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Use of the integrated minimum function in heavy-atom structures

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Summary. A method for identifying a structure image from Patterson maps when the heavy atoms occupy special positions in the space group is described and an example for a simple structure is given.

Introduction

The integrated minimum function of Raman and Lipscomb (1961) is defined as:

$$\mathrm{MA}(\vec{u}) = \sum_{\vec{r}} \mathrm{Min}\,[\mathrm{P}(\vec{r}), \mathrm{P}(\vec{r} + \vec{u})],$$

where the summation is taken over all $\vec{r}$ in the Patterson space. $\mathrm{P}(\vec{r})$ and $\mathrm{P}(\vec{r} + \vec{u})$ are the Patterson function at argumente $\vec{r}$ and $\vec{r} + \vec{u}$, and Min $[\mathrm{P}(\vec{r}), \mathrm{P}(\vec{r} + \vec{u})]$ is the minimum at these two argumente. This function attains a maximum whenever $\vec{u}$ is an interatomic vector in the crystal, and gives all information regarding the function at a single value of the argument $\vec{u}$.

Very often it happens that some atoms lie in special positions in the space group and do not contribute to certain reflections. Let the atoms in the special positions be called S atoms and those in general positions G atoms. Let $\mathrm{P_G}$ denote the Patterson function for which only the atoms in the general positions contribute and let $\mathrm{P_{GS}}$ indicate the Patterson function for which all the atoms contribute. $\mathrm{P_G}$ is calculated by summing the reflections for which the atoms in special positions do not contribute. This distinction is possible only when considerable number of reflections exist for which S atoms do not contribute. Let SS, SG, and GG denote the interatomic vectors between the S and G atoms. Let $\mathrm{MA_G}(\vec{u})$ and $\mathrm{MA_{GS}}(\vec{u})$ denote the respective integrated minimum functions.

$$\text{Let } R = \frac{\mathrm{MA_{GS}}(\vec{u})}{\mathrm{MA_G}(\vec{u})}.$$

Patterson function $\mathrm{P_G}$ does not contain any vector of the type SS and SG, whereas the function $\mathrm{P_{GS}}$ contains SS, SG, and GG vectors. Hence the ratio R

Table 1

Vector type	R	Patterson peak height	Vector type	R	Patterson peak height
KB	1.3	23	BB	1.21	−13
KB	1.3	28	BB	1.25	139
KB	1.3	47	BB	0.92	97
KB	1.5	26	BB	1.10	−8
KB	1.39	36	BB	0.99	92
KB	1.39	21	OO	1.26	51
KO	1.36	197	OO	1.00	−3
KO	1.35	36	OO	1.11	138
KO	1.30	86	OO	1.19	88
KO	1.32	73	OO	1.23	74
KO	1.16	138	OO	1.15	25

will give a value close to 1 whenever $\vec{u}$ is a GG vector, and a value greater than 1when $\vec{u}$ is either a SS or a SG vector. This is possible only when the S atoms are heavy and contribute significantly above the background.

Data and results

The effectiveness of this method was put to test by using the date for $KB_5O_6(OH)_4 \cdot 2H_2O$ (Zachariasen and Plettinger, 1963). This compound is orthorhombic, the space group is *Aba* and there are four molecules per unit cell. The potassium atoms lie in special positions and do not contribute to reflections of the type $h + k = 2n$ and $k + l = 2n$.

P_G and P_{GS} were computed using these data and the ratio R was calculated for different vectors. KK vectors were not used since the potassium positions are special.

The results for different vectors and the corresponding R values and Patterson function values are shown in Table 1. We find that all the KB and KO vectors have R values greater than 1.29, with the exception of one KO vector, whereas all the BB and OO vectors have R values smaller than 1.26 and many have values close to unity. We also note that most of the KB and KO peaks cannot be picked out from the Patterson maps, as their values are similar to OO and BB peaks.

This method seems capable of distinguishing between the GS and GG vectors, thereby aiding the construction of the image to the structure.

References

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