeared atom is *rigid-body vibration*. According to this assumption the vibrational smearing function $t(\boldsymbol{r})$ and the charge density $\rho_0(\boldsymbol{r})$ of the atom at rest define the dynamic atomic charge density as the convolution integral (see Chapter II)

$$\rho(\boldsymbol{r}) = \int t(\boldsymbol{r}')\rho_0(\boldsymbol{r} - \boldsymbol{r}')d^3r'. \qquad (1)$$

The corresponding atomic scattering amplitude is

$$f(\boldsymbol{S}) = T(\boldsymbol{S})f_0(\boldsymbol{S}), \qquad (2)$$

where the temperature factor $T(\boldsymbol{S})$ and the scattering amplitude of the atom at rest $f_0(\boldsymbol{S})$ are Fourier transforms of t and ρ_0.

The smearing function can be given a unique meaning by defining it as the average nuclear distribution. The at-rest charge density ρ_0 is already a more questionable concept. It should represent the contribution of the atom to the total charge density of a "frozen crystal", and a direct approach to the concept would be possible by theoretical calculation only. It forms, however, the necessary bridge between the free atom and the model, since calculation of free-atom charge densities gives at-rest densities.

The great importance of this model in charge-density analysis is established through the basic statement that the system nucleus-plus-core is rigid, unaffected both by vibrations and by bonding (see Chapter XIII). Thus, the free atom will produce correctly the core part of $\rho_0(\boldsymbol{r})$ and, further, when combined with the correct smearing function, also $\rho(\boldsymbol{r})$ in the core region. In reciprocal space this is equivalent to saying that the vibrating *rigid free-atom model is correct asymptotically for large scattering vectors* $\boldsymbol{S}$. Some comments on the validity of this statement should be made: (a) Since the core is spherical, possible librational motion does not affect the validity of the statement. (b) Existence of a core is necessary. Therefore the validity is reduced, particularly for hydrogen. (c) In practice we should be able to apply the statement to *theoretical* free atoms. Then the validity will naturally depend on the reliability of the theoretical calculation. which reduces the validity for heavy atoms. (d) All estimates of the core polarization thus far indicate that non-rigidity of the nucleus-plus-core will have no observable effect on charge density. (Still it may possibly yield significant dipole moments.)

The nuclear distribution functions $t(\boldsymbol{r})$ are directly observable by neutron diffraction. In principle, the experimental $t(\boldsymbol{r})$ thus obtained can be used as the smearing function in the rigid-atom model for charge-density studies by X-rays. In practice parametrization of $t(\boldsymbol{r})$ is necessary. The obvious first-order model for this is harmonic vibration, yielding a Gaussian smearing function with the center (position), the principal axes and the principal rms amplitudes as adjustable parameters (to the extent they are not fixed by the site symmetry). The asymptotic validity of this harmonic rigid-atom model can be studied by comparison of the neutron values and large-scattering-angle X-ray values of the parameters (cf. Coppens, Chapter XI).

The rigid-atom model can be used as an ordinary deformation model if deviations of $\rho_0(\boldsymbol{r})$ from the free atom are allowed. Then it becomes important to know how the translational vibration affects a multipole expansion.

If $t(\boldsymbol{r})$ too is written as a multipole expansion this question is most easy to approach in reciprocal space, where Eq. (2) applies. The dynamic atomic scattering factor $f(\boldsymbol{S})$ can then also be written in the form of a

multipole expansion just by application of the conventional multiplication rules for spherical harmonics on the expansions of $T(\boldsymbol{S})$ and $f_0(\boldsymbol{S})$.

For the multipole moments which are integrals of the radial densities (Chapter IV, eqs. (10), (10')) one simple rule can be stated: the *lowest-order non-vanishing multipole moment* of any charge distribution is independent of the choice of origin. Therefore it is unaffected by any translational motion. For an electron distribution this is always the monopole moment, i.e. the charge, unless we are able, for a neutral atom, to include the nuclear charge in the treatment.

