A Method for Determining the Charge in the Peaks of Deformation Densities

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Abstract

If electron density distributions of different provenance need to be compared, the evaluation of the charge contents of peaks in deformation densities is useful (besides the usual comparison of density sections). Since deformation peaks are often of approximately ellipsoidal shape, a procedure is proposed in which a rotation ellipsoid is placed in the peak position so that it encloses the peak and separates it from the neighbouring peaks. The charge contents of the peaks are calculated by numerical integration where positive; zero and negative values of the electron density are treated separately. This can be achieved by a minor alteration of a standard Fourier program. Numerical results are presented for *p*-dicyanobenzene. The C—C bond peaks contain 0·19–0·26 electrons, and the C—N bond peak about 0·26 electrons.

General considerations

When we compared experimental and theoretical deformation densities for *p*-dicyanobenzene (Drück, Kutoglu, Scheringer, Dannöhl & Schweig, 1983) we found that the experimental bond peak in the C—N bond was only half as high as the theoretical one but was broader. Integration of the density in the peaks revealed that the charge contents were nearly equal. Hence, the experimental and theoretical density distributions did not differ as much as we had assessed by merely comparing the density sections and the peak heights.

The obvious procedure to determine the charge in a peak is to calculate a Fourier series and to sum up the density values in a region around the peak. With standard programs for Fourier synthesis, such as, for example, the program of Finger & Prince (1975) and the XRAY76 system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976), the density is calculated in a parallelepiped whose edges lie parallel to the crystal axes. In most cases, it can hardly be avoided that the parallelepiped chosen to enclose the peak also contains parts of the neighbouring peaks. By transformation to Cartesian coordinates, rectangular parallelepipeds could be generated which may fit the

shape of the peak better; however, the effort needed for additional programming is large. Berkovitch-Yellin & Leiserowitz (1975) have performed integrations over the density in deformation peaks, but they only note that 'the net charge in each bond was computed by numerical integration'.

Our approach is based on the observation that peaks of deformation densities are frequently of approximately ellipsoidal shape. Thus, we place a rotational ellipsoid around the peak. The position and shape of the ellipsoid are chosen to enclose the peak fully and separate it as well as possible from the neighbouring peaks. The Fourier synthesis is calculated in a parallelepiped (with edges parallel to the crystal axes) which encloses the ellipsoid but should not be unnecessarily large (if only one peak at a time is treated). A method for routinely determining the initial and final coordinates of such a parallelepiped is described below. When the Fourier summation is performed in the parallelepiped the condition is examined if the grid point is located inside the ellipsoid; for these grid points, the positive, zero and negative values of the density are summed up separately. From the grid points with positive density, the electronic charge in the peak is calculated according to

$$Q = \sum_i \rho(\mathbf{x}_i)\, v_i = \frac{V}{N} \sum_i \rho(\mathbf{x}_i). \tag{1}$$

v_i is the volume around the grid point $\mathbf{x}_i$ and is the same for all grid points, $v_i = v = V/N$, where V is the volume of the unit cell and N is the number of points in the unit cell.

Weiss (1966), Coppens & Hamilton (1968) and Coppens, Moss & Hansen (1980) have derived expressions for the average density $\bar{\rho}$ in a parallelepiped of any shape and orientation. The position of the parallelepiped is given by the coordinates of its centre. For a single parallelepiped around the grid point $\mathbf{x}_i$, the charge in the parallelepiped is thus given exactly by $Q_i = \bar{\rho}_i v_i$. A corresponding expression for the average density $\bar{\rho}$ in an ellipsoid of any shape and orientation was derived by Kurki-Suonio (1959); see also Coppens & Hamilton (1968). Thus, there seem to be two solutions other than ours. Firstly, in (1) $\bar{\rho}(\mathbf{x}_i)$ is used instead of $\rho(\mathbf{x}_i)$ for every subunit v_i. Within the peak,

more exact values for the charges Q_i are then calculated. However, at the margin of the peak the subunits can also contain negative densities which do not belong to the peak and, therefore, the charge Q_i becomes falsified when $\bar{\rho}(\mathbf{x}_i)$ values are used. For comparison, we have evaluated (1) with ρ and $\bar{\rho}$ and will discuss the numerical results below. The second solution consists of calculating the average density in the whole ellipsoid around the peak with Kurki-Suonio's (1959) expression. This has the advantage that one had to calculate the Fourier synthesis at only one grid point (the centre of the ellipsoid). Since, however, the peaks never assume the shape of an ellipsoid exactly, this approach is not used. (With our approach, we choose too large an ellipsoid and then exclude the regions of negative density.)

