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Direct Calculation of Dynamic Densities

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It will be shown that, in the convolution approximation, dynamic densities of molecules can be calculated directly from temperature factors and quantum-chemically calculated (static) densities, *i.e.* without recourse to numerical integration and without calculating Fourier coefficients and series. The application of the proposed method to the case of density units, derived from two-centre orbital products, is discussed in detail.

In calculating dynamic densities one intends thermally to smear out static densities, which were calculated by quantum chemical methods, in order to compare static density distributions with those obtained by diffraction experiments on crystals. In quantum chemical calculations of the density distribution of polyatomic molecules the atomic orbitals, and hence the density units, are in most cases represented by Gaussian functions and their derivatives (Boys, 1950; Stewart, 1969). Gaussian functions are used, *e.g.*, in the programs *IBMOL*, *POLYATOM*, and *GAUSSIAN* 70 (QCPE, 1974). Let the static density in the position $\mathbf{x}$ of the molecule be represented by

$$\varrho(\mathbf{x})_{\rm stat} = \sum P_{\mu\nu}\varphi_\mu(\mathbf{x})\varphi_\nu(\mathbf{x}) = \sum_{\mu,\nu=1}^{N} P_{\mu\nu} \sum_{i,j=1}^{n} d_{\mu i}d_{\nu j}q_{\mu i}(\mathbf{x})q_{\nu j}(\mathbf{x}), \qquad (1)$$

where the $P_{\mu\nu}$ are the population parameters, the $d_{\mu i}$, $i=1\ldots n$, expansion coefficients for the orbital φ_μ, and $q_{\mu i}(\mathbf{x})$ the respective Gaussian functions or their partial derivatives. The basic density unit in (1) is a product $P_{\mu\nu}d_{\mu i}d_{\nu j}q_{\mu i}(\mathbf{x})q_{\nu j}(\mathbf{x})$. Let both the orbitals μ and ν be of s type and both $q_{\mu i}$ and $q_{\nu j}$ be Gaussian, then the product $q_{\mu i}q_{\nu j}$ is also Gaussian and may be written in a general and normalized form as

$$g(\mathbf{x})_{\rm stat} = (2\pi)^{-3/2}(\det \mathbf{G})^{1/2}\exp\left[-\tfrac{1}{2}(\mathbf{x}-\mathbf{c})^T\mathbf{G}(\mathbf{x}-\mathbf{c})\right]. \qquad (2)$$

$\mathbf{G}$ is a 3×3 symmetric, positive definite matrix, $\mathbf{c}$ is a 3×1 column matrix representing the point in the molecule where the Gaussian is centred; and the superscript T indicates the transpose matrix. Products $q_{\mu i}q_{\nu j}$ containing higher orbitals (p, d, or f) will be considered below. The average thermal motion of a density unit, in the harmonic approximation, is described by a smearing function of the form

$$f(\mathbf{u}) = (2\pi)^{-3/2}(\det \mathbf{U}^{-1})^{1/2}\exp\left(-\tfrac{1}{2}\mathbf{u}^T\mathbf{U}^{-1}\mathbf{u}\right). \qquad (3)$$

$\mathbf{U}$ is the anisotropic vibration tensor of the density unit, $f(\mathbf{u})$ is known to be the Fourier transform of the temperature factor, and the displacement vector $\mathbf{u}$ is measured from the equilibrium position $\mathbf{c}$ of the density unit. The dynamic density, generated by thermal displacement of the static (rigid) unit (convolution approximation of Coulson & Thomas, 1971), is then given by the convolution integral

$$g(\mathbf{x})_{\rm dyn} = \int_{-\infty}^{+\infty} g(\mathbf{x}-\mathbf{c}-\mathbf{u})_{\rm stat} f(\mathbf{u})\,{\rm d}\mathbf{u}. \qquad (4)$$

