

$$C_2 = \mu_2(x) = m_2 - m_1^2$$

$$C_3 = \mu_3(x) = m_3 - 3m_1m_2 + m_1^3$$

$$C_4 = \mu_4(x) - 3\mu_2^2(x) = m_4 + 12m_2m_1^2 - 6m_1^4 - 4m_1m_3 - 3m_2^2$$

d'où:

$$\varphi_{(L)} = \exp iLC_1 - \frac{L^2}{2} C_2 - \frac{iL^3}{6} C_3 + \frac{L^4}{24} C_4 - \dots$$

et en revenant à la fonction  $C_{(L)}^e = \langle \exp -2i\pi L \varepsilon_L S b \rangle$

$$C_{(L)}^e = \exp(-2i\pi L S b \langle \varepsilon_L \rangle - 2\pi^2 L^2 S b^2 \varepsilon_L^2 + 4i\pi^3 L^3 S b^3 \varepsilon_L^3 + \frac{2}{3}\pi^4 L^4 S b^4 \varepsilon_L^4 - \dots).$$

En ne conservant que les premiers termes du développement en cumulant:

$$A_{(L)}^e \simeq \exp(-2\pi^2 L^2 S b^2 \varepsilon_L^2 + \frac{2}{3}\pi^4 L^4 S b^4 \varepsilon_L^4 + \dots).$$

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## Calculation of Dynamic Electron Density Distributions from Static Molecular Wave Functions

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A procedure is described for calculating dynamic molecular densities, within the convolution approximation, from rigid-body translational and librational thermal motions and static wave functions calculated with Gaussian basis orbitals. Fourier transformation of the libratorially smeared wave function is shown to be equivalent to convolution of the molecular scattering factor with a distribution of orientations of the scattering vector. The proper thermal parameters to be applied to two-center products are well defined in this procedure. Static and dynamic molecular deformation densities are plotted for an extended-basis-set wave function of the azide ion,  $N_3^-$ , with rigid-body thermal parameters as determined in the crystal structures of  $NaN_3$  and  $KN_3$ .

### Introduction

Since the electron density distributions determined by X-ray diffraction are time-averages over the thermal motion of a crystal, comparison of experimental results with theoretical densities calculated from static wave functions requires that either the thermal motions be deconvoluted from the experimental densities, or the theoretical densities be thermally smeared.

Experimental densities may be deconvoluted (to some extent) by fitting charge-deformation and thermal-vibration parameters to the experimental measurements (Hirshfeld, 1976). However, in such a deconvolution scheme, the uncertainties in the nature of the

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charge-density model are introduced into the experimental results. For quantitative comparisons between theory and experiment, thermal smearing of the theoretical density appears more desirable and is considered here.

In the usual X-ray model, the atomic thermal parameters are refined assuming independent thermal motion of the atoms. Within a molecule, however, the motions are highly correlated. In addition, uncertainty arises in the correct thermal smearing to be applied to the two-center products of the molecular wave function.

Since the main part of the thermal motion in a molecular crystal is due to the translational and librational external modes, the proper treatment of

rigid-body motions is of major importance. The thermal smearing to be applied to two-center orbital products will be discussed here. The rigid-body librational and translational parameters can be refined directly from the data (Pawley, 1972) or fitted to the individual atomic thermal parameters (Schomaker & Trueblood, 1968).

Rigid-body smearing has been applied to a wave function of the acetylene molecule by Ruysink & Vos (1974). For Gaussian basis orbitals, the application of translational smearing is straightforward. For librational motions, however, the expressions are more difficult to evaluate. The librational smearing applied to acetylene (Ruysink & Vos, 1974; Ruysink, 1973) is only valid for small librations. In this work, analytical expressions are derived which allow rigid-body librational smearing to be applied to wave functions of Gaussian orbitals for any finite librations.