The effect of rigid-body librations on a multipole expansion is multiplication of each term except the spherical one by a coefficient $c_{lmp} < 1$ depending just on the orientational distribution function of the libration. The elementary discussion of Kurki-Suonio et al.[1] shows the validity of this statement in some cases of high symmetry.

RADIAL BASES FOR MULTIPOLE EXPANSION

As discussed in Chapter IV, symmetry requires the atomic charge density $\rho(\boldsymbol{r})$, as well as the smearing function $t(\boldsymbol{r})$ and the at-rest density $\rho_0(\boldsymbol{r})$, to be completely site symmetric. Each of them is therefore representable in terms of any complete site-symmetrized basis of functions. For simplicity we shall use a local Cartesian coordinate system adapted to the atomic site symmetry as defined in Chapter IV, table 4. Then we can in particular write the site-symmetric multipole expansion

$$\rho(\boldsymbol{r}) = \sum_{lmp} \frac{1}{N_{lmp}} \rho_{lmp}(r) y_{lmp}(\theta, \varphi), \tag{3}$$

as defined in Chapter IV, eq. 8, and similar expansions for $\rho_0(\boldsymbol{r})$ and $t(\boldsymbol{r})$, as well as for the corresponding reciprocal-space quantities $f(\boldsymbol{S})$, $f_0(\boldsymbol{S})$ and $T(\boldsymbol{S})$. Equation (3) is valid for the non-cubic site symmetries. In this paper we shall omit the obvious parallel representation for cubic symmetries (cf. eq. (8') of Chapter IV).

By this expansion the representation of the three-dimensional density $\rho(\boldsymbol{r})$ is reduced to a set of radial functions $\rho_{lmp}(r)$, each coupled to a well defined angular behaviour. If the number of terms is small, this representation gives a clear overall picture of the total three-dimensional density function.

We may also make one further step and define some complete orthogonal sets of radial functions $R_{nlmp}(r)$ with

$$\int_0^\infty R_{nlmp}(r) R_{n'lmp}(r) r^2 dr = \delta_{nn'} M^2_{nlmp} \tag{4}$$

to obtain

$$\rho(\boldsymbol{r}) = \sum_{nlmp} C_{nlmp} \frac{1}{M_{nlmp} N_{lmp}} R_{nlmp}(r) y_{lmp}(\theta, \varphi). \tag{5}$$

By this step the deformation model is completely parametrized, and the representation of the three-dimensional atomic charge density is reduced to a set of numbers $\{C_{nlmp}\}$,

$$\begin{aligned} C_{nlmp} &= \frac{1}{M_{nlmp} N_{lmp}} \int \rho(\boldsymbol{r}) R_{nlmp}(r) y_{lmp}(\theta, \varphi) d^3 r \\ &= \frac{1}{M_{nlmp}} \int_0^\infty \rho_{lmp}(r) R_{nlmp}(r) r^2 dr. \end{aligned} \tag{6}$$

The choice of the radial basis $\{R_{nlmp}(r)\}$ is in principle arbitrary, except that analytic angular behaviour requires $R_{nlmp} r^{-1}$ *to be finite at the origin* (cf. Stewart, Chapter V). In practice either Gaussian or Slater type functions have been used. They originate from the two well known complete sets of functions, the radial harmonic-oscillator wave functions

$$R_{nl}(r) = (ar)^l \exp\{-\tfrac{1}{2} a^2 r^2\} (L^{l+\frac{1}{2}}_{\frac{1}{2}(n-l)})(a^2 r^2); \quad n = l, l+2, l+4, \ldots \tag{7}$$

with the normalization

$$M^2_{nl} = \frac{\Gamma(\frac{1}{2}(n+l+3))}{2a^3[\frac{1}{2}(n-l)]!} \tag{8}$$

and the radial Coulomb wave functions

$$R_{nl}(r) = \left(\frac{ar}{n}\right)^l \exp\left\{-\frac{ar}{2n}\right\} L^{2l+1}_{n-l-1}\left(\frac{ar}{n}\right); \quad n = l+1, l+2, \ldots \tag{9}$$

with the normalization

$$M^2_{nl} = \frac{2n^4 (n+l)!}{a^3 (n-l-1)!}. \tag{10}$$

Both expressions involve the associated Laguerre polynomials

$$L^k_m(z) = \frac{1}{m!} e^z z^{-k} \frac{d^m}{dz^m} (e^{-z} z^{m+k}) \tag{11}$$

and a parameter a, which can be chosen separately for each angular function y_{lmp}. (In fact, the set (9) is not complete without inclusion of the continuum wave functions. Correspondingly, the summation over n in the expansion (5) must be understood to comprise a sum plus an integral.)

