Fig. 1 shows that the various coordinates in (15) can be replaced as follows:

$$Y_1 = r_{12} \sin \varphi_1 \qquad Z_1 = r_{12} \cos \varphi_1$$
$$Z_3 = r_{23} \qquad Z_4 = r_{23} - r_{34} \cos \varphi_2$$
$$(X_4^2 + Y_4^2)^{1/2} = r_{34} \sin \varphi_2 \,,$$

where r_{mn} is the distance between atoms m and n. Equation (15) for the variance of the torsion angle, τ, then becomes:

$$\begin{aligned}\sigma^2(\tau) = & \frac{\sigma_1^2}{r_{12}\sin^2\varphi_1} + \frac{\sigma_2^2}{r_{23}^2}\left[\left(\frac{r_{23}-r_{12}\cos\varphi_1}{r_{12}\sin\varphi_1}\right)^2 \right. \\ & \left. -2\left(\frac{r_{23}-r_{12}\cos\varphi_1}{r_{12}\sin\varphi_1}\right)\cot\varphi_2\cos\tau + \cot^2\varphi_2\right] \\ & + \frac{\sigma_3^2}{r_{23}^2}\left[\cot^2\varphi_1 - 2\left(\frac{r_{23}-r_{34}\cos\varphi_2}{r_{34}\sin\varphi_2}\right)\cot\varphi_1\cos\tau \right. \\ & \left. + \left(\frac{r_{23}-r_{34}\cos\varphi_2}{r_{34}\sin\varphi_2}\right)^2\right] + \frac{\sigma_4^2}{r_{34}^2\sin^2\varphi_2}\,. \end{aligned} \qquad (16)$$

Use of the special coordinates in (8′) leads to the torsion angle:

$$|\tau| = \cos^{-1}\frac{Y_4}{(X_4^2+Y_4^2)^{1/2}}\,. \qquad (17)$$

The convention of the 'right-hand rule' (Klyne & Prelog, 1960) is used to fix the sign of τ. In order to determine the sign, in a right-handed system with $Y_1 > 0$ and $Z_3 > 0$, it is necessary only to examine X_4. The sign of τ is the sign of $-X_4$.

For the purpose of programming a computer to calculate the standard deviation of the torsion angle, equation (15) seems most appropriate. If, however, the six structural parameters are known, then equation (16) would be more suitable.

The function-and-error program of Busing & Levy (1961) included a provision for calculating the dihedral angle and its standard error for two planes each defined by three atoms. The torsion-angle calculation is a special case in which two atoms are common to both planes. In this program the standard error is calculated from the full covariance matrix, and the necessary derivatives are evaluated by numerical differentiation.

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Normal probability plot analysis of small samples.*

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In using normal probability plots for comparing two sets of crystallographic data [Abrahams, S. C. & Keve, E. T. (1971), *Acta Cryst.* A**27**, 157] note should be taken of the fact that the expected values of normal order statistics are not given exactly by the percentage points of the normal distribution. This becomes an important consideration only for small samples. Tables of expected ranked exact moduli of normal observations, for sample sizes to 41, are presented: these are useful for half-normal probability plots.

Differences between independent measurements or calculated values of the same ith crystallographic quantity, $\Delta_i = F(1)_i - F(2)_i$, are readily analyzed by the normal probability plot method (Abrahams & Keve, 1971) in terms of the pooled standard deviation $\sigma_i = [\sigma^2 F(1)_i + \sigma^2 F(2)_i]^{1/2}$. A plot of the j ranked values of the weighted deviations Δ_i/σ_i (where $i=1$ refers to the largest Δ_i/σ_i) against the expected values $\xi(i|j)$ should result in a scatter of points about a straight line of unit slope that passes through the origin. If the weighted deviations are drawn from a normal distribution, a reasonable assumption for a crystallographic experiment, then the expected values for large j are given approximately by the percentage points X_i of the normal distribution, with

$$P(X_i) = \frac{l}{\sqrt{2\pi}}\int_{-X_i}^{X_i} \exp(-\alpha^2/2)\,d\alpha = |(j-2i+1)/j| \qquad (1)$$

For small values of j, especially for $j < 50$, the deviations between the values given by equation (1) and the exact values as tabulated by Harter (1961) become appreciable, especially at the extremes of the array. Four examples are given in Table 1. The exact values should always be used for small samples.