### Translations and librations

The displacement  $\mathbf{u}_{\text{lib}}$ , of a point at  $\mathbf{r}$ , in a rigid molecule due to libration about an axis  $\boldsymbol{\omega}$  with a magnitude  $|\omega|$  is given by

$$\mathbf{u}_{\text{lib}} = \frac{\sin \omega}{\omega} \begin{pmatrix} 0 & -\omega_3 & \omega_2 \\ \omega_3 & 0 & -\omega_1 \\ -\omega_2 & \omega_1 & 0 \end{pmatrix} \begin{pmatrix} r_1 \\ r_2 \\ r_3 \end{pmatrix} + \left( \frac{1 - \cos \omega}{\omega^2} \right) \begin{pmatrix} -\omega_2^2 - \omega_3^2 & \omega_1 \omega_2 & \omega_1 \omega_3 \\ \omega_1 \omega_2 & -\omega_1^2 - \omega_3^2 & \omega_2 \omega_3 \\ \omega_1 \omega_3 & \omega_2 \omega_3 & -\omega_1^2 - \omega_2^2 \end{pmatrix} \times \begin{pmatrix} r_1 \\ r_2 \\ r_3 \end{pmatrix} \quad (1)$$

where  $\omega_1, \omega_2, \omega_3$  and  $r_1, r_2, r_3$  are the components of  $\boldsymbol{\omega}$  and  $\mathbf{r}$ . Expression (1) is exact for any finite libration (Schomaker & Trueblood, 1968).

The static density  $\varrho(\mathbf{r})$  corresponding to a wave function of molecular orbitals  $\varphi(\mathbf{r})$  is, for a closed-shell system, given by

$$\varrho(\mathbf{r}) = 2 \sum_i^N \varphi_i^*(\mathbf{r}) \varphi_i(\mathbf{r}) = 2 \sum_i^N \sum_{\mu\nu} C_{\mu i} C_{\nu i}^* \chi_{\mu}(\mathbf{r} - \mathbf{r}_a) \chi_{\nu}(\mathbf{r} - \mathbf{r}_b) \quad (2)$$

where  $N$  is the number of occupied orbitals, the  $C_{\mu i}$  are the molecular orbital coefficients, and the  $\chi_{\mu}(\mathbf{r})$  are basis orbitals. The dynamic molecular density  $\varrho_{\text{dyn}}(\mathbf{r})$  is obtained by a convolution of the static density with the probability distribution function  $P(\mathbf{u})$  for a displacement  $\mathbf{u}$ .

$$\varrho_{\text{dyn}}(\mathbf{r}) = \int_{-\infty}^{\infty} \varrho(\mathbf{r} - \mathbf{u}) P(\mathbf{u}) d\mathbf{u}. \quad (3)$$

Both translational and librational motions are assumed here to be harmonic and the correlations between translation and libration (the screw tensor  $\mathbf{S}$ ) are

assumed to be zero. When the wave function is composed of Gaussian basis functions, convolution with the translational distribution function is easily performed (Stewart, 1968), since the displacements are identical for all orbital products in the molecule.

Calculation of the smeared density due to libration, however, is more difficult since one needs to evaluate the convolution

$$\varrho_{\text{lib}}(\mathbf{r}) = \int_{-\infty}^{\infty} \varrho(\mathbf{R}\mathbf{r}) P(\boldsymbol{\omega}) d\boldsymbol{\omega} \quad (4)$$

with (in the harmonic approximation)

$$P(\boldsymbol{\omega}) = (2\pi)^{-3/2} |\mathbf{L}^{-1}|^{1/2} \exp(-\frac{1}{2} \boldsymbol{\omega}^T \mathbf{L}^{-1} \boldsymbol{\omega}), \quad (5)$$

where  $\mathbf{L}$  is the tensor describing the mean square amplitudes of libration of the molecule.  $\mathbf{R}$  is the rotation matrix corresponding to the rotation  $\boldsymbol{\omega}$  such that  $\mathbf{R}\mathbf{r} = \mathbf{r} + \mathbf{u}_{\text{lib}}$ .

Ruysink & Vos (1974) were able to obtain an approximate analytical expression for (4) by assuming small librations ( $\omega, \omega_a \cong 0$ ,  $\sin \omega \cong \omega$ ). Exact expressions can be obtained for the librational smearing by considering the Fourier transform of the smeared density. The coherent scattering factor for the librating molecule is given by

$$f_{\text{lib}}(\mathbf{h}) = \int_{-\infty}^{\infty} \varrho_{\text{lib}}(\mathbf{r}) \exp(2\pi i \mathbf{h}^T \mathbf{r}) d\mathbf{r}. \quad (6)$$

Since  $\mathbf{R}^{-1} = \mathbf{R}^T$ , one obtains from expression (4)

$$f_{\text{lib}}(\mathbf{h}) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \varrho(\mathbf{R}\mathbf{r}) \exp(2\pi i \mathbf{h}^T \mathbf{R}^T \mathbf{r}) d\mathbf{r} P(\boldsymbol{\omega}) d\boldsymbol{\omega}. \quad (7)$$

