Acta Cryst. (1979). A**35**, 838–844

Anharmonic Contributions to Dynamic Electron Densities Caused by Large Librations of Molecules

By C. Scheringer

Institut für Mineralogie der Universität Marburg, D 3550 Marburg/Lahn, Federal Republic of Germany

(*Received* 2 *April* 1979; *accepted* 9 *May* 1979)

Abstract

The effect of large librations of molecules on electron density distributions is investigated with the already published structures of β-NaN$_3$, *p*-nitropyridine *N*-oxide and anthracene, and with some model calculations for C, N, O atoms. For this purpose, the temperature factor of the atom concerned is expanded with cumulants, and the smearing function of the nuclear positions and the dynamic electron density is calculated by an Edgeworth series. The results are represented as difference densities ρ(anharmonic) − ρ(harmonic) $\equiv \rho(A - H)$ maps. For the end N atom in β-NaN$_3$ at 295 K and for the C(7) atom in *p*-nitropyridine *N*-oxide at 30 K, these maps contain minima of 0·53 e Å^{-3} (N) and 0·22 e Å^{-3} [C(7)] in front of the nuclei, and maxima of 0·44 e Å^{-3} (N) and 0·21 e Å^{-3} [C(7)] behind the nuclei. Thus, due to large librations, the density is shifted from in front of the nuclei towards the back of the nuclei, as viewed from the centre of libration. The magnitude of the region of non-vanishing $\rho(A - H)$ density largely depends on the magnitude of the atomic motions (temperature). With the end N (295 K) mentioned above the radius of this region around the nucleus is about 0·5 Å, and with C(7) about 0·2 Å. Apart from the temperature, the $\rho(A - H)$ densities are essentially determined by the distance of the atom from the centre of libration, and by the ratio of the librational/translational contributions to the atomic motions. A procedure is described to estimate the extrema in the $\rho(A - H)$ densities in an actual structure.

Introduction

In the calculation of *X–N* maps, the use of correct temperature factors is of primary importance (Scheringer, Kutoglu & Mullen, 1978). One may expect that neglect of anharmonic contributions to the atomic motions which arise from large librations of molecules can also lead to significant errors in electron density distributions. In this paper, we investigate the magnitude of such errors by calculating the densities ρ(anharmonic) − ρ(harmonic) $\equiv \rho(A - H)$ for some different situations. We choose, as examples, the end N atom of β-NaN$_3$ at 295 K (Stevens & Hope, 1977 – hereafter referred to as SH), and C(7) in *p*-nitropyridine *N*-oxide at 30 K (Wang, Blessing, Ross & Coppens, 1976 – hereafter referred to as WBRC). Moreover, we shall perform model calculations for C, N and O atoms for different distances of the atom from the centre of libration, for different ratios of the librational/translational contributions to the atomic motions, and for different magnitudes of the atomic motions (temperatures). With this type of model calculation one can estimate, for an actual structure, how much the contributions of the anharmonic motions due to large librations affect the density distribution around the atoms.

Temperature factors with anharmonic contributions are best described by the cumulant expansion, and the respective smearing function of the nuclear positions by an Edgeworth series (Johnson, 1969, 1970; Scheringer, 1977). If large librations of molecules are the only cause of anharmonicity, then the cumulants can be calculated from the rigid-body vibration tensors **TLS** and the position of the centre of libration, $\boldsymbol{\rho}$ (Scheringer, 1978). Convolution of the smearing function for the nuclear position with the distribution of the density of the atom at rest then leads to the dynamic density. We shall show that convolution of a Gaussian distribution with an Edgeworth distribution leads to an Edgeworth distribution. Therefore, we shall use a sum of Gaussian functions to describe the static density of an atom, and can then calculate the dynamic density by means of an Edgeworth series.

Representation of the smearing function by an Edgeworth series

In the harmonic approximation of the nuclear motions, the smearing function is known to be a Gaussian distribution about the mean nuclear position. We denote it by $g(\mathbf{y})$ and the covariance matrix (vibration tensor) by $\mathbf{U}$. The smearing function which contains anharmonic

0567-7394/79/050838-07$01.00

deviations from the Gaussian distribution is then given, to a good approximation, by the Edgeworth expansion

$$\begin{aligned} f(\mathbf{y}) = g(\mathbf{y}) \Big[1 &+ \sum_i {}^1\kappa^i\, {}^1H_i(\mathbf{y}) + \tfrac{1}{6} \sum_{ijk} {}^3\kappa^{ijk}\, {}^3H_{ijk}(\mathbf{y}) \\ &+ \tfrac{1}{2} \sum_{ij} ({}^1\kappa^i\, {}^1\kappa^j + {}^2\kappa^{ij})\, {}^2H_{ij}(\mathbf{y}) \\ &+ \tfrac{1}{6} \sum_{ijkl} ({}^1\kappa^i\, {}^3\kappa^{jkl} + \tfrac{1}{4}\, {}^4\kappa^{ijkl})\, {}^4H_{ijkl}(\mathbf{y}) \\ &+ \tfrac{1}{72} \sum_{ijklmn} {}^3\kappa^{ijk}\, {}^3\kappa^{lmn}\, {}^6H_{ijklmn}(\mathbf{y}) + \ldots \Big] \end{aligned} \tag{1}$$