So far, only special solutions of (4) are known. Hosemann & Bagchi (1962) give the solution for the case $\mathbf{G}=\alpha\mathbf{E}$, $\mathbf{U}^{-1}=\gamma\mathbf{E}$, where $\mathbf{E}$ is the unit matrix. Stewart (1968) gives the solution for $\mathbf{G}=\alpha\mathbf{E}$, $\mathbf{U}$ being diagonal, applied to the case of one-centre orbital products. In favourable situations, the problem can be adapted to these solutions and (4) can be worked out analytically, as was done by Ruysink & Vos (1974) in calculating the dynamic density of the C_2H_2 molecule. In all other cases one is forced either to integrate (4) numerically or to calculate the Fourier transform of the static density, introduce temperature factors, and calculate the Fourier series with the (dynamic) structure factors so obtained. Both procedures are usually time-consuming. The more so in the first case, the more points of the dynamic density that are calculated. In the second case the procedure becomes less economic, the fewer the points that are desired, since all Fourier coefficients are needed. In this paper we shall give the general solution for (4), and shall discuss the case where the two orbitals of a given product are centred at two different nuclei.

The convolution product of two functions in direct space is known to correspond to the product of the Fourier transforms in reciprocal space. We will find the analytical solution of (4) by transforming the product of the transforms back to direct space. The transform of (2) is

$$F(\mathbf{h})_{\text{stat}}=\exp\left(-2\pi^2\mathbf{h}^T\mathbf{G}^{-1}\mathbf{h}\right)\exp\left(2\pi i\mathbf{h}^T\mathbf{c}\right), \qquad (5)$$

and the transform of (3) is the temperature factor

$$T(\mathbf{h})=\exp\left(-2\pi^2\mathbf{h}^T\mathbf{U}\mathbf{h}\right). \qquad (6)$$

In the product of (5) and (6), we have the quadratic form $\mathbf{h}^T(\mathbf{G}^{-1}+\mathbf{U})\,\mathbf{h}$ in the exponent. Apart from this, the product has the form (5) and now, with the vibration tensor $\mathbf{U}$ being incorporated, represents the Fourier transform of the dynamic density. Hence, transformation to direct space yields

$$g(\mathbf{x})_{\text{dyn}}=(2\pi)^{-3/2}[\det(\mathbf{G}^{-1}+\mathbf{U})^{-1}]^{1/2} \times \exp\left[-\tfrac{1}{2}(\mathbf{x}-\mathbf{c})^T(\mathbf{G}^{-1}+\mathbf{U})^{-1}(\mathbf{x}-\mathbf{c})\right]. \qquad (7)$$

If we define the displacement vector $\mathbf{u}$ also with respect to the origin of $\mathbf{x}$ (and not w.r.t. $\mathbf{c}$), then the temperature factor (6) would also have a phase factor; and in our result (7) we would obtain $\mathbf{x}-2\mathbf{c}$ (instead of $\mathbf{x}-\mathbf{c}$), in full agreement with Hosemann & Bagchi's (1962) result. In our case however, it is necessary, as is customary in the crystallographic literature, to refer $\mathbf{u}$ to the equilibrium position $\mathbf{c}$, because only in this case the Gaussian distribution of the dynamic density remains centred at the point $\mathbf{c}$.

Now we shall apply (7) to the products $q_{\mu i}q_{\nu j}$ of (1). The higher orbitals (p, d, or f) can be obtained by partial differentiation of the s orbitals with respect to the nuclear coordinates (Boys, 1950). This differentiation can be carried out after the integration (4) has been performed, but then the nuclear coordinates must be accessible in the expression for the dynamic density of the s,s orbital products. Let us write representatively for the product $q_{\mu i}q_{\nu j}$ which belongs to two s orbitals, which are centred at the nuclei $\mathbf{a}$ and $\mathbf{b}$ respectively,

$$g(\mathbf{x},ss)_{\text{stat}}=\exp\left[-\tfrac{1}{2}(\mathbf{x}-\mathbf{a})^T\mathbf{A}(\mathbf{x}-\mathbf{a})\right] \times \exp\left[-\tfrac{1}{2}(\mathbf{x}-\mathbf{b})^T\mathbf{B}(\mathbf{x}-\mathbf{b})\right]. \qquad (8)$$