Substituting  $\mathbf{r}' = \mathbf{R}\mathbf{r}$  gives

$$f_{\text{lib}}(\mathbf{h}) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \varrho(\mathbf{r}') \exp[2\pi i (\mathbf{R}\mathbf{h})^T \mathbf{r}'] d\mathbf{r}' P(\boldsymbol{\omega}) d\boldsymbol{\omega} \quad (8)$$

with  $d\mathbf{r}' = d\mathbf{r}$ , since  $\mathbf{R}$  is unitary and

$$f_{\text{lib}}(\mathbf{h}) = \int_{-\infty}^{\infty} f(\mathbf{R}\mathbf{h}) P(\boldsymbol{\omega}) d\boldsymbol{\omega} \quad (9)$$

where  $f(\mathbf{h})$  is the static molecular scattering factor. Thus, the dynamic scattering factor may be obtained by convolution of  $f(\mathbf{h})$  over the distribution of orientations of  $\mathbf{h}$  with respect to the molecule.

For  $s$ -type Gaussian basis orbitals centered at  $\mathbf{r}_a$  and  $\mathbf{r}_b$ , the product

$$\chi_a(\mathbf{r}) \chi_b(\mathbf{r}) = \exp(-A|\mathbf{r} - \mathbf{r}_a|^2) \exp(-B|\mathbf{r} - \mathbf{r}_b|^2) \quad (10)$$

can be reduced to a single center

$$\chi_a(\mathbf{r}) \chi_b(\mathbf{r}) = \exp[-(A+B)|\mathbf{r} - \mathbf{r}_c|^2] \times \exp\left(-\frac{AB}{A+B} |\mathbf{r}_a - \mathbf{r}_b|^2\right) \quad (11)$$

where the 'center of density'  $\mathbf{r}_c$ , is given by

$$\mathbf{r}_c = (A\mathbf{r}_a + B\mathbf{r}_b)/(A+B). \quad (12)$$

The molecular scattering factor for *s*-type basis orbitals is given by

$$\begin{aligned} f_{\text{stat}}^{s,s}(\mathbf{h}) &= C_a C_b \int_{-\infty}^{\infty} \chi_a(\mathbf{r}) \chi_b(\mathbf{r}) \exp(2\pi i \mathbf{h}^T \mathbf{r}) d\mathbf{r} \\ &= C_a C_b \exp\left(-\frac{AB}{A+B} |\mathbf{r}_a - \mathbf{r}_b|^2\right) \left(\frac{\pi}{A+B}\right)^{3/2} \\ &\quad \times \exp\left(-\frac{\pi^2 |\mathbf{h}|^2}{A+B}\right) \exp(2\pi i \mathbf{h}^T \mathbf{r}_c) \end{aligned} \quad (13)$$

where the  $C_a$  and  $C_b$  include the molecular orbital coefficients and normalization factors. The only term in (13) which depends on the direction of  $\mathbf{h}$  is  $\exp(2\pi i \mathbf{h}^T \mathbf{r}_c)$ . Substituting (13) into (9) and using

$$(\mathbf{R}\mathbf{h})^T \mathbf{r} = \mathbf{h}^T \mathbf{R}^T \mathbf{r} = \mathbf{h}^T \mathbf{r} - (\mathbf{R}\mathbf{h})^T \mathbf{u}_{\text{lib}}$$

where  $\mathbf{u}_{\text{lib}}$  is the displacement due to libration, gives for the librational averaged temperature factor:

$$\begin{aligned} f_{\text{dyn}}^{s,s} &= \int_{-\infty}^{\infty} f_{\text{stat}}^{s,s}(\mathbf{R}\mathbf{h}) P(\omega) d\omega \\ &= f_{\text{stat}}^{s,s}(\mathbf{h}) \int_{-\infty}^{\infty} \exp[-2\pi i (\mathbf{R}\mathbf{h})^T \mathbf{u}_{\text{lib}}^c] P(\omega) d\omega \end{aligned} \quad (14)$$

where the superscript *c* indicates that the displacement is for the point  $\mathbf{r}_c$ . Note that the integral in (14) is the librational temperature factor multiplied by the static scattering factor. The librational temperature factor, derived by Pawley & Willis (1970), is given by