(Johnson, 1969, 1970). ${}^1\boldsymbol{\kappa}$, ${}^2\boldsymbol{\kappa}$, ${}^3\boldsymbol{\kappa}$, ${}^4\boldsymbol{\kappa}$ are the cumultants, and ${}^2\boldsymbol{\kappa}$ contains only anharmonic contributions, *i.e.* the deviations from the vibration tensor **U**. $H(\mathbf{y})$ are the Hermitian polynomials. To evaluate (1), we have to calculate the cumulants as functions of the positional parameters **x** of the atom, and of the libration tensor **L** of the molecule, and the Hermitian polynomials as a function of the space coordinates **y** and the inverse covariance matrix $\mathbf{U}^{-1}$. To simplify our description, we choose a special Cartesian coordinate system (**x** system). We put the atom on the x_1 axis at the position x_1, $x_2 = x_3 = 0$. Since the librations about the x_1 axis revolve the atom into itself, we have $L_{11} = 0$ for this atom (this description does not imply a loss of generality). We now introduce the restrictions that **T** and **L** are diagonal and **S** = 0. Then, in our special coordinate system,

$$U_{11} = T_{11},\ U_{22} = T_{22} + x_1^2 L_{33},\ U_{33} = T_{33} + x_1^2 L_{22}, \tag{2}$$

and **U** is also diagonal. The restrictions expressed in (2) simplify our calculation considerably, but do not essentially falsify our $\rho(A - H)$ maps. In the **x** system we obtain for the cumulants

$$\begin{aligned} &{}^1\kappa^1 = [-\tfrac{1}{2}(L_{22} + L_{33}) + \tfrac{1}{8}(L_{22}^2 + L_{33}^2) + \tfrac{1}{12} L_{22} L_{33}] x_1, \\ &{}^2\kappa^{11} = \tfrac{1}{2}(L_{22}^2 + L_{33}^2) x_1^2, \\ &{}^2\kappa^{22} = -(L_{33}^2 + \tfrac{1}{3} L_{22} L_{33}) x_1^2, \\ &{}^2\kappa^{33} = -(L_{22}^2 + \tfrac{1}{3} L_{22} L_{33}) x_1^2, \\ &{}^3\kappa^{221} = -L_{33}^2 x_1^3,\ {}^3\kappa^{331} = -L_{22}^2 x_1^3, \end{aligned} \tag{3}$$

where all cumulants equal to zero are not written out (Pawley & Willis, 1970; Scheringer, 1978). The three-dimensional Hermitian polynomials ${}^1H$, ${}^2H$ and ${}^3H$ are given by Johnson (1970), the one-dimensional polynomials ${}^4H$ and ${}^6H$ by Kendall & Stuart (1969). The extension to three dimensions was performed by us; the appropriate rules can be found from the symmetry restrictions on the indices. The space coordinates **y** of the smearing function (1) refer to the point $(x_1,0,0)$ and the axes of the **y** system are parallel to those of the **x** system. Further simplification is obtained if we restrict ourselves to density sections $y_3 = 0$ (after interchanging the axes 2 and 3 we can also obtain sections $y_2 = 0$). We abbreviate $y_i/U_{ii} = z_i$, and then obtain for the Hermitian polynomials $H(\mathbf{z})$ $[H(\mathbf{y})]$

$$\begin{aligned} &{}^1H_1 = z_1,\ {}^1H_2 = z_2,\ {}^1H_3 = z_3 = 0, \\ &{}^2H_{ii} = z_i^2 - 1/U_{ii},\ i = 1, 2, 3, \\ &{}^3H_{221} = z_2^2 z_1 - z_1/U_{22},\ {}^3H_{331} = -z_1/U_{33}, \\ &{}^4H_{1122} = z_1^2 z_2^2 - z_1^2/U_{22} - z_2^2/U_{11} + 1/(U_{11} U_{22}), \\ &{}^4H_{1133} = -z_1^2/U_{33} + 1/(U_{11} U_{33}), \\ &{}^6H_{112233} = -z_1^2 z_2^2/U_{33} + z_1^2/(U_{22} U_{33}) \\ &\qquad + z_2^2/(U_{11} U_{33}) - 1/(U_{11} U_{22} U_{33}). \end{aligned} \tag{4}$$

In (4) only those polynomials are listed which, with the cumulants of (3), lead to non-zero terms in (1). If we make use of the fact that the indices of the cumulants are pair-wise interchangeable and, hence, that several terms in (1) give identical contributions, then we finally obtain from (1), (3) and (4) for the sections $y_3 = 0$

$$\begin{aligned} f(y_1, y_2) = g(y_1, y_2)\, (1 &+ {}^1\kappa^1\, {}^1H_1 \\ &+ \tfrac{1}{2} \{[({}^1\kappa^1)^2 + {}^2\kappa^{11}]\, {}^2H_{11} + {}^2\kappa^{22}\, {}^2H_{22} \\ &+ {}^2\kappa^{33}\, {}^2H_{33} + {}^3\kappa^{221}\, {}^3H_{221} + {}^3\kappa^{331}\, {}^3H_{331} \\ &+ {}^1\kappa^1\, {}^3\kappa^{221}\, {}^4H_{1122} + {}^1\kappa^1\, {}^3\kappa^{331}\, {}^4H_{1133} \\ &+ \tfrac{1}{4}\, {}^3\kappa^{221}\, {}^3\kappa^{331}\, {}^6H_{112233}\}). \end{aligned} \tag{5}$$