Details of programming

The only essential change in a standard program for Fourier synthesis is to add a section for computing $\sum \rho_i(\text{peak})$ in the loops over all grid points. Here, one has to find out if a grid point $\mathbf{x}_i$ is located within the ellipsoid or not. For this purpose we use the polar equation

$$r^2 = a^2/[1 - \cos^2 \theta(1 - a^2/b^2)] \qquad (2)$$

(Rottmann, 1960), where $2a$ is the rotation axis of the ellipsoid. Equation (2) is valid for all ratios of a/b. With the distances and angles which are defined in Fig. 1, we have $\cos \varphi = (s^2 + a^2 - t^2)/(2as)$. Since $\cos^2 \theta = 1 - \cos^2 \varphi$ for $\varphi = 90 - \theta$ and for $\varphi = 90 + \theta$, we obtain for all points P in space

$$r^2 = a^2 \bigg/ \left[\frac{(s^2 + a^2 - t^2)^2}{4a^2 s^2} (1 - a^2/b^2) + a^2/b^2 \right]. \qquad (3)$$

In addition to the standard parameters of the Fourier program, the coordinates of the points A and Z (in lattice units) and the half axes of the ellipsoids, a and b (in Å) are read in. In the loop over the grid points, s^2, t^2 and r^2 are computed, and the condition $s^2 \leq r^2$ is examined. If it holds, the density of the grid point is summed; this is done separately for positive, zero and negative values of the density. As a control, the volume of the ellipsoid is calculated according to $V(\text{ellipsoid}) = 4\pi ab^2/3$, and from the number M of grid points found in the ellipsoid according to $V(\text{ellipsoid}) = Mv$.

In order to determine routinely the initial and final coordinates of a parallelepiped of practical size in which the Fourier synthesis is to be calculated, we have written a special program. The user has to specify two points in the unit cell (as a rule atomic positions) which mark the line of the rotation axis. With reference to these two points, the exact position and shape (half axis) of the ellipsoid has to be specified. A Cartesian

coordinate system is established in the program with a third lattice point. The Cartesian coordinates of the points A and Z in Fig. 1, and those of the eight vertices of a rectangular parallelepiped which enveloped the ellipsoid, are calculated. All Cartesian coordinates are then transformed into lattice units. The three smallest and the three largest coordinates x,y,z of the eight vertices are then chosen to define the parallelepiped in which the Fourier synthesis is calculated. The volume of the parallelepiped thus obtained is always larger by a factor of $6/\pi = 1\cdot91$ then the volume of the ellipsoid. It may further be larger by a factor of at the most $3\sqrt{3}$ approximately if the enveloping rectangular parallelepiped is located with oblique angles towards the crystal axes.

If there are several peaks to be integrated at one time, the calculation of the Fourier series over the complete cell may be a reasonable alternative.

Application

With our modified Fourier program we have calculated the charges in the peaks of the deformation density of p-dicyanobenzene (Drück et al., 1983). To test the procedure we used ellipsoids of different sizes, between 2 and 6 Å^3. With the $X - X$ map, we found for the C—C bond peaks in the ring charges of $0\cdot19$–$0\cdot27$e (variation for the three independent peaks and different volumes), and for the C—H bonds $0\cdot19$–$0\cdot23$e. For the C—N triple bond, we found $0\cdot253$e for an ellipsoid volume of $2\cdot14$ Å^3, and $0\cdot289$e for a volume of $5\cdot41$ Å^3. The dynamic deformation density calculated from a charge-cloud model has charges of the same order (mostly a little smaller). With the static deformation density of the same model, the charges are 15–30% larger because the peaks are higher but not correspondingly reduced in width. Furthermore, the charges cannot be determined unequivocally because there is some overlap of the peaks in our deformation densities. Our values for the peak charges are in good
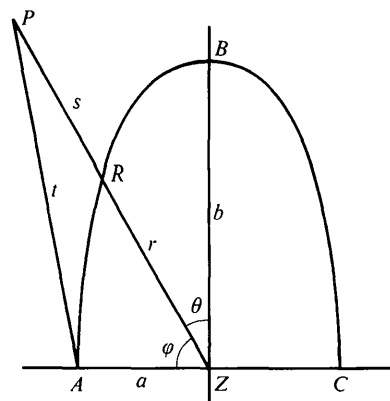

Fig. 1. Definitions referring to the ellipsoid; axis of rotation $= AC$, $a = AZ$, $b = BZ$, $s = PZ$, $t = PA$, $r = RZ$.

agreement with those found by Berkovitch-Yellin & Leiserowitz (1975, 1977).

For two peaks, we have calculated the charge with several grids and also with $\bar{p}$ instead of p. For the C—N peak of p-dicyanobenzene ($X - X$ map), the results are given in Table 1. We may draw the following conclusions. Even with a coarse grid of only 25 points per cell edge ($\Delta = 0.15, 0.26, 0.29$ Å, respectively, 233 grid points in the ellipsoid of 2.41 Å^3) we obtain a numerical accuracy of 0.001e (calculated with p). For fine grids, the calculations with p and $\bar{p}$ produce nearly identical results (100 points per cell edge give rise to a difference of only 0.0005e). This is expected since the factor $S_1 S_2 S_3$ of Coppens & Hamilton (1968) is now nearly one. If we make the grid coarser, the charge calculated from p increases whereas that from $\bar{p}$ decreases. Here the different treatment of the subunits located at the margin of the peak becomes obvious. With p, the negative density outside the peak is neglected, whereas with $\bar{p}$ it is fully taken into account. Since we are only interested in the region with positive density, the calculation with $\bar{p}$ is less accurate for coarse grids, see Table 1 for grids 25 and 10 compared to grid 100. Thus, as long as one uses grids with subunits of equal size (which cannot be avoided with standard Fourier programs), the simpler calculation with p is to be preferred. That such a coarse grid of 25 points per cell edge ($a = 3.78, b = 6.46, c = 7.28$ Å) will do may be because experimental deformation densities do not possess large gradients. With theoretical static deformation densities which have more pointed peaks, this situation may be different and finer grids may be required. The figures in Table 1 also show that the exact separation of a peak from its neighbours will be, in many cases, the crucial problem and not the numerical accuracy.

Finally, we remark that, as a control, we have also calculated the charges with IBM double precision (64 bits). The deviations from the values given in Table 1 are at most 0.0004e and thus can be neglected. [However, we point out that, with numerical integration over larger volumes than ellipsoids around peaks, there are deviations from the expected results when fine grids and single IBM precision (32 bits) are used. Thus, with integration over the full unit cell which we performed as a program control, we found only

Table 1. *Results of the integration for the* C—N *peak in p-dicyanobenzene*

The volume of the chosen ellipsoid is 2.41 Å^3. 'Grid' denotes the number of points per cell edge. M is the number of points in the volume of the ellipsoid with the respective grid.

Grid	M	Q from p	Q from $\bar{p}$
100	15058	0.2535	0.2530
75	6366	0.2537	0.2528
50	1885	0.2543	0.2522
25	233	0.2544	0.2463
10	12	0.2721	0.1909

63.5e instead of the expected 66e when grid 100 was used. With double precision these losses did not occur and the 66e were found accurately to six decimal places.]

The proposed method indicates that peak integration can be performed without an essential reorganization of a standard Fourier program and with little computing time, and thus can be routinely performed in the study of deformation densities.

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