In order to be able to apply our solution (7) we have to express $\mathbf{a}$ and $\mathbf{b}$ in (8) in terms of the centre $\mathbf{c}$ of that Gaussian which is the product of the two factors in (8). Re-ordering of terms in (8) yields

$$g(\mathbf{x},ss)_{\text{stat}}=\exp\left[-\tfrac{1}{2}(\mathbf{x}-\mathbf{c})^T\mathbf{G}(\mathbf{x}-\mathbf{c})\right] \times \exp\left[-\tfrac{1}{2}(\mathbf{a}^T\mathbf{A}\mathbf{a}+\mathbf{b}^T\mathbf{B}\mathbf{b}-\mathbf{c}^T\mathbf{G}\mathbf{c})\right], \qquad (9a)$$

where

$$\mathbf{G}=\mathbf{A}+\mathbf{B}, \quad \mathbf{c}=\mathbf{G}^{-1}(\mathbf{A}\mathbf{a}+\mathbf{B}\mathbf{b}). \qquad (9b)$$

In general, the density unit under consideration will be placed somewhere between the positions $\mathbf{a}$ and $\mathbf{b}$ of the nuclei. Vibration tensors for such internuclear density units are derived by Scheringer (1976). The question of what tensor should be applied to a given density unit is discussed below. We introduce the vibration tensor $\mathbf{U}$ and, by properly taking into account the normalization factors, we obtain from (7) and (9):

$$g(\mathbf{x},ss)_{\text{dyn}}=[\det\mathbf{G}^{-1}\det(\mathbf{G}^{-1}+\mathbf{U})^{-1}]^{1/2} \times \exp\left[-\tfrac{1}{2}(\mathbf{x}-\mathbf{c})^T(\mathbf{G}^{-1}+\mathbf{U})^{-1}(\mathbf{x}-\mathbf{c})\right] \times \exp\left[-\tfrac{1}{2}(\mathbf{a}^T\mathbf{A}\mathbf{a}+\mathbf{b}^T\mathbf{B}\mathbf{b}-\mathbf{c}^T\mathbf{G}\mathbf{c})\right]. \qquad (10)$$

The dynamic densities of the orbital products p_is and p_ip_j ($i,j=1,2,3$ for the three directions of space) will only be given for the special cases

$$\mathbf{A}=\alpha\mathbf{E}, \quad \mathbf{B}=\beta\mathbf{E}, \quad \mathbf{G}=(\alpha+\beta)\mathbf{E}, \quad \mathbf{c}=\frac{\alpha\mathbf{a}+\beta\mathbf{b}}{\alpha+\beta} \qquad (11)$$

which are predominantly used in quantum chemical calculations. Let the p_i orbital be centred at the nucleus $\mathbf{a}$ and the s orbital at the nucleus $\mathbf{b}$, and we obtain from (10) and (11)

$$g(\mathbf{x},p_is)_{\text{dyn}}=\frac{1}{\alpha}\,\frac{\partial g(\mathbf{x},ss)_{\text{dyn}}}{\partial a_i} = P_i(\alpha+\beta)^{-1}g(\mathbf{x},ss)_{\text{dyn}}, \qquad (12a)$$

where

$$P_i=[(\mathbf{x}-\mathbf{c})^T\mathbf{F}]_i+\beta(b_i-a_i), \quad \mathbf{F}=[(\alpha+\beta)^{-1}\mathbf{E}+\mathbf{U}]^{-1}. \qquad (12b)$$

If the orbital p_i is centred at the nucleus $\mathbf{a}$ and the orbital p_j is centred at the nucleus $\mathbf{b}$, then we obtain

$$g(\mathbf{x},p_ip_j)_{\text{dyn}}=\frac{1}{\alpha\beta}\,\frac{\partial^2 g(\mathbf{x},ss)_{\text{dyn}}}{\partial a_i\partial b_j} =(\alpha+\beta)^{-2}[P_iP_j+(\alpha+\beta)\delta_{ij}-F_{ij}]g(\mathbf{x},ss)_{\text{dyn}}, \qquad (13)$$

where $\delta_{ij}=1$ for $i=j$, and $\delta_{ij}=0$ for $i\neq j$. In order to obtain the dynamic densities of the d and f orbital products, the respective higher derivatives have to be formed.