Calculation of the dynamic density

We wish to describe the density distribution of the atom at rest by Gaussian functions. In order to obtain the necessary parameters, we make use of the representation of the scattering factors as given in *International Tables for X-ray Crystallography* (1974),

$$f(\sin\theta/\lambda) = \sum_{r=1}^{4} a_r \exp(-b_r \sin^2\theta/\lambda^2) + a_5. \tag{6}$$

From (6) we obtain the density distribution by inverse Fourier transformation, and thus obtain

$$\begin{aligned} \rho(\mathbf{y}) = \sum_{r=1}^{4} &a_r (2\pi b_r/8\pi^2)^{-3/2} \\ &\times \exp\left[-\frac{1}{2}\frac{8\pi^2}{b_r}(y_1^2 + y_2^2 + y_3^2)\right] + a_5 \\ &\times \delta\text{-function}. \end{aligned} \tag{7}$$

The constants a_r and b_r are given for all atoms in *International Tables for X-ray Crystallography* (1974). For the convolution of Gaussian functions, the theorem holds that the convolute product is again a Gaussian, and that the covariance matrix of the convolute is the sum of the two respective covariance matrices (Scheringer & Reitz, 1976). Hence, for harmonic motions, convolution of the static density $\rho(\mathbf{y})$ with the smearing function $g(\mathbf{y})$ yields the dynamic density, $\mathbf{U}$ being diagonal,

$$\rho(\mathbf{y})^{\text{harm}}_{\text{dyn}} = \sum_{r=1}^{5} a_r g_r(\mathbf{y}, \mathbf{U}, b_r), \tag{8a}$$

$$g_r(\mathbf{y}, \mathbf{U}, b_r) = (2\pi)^{-3/2} \prod_{i=1}^{3} (U_{ii} + b_r/8\pi^2)^{-1/2} \times \exp\left(-\frac{1}{2}\sum_{i=1}^{3} \frac{y_i^2}{U_{ii} + b_r/8\pi^2}\right), \tag{8b}$$

where $b_5 = 0$. Obviously, the dynamic density (8) is the sum of five Gaussian functions. Since it does not matter in the Edgeworth expansion what the physical nature of the covariance matrix is (either a vibration tensor or a density tensor or the sum of both tensors), we obtain, in the anharmonic case, the dynamic density by expanding the Edgeworth series about each single Gaussian $g_r(\mathbf{y}, \mathbf{U}, b_r)$ of (8) and then form the sum

$$\rho(\mathbf{y})_{\text{dyn}} = \sum_{r=1}^{5} a_r f_r(\mathbf{y}). \tag{9}$$

The Hermitian polynomials to be used in (9) have to be changed accordingly, *i.e.* instead of $z_i = y_i/U_{ii}$ we now have to use $z_i = y_i/(U_{ii} + b_r/8\pi^2)$.

In the calculation of the $\rho(A-H)$ densities one has to ensure that the density (8*a*), which is the type usually obtained in structure refinement, is not centred at the point x_1,0,0, but rather at a point x_1(uncorrected),0,0. This point is closer to the centre of libration. This is the well-known effect of bond shortening in standard refinements, whereas in our model the correct distance from the centre of libration is assumed by definition. Hence, the position x_1(uncorrected) has first to be calculated from the first cumulant (reverse librational correction), and the Gaussian distribution (8*a*) has to be centred at this point, and then subtracted from the distribution (9). Another, but less accurate, way of achieving this is to calculate the Edgeworth series (5) without the terms $1 + {}^1\kappa^1\,{}^1H_1$ (the term $\sum_i {}^1\kappa^i\,{}^1H_i$ shifts the Gaussian distribution only to a first approximation). We use the more accurate procedure and calculate the density according to

$$\rho(\mathbf{y}, A-H) = \sum_{r=1}^{5} a_r[f_r(\mathbf{y}, x_1) - g_r(\mathbf{y}, x_1^{\text{unc}})], \tag{10}$$

where x_1 and x_1^{unc} denote the respective origins of the $\mathbf{y}$ systems.

The end N atom in β-NaN$_3$

The structure of β-NaN$_3$ at room temperature was determined by Choi & Prince (1976) with neutron data, and by SH with X-ray data. In this investigation, the end N atom [N(1) in the azide ion] is of interest; its site symmetry is $3m$. Choi & Prince (1976) determined the rigid-body vibration tensors $\mathbf{T}$ and $\mathbf{L}$ ($\mathbf{S} = \mathbf{0}$) by including third cumulants for the end N atom in the refinement, see Prince & Finger (1973). Similar values for $\mathbf{T}$ and $\mathbf{L}$ were obtained by SH in the harmonic approximation of the atomic motions. Furthermore, SH determined third cumulant parameters for the end N atom in the refinement for various sorts of scattering factors. Then SH calculated difference densities with and without inclusion of the third cumulants and found remarkable differences in the density around the end N atom (a change of four contour lines out of nine).