When orthogonality is not important the sets (7) and (9) can be replaced simply by

$$R_{nl}(r) = r^n e^{-\alpha r^2}; \quad n = l, l+2, l+4, \ldots \tag{12}$$

$$R_{nl}(r) = r^{n-1} e^{-\alpha r/n}; \quad n = l+1, l+2, \ldots \tag{13}$$

with the parameter α independent for each (lmp), which up to any value of n span the same subspaces of functions, respectively. However, because of the non-orthogonality of these sets the straightforward relation (6) between the charge density $\rho(\boldsymbol{r})$ and its expansion coefficients C_{nlmp} is lost.

The expansion (5) of a real-space quantity, $\rho(\boldsymbol{r})$ or $t(\boldsymbol{r})$, gives, through Fourier transformation, the same type of expansion for the corresponding reciprocal-space quantity, $f(\boldsymbol{S})$ or $T(\boldsymbol{S})$,

$$f(\boldsymbol{S}) = \sum_{nlmp} C_{nlmp} \frac{1}{M_{nlmp} N_{lmp}} s_{nlmp}(S) y_{lmp}(\theta_S, \varphi_S) \tag{14}$$

with the radial functions

$$s_{nlmp}(S) = 4\pi i^l \int_0^\infty R_{nlmp}(r) j_l(2\pi S r) r^2 dr \tag{15}$$

(cf. eq. (24) of Chapter IV). Since the Fourier transformation conserves both orthogonality and normalization there is no other difference between the real and reciprocal-space expansions, or their uses, than that of the radial functions.

For the radial basis (7) even the functional forms of the expansions (5) and (14) are equal because of the Fourier invariance of the harmonic-oscillator wave functions: Fourier transformation of the equation

$$\nabla^2\psi(\boldsymbol{r}) + a^2(2\varepsilon - a^2r^2)\psi(\boldsymbol{r}) = 0, \qquad (16)$$

which is essentially the Schrödinger equation of the isotropic harmonic oscillator, yields

$$\nabla^2\varphi(\boldsymbol{S}) + A^2(2\varepsilon - A^2S^2)\varphi(\boldsymbol{S}) = 0,$$

$$\text{with } Aa = 2\pi, \quad (16)'$$

which is identical in form to (16). Since an eigenfunction of an equation is transformed into an eigenfunction of the transformed equation with the same eigenvalue, and since, moreover, the normalization is conserved, the transform of any normalized eigenfunction $\psi = f(a\boldsymbol{r})$ of (16) to any eigenvalue $\varepsilon = n + 3/2$ is obtained just by inserting $A\boldsymbol{S}$ instead of $a\boldsymbol{r}$ and possibly multiplying by a phase factor. Detailed calculation shows that this phase factor is i^n. Now, with the radial functions (7), $R_{nl}(r)y_{lmp}(\theta, \varphi)/M_{nl}N_{lmp}$ are normalized eigenfunctions of Eq. (16) to the eigenvalue $n + 3/2$ and we can directly apply the above replacement rule to obtain

$$s_{nl}(S) = i^n(a/A)^3(AS)^l \times \exp\{-\tfrac{1}{2}A^2S^2\}L^{l+\frac{1}{2}}_{\frac{1}{2}(n-l)}(A^2S^2). \qquad (17)$$

For transforms of other radial functions see e.g. the review article by Kaijser and Smith.[2]

There are obvious differences in the behaviour of the functions of the two bases (7) and (9), or (12) and (13), due to the different nature of the two physical systems from which they originate. Particularly, the singularity of the Coulomb potential means that the Coulomb functions are not analytic at the origin — as the oscillator functions are — but have their derivatives defined only up to a finite order or have a cusp. In the corresponding reciprocal-space radial functions (15) this is reflected in the asymptotic behaviour at large S, which is also Gaussian for the oscillator functions but like a finite negative power of S for the Coulomb functions.