If the sign of Δ_i is without significance, as in comparison of two sets of position parameters, the half-normal probability plot should be used (Abrahams & Keve, 1971). For large samples, the expected values may again be obtained from the percentage points of the normal distribution, with $P(X_i) = (2j-2i+1)/2j$.† For j small, these approximate values are appreciably in error, and the exact values should be used. The expected value of the ith largest modulus of

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† The expression given for this quantity in Abrahams & Keve (1971) is misprinted as $(2i+1)/2j$; it should have read $(2i-1)/2j$, where $i=1$ refers to the smallest observation. For consistency with the full-normal case notation, we use the expression above, where $i=1$ refers to the largest observation.

Table 1. *Expected values of normal order statistics*

Approximate values are obtained from percentage points of the normal distribution as proposed by Abrahams & Keve (1971). Exact values are from Harter (1961). Note that $\xi(j+1-i \mid j) = -\xi(i \mid j)$.

i	$P(X_i)$	Approx. $\xi(i \mid j)$	Exact $\xi(i \mid j)$
		$j=5$	
1	0·80	1·282	1·163
2	0·40	0·524	0·495
3	0·00	0·000	0·000
		$j=10$	
1	0·90	1·645	1·539
2	0·70	1·036	1·001
3	0·50	0·675	0·656
4	0·30	0·385	0·376
5	0·10	0·126	0·123
		$j=25$	
1	0·96	2·054	1·965
2	0·88	1·555	1·524
3	0·80	1·282	1·263
4	0·72	1·080	1·067
5	0·64	0·915	0·905
6	0·56	0·772	0·764
7	0·48	0·643	0·637
8	0·40	0·524	0·519
9	0·32	0·412	0·409
10	0·24	0·305	0·303
11	0·16	0·202	0·200
12	0·08	0·100	0·100

i	$P(X_i)$	Approx. $\xi(i \mid j)$	Exact $\xi(i \mid j)$
		$j=50$	
1	0·98	2·326	2·249
2	0·94	1·881	1·855
3	0·90	1·645	1·629
4	0·86	1·476	1·464
5	0·82	1·341	1·331
6	0·78	1·226	1·218
7	0·74	1·126	1·119
8	0·70	1·037	1·030
9	0·66	0·954	0·949
10	0·62	0·878	0·873
11	0·58	0·806	0·802
12	0·54	0·739	0·735
13	0·50	0·674	0·671
14	0·46	0·613	0·610
15	0·42	0·553	0·551
16	0·38	0·496	0·494
17	0·34	0·440	0·438
18	0·30	0·385	0·384
19	0·26	0·332	0·330
20	0·22	0·279	0·278
21	0·18	0·228	0·227
22	0·14	0·176	0·176
23	0·10	0·126	0·125
24	0·06	0·075	0·075
25	0·02	0·025	0·025

Table 2. *Expected values of half-normal order statistics (ranked moduli of normal observations)*

Approximate values are obtained from percentage points of the normal distribution: exact values have been calculated from equation (2).

i	$P(X_i)$	Approx. $\xi_{1/2}(i \mid j)$	Exact $\xi_{1/2}(i \mid j)$
		$j=5$	
1	0·90	1·645	1·570
2	0·70	1·036	1·044
3	0·50	0·675	0·712
4	0·30	0·385	0·448
5	0·10	0·126	0·216
		$j=10$	
1	0·95	1·960	1·881
2	0·85	1·440	1·424
3	0·75	1·150	1·151
4	0·65	0·935	0·944
5	0·55	0·755	0·772
6	0·45	0·598	0·621
7	0·35	0·454	0·483
8	0·25	0·319	0·355
9	0·15	0·189	0·233
10	0·05	0·063	0·115

i	$P(X_i)$	Approx. $\xi_{1/2}(i \mid j)$	Exact $\xi_{1/2}(i \mid j)$
		$j=25$	
1	0·98	2·326	2·254
2	0·94	1·881	1·860
3	0·90	1·645	1·635
4	0·86	1·476	1·470
5	0·82	1·341	1·338
6	0·78	1·227	1·226
7	0·74	1·126	1·128
8	0·70	1·036	1·039
9	0·66	0·954	0·958
10	0·62	0·878	0·883
11	0·58	0·806	0·813
12	0·54	0·739	0·746
13	0·50	0·675	0·683
14	0·46	0·613	0·622
15	0·42	0·553	0·564
16	0·38	0·496	0·507
17	0·34	0·440	0·452
18	0·30	0·385	0·399
19	0·26	0·332	0·347
20	0·22	0·279	0·295
21	0·18	0·228	0·245
22	0·14	0·176	0·195
23	0·10	0·126	0·146
24	0·06	0·075	0·097
25	0·02	0·025	0·048

