SHORT COMMUNICATIONS

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An alternative derivation of peaks in the γ' synthesis.

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Abstract

By Taylor expansion, peak position and peak heights in the γ' synthesis are derived. The first approximation gives a fairly good evaluation for heights of P and Q peaks in the range of convergence.

An approximate derivation of peaks in the γ' synthesis was presented by Ramachandran & Srinivasan (1970) by convolution of the modulus $|F_N|$ and phase $\exp(i\varphi_P)$ syntheses. An alternative derivation is presented here.

Notation

F_N = structure factor of the complete structure
F_P = structure factor of the known atoms
F_Q = structure factor of the unknown atoms
φ_P = phase of F_P
f_{Pi}, f_{Qi} = scattering factors of the P and Q atoms
$\Sigma_P = \sum_{i=1}^{P} f_{Pi}^2$,
$\Sigma_Q = \sum_{i=1}^{Q} f_{Qi}^2$
$\mathbf{x}_{Pi}, \mathbf{x}_{Qi}$ = positions of the P and Q atoms

The γ' synthesis for noncentrosymmetric structures is calculated with coefficients

$$\Phi = |F_N| \exp(i\varphi_P) = (|F_N|^2/|F_P|^2)^{1/2} F_P. \quad (1)$$

Substitution of $|F_N|^2$ by $(F_P + F_Q)(F_P^* + F_Q^*)$ gives

$$\Phi = (1 + |F_Q|^2/|F_P|^2 + F_Q^*/F_P^* + F_Q/F_P)^{1/2} F_P. \quad (2)$$

In cases where the greater part of structure is known, $|F_P| > |F_Q|$, a Taylor expansion

$$\sqrt{1+x} = \sum_{k=0}^{\infty} \binom{\frac{1}{2}}{k} x^k = 1 + \tfrac{1}{2}x - \tfrac{1}{8}x^2 + \tfrac{1}{16}x^3 \ldots \quad (3)$$

can be used. The series is convergent for $x < 1$, that means for $|F_Q/F_P| < \sqrt{2} - 1$. Coefficients of γ' can be expressed by

$$\Phi = \sum_{k=0}^{\infty} \binom{\frac{1}{2}}{k} \sum_{i=0}^{k} \binom{k}{i} \times \sum_{j=0}^{i} \binom{i}{j} \left(\frac{F_Q}{F_P}\right)^j \left(\frac{F_Q^*}{F_P^*}\right)^{i-j} \left(\frac{|F_Q|}{|F_P|}\right)^{2(k-i)} F_P \quad (4)$$

and in the first approximation we have

$$|F_N| \exp(i\varphi_P) \doteq F_P + \frac{|F_Q|^2}{2F_P^*} + \frac{F_Q^*}{2} \exp(2i\varphi_P) + \tfrac{1}{2}F_Q. \quad (5)$$

Peak heights from this derivation in Table 1 are slightly different from that of Ramachandran & Srinivasan (1970). For comparison with the β or weighted γ' syntheses see Main (1979). From the second approximation comes dependence of the Q peak height on the Σ_Q/Σ_P and it is $0{\cdot}5 f_{Qi}(1 - \Sigma_Q/2\Sigma_P)$.

To analyze the relative heights of the P and Q peaks we selected from the Taylor expansion the coefficients of F_P and F_Q. The other terms contribute to general background. The partial sums are abbreviated by $R_P F_P$ and $R_Q F_Q$, where R_P and R_Q are real coefficients:

$$R_P = \sum_{k=0}^{\infty} \binom{\frac{1}{2}}{k} \sum_{i=0}^{[k/2]} \binom{k}{2i} \binom{2i}{i} (|F_Q|^2/|F_P|^2)^{k-i} \quad (6)$$

$$R_Q = \sum_{k=1}^{\infty} \binom{\frac{1}{2}}{k} \sum_{i=0}^{[(k-1)/2]} \binom{k}{2i+1} \binom{2i+1}{i+1} (|F_Q|^2/|F_P|^2)^{k-i-1}, \quad (7)$$

$[x]$ is the integer part of x.

The Fourier transform of $(|F_Q|^2/|F_P|^2)^n F_X$ (where $X = P$ or Q) is difficult to interpret from the point of peak heights and peak positions. The resulting synthesis is a convolution of F_X with $(|F_Q|^2/|F_P|^2)^n$. The latter is calculated with real and positive coefficients so that the highest peak is at the origin and the dominant peaks in the resulting synthesis are the same as in individual F_P and F_Q syntheses. From