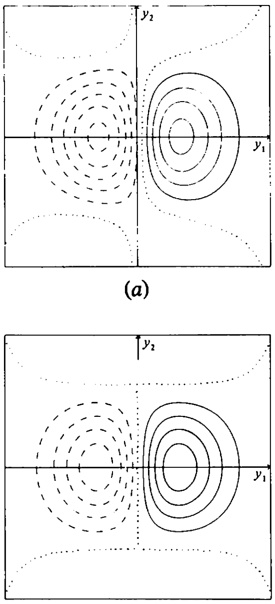
We consider the end N atom in β-NaN$_3$ as a test case for our procedure, and shall do the following: firstly, we try to interpret the values of the third cumulants which were obtained by SH in the refinement, by means of large librations of the azide ion; secondly we calculate the $\rho(A-H)$ density and compare it with the maps of SH with and without inclusion of the third cumulants.

In SH's notation, the three third cumulants of the end N atom are C_{111}, C_{333} and C_{113}. For C_{113} SH find values ranging from $-0{\cdot}0180$ to $-0{\cdot}0225$ rad^4 for high-order refinements with different scattering factors. We calculate the cumulants from our model of large librations; in our equations (1)–(5) we have to interchange the x and z directions and also use $C_{ijk} = \frac{4}{3}\pi^3 \kappa^{ijk}$. We find $C_{111} = C_{333} = 0$ for all values of $\mathbf{L}$, *i.e.* these two cumulants cannot be interpreted as being due to librations. Thus, with SH, they either represent other anharmonic effects or are only non-zero within the error limits. To calculate the value of C_{113}, we use the neutron parameters of Choi & Prince (1976), $L_{11} = L_{22} = 0{\cdot}0150$ rad^2, $L_{33} = L_{12} = L_{13} = L_{23} = 0$, x_1 = distance N(1)–N(2) corrected for libration = 1·180 Å, and find $C_{113} = -0{\cdot}0153$ Å^3 rad^4. The agreement with SH's values is good and becomes even more obvious if we calculate the r.m.s. librational amplitudes. Let us use the most deviant value of SH, $C_{113} = -0{\cdot}0225$ Å^3 rad^4 and $x_1 = d_z$(corrected) = 1·188 Å (SH, Table 3, column HF, high angle parameters), we obtain $L_{11} = 0{\cdot}0180$ rad^2, $\sqrt{L_{11}} = 7{\cdot}69°$, whereas Choi & Prince's values (which we used) are $L_{11} = 0{\cdot}0150$ rad^2, $\sqrt{L_{11}} = 7{\cdot}02°$. Hence the maximum deviation for $\sqrt{L_{11}}$ is only 0·67°, which underlines the fact that C_{113} of SH can well be interpreted as a librational cumulant. We note that SH's values of L_{11}, 0·0139 and 0·0147 rad^2, ($\sqrt{L_{11}}$ = 6·75 and 6·95°) are closer to Choi & Prince's neutron parameter than to the values obtained from C_{113}. This is probably due to the fact that the third cumulants can be determined less accurately in the refinement.

For calculating the density $\rho(A-H)$ we further need $\mathbf{T}$ and x_1(uncorrected) which we also take from Choi & Prince. $T_{11} = T_{22} = 0{\cdot}0229$, $T_{33} = 0{\cdot}0192$ Å^2, x_1[uncorrected distance N(1)–N(2)] = 1·162 Å. Fig.

1(*a*) shows the $\rho(A - H)$ section $y_3 = 0$ along the N(1)—N(2) axis for the N(1) atom, with the origin $x_1 = 1\cdot180$ Å. There is a maximum of 0·44 e Å^{-3} at $y_1 = 0\cdot17$ Å, and a minimum of $-0\cdot53$ e Å^{-3} at $y_1 = -0\cdot15$ Å. Thus the librations of the molecule cause a shift of density from the N(1)—N(2) bond region towards the lone-pair region of N(1). Fig. 1(*a*) is asymmetric with respect to the y_2 axis. If one takes into account only the third cumulant in calculating the Edgeworth series ($^1\boldsymbol{\kappa} = {}^2\boldsymbol{\kappa} = \mathbf{0}$), one obtains an antisymmetric distribution with respect to the y_2 axis, Fig. 1(*b*). Thus, the first two cumulants change only the details of the density; they model Fig. 1(*b*) into Fig. 1(*a*) with density shifts of at most 0·08 e Å^{-3}.

We now compare our result, Fig. 1(*a*), with the densities found by SH. Our $\rho(A - H)$ map of Fig. 1(*a*) corresponds to the difference SH Fig. 4(*b*) − SH Fig. 4(*c*), since $X - X(\mathbf{U}) - [X - X(^3\boldsymbol{\kappa})] = X(^3\boldsymbol{\kappa}) - X(\mathbf{U})$. Behind the end N atom (in the lone-pair region), SH Fig. 4(*c*) shows four lines less than SH Fig. 4(*b*), whereas in the bond region there are several lines more in SH Fig. 4(*c*). This fully corresponds to our $\rho(A - H)$ map, Fig. 1(*a*). Also, the details of the shapes of the lone-pair and bond peaks of the end N atom in SH's maps are in agreement with our calculation (Fig. 1*a*). Thus, the change of the density distribution, as observed by SH with the inclusion of the third cumulants, can largely be explained by the occurrence of large librations of the azide ion.