$$\begin{aligned} &\int_{-\infty}^{\infty} \exp(2\pi i \mathbf{h}^T \mathbf{u}) P(\omega) d\omega \\ &= \exp\{2\pi i h_1(-\frac{1}{2}\Omega_2 - \frac{1}{2}\Omega_3)r_1 + \dots + \dots\} \\ &\quad \text{(first cumulant)} \\ &+ 4\pi^2 h_1^2(-\frac{1}{2}\Omega_2 r_3^2 - \frac{1}{2}\Omega_3 r_2^2) + \dots + \dots \\ &+ 4\pi^2 h_2 h_3 (\Omega_1 r_2 r_3) + \dots + \dots \\ &\quad \text{(second cumulant)} \\ &+ 8\pi^3 i h_3^3 [(\Omega_2^2 r_3^2 + \Omega_3^2 r_2^2) \frac{1}{2} r_1] + \dots + \dots \\ &+ 8\pi^3 i h_1^2 h_2 [\Omega_3^2 (\frac{1}{2} r_2^2 - r_1^2) \\ &+ (\Omega_2 \Omega_3 - \Omega_3 \Omega_1 + \Omega_1 \Omega_2) \frac{1}{2} r_3^2] r_2 + \dots + \dots \\ &+ 8\pi^3 i h_1^2 h_3 [\Omega_2^2 (\frac{1}{2} r_3^2 - r_1^2) \\ &+ (\Omega_2 \Omega_3 + \Omega_3 \Omega_1 - \Omega_1 \Omega_2) \frac{1}{2} r_2^2] r_3 + \dots + \dots \\ &+ 8\pi^3 i h_1 h_2 h_3 [-(\Omega_2 \Omega_3 + \Omega_3 \Omega_1 + \Omega_1 \Omega_2) r_1 r_2 r_3] \} \\ &\quad \text{(third cumulant)} \end{aligned} \quad (15)$$

where  $\Omega_1, \Omega_2, \Omega_3$  are the diagonal elements of the librational tensor after a transformation of the coordinates to diagonalize  $\mathbf{L}$ , and  $h_1, h_2, h_3$  and  $r_1, r_2, r_3$  are the components of  $\mathbf{h}$  and  $\mathbf{r}_c$  in the transformed system.

Thus, the correct librational motion to assign to the two-center product,  $\chi_a(\mathbf{r})\chi_b(\mathbf{r})$ , is the motion of the center of density  $\mathbf{r}_c$  as defined in (12). For Gaussian lobe basis functions in which *p*-type and higher basis functions are constructed from *s* functions displaced

from the nuclei (Whitten, 1966), (14) can be applied to the entire wave function.

For Gaussian basis functions of the type

$$\chi_a(\mathbf{r}) = (x - x_a)^m (y - y_a)^n (z - z_a)^p \exp(-A|\mathbf{r} - \mathbf{r}_a|^2) \quad (16)$$

the scattering factor for a two-center product is given by (Miller & Krauss, 1967)

$$\begin{aligned} f_{\text{stat}}^{a,b}(\mathbf{h}) &= C_a C_b \int_{-\infty}^{\infty} \chi_a(\mathbf{r}) \chi_b(\mathbf{r}) \exp(2\pi i \mathbf{h}^T \mathbf{r}) d\mathbf{r} \\ &= C_a C_b \exp\left[-\frac{AB}{A+B} (\mathbf{r}_a - \mathbf{r}_b)^2\right] \left(\frac{\pi}{A+B}\right)^{3/2} \\ &\quad \times \exp\left(-\frac{\pi^2 |\mathbf{h}|^2}{A+B}\right) \\ &\quad \times \exp(2\pi i \mathbf{h}^T \mathbf{r}_c) F_{a,b}^x(h_1) F_{a,b}^y(h_2) F_{a,b}^z(h_3) \end{aligned} \quad (17)$$

where

$$\begin{aligned} F_{a,b}^x(h_1) &= \sum_{\mu=0}^{m_a} \binom{m_a}{\mu} (x_c - x_a)^{m_a - \mu} \sum_{\nu=0}^{m_b} \binom{m_b}{\nu} (x_c - x_b)^{m_b - \nu} \\ &\quad \times \left(\frac{i}{2(A+B)^{1/2}}\right)^{\mu + \nu} H_{\mu + \nu} \left(\frac{\pi h_1}{(A+B)^{1/2}}\right) \end{aligned}$$

and the  $H_m(x)$  are Hermite polynomials of order *m*.