OPTIMIZATION OF THE MODEL

The application of multipole expansions to deformation models is far from straightforward. Any complete basis can give a representation to any given accuracy if any number of terms is allowed. However, the main problem is the optimization of the basis so that a good representation can be achieved with a minimum number of parameters. The whole success of the analysis by deformation models depends on the degree of optimization one is able to achieve. In this section some arguments are discussed which have been or may be used in this process. Several important ones lie already behind the preceding developments and the significance of some of them is still open to discussion.

Symmetry

Restriction of the treatment to the subspace of completely symmetrized functions means essential exclusion of useless degrees of freedom. This is seen very clearly in the index picking rules of tables 4 & 5 of Chapter IV for symmetrized multipole expansions. For atoms with low site symmetry an appropriate further reduction is often possible by assuming the approximate higher symmetry of the immediate neighbourhood to be valid. This and other related possibilities based on assuming the free-molecule symmetry or other approximate symmetry to be valid will not be elaborated further in this context, but their significance will be evident in several examples treated by Hirshfeld (Appendix 2).

Regularity

The analyticity of the representation is an obvious requirement, except for the cusp of charge density at the nuclear position, where the Coulomb potential has a singularity. This affects the behaviour of the radial basis at the origin in real space and at infinity in reciprocal space. The oscillator or Gaussian basis (7) or (12) shows the correct behaviour for representations which are analytic also at the origin. The Coulomb or Slater basis (9) or (13) has the correct behaviour for representing functions with the Coulomb cusp at the origin. This does *not* mean that a Gaussian expansion would be unable to represent a cusp. Based on a complete set it can represent any square-integrable function. However, since every partial sum will be analytic the expansion converges slowly at the cusp, while in the Slater expansion all partial sums already have a cusp and it is probable that by a proper choice of the parameters a rapid convergence is obtained even at the origin. Thus, as regards the behaviour at the nuclear position, the oscillator basis is the better one for representing $t(\boldsymbol{r})$ and $T(\boldsymbol{S})$ while the Slater basis is better for $\rho_0(\boldsymbol{r})$ and $f_0(\boldsymbol{S})$.

Approximate Free-Atom Nature

This gives a qualitative reason to expect that a multipole expansion of the atomic charge density will converge rapidly towards larger values of l. For a free atom only the spherical term $l = 0$ exists. Even for an oriented free atom, which means an atom in a site-symmetric field of zero strength, the highest l occurring in the expansion cannot be larger than twice the angular-momentum quantum number of the unfilled shell. If the free atom can be understood as a zeroth approximation in the sense of perturbation theory, the high energies of the orbitals with high angular momenta effectively suppress the high multipole terms which these contribute to the charge density.

The same qualitative argument may be used for the expansion with respect to the radial quantum number, if radial functions closely enough related to the free-atom orbitals are used. The problem, however, concerns mainly the representation of the contribution of the valence electrons, which feel most strongly the presence of neighbours and the effect of bonding. Therefore the choice of the radial functions must be a compromise between several trends. The free-atom approximation suggests Slater type, the presence of neighbours and the necessary *locality* of the atom makes it desirable to suppress their long tails.

Approximate Harmonicity of the Motion

In cases where this argument is valid it is clear that the harmonic-oscillator wave functions will give a proper basis for representing the smearing function and the temperature factor. There is an essential difference between this argument and the preceding one in that the physical circumstances on which the validity depends, i.e. the temperature, can be varied. The number of significant parameters can be reduced to those necessary for the harmonic motion just by doing the charge-density studies at low temperature.