Table 1. *Peaks in the γ' synthesis for a non-centrosymmetric structure*

Term	Position	Scattering factor	Number	Type
F_P	$\mathbf{x}_{Pi}$	f_{Pi}	P	Known
$\frac{1}{2}F_Q$	$\mathbf{x}_{Qi}$	$\frac{1}{2}f_{Qi}$	Q	Wanted
$\frac{1}{2}F_Q^* \exp(2i\varphi_P)$	$2\mathbf{x}_{Pi} - \mathbf{x}_{Qj}$	$\frac{1}{2}f_{Pi}f_{Qj}/\Sigma_P$	PQ	Background
	$\mathbf{x}_{Pi} + \mathbf{x}_{Pj} - \mathbf{x}_{Qk}$	$f_{Pi}f_{Pj}f_{Qk}/\Sigma_P$	$P(P-1)Q/2$	Background
$\dfrac{\lvert F_Q\rvert^2}{2F_P^*}$	$\mathbf{x}_{Pi}$	$\frac{1}{2}f_{Pi}\Sigma_Q/\Sigma_P$	P	Known
	$\mathbf{x}_{Qi} - \mathbf{x}_{Qj} + \mathbf{x}_{Pk}$ $(i \neq j)$	$\frac{1}{2}f_{Qi}f_{Qj}f_{Pk}/\Sigma_P$	$PQ(Q-1)$	Background
	$\mathbf{x}_{Pi} + \mathbf{x}_{Pj} - \mathbf{x}_{Pk}$ $(i \neq j, j \neq k)$	$-\frac{1}{2}f_{Pi}f_{Pj}f_{Pk}\Sigma_Q/\Sigma_P^2$	$P^2(P-1)$	Background

0108-7673/84/020161-02$01.50

the interpretation of $(|F_Q|^2/|F_P|^2)F_P$ (Ramachandran & Srinivasan, 1970) and from n successive convolutions of $|F_Q|^2/|F_P|^2$ terms one can evaluate the contribution to peak heights as $(\Sigma_Q/\Sigma_P)^n f_X$. A lot of lesser peaks from this synthesis in more general positions will contribute to the general background.

The results of numerical summation for R_P and R_Q, Table 2, showed that in the range of convergence the peak heights of P and Q atoms are not very sensitive to the value of Σ_Q/Σ_P. The P enhancement obtained from the first approximation and the Σ_Q/Σ_P dependence of the Q peak heights from the second approximation are overestimated. But all of this is derived for the rather limited range of Σ_Q/Σ_P.

Table 2. *The numerical values of R_P and R_Q obtained by summation of the first* 51 *terms* ($k_{max} = 50$) *of the expansion*

$\|F_Q\|/\|F_P\|$	R_P	R_Q
0·00	1·000	0·500
0·10	1·002	0·499
0·20	1·010	0·498
0·30	1·023	0·494
0·40	1·040	0·490

The fact that the peak heights are almost insensitive to Σ_Q/Σ_P shows that the γ' synthesis is a very good tool for location of unknown atoms and for refinement of atom positions and electron density (especially as $2F_o - F_c$ synthesis) in the final stages of structure determination and no special synthesis seems to be necessary.

References

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The consequences of the neglect of TDS correction for temperature parameters: erratum.

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Abstract

In the paper by Stevenson & Harada [*Acta Cryst.* (1983), A**39**, 202–207] the calculated values of Δ' (and consequently $\delta\bar{B}$) in Table 1 are in error. For KCl and BaF_2 the conventional (rather than primitive) unit-cell volumes were mistakenly used when calculating q_{ZB}. For CdS and CdSe the factor used to get q'_{ZB} from q_{ZB} was incorrect. The new (corrected) Table 1 is given below. The agreement between $\delta\bar{B}$ and $\delta\bar{B}_{obs}$ is, with the new $\delta\bar{B}$ values, generally better; with $\delta\bar{B}$ for KCl closer to the $\delta\bar{B}_{obs}$ value given by Cooper & Rouse [*Acta Cryst.* (1968), A**24**, 405–410], namely 0·16 Å^2. The calculated value of the '*overall*' temperature parameter for CdS becomes 1·29 Å^2. It should also be noted that there is a factor of 2 missing from the denominator of equation (15).

Table 1. *Details for comparison of experimental and theoretical Δ' values for each of four studies*

The size of the detector aperture is given with the width first in each case.

	Experimental conditions							Results			
	Scan mode	Scan width (°θ)	Detector aperture (°)	Lattice parameters a (Å)	c (Å)	q_s (Å^{-1})	q_{ZB} (Å^{-1})	Δ'	Δ'_{obs}	$\delta\bar{B}$ (Å^2)	$\delta\bar{B}_{obs}$ (Å^2)
KCl	ω	2·5	1·5×1·5	6·290	–	0·1702	0·9837	0·073	0·087 (0·105)	0·14	0·16 (0·20)
CdS	ω–2θ	3·0	2·0×1·5	4·136	6·713	0·1991	0·8413	0·080	0·057	0·11	0·08
CdSe	ω–2θ	3·0	2·0×1·5	4·299	7·010	0·1991	0·8081	0·083	0·072	0·12	0·11
BaF_2	ω–2θ	2·4	2·2×3·2	6·196	–	0·1682	0·9986	0·062	0·066	0·05	0·05

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