Because of the additional dependence of  $\mathbf{h}$ , when (17) is substituted into (9) the static scattering factor cannot be factored out as it was for the *s, s* product in (14). For example, for the product  $p_x, s$ ,

$$\begin{aligned} f_{\text{dyn}}^{p_x, s} &= \int_{-\infty}^{\infty} f_{\text{stat}}^{p_x, s} P(\omega) d\omega \\ &= C_a C_b \exp\left(-\frac{AB}{A+B} |\mathbf{r}_a - \mathbf{r}_b|^2\right) \left(\frac{\pi}{A+B}\right)^{3/2} \\ &\quad \times \exp\left(-\frac{\pi^2 |\mathbf{h}|^2}{A+B}\right) \\ &\quad \times \int_{-\infty}^{\infty} \left[\frac{i}{2(A+B)^{1/2}} H_1 \frac{\pi \mathbf{h}'}{(A+B)^{1/2}} + x_c - x_a\right] \\ &\quad \times \exp[2\pi i (\mathbf{R}\mathbf{h})^T \mathbf{r}_c] P(\omega) d\omega \end{aligned} \quad (18)$$

where  $\mathbf{h}' = \mathbf{R} \begin{pmatrix} h_1 \\ 0 \\ 0 \end{pmatrix}$ .

Let

$$\begin{aligned} K_{a,b}(h^2) &= C_a C_b \exp\left(-\frac{AB}{A+B} |\mathbf{r}_a - \mathbf{r}_b|^2\right) \\ &\quad \times \left(\frac{\pi}{A+B}\right)^{3/2} \exp\left(-\frac{\pi^2 |\mathbf{h}|^2}{A+B}\right) \end{aligned}$$

for convenience. Using a series expansion for  $(\sin \omega)/\omega$  and  $(1 - \cos \omega)/\omega^2$  in (1) gives

$$\begin{aligned} h' &= h_1 - \omega_3 h_2 + \omega_2 h_3 - \frac{1}{2} \omega_3^2 h_1 - \frac{1}{2} \omega_2^2 h_1 \\ &\quad + \frac{1}{2} \omega_1 \omega_2 h_2 + \frac{1}{2} \omega_1 \omega_3 h_3 + \dots \end{aligned} \quad (19)$$

With  $H_1(x)=2x$ , one obtains for (18),

$$\begin{aligned} f_{\text{dyn}}^{p_{x^2}, s} &= f_{\text{stat}}^{p_{x^2}, s} \int_{-\infty}^{\infty} \exp(-2\pi i h^T \mathbf{u}_{\text{lib}}^c) P(\omega) d\omega \\ &- K_{a,b}(h^2) \int_{-\infty}^{\infty} \omega_3 h_2 \left( \frac{\pi i}{(A+B)} \right) \\ &\times \exp(-2\pi i h^T \mathbf{u}_{\text{lib}}^c) P(\omega) d\omega \\ &+ K_{a,b}(h^2) \int_{-\infty}^{\infty} \omega_2 h_3 \left( \frac{\pi i}{(A+B)} \right) \\ &\times \exp(-2\pi i h^T \mathbf{u}_{\text{lib}}^c) P(\omega) d\omega - \dots \end{aligned} \quad (20)$$

Note that the first term in (20) is the same as (14). The remaining terms may be considered as corrections (normally small) which account for the change of orientation of the basis orbitals with libration. Expressions for these integrals are similar to (15) and can be derived in the same manner. In the derivation, terms of order  $\omega^n$  with  $n > 2$  have been neglected.

The smeared density is obtained from the total dynamic molecular scattering factor by the usual Fourier transform

$$\varrho_{\text{dyn}}(\mathbf{r}) = \frac{1}{V} \sum f_{\text{dyn}}(\mathbf{h}) \exp(-2\pi i \mathbf{h}^T \mathbf{r}). \quad (21)$$

Since a finite number of terms are included in the summation,  $\varrho_{\text{dyn}}(\mathbf{r})$  will include series-termination error. This is desirable, however, for comparison with experimental densities which also include series-termination errors.

### Internal modes

The density averaged over the internal vibrational modes, in the Born–Oppenheimer approximation, may be obtained from

$$\begin{aligned} \varrho_{\text{int}}(\mathbf{r}) &= \int \varrho(\mathbf{r}, \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N) \\ &\times P(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N) d\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N \end{aligned} \quad (22)$$

where  $P(\mathbf{R}_1, \dots, \mathbf{R}_N)$  is the distribution function for the  $\mathbf{R}_1, \dots, \mathbf{R}_N$  nuclear position vectors. Evaluation requires calculating the wave function at a large number of internuclear geometries.