(*a*)

(*b*)

Fig. 1. $\rho(A - H)$ sections ($y_3 = 0$) for the end N in the azide ion of the β-NaN$_3$ structure at room temperature (SH). (*a*) and (*b*) each represent an area of 1 × 1 Å^2. The origin for the coordinates y_1, y_2 is the position of the end N, corrected for librations $\{z[\mathrm{N}(1)] = 1\cdot180$ Å, see text$\}$. (*a*) Edgeworth series calculated with all (first three) cumulants, (*b*) series calculated only with the third cumulants. Contour interval: 0·1 e Å^{-3}. Positive: full lines, zero: dotted, negative: dashed.

The C(7) atom in *p*-nitropyridine *N*-oxide

p-Nitropyridine *N*-oxide was studied by WBRC at 30 K and is thus suitable for investigating the relevance of anharmonic contributions to electron densities at low temperatures. Large librations occur mainly about the long axis of the molecule; for our considerations, C(6), C(7), C(9) and C(10) are (nearly) equivalent. WBRC have shown that the translations and librations of the molecule can be assumed to be harmonic. With (3) we also make this assumption, see Scheringer (1978).

Since the molecule has only symmetry *m* (and no longer $\bar{1}$), the centre of libration (coordinate origin) is not immediately given. In such a case we assume that the centre of gravity can most likely be regarded as the centre of libration (unless the molecule is not one-sidedly anchored) (Scheringer, 1978). The centre of gravity is on the long axis of the molecule, and since the librations about this axis are the largest, the intersection of the long axis with the perpendicular through C(7) is used as the centre of libration. From the molecular geometry we calculate the distance $x_1 = 1\cdot20$ Å for C(7).

The thermal parameters which we need are contained in WBRC, Table 5. The principal axes of **L** are given, to a very good approximation, by the principal inertial axes of the molecule, but for **T** the approximation is poorer. This, however, causes no trouble since **T** is nearly isotropic. With the definition of our coordinate system in (2)–(4), we choose the long axis of the molecule as x_2, and the axis in the molecular plane through C(7) as x_1. Then we obtain with the data of WBRC, Table 5: $L_{11} = L_{33} = 0\cdot0006$, $L_{22} = 0\cdot0020$ rad^2, $T_{11} = 0\cdot0043$, $T_{22} = 0\cdot0057$, $T_{33} = 0\cdot0049$ Å^2, and further, $\sqrt{L_{11}} = \sqrt{L_{33}} = 1\cdot40$, $\sqrt{L_{22}} = 2\cdot56°$.

With these components of **T** and **L**, and with $x_1 = 1\cdot20$ Å, we calculate the $\rho(A - H)$ section for C(7) in the plane of the molecule (Fig. 2). The minimum of $-0\cdot22$ e Å^{-3} lies inside the ring at a distance of 0·08 Å from the nucleus of C(7). As with the end N in the azide ion, density is shifted from the region in front of to a region behind the nucleus. Because of the smaller vibrations of C(7) (30 K), the redistribution of the density with C(7) occurs closer to the nucleus and is completed within a region of about 0·25 Å around the nucleus. For the end N in the azide ion, this region extends to about 0·5 Å around the nucleus, *cf.* Figs. 1 and 2, but note the difference in scale.

For C(6), C(9) and C(10), we expect the same results as for C(7). For C(9) this is immediately obvious, since with our location of the centre of libration we also obtain $x_1 = 1\cdot20$ Å for C(9). For C(6) and C(10) we had to shift the centre of libration to the intersection of the long axis with the perpendicular through C(6). Since $L_{11} = L_{33} \ll L_{22}$ such a shift is allowed in a first approximation. If $L_{11} = L_{33} = 0$, there is only one *axis* of libration, and then the centre of libration is that point which lies on the axis at the shortest (perpendicular) distance to the nucleus.

This example shows that, even for low temperatures, one cannot generally assume that the effect of anharmonic motions of the atoms on the (dynamic) density distribution can be neglected. Thus one should search for a method which enables one to judge in advance how large the anharmonic contributions to the dynamic density may be in an actual structure. One such method is given by our approach of calculating $\rho(A - H)$ sections for all atoms in the structure. On an electronic computer, this is only a matter of seconds and thus involves little effort. In this context, we offer our program to other interested workers. The structural input is x_1, L_{22}, L_{33}, T_{11}, T_{22}, T_{33} referred to the above-mentioned Cartesian coordinate system, and the constants for the Gaussian functions of the respective atom as given in *International Tables for X-ray Crystallography* (1974, Table 2.2*B*).

Estimating the effects of large librations without calculating an Edgeworth distribution

In this section we shall work out a procedure that enables one, without calculating an Edgeworth series, to estimate roughly the effects of large librations on the dynamic electron density distribution with an actual structure. For this purpose, we first discuss the main factors which determine the anharmonic contributions to the densities. The numerical aspects of these factors will then be studied by means of model calculations. Finally, we shall describe our procedure.