Table 3. *Expected values of ranked moduli of normal observations, calculated by numerical integration of Epuation* (2)

j is the sample size, *i* is the rank of the observation, and $i=1$ is the largest observation: $j=2[1]\ 41$, $i=1, j$.

i \ j	2	3	4	5	6	7	8	9
1	1.128	1.326	1.465	1.570	1.654	1.724	1.783	1.835
2	.467	.732	.911	1.044	1.149	1.235	1.307	1.370
3		.335	.553	.712	.835	.934	1.018	1.089
4			.262	.448	.589	.702	.796	.875
5				.216	.377	.504	.608	.696
6					.183	.326	.442	.538
7						.160	.288	.393
8							.141	.257
9								.127

i \ j	10	11	12	13	14	15	16	17
1	1.881	1.921	1.958	1.992	2.023	2.051	2.077	2.102
2	1.424	1.473	1.517	1.556	1.592	1.626	1.656	1.685
3	1.151	1.206	1.255	1.299	1.339	1.376	1.410	1.442
4	.944	1.005	1.059	1.107	1.151	1.191	1.229	1.263
5	.772	.838	.897	.949	.997	1.040	1.080	1.117
6	.621	.693	.756	.813	.864	.910	.953	.992
7	.483	.561	.629	.690	.745	.794	.839	.881
8	.355	.439	.512	.577	.635	.688	.736	.780
9	.233	.323	.402	.471	.533	.589	.640	.686
10	.115	.213	.297	.371	.437	.496	.550	.599
11		.105	.196	.275	.345	.408	.464	.516
12			.097	.182	.256	.322	.382	.436
13				.090	.169	.239	.302	.359
14					.084	.158	.225	.285
15						.079	.149	.212
16							.074	.140
17								.070

i \ j	18	19	20	21	22	23	24	25
1	2.125	2.146	2.167	2.186	2.204	2.221	2.238	2.254
2	1.712	1.737	1.760	1.782	1.803	1.823	1.842	1.860
3	1.471	1.499	1.525	1.549	1.572	1.594	1.615	1.635
4	1.295	1.324	1.352	1.379	1.403	1.427	1.449	1.470
5	1.151	1.183	1.213	1.241	1.267	1.292	1.316	1.338
6	1.028	1.062	1.094	1.123	1.151	1.177	1.202	1.226
7	.919	.955	.988	1.020	1.049	1.077	1.103	1.128
8	.820	.858	.893	.926	.957	.986	1.013	1.039
9	.729	.769	.806	.840	.872	.902	.931	.958
10	.644	.685	.724	.760	.793	.825	.855	.883
11	.563	.606	.647	.684	.719	.752	.783	.813
12	.486	.531	.573	.612	.649	.683	.716	.746
13	.411	.459	.503	.544	.582	.618	.651	.683
14	.339	.389	.435	.478	.517	.555	.589	.622
15	.269	.321	.369	.414	.455	.494	.530	.564
16	.200	.255	.305	.352	.395	.435	.472	.507
17	.133	.190	.243	.291	.336	.377	.416	.452
18	.066	.126	.181	.231	.278	.321	.361	.399
19		.063	.120	.173	.221	.266	.308	.347
20			.060	.115	.165	.212	.255	.295
21				.057	.110	.158	.203	.245
22					.055	.105	.152	.195
23						.052	.101	.146
24							.050	.097
25								.048