When the wave function is available at only the equilibrium geometry, further approximations must be considered. It has been found (Coulson & Thomas, 1971) in the evaluation of (22) for the  $\text{H}_2$  molecule that density near the nucleus follows the nuclear motions and thus would be well approximated by a convolution

$$\varrho_{\text{int}}(\mathbf{r}) = \int \varrho(\mathbf{r} - \mathbf{u}) P(\mathbf{u}) d\mathbf{u}. \quad (23)$$

The convolution approximation assumes that the wave function does not change as a function of the nuclear positions. The correct thermal smearing to be applied to the two-center terms is not obvious in this approximation, however.

In treating the internal modes of acetylene,

Ruysink & Vos (1974) avoided this problem by employing the convolution

$$\varrho_{\text{int}}(\mathbf{r}) = \iint \chi_a(\mathbf{r} - \mathbf{u}_i) \chi_b(\mathbf{r} - \mathbf{u}_j) P(\mathbf{u}_i) P(\mathbf{u}_j) d\mathbf{u}_i d\mathbf{u}_j. \quad (24)$$

This approach has recently been criticized by Scheringer & Reitz (1976) as being inconsistent with the Born–Oppenheimer approximation since, in the limit of independent vibrations, it reduces to a smearing of the individual orbitals rather than the orbital product. It should be noted, however, that any approach in which a wave function calculated at a single geometry is used will be inconsistent with the Born–Oppenheimer approximation. The ultimate criterion for judging the validity of an approximation should be its ability to reproduce the results of (22).

As shown above, the correct thermal smearing to be applied to a two-center product for librational rigid-body motion is the motion of the center of density  $\mathbf{r}_c$ . As the motion of  $\mathbf{r}_c$  is obviously also appropriate for translational rigid-body smearing, it would appear to be a reasonable approximation for the treatment of internal vibrations as well. For a product  $\chi_a(\mathbf{r})\chi_b(\mathbf{r})$  in which the nuclei are displaced by  $\mathbf{u}_a$  and  $\mathbf{u}_b$  respectively, the displacement of the center of density would be

$$\mathbf{u}_c = (A\mathbf{u}_a + B\mathbf{u}_b)/(A+B) \quad (25)$$

and in the convolution approximation

$$\varrho_{\text{int}}^{a,b}(\mathbf{r}) = \int \varrho^{a,b}(\mathbf{r} - \mathbf{u}_c) P(\mathbf{u}_c) d\mathbf{u}_c. \quad (26)$$

Ruysink & Vos (1974) have also considered the dependence of the normalization factors of the molecular orbitals on geometry. Rather than include the normalization factors in the convolution, they used an average over all geometries. Whether the change in normalization factors can be ignored, taken as the average, or must be included in the convolution cannot be answered without further testing of (24) and (26) with Born–Oppenheimer results.

### Results

Dynamic densities have been calculated for the azide ion,  $\text{N}_3^-$ , from a static molecular wave function and the librational and translational thermal parameters as determined in the crystal structures of  $\text{NaN}_3$  and  $\text{KN}_3$ . The molecular wave function was calculated using an extended basis set of Cartesian-Gaussian basis orbitals as in (16). The rigid-body thermal parameters

Table 1. *Rigid-body thermal parameters*

$\text{NaN}_3$ : Molecular axis along  $z$  ( $\bar{3}$  in space group  $R\bar{3}m$ )

$$\begin{array}{ll} U_{11} (= U_{22}) = 0.0248 \text{ \AA}^2 & L_{11} (= L_{22}) = 0.047 \text{ rad}^2 \\ U_{33} = 0.0204 & L_{33} = 0.0 \end{array}$$

$\text{KN}_3$ : Molecular axis along  $x$ ,  $[(1,1,0)$  in space group  $I4/mcm$ ],  $z$  along  $c$

$$\begin{array}{ll} U_{11} = 0.0182 \text{ \AA}^2 & L_{11} = 0.0 \text{ rad}^2 \\ U_{22} = 0.0155 & L_{22} = 0.0110 \\ U_{33} = 0.0240 & L_{33} = 0.0062 \end{array}$$