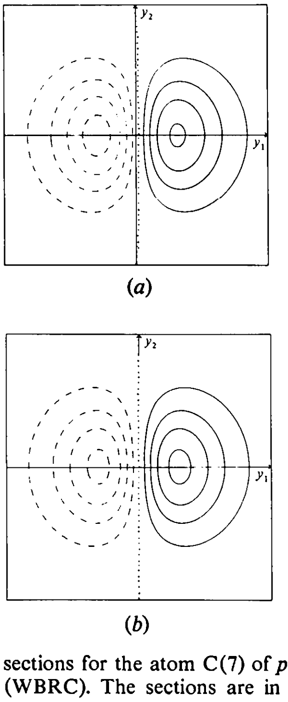


Fig. 2. $\rho(A - H)$ sections for the atom C(7) of *p*-nitropyridine *N*-oxide at 30 K (WBRC). The sections are in the plane of the molecule; the negative y_1 axis points to the long axis of the molecule. (*a*) and (*b*) each represent an area of 0·5 × 0·5 Å^2. Contour interval 0·05 e Å^{-3}. Otherwise as Fig. 1.

Factors affecting anharmonic contributions to electron densities

In the main, there are three such factors:

(1) the distance x_1 of the atom from the centre of libration,

(2) the ratio of the librational to the translational parts in the atomic motions,

(3) the absolute magnitude of the atomic motions (temperature).

The larger the distance x_1, the more the arc, along which the atom moves, converges towards a straight line (tangent on the arc). For small values of x_1 the arc is more curved, and hence we expect larger anharmonic contributions (for a constant amplitude of atomic motion).

Since we assume the translations of the molecule, referred to the librational origin, to be harmonic, the translations of the atoms are harmonic (in this coordinate system). Thus, anharmonic contributions to the atomic motions arise only from the librations. Since the atomic motions form the sum of translational and librational contributions (in our approximation with $\mathbf{S} = \mathbf{0}$), the anharmonic contributions to the dynamic density are larger, the larger the ratio of librational to translational contributions. For an atom at $(x_1,0,0)$, we define this ratio to be

$$V = \frac{3}{2}\frac{x_1^2(L_{22} + L_{33})}{T_{11} + T_{22} + T_{33}}. \qquad (11)$$

Equation (11) is formulated with respect to our special Cartesian coordinate system, but the components L_{22} and L_{33} can always be calculated from $\mathbf{L}$ (referred to an arbitrary coordinate system) by appropriate transformation. For an atom, there are only two degrees of freedom of libration, since libration about the x_1 axis revolves the (spherically symmetric) atom into itself. We have included the factor 3/2 in (11) to even out the difference in the numbers of degrees of freedom for librations and translations. Because of the equidistribution of energy to the various degrees of freedom we expect $V \le 1$ with actual structures. $V < 1$ we expect mainly for atoms close to the centre of the molecule, since for smaller values of x_1 the librational amplitudes of the atoms become smaller. For the end N in the azide ion we calculate $V = 0{\cdot}96$, for C(7) in *p*-nitropyridine *N*-oxide $V = 0{\cdot}38$, and for the C atoms *A*, *B*, *C*, *D* in anthracene at room temperature

Table 1. *Values of* $\sqrt{L_{33}}$ *and* $\rho_{\max}$, *calculated under the conditions* $L_{22} = L_{33}$, $L_{11} = 0$, $T_{11} = T_{22} = T_{33}$, $U_{11} = T_{11}$, $U_{22} = U_{33} = T_{22} + x_1^2 L_{33}$

x_1 in Å, U_{22} in Å^2, $\sqrt{L_{33}}$ in °. $\rho_{\max}$, in e Å^{-3} × 100, are the extreme (negative) values found in the $\rho(A - H)$ section $y_3 = 0$ (on the y_1 axis).

		$x_1 = 1\cdot2$		$x_1 = 1\cdot5$		$x_1 = 2\cdot0$		$x_1 = 4\cdot0$		$x_1 = 6\cdot0$	
V	U_{22}	$\sqrt{L_{33}}$	$\rho_{\max}$	$\sqrt{L_{33}}$	$\rho_{\max}$	$\sqrt{L_{33}}$	$\rho_{\max}$	$\sqrt{L_{33}}$	$\rho_{\max}$	$\sqrt{L_{33}}$	$\rho_{\max}$
1·0	0·04	6·75	47	5·40	37	4·05	27	2·03	13	1·35	9
1·0	0·02	4·77	61	3·82	48	2·86	36	1·43	17	0·95	11
1·0	0·01	3·38	71	2·70	56	2·03	42	1·01	20	0·68	13
0·8	0·04	6·37	35	5·09	27	3·82	20	1·91	10	1·27	6
0·8	0·02	4·50	45	3·60	35	2·70	26	1·35	13	0·90	8
0·8	0·01	3·18	53	2·55	41	1·91	31	0·95	15	0·64	10
0·6	0·04	5·85	22	4·68	18	3·51	13	1·75	6	1·17	4
0·6	0·02	4·13	30	3·31	23	2·48	17	1·24	8	0·83	6
0·6	0·01	2·92	34	2·34	27	1·75	20	0·88	10	0·58	7

(Cruickshank, 1956, Fig. 2), approximately, $V = 0\cdot92$, $0\cdot52$, $0\cdot13$, $0\cdot23$ respectively.