On the other hand this would suggest analysis of neutron diffraction data, e.g. for studies of anharmonicity, in terms of the harmonic-oscillator wave functions. In the cubic site symmetries, where the harmonic oscillator is necessarily spherical, this would be just the multipole expansion with the radial basis (9). In axial and general

non-axial site symmetries the wave functions of the axial harmonic oscillator and of the general three-dimensional one, respectively, lead to shorter expansions. It is, however, obvious that refinement of a model where $t(\boldsymbol{r})$ and $\rho_0(\boldsymbol{r})$ are both represented by expansions, though short, will already contain too many parameters. Therefore, unless an independent determination of $t(\boldsymbol{r})$ is made, one must be content with the harmonic approximation.

Orthogonality and Independence of Parameters

Independence of the parameters is a necessary condition when the number of parameters is to be minimized. Often it can be obvious from the physical nature of the parameters. So, intuitively we understand that positions and thermal parameters of an atom as well as parameters of two different atoms should be independent. In a practical analysis we know, however, that correlations occur. One possible way to discuss this problem can be based on orthogonality.

Orthogonality represents the ultimate degree of independence. The best possible representation $\Sigma_n c_n u_n(\boldsymbol{r})$ of a function $\rho(\boldsymbol{r})$ with an incomplete set of orthogonal function $u_n(\boldsymbol{r})$ is unique and can be defined as the projection of $\rho(\boldsymbol{r})$ on the subspace spanned by the set $\{u_n\}$. The unique least-squares values of the coefficients are $c_n = \int u_n \rho d^3r / \int u_n^* u_n d^3r$ obtained by projecting ρ on u_n. Each parameter c_n can thus be determined separately and independently even without knowing what other *orthogonal* functions u_n are used. Similarly any two parameters included in two mutually orthogonal terms of a representation are independent and can be called orthogonal.

One of the major problems in the charge-density analysis is that we have experimental information only about a finite number of Fourier coefficients of ρ, i.e. about the projection of ρ on a finite-dimensional subspace spanned by the plane waves $\exp(-2\pi i \boldsymbol{H}\cdot\boldsymbol{r})$ with $H < 2/\lambda$. Therefore, it is not really the orthogonality of the functions u_n themselves that counts, but the orthogonality of their projections on this subspace. We shall not elaborate this point further, since our purpose is just to give a qualitative understanding of the close connection between independence and orthogonality and to indicate why it is useful to look at the parametrization from this point of view. Although, strictly speaking, orthogonality is neither quite necessary nor sufficient for independence of the parameters, it is a promising property to start with. In the limit of very large data sets it will lead to independence. Also, a severe lack of orthogonality in any case indicates close correlation of the corresponding parameters.

Parameters of different atoms are necessarily almost orthogonal. In the limit of zero overlapping of the functions used for representation of different atoms the orthogonality is exact. Parameters belonging to different terms (lmp) of the same multipole expansion (3) are orthogonal due to the orthogonality of $y_{lmp}(\theta, \varphi)$. Position parameters belong to the dipole terms, the isotropic temperature factor to the monopole term and the parameters describing the harmonic anisotropy to the quadrupole terms. Provided x, y, and z are coordinates in the specific symmetry-adapted local Cartesian coordinate system formed by the principal axes of the thermal ellipsoid, this correspondence is that given in Table 1.

This correspondence refers most directly to the behaviour of the radial smearing functions $t_{lmp}(r)$ but applies also to the radial densities $\rho_{lmp}(r)$ of the thermally

Table 1. Correspondence between the Atomic Parameters and the Terms of the Multipole Expansion

lmp	corresponding parameter
00+	isotropic temperature factor $\bar{B}$ $= \frac{1}{3}(B_x + B_y + B_z)$
11+	x-coordinate of the position
11−	y-coordinate of the position
10+	z-coordinate of the position
20+	prolateness $B_Z - \bar{B}$ of the thermal ellipsoid
22+	non-axiality $B_x - B_y$ of the thermal ellipsoid
22−	direction of the x-axis in the plane $\perp$ z-axis
21+	direction of the z-axis in the plane $\perp$ y-axis
21−	direction of the z-axis in the plane $\perp$ x-axis