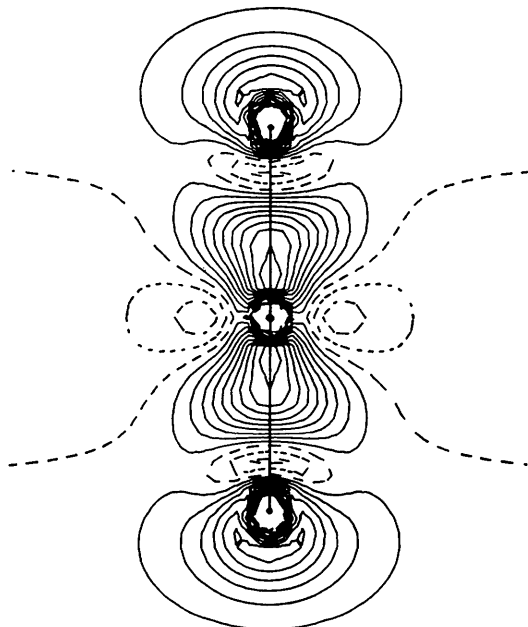


Fig. 1. Static deformation density of  $N_3^-$ . Contours at  $0.10 \text{ \AA}^{-3}$ , negative contours dashed. Large negative contours near the nuclei have been omitted.

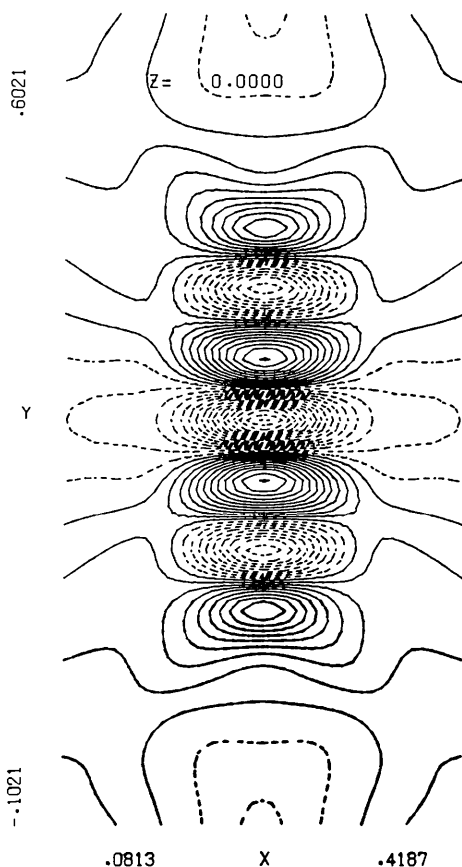


Fig. 2. Dynamic deformation density calculated with rigid-body thermal parameters of the  $N_3^-$  ion as found in the crystal structure of  $KN_3$ . Contours at  $0.05 e \text{ \AA}^{-3}$ .

used in the calculation are given in Table 1. Details of the theoretical calculation and comparison with experimental densities will be given elsewhere (Stevens, Rys & Coppens, 1977*a,b*).

The internal vibrations have been neglected. Since the amplitudes of displacement due to the internal modes are small, their contribution to the total thermal motion is very small at room temperature (Scheringer, 1972), though their relative importance may increase when the amplitudes due to external modes are reduced by cooling of the specimen. In addition, when the rigid-body thermal parameters have been obtained from diffraction data, the translational and librational parameters will include, to some extent, the internal vibrations.

In Fig. 1, the static difference density

$$\Delta \rho_{\text{stat}} = \rho_{\text{stat}}(\text{molecule}) - \rho_{\text{stat}}(\text{atoms}) \quad (27)$$

is plotted for the theoretical density of  $N_3^-$ . Molecular scattering factors of the thermally smeared density are calculated from (9) at  $h, k, l$  values corresponding to each of the experimental intensity measurements of  $NaN_3$  and  $KN_3$ . The series-terminated dynamic density

$$\Delta \rho_{\text{dyn}} = \rho_{\text{dyn}}(\text{molecule}) - \rho_{\text{dyn}}(\text{atoms}) \quad (28)$$

is obtained by the Fourier summation

$$\Delta \rho_{\text{dyn}} = \frac{1}{V} \sum (f_{\text{dyn}}^{\text{mol}} - f_{\text{dyn}}^{\text{atoms}}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}). \quad (29)$$

The result for  $KN_3$  is plotted in Fig. 2 and for  $NaN_3$  in Fig. 3. In both cases the resolution limit,  $(\sin \theta/\lambda)_{\text{max}}$ , is about  $1.20 \text{ \AA}^{-1}$ .

