Pseudo-Gaussian peak integrals for Fourier-map interpretation. By F. PAVELČÍK, *Department of Inorganic Chemistry, Faculty of Natural Sciences, Komensky University, 842 15 Bratislava, Slovak Republic*

Abstract

For the purpose of the automatic assignment of atomic types to electron-density peaks, the use of peak integrals calculated in the pseudo-Gaussian approximation, instead of peak heights, is suggested. A simple formula is derived.

In the final stage of an automatic structure determination, or in automatic structure refinement, it is necessary to assign atomic types to individual Fourier peaks. This is usually done on the basis of peak heights (Pavelčík, 1986b; Cascarano, Giacovazzo, Camalli, Spagna & Watkin, 1991). Problems can arise with the assignment of atomic types to atoms of similar atomic number but different thermal motion. For example, an O atom in a terminal group or a solvent molecule can have a peak height lower than that of an N or C atom located near the centre of gravity of the molecule. To overcome this problem, the use of pseudo-Gaussian peak integrals instead of peak heights is suggested. The peak integral is defined as the total number of electrons in the peak volume.

An electron-density peak can be approximated by

$$\rho(x,y,z) = H \exp\left[-\left(x^2 a_x^{-2} + y^2 a_y^{-2} + z^2 a_z^{-2}\right)\right], \quad (1)$$

where H is the peak height in e Å^{-3} and x, y and z are Cartesian coordinates in the local coordinate system with its origin at the atomic centre.

The integral of this peak is

$$I = kH a_x a_y a_z, \quad (2)$$

where k contains integration constants. In the process of peak-position interpolation (Rollett, 1965; Pavelčík, 1986a), curvatures at peak maxima are estimated ($d_{xx} = \partial^2\rho/\partial x^2$, $d_{yy} = \partial^2\rho/\partial y^2$, $d_{zz} = \partial^2\rho/\partial z^2$). The second derivative for a Gaussian peak at maximum is

$$\partial^2\rho/\partial x^2 = -2H a_x^{-2}. \quad (3)$$

The integral of the electron-density peak can be approximated by

$$I = kH[(-2H/d_{xx})(2H/d_{yy})(2H/d_{zz})]^{1/2} \quad (4)$$

(the same formula is also valid for fractional coordinates). The peak integrals can be normalized on the basis of the known contents of the unit cell,

$$F(000) = \sum I_i, \quad (5)$$

where $F(000)$ is the total number of electrons and summation is over all peaks found in the Fourier map in the final stage of structure determination (*e.g.* partially refined with $R < 0.15$).

Table 1. *Result of Fourier calculation of isotropically refined structure* ($R = 0.137$) *of FUNG*

Atom types ('Name') are assigned automatically on the basis of peak heights. Pseudo-Gaussian peak integrals (PGPI), correct atom types ('Type') and isotropic temperature factors [B_{iso} (Å^2)] are also given.

No.	Name	x	y	z	Height	PGPI	Type	B_{iso}
1	Cl(1)	0.0888	0.4147	0.1458	17.11	16.48	P	5.23
2	S(2)	0.1269	0.4934	−0.3071	15.96	17.22	S	6.32
3	S(3)	0.1721	0.4218	0.2798	14.17	15.24	S	7.46
4	P(4)	0.0078	0.3126	0.3704	11.46	17.01	Cl	10.40
5	O(5)	0.0711	0.4535	0.0095	7.67	8.64	O	5.71
6	O(6)	0.0848	0.3762	0.0115	7.21	8.67	O	6.50
7	O(7)	0.0165	0.4108	0.2404	6.98	7.95	O	6.51
8	O(8)	0.1565	0.5907	−0.1947	6.76	9.55	O	6.07
9	N(9)	0.1217	0.5823	0.0888	6.45	6.73	N	4.81
10	N(10)	0.0925	0.5591	0.2295	5.85	7.13	N	6.10
11	C(11)	0.1173	0.5193	−0.1065	5.61	6.13	C	4.29
12	C(12)	0.1317	0.5667	−0.0766	5.47	6.27	C	4.59
13	C(13)	0.0917	0.4980	0.0326	5.41	6.05	C	4.58
14	C(14)	0.1359	0.6283	0.1345	5.00	6.03	C	5.39
15	C(15)	0.0792	0.5188	0.1984	4.93	5.95	C	5.19
16	C(16)	0.0916	0.6604	0.0556	4.54	6.01	C	6.18
17	C(17)	0.0076	0.4006	0.4199	4.34	6.04	C	7.19
18	C(18)	0.2041	0.5170	−0.4027	4.30	5.81	C	5.77
19	C(19)	0.1912	0.6389	0.2387	4.14	6.19	C	7.04
20	C(20)	0.1414	0.3682	−0.1128	4.11	5.32	C	7.17
21	C(21)	0.1042	0.7040	0.1065	4.01	5.72	C	7.44
22	C(22)	0.1609	0.7139	0.2105	3.99	5.86	C	8.12
23	C(23)	0.2057	0.6830	0.2806	3.95	5.19	C	8.11
24	C(24)	−0.0374	0.3599	0.4424	3.85	5.23	C	7.60
25	C(25)	0.1304	0.3268	−0.2052	3.42	5.05	C	10.65
26	C(26)	0.1217	0.2877	−0.0826	3.03	4.83	C	12.01
27	C(27)	0.1884	0.3175	−0.3315	2.81	4.46	C	11.59
28	C(28)	0.0817	0.4143	0.4992	1.48	1.26	−	−

The peak integrals are conveniently expressed in electrons. They are still affected by Fourier ripples, anisotropic motion and redistribution of electrons due to chemical bonding.

The test calculations showed that there is in general smaller dispersion in peak integrals of atoms of the same type and atoms of different atomic types are better clustered in comparison with peak heights. An example for FUNG [$C_{17}H_{22}ClN_2O_4PS_2$, $Z = 8$, *Pccn* (Vrabel, Pavelčík, Kello, Miertus, Konečny & Lokaj, 1987)] is given in Table 1. Chlorine is a terminal atom, whereas phosphorus is the central atom in a thiophosphate group. The minimum and maximum peak heights for C atoms are 2.81 and 5.61; the difference is 2.80. The minimum and maximum peak integrals are 4.46 and 6.13; the difference is 1.67.

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