For low temperatures it is commonly assumed that, with the decrease of the atomic vibrations, the anharmonic contributions will decrease so much that they can be neglected. The correct part of this assumption is that, with lower temperature, the smearing functions of the nuclei contract to a smaller space around the nuclei. It does not hold, however, that the relative effect of the anharmonic motions on the density distributions will also decrease. As is shown by the following calculations, the contraction of the smearing function has the effect that, for given values of x_1 and V, the extrema of the $\rho(A - H)$ densities even increase.

Model calculations

To obtain results for three different temperatures we proceed as follows: For $T = 300$, 100, 30 K the components U_{ii} are about 0·04, 0·02, 0·01 Å^2 respectively, on average. We assume these values for U_{22} and U_{33} in order to represent these three temperatures approximately. For the sake of simplicity, we assume **T** to be isotropic, and $L_{22} = L_{33}$. Then $U_{22} = U_{33} = T_{22} + x_1^2 L_{33}$. With (2) we have $U_{11} = T_{11}$, and **U** is not isotropic. Equation (11) reduces to $VT_{22} = x_1^2 L_{33}$. Now we assume six values of x_1, three values of U_{22} and three values of V and calculate **T** and **L** according to: $T_{22} = U_{22}/(1 + V)$, $T_{11} = T_{33} = T_{22}$, $L_{33} = VU_{22}/[x_1^2(1 + V)]$, $L_{22} = L_{33}$. With x_1, **T** and **L** we calculate $\rho(A - H)$ sections $y_3 = 0$.

To describe our results in a more concise form, we state only the absolutely largest value of the $\rho(A - H)$ section, *i.e.* the minimum on the negative y_1 axis, see Figs. 1 and 2. This minimum represents the largest change of density in the environment of the nucleus that is needed to correct the dynamic density calculated in the harmonic approximation. Hence, we abbreviate this extremum of the $\rho(A - H)$ density by $\rho_{\max}$. The results of our calculation for a C atom are given in Table 1. To be able to envisage the magnitude of the librations in each particular case, $\sqrt{L_{33}}$ is also listed in Table 1.

To complement the survey given in Table 1 with respect to the dependence on V, we have calculated $\rho_{\max}$ as a function of V for some values of x_1 and U_{22}, and represented the results graphically in Fig. 3. For each curve in Fig. 3, 16 points ($\rho_{\max}$, V) were calculated and the remainder of the curve was drawn by interpolation. The curves for $V > 1$ are of only academic interest, since it is unlikely that this part of the curve corresponds to nature. Fig. 3 shows that $\rho_{\max}$ increases practically linearly in the region

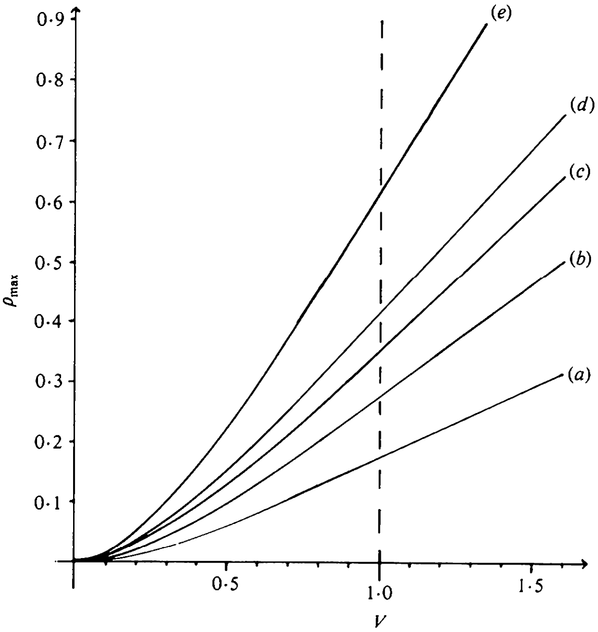


Fig. 3. Plots of $\rho_{\max}$ as a function of V for the following pairs of x_1(Å) and U_{22}(Å^2): (*a*) 4·0, 0·02; (*b*) 2·0, 0·04; (*c*) 2·0, 0·02; (*d*) 2·0, 0·01; (*e*) 1·2, 0·02. Conditions for **L** and **T** as in Table 1.

$0 \cdot 5 \leq V \leq 1 \cdot 5$. Hence, $\rho_{\max}$ can well be obtained for intermediate values of V in Table 1 by linear interpolation.

We also calculated a corresponding table (not given here) for N and O atoms. It appears that the $\rho_{\max}$ values for these atoms can be obtained to a sufficient approximation by enlarging the $\rho_{\max}$ values of Table 1 by 17 and 33% respectively. This corresponds to the increase in the number of electrons for N and O relative to C.