To assess the importance of the higher-order terms which occur in (9) when the orbital products are not of the  $s, s$  type, as in (20), the calculation on  $NaN_3$  has been repeated neglecting all but the first term in the orbital product scattering expressions. The dynamic difference density calculated in this manner is very close to the correct treatment. The maximum difference,  $0.03 e \text{ \AA}^{-3}$ , is less than the estimated experimental error. Because of the additional dependence on  $\omega^m$  for an orbital product of order  $m$ , (where  $m$  is the sum of the  $l$  quantum numbers of the atomic orbitals), the correction terms of higher-order orbital products are more sensitive to the magnitude of the libration than the  $s, s$  products would be, but are generally small when the librations are small.

Calculation of the dynamic density has also been repeated neglecting the first and third cumulant terms in (15). The differences are again found to be small,  $< 0.02 e \text{ \AA}^{-3}$ , provided the same terms have been neglected in calculating  $f_{\text{dyn}}^{\text{atoms}}$  in (29). Of course, the extent to which either of these simplifications is valid depends on the magnitude of  $\omega$ , the distance from the center of libration, and the magnitude of  $\mathbf{h}$ . The neglect of higher-order terms will also become more severe when higher angular terms such as  $d$ -orbitals are more heavily populated.

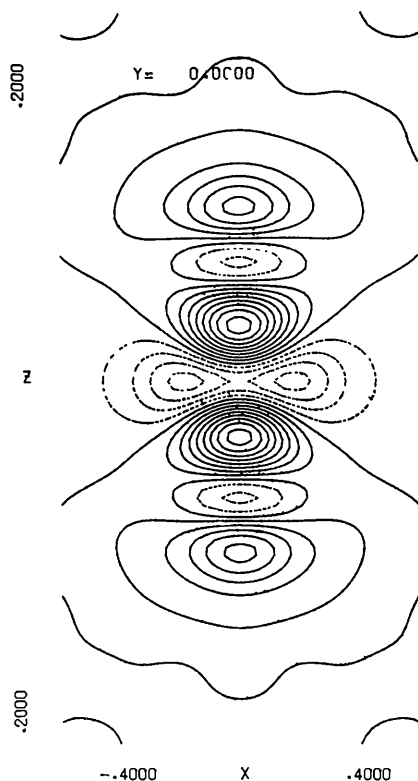


Fig. 3. Dynamic deformation density calculated with rigid-body thermal parameters as found in  $\text{NaN}_3$ . Contours at  $0.05 \text{ e } \text{\AA}^{-3}$ .

### Conclusions

We have shown that the time-averaged molecular electron density distribution for rigid-body librations can be obtained by a convolution of the molecular scattering factors with the distribution of orientations of the scattering vector  $\mathbf{h}$ . The correct libration amplitude to be applied to two-center orbital products is found to be the motion of the center of density point,  $r_c$ . Starting with a static molecular density, the dynamic

density smeared by rigid-body translations and librations can be obtained for any magnitude of  $\mathbf{T}$  and  $\mathbf{L}$ .

The dynamic density obtained in this manner contains series termination effects, but for extended data sets the effects will be relatively small when the difference density,  $\Delta\rho_{\text{dyn}}$ , is calculated. In addition, if the object of calculating the dynamic density is for comparison with X-ray diffraction results, which are also obtained from a finite series, then series-termination effects may be included in the theory to the same extent as in the experiment. Although the results given here are for a linear molecule, the method is applicable to molecules of general geometry.

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## Magnetic Properties of Crystals: An Alternative Method

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A method, based on the group-theoretical concept of the factor groups contained in a composition series, of obtaining the number of the constants required to describe a magnetic property in respect of the 90 magnetic point groups is described. The advantage of the method presented here is that one can enumerate simultaneously the constants needed for the description of the magnetic property for all the point groups involved in a composition series and their magnetic variants. Piezomagnetism is worked out in detail for one composition series.

### 1. Introduction

The character method developed by Bhagavantam (1942) has been successfully applied by Bhagavantam

& Suryanarayana (1949), Bhagavantam & Pantulu (1964) and Bhagavantam (1966) for enumerating physical constants needed for the description of various physical properties in respect of the 90 magnetic sym-