i \ j	26	27	28	29	30	31	32	33
1	2.269	2.283	2.297	2.310	2.323	2.335	2.347	2.359
2	1.877	1.894	1.910	1.925	1.939	1.953	1.967	1.980
3	1.653	1.671	1.689	1.705	1.721	1.736	1.751	1.765
4	1.490	1.510	1.528	1.546	1.562	1.579	1.594	1.609
5	1.359	1.380	1.399	1.418	1.436	1.453	1.469	1.485
6	1.248	1.270	1.290	1.310	1.329	1.347	1.364	1.380
7	1.151	1.174	1.195	1.215	1.235	1.254	1.272	1.289
8	1.064	1.087	1.109	1.131	1.151	1.171	1.189	1.207
9	.984	1.008	1.031	1.053	1.075	1.095	1.114	1.133
10	.910	.935	.959	.982	1.004	1.025	1.045	1.064
11	.840	.867	.892	.915	.938	.960	.981	1.001
12	.775	.802	.828	.853	.876	.899	.920	.941
13	.712	.741	.767	.793	.817	.840	.863	.884
14	.653	.682	.710	.736	.761	.785	.808	.830
15	.596	.626	.654	.682	.707	.732	.756	.778
16	.540	.571	.601	.629	.656	.681	.705	.729
17	.486	.519	.549	.578	.606	.632	.657	.681
18	.434	.468	.499	.529	.557	.584	.610	.634
19	.383	.418	.450	.481	.510	.538	.564	.589
20	.333	.369	.402	.434	.464	.492	.520	.546
21	.284	.321	.355	.388	.419	.448	.476	.503
22	.235	.273	.309	.343	.375	.405	.434	.461
23	.188	.227	.264	.298	.331	.362	.392	.420
24	.140	.181	.219	.255	.288	.320	.351	.380
25	.093	.135	.174	.211	.246	.279	.310	.340
26	.047	.090	.130	.168	.204	.238	.270	.301
27		.045	.087	.126	.163	.198	.231	.262
28			.043	.084	.122	.158	.192	.224
29				.042	.081	.118	.153	.186
30					.040	.079	.114	.148
31						.039	.076	.111
32							.038	.074
33								.037

i \ j	34	35	36	37	38	39	40	41
1	2.370	2.380	2.391	2.401	2.411	2.420	2.429	2.438
2	1.993	2.005	2.016	2.028	2.039	2.050	2.060	2.070
3	1.779	1.792	1.804	1.817	1.829	1.840	1.852	1.863
4	1.624	1.638	1.651	1.665	1.677	1.690	1.702	1.713
5	1.501	1.515	1.530	1.543	1.557	1.570	1.582	1.594
6	1.397	1.412	1.427	1.441	1.455	1.469	1.482	1.495
7	1.306	1.322	1.337	1.352	1.367	1.381	1.395	1.408
8	1.225	1.241	1.258	1.273	1.288	1.303	1.317	1.330
9	1.151	1.168	1.185	1.201	1.217	1.232	1.246	1.260
10	1.083	1.101	1.118	1.135	1.151	1.166	1.182	1.196
11	1.020	1.038	1.056	1.073	1.090	1.106	1.121	1.136
12	.960	.980	.998	1.016	1.033	1.049	1.065	1.080
13	.904	.924	.943	.961	.979	.996	1.012	1.028
14	.851	.871	.891	.909	.927	.945	.962	.978
15	.800	.821	.841	.860	.878	.896	.913	.930
16	.751	.772	.793	.812	.831	.850	.867	.885
17	.704	.726	.747	.767	.786	.805	.823	.841
18	.658	.680	.702	.723	.743	.762	.781	.798
19	.613	.637	.659	.680	.701	.720	.739	.758
20	.570	.594	.617	.639	.660	.680	.699	.718
21	.528	.553	.576	.598	.620	.640	.660	.680
22	.487	.512	.536	.559	.581	.602	.622	.642
23	.447	.472	.497	.520	.543	.564	.585	.605
24	.407	.433	.458	.482	.506	.528	.549	.570
25	.368	.395	.421	.445	.469	.492	.513	.534
26	.330	.357	.384	.409	.433	.456	.479	.500
27	.292	.320	.347	.373	.398	.421	.444	.466
28	.254	.283	.311	.338	.363	.387	.411	.433
29	.217	.247	.275	.303	.329	.353	.377	.400
30	.181	.211	.240	.268	.295	.320	.344	.368
31	.144	.175	.205	.234	.261	.287	.312	.336
32	.108	.140	.171	.200	.228	.254	.280	.304
33	.072	.105	.136	.166	.195	.222	.248	.273
34	.036	.070	.102	.133	.162	.190	.216	.242
35		.035	.068	.099	.129	.158	.185	.211
36			.034	.066	.097	.126	.154	.180
37				.033	.064	.094	.123	.150
38					.032	.063	.092	.120
39						.031	.061	.090
40							.031	.060
41								.030

an observation in a sample of size j drawn from a normal population with zero mean and unit variance is given exactly by

$$\xi_{1/2}(i|j)=\frac{2j!}{(j-i)!\,(i-1)!} \times \int_0^\infty \frac{x\exp(-x^2/2)}{\sqrt{2\pi}}(2P-1)^{j-i}(2-2P)^{i-1}\mathrm{d}x \quad (2)$$

where

$$P=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{X}\exp(-\alpha^2/2)\mathrm{d}\alpha .$$