smeared density $\rho(\boldsymbol{r})$. Positive slope of t_{11+}, t_{11-} or t_{10+} at $r = 0$ indicates that the correct position has positive x, y or z coordinate shift, respectively. Similarly, deviation of the second derivatives $t''_{00+}(0)$, $t''_{20+}(0)$ or $t''_{22+}(0)$ of the model from those of the function to be represented indicates a necessary correction of $\bar{B}$, $B_z - \bar{B}$ or $B_x - B_y$, respectively; and non-vanishing $t''_{22-}(0)$, $t''_{21+}(0)$ or $t''_{21-}(0)$ indicates erroneous directions of the principal axes of thermal motion in the way indicated in Table 1. Correspondingly, a site symmetry which does not allow occurrence of the components (20+) (22+), (22−) or (21±), respectively, requires sphericity, requires axial symmetry and defines the direction of the x-axis or of the z-axis (cf. tables 4 & 5 of Chapter IV).

The statements above refer closely to a kind of difference-series thinking. This becomes explicit when we notice that the radial densities $\rho_{lmp}(r)$ (Chapter IV, eq. (15)) of the multipole expansion (3) for the total crystal charge density have the derivatives

$$\rho''_{00+}(0) = -\frac{4\pi^2}{3V}\sum F_{\boldsymbol{H}} H^2$$

$$\left.\begin{matrix}\rho'_{11+}(0)\\ 11-\\ 10+\end{matrix}\right\} = -\frac{2\pi i}{V}\sum F_{\boldsymbol{H}} \begin{Bmatrix} h_{\boldsymbol{H}} \\ k_{\boldsymbol{H}} \\ l_{\boldsymbol{H}} \end{Bmatrix}$$

$$\left.\begin{matrix}\rho''_{20+}(0)\\ 22+\\ 22-\\ 21+\\ 21-\end{matrix}\right\} = -\frac{4\pi^2}{V}\sum F_{\boldsymbol{H}} \begin{Bmatrix} (l_{\boldsymbol{H}}^2 - \frac{1}{3}H^2) \\ \frac{1}{2}(h_{\boldsymbol{H}}^2 - k_{\boldsymbol{H}}^2) \\ h_{\boldsymbol{H}} k_{\boldsymbol{H}} \\ h_{\boldsymbol{H}} l_{\boldsymbol{H}} \\ k_{\boldsymbol{H}} l_{\boldsymbol{H}} \end{Bmatrix}$$

where $h_{\boldsymbol{H}} k_{\boldsymbol{H}} l_{\boldsymbol{H}}$ denote the components of the reciprocal-lattice vector $\boldsymbol{H}$ in the local Cartesian coordinate system. Requiring that all the right-hand-side series vanish when written as difference series (with $F_{obs} - F_{calc}$ instead of F) we get conditions equivalent to the equations of the conventional difference Fourier determination of the positions and Debye–Waller factors.

Further, it is intuitively clear from the orthogonality point of view that parameters of the smearing function and those of the at-rest charge density of an atom will correlate, especially if the model allows core deformation, i.e. charge-density parameters effective in the core region. Particularly we can note that, as to the radial dependence of the smearing function, the position is coupled to the dipole terms with linear behaviour and the

temperature parameters to the monopole and quadrupole terms with quadratic behaviour at the origin. In the deformation model they are convoluted with a Slater-type expansion of $\rho_0(\boldsymbol{r})$. One can argue that the closest correlations should occur between terms which, except for the exponetials, behave similarly at the origin. Thus, one should expect that charge-density parameters of the dipole terms linear in r would correlate most with position parameters, the monopole and quadrupole terms quadratic in r with the thermal parameters.

N-Representability

This is the obvious requirement that, since electrons are fermions, the charge density of an N-electron system must correspond to an antisymmetric N-particle wave function (cf. *Smith*, Chapter 1). In fact, any non-negative $\rho(\boldsymbol{r})$ with $\int \rho(\boldsymbol{r}) d^3r = N$ is N-representable. (In the ordinary use of the concept, N-representability is demanded in a restricted space of states with a fixed finite basis, which is a far less simple problem.) The proof is simple: Make an arbitrary division $\rho = \sum_{i=1}^{N} \rho_i$ into N non-overlapping parts ρ_i with $\int \rho_i d^3r = 1$. A state where each of the N single-particle states $\psi_i = \rho_i^{1/2}(\boldsymbol{r})$ is singly occupied, i.e. the corresponding Slater determinant, is an example of an antisymmetric N-particle state with the charge density $\rho(\boldsymbol{r})$.

The discontinuity of the functions ρ_i does not invalidate the argument, because according to the mathematical foundations of quantum mechanics the space of possible wave functions is that of all square-integrable functions. It is true that the expectation value of kinetic energy in such a state is infinite. Still, it has a definite momentum distribution $\varphi_i^*(\boldsymbol{p})\varphi_i(\boldsymbol{p})$, where $\varphi_i(\boldsymbol{p})$ is the Fourier transform of $\psi_i(\boldsymbol{r})$, and, thus, also a definite probability distribution of the kinetic energy.

In building a deformation model the number of electrons fixes the normalization of the monopole term. The positivity, on the contrary, cannot be used to simplify the model. It must be taken as an extra condition restricting the possible values of the parameters.

DETERMINATION OF THE MODEL FROM DATA

The discussion of the validity of the rigid-atom model suggests a natural division of the charge-density analysis into two stages. At first *an asymptotic parametrization* of the rigid-atom model to fix positions and Debye–Waller factors without charge-density parameters should be performed. (Conventional treatment of rigid molecular librations belongs clearly to this stage when necessary.) This could be done either from neutron diffraction data or by a high-order fitting procedure from X-ray data (cf. Coppens, Chapter XI). At least in case of accurate data and a simple structure this would be equivalent to a difference Fourier determination.

The second stage would be the ordinary specification and refinement of the deformation model, keeping the first-stage parameters more or less fixed. There are in principle two possible strategies. One is to search for *complete parametrization*, which could exhaust all the information of the data, and to determine all parameters by least-squares methods. All arguments of the kind discussed in the preceding section are then necessary. Also all assumptions made are then built into the model and affect the significance of the resulting parameters.

The other possibility is to use the series (15) or (15′) of Chapter IV for *direct calculation* of radial densities $\rho_{lmp}(r)$ or the radial accumulation functions $r^{l+2}\rho_{lmp}(r)$ of the multipole moments or to calculate any other relevant physical quantities represented by a series of the form[3,4] $X = (1/V)\Sigma C_H F_H$ (cf. Coppens and Hansen, Chapter XII). This possibility is mostly used in the form of a difference series, for instance in calculation of deformation densities or valence densities, without explicit calculation of the residual term. However, the series-termination error is present also in all such calculations. It is equal to the difference between the true residual term and the theoretical one. Therefore they, too, require the asymptotic parametrization. But particularly in calculation of integrated quantities like electron counts in specific regions, multipole moments, etc., the evaluation of the residual term is necessary for determination of the experimental value of the desired quantity. This can be done simply by subtracting the truncated series corresponding to the model from the ordinary model value, which can be calculated directly using the analytic form of the model charge density.[4,5] (This procedure was first suggested by Hosemann[7] for charge-density calculations.)

The advantage of this direct calculation is that it can be done independently for each interesting quantity. It has been used in calculation of charges and dipole momenta (cf. Chapter XII) and radial charge densities .[5,6] It can be applied to the analysis of molecular librations[1] and anharmonicity[8] from neutron-diffraction data. It can also be used to give a quick indication about the significance of different multipole components of the atoms for development of the deformation model beyond the asymptotic parametrization.

Many of the problems and ideas presented here are discussed in more detail in other Chapters, particularly those by Smith (Chapter I), Stewart (Chapter V), Coppens (Chapters XI, XII) and Hirshfeld (Chapter XIII, Appendix 2). As further general references on this subject the review lectures by Becker[9] and Smith[10] at the Sagamore V Conference should be consulted.

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