Ruysink & Vos (1974) have treated the two-centre case ($\mathbf{a}+\mathbf{b}$) in a different manner. They displace the orbitals and their respective nuclei and, from the displaced orbitals, they calculate the density. Such an approach is inconsistent with the Born–Oppenheimer approximation: for a given thermal configuration $\mathbf{a}, \mathbf{b}$ of the nuclei, the density, *i.e.* the orbital product $\varphi_a\varphi_b$, is formed immediately and then – if at all – the density unit is thermally, *i.e.* relatively slowly, displaced, but not the single orbitals. The effect of such an approach is dependent on the degree of correlation between the vibrations of the two nuclei **a** and **b**. For rigid-body translation the displacement of the orbitals is obviously equal to the displacement of the density. For the case of independent vibrations, Ruysink & Vos's (1974) integral (10) can be shown to break down into two convolution integrals over the single orbitals φ_a and φ_b respectively. Hence, in this case two thermally averaged orbitals are calculated in the first place and are then multiplied to form the density. For other cases of correlation Ruysink & Vos's integral (10) cannot easily be analysed. We are not able to judge to what extent the inconsistency of Ruysink & Vos's (1974) approach with the Born–Oppenheimer approximation will be numerically relevant.

The question remaining to be discussed is what vibration tensors **U** have to be used in (10) for the dynamic density. In this context we point out that, in the convolution approximation used here, the dynamic density is not uniquely defined because the bond densities do not behave physically according to the pattern of the convolution approximation. Only in the 'exact description' of a vibrating molecule is the dynamic density uniquely defined (within the framework of the Born–Oppenheimer approximation), *cf.* Scheringer (1976); but this description does not yield precepts of how the density distribution is to be divided into vibrating rigid units since, in principle, there are no such units in this description. Since the dynamic density is generally not calculated for its own sake, but rather for comparison with experimental results, these being also described in the convolution approximation, we obtain a clear-cut precept concerning the vibration tensors: These tensors must be taken from the dynamic model used in the refinement of the electron density, even if the tensors of this model are not correct. This precept can easily be satisfied when the experimental model of the density distribution is also formulated by means of orbital products, such as that of Coppens, Willoughby & Csonka (1971). For the two-centre orbital products, these authors used temperature factors which refer to the midpoint $(\mathbf{a}+\mathbf{b})/2$ between the nuclei. However there are several other experimental models which are not formulated in terms of orbital products but are rather constructed from points of view relevant to structure analysis, *cf. e.g.* Hirshfeld & Rabinovich (1967); Hirshfeld (1971); Brill, Dietrich & Dierks (1971). In such cases, the dynamic density can only approximately be calculated from an LCAO approach by trying to simulate the experimental model as much as possible.

How much gain in computing time is obtained with the analytical formulae presented here? We first compare the calculation of the dynamic density with the calculation of the static density. Our equations (10), (12), and (13) contain the matrices $\mathbf{F}=(\mathbf{G}^{-1}+\mathbf{U})^{-1}$ in places where the corresponding formulae for the static density would have **G**. Having introduced the vibration tensor **U**, it is no longer possible to break down the dynamic density units into a product of two dynamic orbitals. Consequently, an advantage which is used in the calculation of the static density can no longer be exploited, for N orbitals need only N elements $\varphi_\mu(\mathbf{x})$ and a (very fast) matrix multiplication $\boldsymbol{\varphi}^T\mathbf{P}\boldsymbol{\varphi}$ can be calculated. For the dynamic density, however, $N(N+1)/2$ products $P_{\mu\nu}\varphi_\mu(\mathbf{x})\varphi_\nu(\mathbf{x})$ must be calculated, since in (1), the products $q_{\mu i}q_{\nu j}$ first arise. This mode of calculation corresponds fully to the calculation of structure factors for the dynamic density; but in place of $q_{\mu i}q_{\nu j}$ we then have the transforms of these products. Since the transforms of orbital products lacking a centre of symmetry are complex, and the density units are always real, the computing time for one density point $\varrho(\mathbf{x})_{\text{dyn}}$ is about half the time needed for one structure factor.

Compared to the calculation of the dynamic density *via* structure factors, the analytical method discussed in this paper is generally much faster. If, for example, 300 density points are desired and 1500 structure factors are needed, the direct calculation is about ten times faster. Obviously the direct calculation is particularly favourable when only a few density points are desired. A further advantage of the analytical solution consists in obtaining the dynamic density without series termination errors which could otherwise only be eliminated by calculating a large number of structure factors.

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