

Contents

	PAGE
PREFACE (U. Shmueli)	xxiii
PART 1: GENERAL RELATIONSHIPS AND TECHNIQUES	1
1.1. RECIPROCAL SPACE IN CRYSTALLOGRAPHY (U. Shmueli)	2
1.1.1. Introduction	2
1.1.2. Reciprocal lattice in crystallography	2
1.1.3. Fundamental relationships	3
1.1.4. Tensor-algebraic formulation	5
1.1.5. Transformations	7
1.1.5.1. Transformations of coordinates	7
1.1.6. Some analytical aspects of the reciprocal space	8
References	9
1.2. THE STRUCTURE FACTOR (P. Coppens)	10
1.2.1. