THE USE OF SIGN RELATIONSHIP IN THE DETERMINATION OF HEAVY
ATOM CONTAINING CRYSTAL STRUCTURES.   I.   A Sign-refinement
Procedure

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ABSTRACT

*For crystals composed entirely of light atoms with atomic numbers close
to each other, the Sayre equation gives the sign relation of the structure
amplitudes.   It has been successfully applied to the determination of
crystal structures of organic compounds.   Nevertheless, for crystals contain-
ing "heavy atoms", the Sayre equation is no longer valid; instead, the so-
called "heavy atom method" is generally used.   In the present work the inter-
relation between the respective signs of structure amplitudes, the Sayre
equations, and heavy atoms has been considered, and the possibility of
combining the heavy atom method and that of Sayre is pointed out.   This leads
to the suggestion of a sign-refinement procedure, with which the initial
signs of heavy atoms can be refined to the correct signs of the structure
amplitudes.   This procedure has been verified with a hypothetical one-
dimensional structure and proved to be satisfactory.   Some problems concern-
ing its application to the actual crystal-structure analysis are also
discussed.*

I.   INTRODUCTION

Ever since Sayre[1] introduced the sign relationship of the structural
amplitude in 1952, this method has been widely applied directly to the
determination of crystal structures.   However, the Sayre equation is only
valid for the crystal structures containing light atoms of the same kind or
with atomic numbers close to each other.   For "heavy atoms", the sign
derived from the Sayre equation no longer represents the true sign of the
structural amplitudes.   To solve this problem, Woolfson[2] has added a
correctional term in the Sayre equation; namely, $B, \frac{1}{V^2} \times \sum_{h'}\sum_{h''} F_{h'} F_{h''} F_{h-h'-h''}$,

which is suitable for the crystal structures containing two kinds of atoms.
However, the computations of the correctional term are rather tedious, not
suitable for general applications.

Starting from another angle of approach and considering a rather easy
determination of the position of the heavy atoms, the author deems it
possible to modify the Sayre equation thus obtained, which not only appears
to be simple but also indicates the interrelation between the respective
signs of "heavy atoms", "Sayre equation", and "structure amplitudes".   The
modified equation may bridge the gap between the "heavy atom method" and the
"sign relationship method".

II. THE MODIFIED SAYRE EQUATION

According to Sayre's[1] derivations, for any crystal structures,

$$F_H^{sq} = \frac{1}{V} \sum_{H'} F_{H'} F_{H-H'} \equiv G_H, \tag{1}$$

in which F_H^{sq} is the structure amplitude of "square crystals". If the crystal contains only one kind of atoms, then

$$F_H^{sq} = f^{sq} \sum_j \exp 2\pi i \, \mathbf{H} \cdot \mathbf{r}_j = \frac{f^{sq}}{f} \sum_j f \exp 2\pi i \, \mathbf{H} \cdot \mathbf{r}_j = \frac{f^{sq}}{f} F_H \equiv \frac{1}{\varphi} F_H, \tag{2}$$

in which f is the atomic scattering factor; f^{sq} is the scattering factor of the "square atom". Here, the sign of the structure amplitude F_H is the same as that of G_H (henceforth called "Sayre sign").

Let the crystal contain two kinds of atoms, light P and heavy Q. We have

$$F_H^{sq} = \sum_P f_P^{sq} \exp 2\pi i \, \mathbf{H} \cdot \mathbf{r}_P + \sum_Q f_Q^{sq} \exp 2\pi i \, \mathbf{H} \cdot \mathbf{r}_Q, \tag{3}$$

Let
$$\varphi_P = f_P / f_P^{sq}; \quad \varphi_Q = f_Q / f_Q^{sq},$$

then
$$F_H^{sq} = \frac{1}{\varphi_P} F_H + \left(\frac{1}{\varphi_Q} - \frac{1}{\varphi_P} \right)(F_H)_Q, \tag{4}$$

in which $(F_H)_Q$ is the contribution of the structure amplitude by the heavy atoms, and its sign will be called "heavy atom sign" henceforth.

Substituting equation (4) into (1), we have

$$F_H = (A_i)_P G_H - \left[\frac{\varphi_P}{\varphi_Q} - 1 \right](F_H)_Q. \tag{5}$$

In comparison with the equivalent terms in Sayre equation, there is only one additional correction term in equation (5), namely,

$$-\left[\frac{\varphi_P}{\varphi_Q} - 1 \right](F_H)_Q.$$

This correction term can easily obtained by knowing the position of the heavy atom.

To verify the validity of equation (5), we shall use Woolfson's[2] one-dimensional crystal model:

Lattice parameter: $a = 20$ Å; Space group: $P\bar{1}$;

Atomic coordinates: $X_{P_1} = \pm 0.0625$; $X_{P_2} = \pm 0.1429$; $X_{P_3} = \pm 0.2500$;
$X_{P_4} = \pm 0.4500$; $X_Q = \pm 0.3333$.

Atomic electron density distributions and scattering factors:

$$(\rho_a)_P = 6\sqrt{2}\,e^{-2\pi u^2}; \quad (\rho_a)_Q = 12\sqrt{2}\,e^{-2\pi u^2};$$

$$f_P = \int_{-\infty}^{\infty}(\rho_a)_P \cos 2\pi S u\, du = 6\,e^{-\frac{1}{2}\pi S^2}; \quad f_Q = 12\,e^{-\frac{1}{2}\pi S^2};$$

$$f_P^{sq} = \int_{-\infty}^{\infty}(\rho_a)_P^2 \cos 2\pi S u\, du = 36\,e^{-\frac{1}{4}\pi S^2}; \quad f_Q^{sq} = 144\,e^{-\frac{1}{4}\pi S^2};$$

$$\varphi_P = \frac{1}{6}\,e^{-\frac{\pi}{4}S^2}; \quad \varphi_Q = \frac{1}{12}\,e^{-\frac{\pi}{4}S^2}.$$

where $S = 2\sin\theta/\lambda$. Now, equation (5) becomes $F_H = \varphi_P G_H - (F_H)_Q$.
See Table 1 for verified results. From the data in Table 1, the deviation
factor of equation (5) is $\quad R = \sum_H \big||\mathscr{F}_H| - |F_H|\big| \Big/ \sum_H |F_H| = 1.8\%$

(all R's thus referred to have the same meaning in this paper). This small
discrepancy is probably due to the broken tail effect of the series as well
as the atomic overlapping.

Although equation (5) is suitable only to the crystal containing one
kind of "heavy atoms", yet when the "heavy atoms" are of more than one kind,
as long as their positions are known, similar correction terms can be added
to the equation (5) so as not to increase the degree of complexity excessive-
ly.

Table 1

H	S	φ_P	G_H	$\varphi_P G_H$	$(F_H)_Q$	$\mathscr{F}_H$	F_H	Δ_H
0	0.00	0.1667	575.7	95.94	24.00	71.94	72.00	0.06
1	0.05	0.1667	−100.43	−16.74	−11.96	−4.88	−4.84	0.04
2	0.10	0.1653	−121.43	−20.07	−11.80	−8.27	−8.34	0.07
3	0.15	0.1633	204.50	33.40	23.15	10.25	10.35	0.10
4	0.20	0.1612	−110.02	−17.74	−11.26	−6.48	−6.66	0.18
5	0.25	0.1587	−178.24	−28.29	−10.89	−17.40	−17.47	0.07
6	0.30	0.1552	174.13	27.03	20.82	6.21	6.31	0.10
7	0.35	0.1512	−87.85	−13.28	−9.90	−3.38	−3.33	0.05
8	0.40	0.1467	−137.79	−20.21	−9.33	−10.88	−11.06	0.18
9	0.45	0.1420	232.28	32.98	17.47	15.51	15.77	0.26
10	0.50	0.1366	−330.16	−45.10	−8.10	−37.00	−37.34	0.34
11	0.55	0.1312	−133.20	−17.48	−7.47	−10.01	−9.95	0.06
12	0.60	0.1252	211.76	26.51	13.63	12.88	13.42	0.54
13	0.65	0.1192	−20.78	−2.48	−6.18	3.70	3.67	0.03
14	0.70	0.1132	−79.71	−9.02	−5.56	−3.46	−3.35	0.11
15	0.75	0.1072	253.36	27.16	9.93	17.23	17.61	0.38
16	0.80	0.1007	5.92	0.60	−4.39	4.99	4.77	0.22
17	0.85	0.0947	−97.88	−9.27	−3.86	−5.41	−6.04	0.63
18	0.90	0.0880	134.19	11.81	6.72	5.09	5.43	0.34
19	0.95	0.0820	−94.47	−7.75	−2.90	−4.85	−5.19	0.34
20	1.00	0.0760	20.92	1.59	−2.49	4.08	4.05	0.03
21	1.05	0.0700	108.72	7.61	4.25	3.36	3.54	0.18
22	1.10	0.0647	−59.14	−3.83	−1.79	−2.04	−2.28	0.24
23	1.15	0.0587	−91.68	−5.38	−1.50	−3.88	−4.10	0.22
24	1.20	0.0540	76.08	4.11	2.50	1.61	1.76	0.15
25	1.25	0.0494	−77.23	−3.82	−1.03	−2.79	−2.91	0.12
26	1.30	0.0440	−79.10	−3.48	−0.85	−2.63	−2.74	0.11

* In Table 1: $\mathscr{F}_H \equiv \varphi_P G_H - (F_H)_Q$;

F_H --- structure amplitude computed by the atomic coordinates and its corresponding scattering factor;

$\Delta_H \equiv |\mathscr{F}_H - F_H|$.

III. INTERRELATION OF "HEAVY ATOM SIGN", AND THE STRUCTURAL AMPLITUDE SIGN

Rewriting equation (5), we have

$$\varphi_r G_H = F_H + \left[\frac{\varphi_r}{\varphi_0} - 1\right](F_H)_0, \tag{6}$$

in which the left-hand side is the "Sayre sign"; the first term on the right-hand side is the structure amplitude sign, and the second term is the heavy-atom sign (Notice that in general $\frac{\varphi_r}{\varphi_0} \geq 1$). It is obvious that when the crystal contains only one kind of atoms, the second term on the right-hand side of equation (6) is zero, and the structure amplitude sign is the same as the "Sayre sign". This is the conclusion reached by Sayre in 1952. When the crystal contains two kinds of atoms, we have the following two cases:

(1) If the heavy-atom sign is the same as the structure-amplitude sign, then the Sayre sign is equal to the structure-amplitude sign;

(2) If the heavy-atom sign is opposite to the structure-amplitude sign, then we again have two cases:

(a) $\underline{If}$ $|F_H| > \left|\left[\frac{\varphi_r}{\varphi_0} - 1\right](F_H)_0\right|,$ then the Sayre sign is still the same as the structure-amplitude sign;

(b) $\underline{If}$ $|F_H| < \left|\left[\frac{\varphi_r}{\varphi_0} - 1\right](F_H)_0\right|,$ then the Sayre sign is the opposite to the structure-amplitude sign.

Hence, it is seen that in spite of the fact that the crystal contains heavy atoms, the majority of the Sayre sign still correctly represents the structure-amplitude sign, and is closer to the actual conditions than the heavy-atom sign. The data in Table 1 can be considered as a verfied instance: among the 26 structure-amplitude signs in Table 1, there are 3 opposite to those of the heavy atom signs, but there is only one with a sign opposite to that of the Sayre sign.

The above-mentioned fact suggests the possibility of combining the heavy atom method and the Sayre method. It further leads to the suggestio: of a sign-refinement procedure of the heavy atom sign from equation (5) to finally obtain the structure amplitude sign.

IV. THE APPLICATION OF THE MODIFIED EQUATION -- SIGN-REFINEMENT TEST

The sign-refinement procedure can be divided into three steps:

Step I. From the starting sign, find the corresponding G_H for every

VI. CONCLUSION

We have introduced the sign-refinement method which has been experimentally tested to be valid with a hypothetical crystal. A further test is needed to verify the validity of this method for a real crystal. However, from the data on hand, it is seen that this may be a practical method to combine the heavy atom method and the sign relation method, and also possesses special features that either the heavy atom method or the sign relation method lacks. In determining the crystal structures containing heavy atoms, the heavy atom method is to utilize the heavy atom signs to obtain the whole structure through the successive electron density syntheses. The method in this paper is in substance a sign-refinement procedure to replace the whole or a part of the electron density approximation procedure. In so doing, there may be two advantages: one being to improve the heavy atom signs without knowing the actual structural model in order to lesson the difficulty in interpreting the electron density maps; the other being easier to standardize or automize than the electron density gradual approximation method. Should we integrate the refinement procedure into the electron computation procedure, under the most favorable conditions, it is possible to start with the heavy atom signs to derive the final electron density maps automatically. Finally, it is to be pointed out that this method as introduced in this paper is also applicable to the noncentrosymmetric crystals by treating the real and imaginary parts of the structure amplitude separately. Relevant discussions in detail can be cited from another article[6] by this author.

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