A comparison of exact [equation (2)] and approximate expected magnitudes of the ranked half-normal order statistics, for three values of j, is given in Table 2. The exact moduli, for values of $j=2[1]\,41$, for all values of i (to our knowledge, not previously published) are presented in Table 3. The normal approximation is satisfactory for intermediate values of i (*cf.* Table 2), but remains in error by about 2% for values of j as high as 400. The extreme smallest value has a limiting exact value which is double that for the normal approximation, although the *absolute* difference between exact and approximate values is of no practical importance for large values of j.

Complete values of the full- and half-normal order statistics will appear in Volume 4 of *International Tables for X-ray Crystallography*.

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Multiple diffraction effects in neutron single-crystal diffractometry.

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The n-beam dynamical theory of diffraction is applied to multiple neutron diffraction. A computer program has been adapted to the neutron case from one originally developed for high energy electron diffraction in reflection. The integrated intensities are computed for the two and multibeam cases of the 002 reflection and compared with experiment. It is shown that only a negligible fraction of the incident beam satisfies the conditions for multiple diffraction.

The importance of multiple neutron diffraction in the Bragg case was recognized early by Moon & Shull (1961) and subsequently by Borgonovi & Caglioti (1962). The latter authors found remarkable effects in the 002 reflection from mosaic crystals such as nickel, aluminum, and pyrite, whereas they were not able to observe any appreciable effect in relatively perfect crystals such as LiF and NaCl. Since multiple diffraction is essentially related to a dynamical interaction among diffracted beams, the reason for this negative result is not clear, and a theoretical evaluation of these effects seems worthwhile.

The appropriate tool for this interpretation is the n-beam dynamical theory of diffraction and, for this purpose, a computer program originally developed for high energy electron diffraction in reflection (Colella, 1971; Colella & Menadue, 1971) has been adapted to the neutron case with a few minor modifications.

In Borgonovi & Caglioti's experiment, the crystal was oriented for the 002 Bragg reflection and then rotated around the [002] normal. The intensity was measured as a function of φ, the azimuthal angle. The divergence of the incident beam in the diffraction plane, of the order of several minutes of arc (Caglioti & Ricci, 1962), was much higher than the Darwin width of the crystal. In this situation, the intensity measured by the counter corresponds to the integrated intensity of the diffraction profile for an ω scan. For the sake of comparison with Borgonovi & Caglioti's experiment, the 002 integrated intensity for an ω scan (Bragg case) was computed when one or two strong reflections other than 002 were simultaneously excited. In relation to the nickel 002 azimuthal plot obtained by Borgonovi & Caglioti, numerous multibeam rocking curves for LiF and NaCl single crystals were computed in the vicinity of $\varphi=36$–$37°$, where the 002 intensity suffers the most drastic changes.† The results are reported in Table 1. The 002 integrated intensity

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† The azimuthal angle $\varphi=0$ corresponds to a [010] axis lying in the diffraction plane.

Table 1. *The effects of simultaneous reflections on the* 002 *integrated intensity*

The simultaneous reflections are listed in the second column from the left. When two simultaneous reflections are involved (four-beam case), their *hkl* indices are indicated by parentheses. The maximum and minimum percentage changes of the 002 integrated intensity are indicated, along with the angular width on the azimuthal scale. I_2 is the 002 two-beam integrated intensity.

Crystal	*hkl*	$\Delta I/I_2$ ($\times 100$)	$\Delta\varphi$ (sec)
LiF	$\bar{1}31$	-15	14
		$+466$	
	$\begin{pmatrix}042\\040\end{pmatrix}$	$+33$	8·3
		-30	
NaCl	$\bar{1}31$	$-2·5$	3·1
		$+31·4$	