The $\rho_{\max}$ values found for the end N atom in the azide ion and for anthracene (atoms A, B, C, D; $\rho_{\max} = 0 \cdot 10$, $0 \cdot 07$, $0 \cdot 02$, $0 \cdot 04$ e Å^{-3} respectively) fit well to the values given in Table 1. Here one has to take into account, however, that with these structures, the thermal parameters are somewhat different from those listed in Table 1, and that N instead of C occurs in the azide ion. For C(7) in *p*-nitropyridine *N*-oxide one would assess from Table 1 too small a value of $\rho_{\max}$ ($\rho_{\max} < 0 \cdot 2$ e Å^{-3}). The larger value of $\rho_{\max} = 0 \cdot 22$ e Å^{-3} actually found arises from the fact that the anharmonicity is largely concentrated in one degree of freedom (large librations only about the long axis of the molecule).

Procedure

With an actual structure, one has first to calculate V from x_1, **T** and **L** (here the harmonic approximation is sufficient). With low temperatures, the translations of the atoms should be increased slightly because of the presence of internal (harmonic) vibrations. For small molecules, like urea, this increase is well below 6% (Ishii & Scheringer, 1979). With site symmetry $\bar{1}$ the centre of libration (coordinate origin) is immediately given; without site symmetry $\bar{1}$ the centre of gravity may be chosen to a first approximation, or a procedure as described with the example of *p*-nitropyridine *N*-oxide may be adopted. With V and by means of Table 1 and Fig. 3, $\rho_{\max}$ can be estimated by interpolation. If one finds $V \leq 0 \cdot 5$ with moderate anisotropic librations, one can always assume that $\rho_{\max} < 0 \cdot 2$ e Å^{-3} holds. With large anisotropy of the librations (*e.g.* *p*-nitropyridine *N*-oxide), the anharmonic contributions to the density are larger, and then we may have $\rho_{\max} \geq 0 \cdot 2$ e Å^{-3} already for $V \geq 0 \cdot 4$. Anisotropy of the translations is not so important, as we could see from a few model calculations. If there are N or O atoms, the values of Table 1 should be enlarged by 17 or 33%. For other atoms, however, a $\rho(A - H)$ map should be calculated.

Conclusion

This investigation has shown that one cannot in every case assume that the anharmonic contributions to the electron density, caused by large librations, can be neglected. However, at first glance, it is often difficult to judge how large the anharmonic contributions may be in an actual case. Thus, for example, we had not expected that one can neglect the anharmonic contributions with the atom A in anthracene, but the $\rho(A - H)$ map shows that one can. The $\rho(A - H)$ density gives a sure hint as to how large the anharmonic contributions will be; less accurate, but simpler to apply is the procedure outlined in the previous section.

The significance of the anharmonic contributions to the electron density must, of course, be judged in comparison with the other (random and systematic) errors which occur in the experimental density distribution. With the present state of accuracy in the experimental determination of electron densities in molecular crystals, the total error in the bond regions may not exceed $0 \cdot 2$ e Å^{-3}, whereas close to the nuclei the total error may be larger. We have seen that, with decreasing atomic motions (decreasing temperature), the non-zero $\rho(A - H)$ densities contract towards the atomic nuclei. With C(7) in *p*-nitropyridine *N*-oxide the $\rho(A - H)$ extrema were at a distance of $0 \cdot 08$ Å from the nuclei, and in this case the experimenters (WBRC) would have to be asked whether or not the remaining errors around C(7) exceeded $0 \cdot 22$ e Å^{-3}. Thus, the significance of the anharmonic contributions to the dynamic electron density in an actual experimental investigation can only be judged by the experimenter, who has carefully to estimate the total error in the density distribution and to relate it to the error caused by large librations.

References

Choi, C. S. & Prince, E. (1976). *J. Chem. Phys.* **64**, 4510–4516.

Cruickshank, D. W. J. (1956). *Acta Cryst.* **9**, 915–923.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Ishii, M. & Scheringer, C. (1979). *Acta Cryst.* A**35**, 613–616.

Johnson, C. K. (1969). *Acta Cryst.* A**25**, 187–194.

Johnson, C. K. (1970). *Thermal Neutron Diffraction*, pp. 132–160. Oxford Univ. Press.

Kendall, M. G. & Stuart, A. (1969). *The Advanced Theory of Statistics*. Vol. I, Ch. 6. London: Griffin.

Pawley, G. S. & Willis, B. T. M. (1970). *Acta Cryst.* A**26**, 260–262.

Prince, E. & Finger, L. W. (1973). *Acta Cryst.* B**29**, 179–183.

Scheringer, C. (1977). *Acta Cryst.* A**33**, 879–884.

Scheringer, C. (1978). *Acta Cryst.* A**34**, 702–709.

Scheringer, C., Kutoglu, A. & Mullen, D. (1978). *Acta Cryst.* A**34**, 481–483.

Scheringer, C. & Reitz, H. (1976). *Acta Cryst.* A**32**, 271–273.

Stevens, E. D. & Hope, H. (1977). *Acta Cryst.* A**33**, 723–729.

Wang, Y., Blessing, R. H., Ross, F. K. & Coppens, P. (1976). *Acta Cryst.* B**32**, 572–578.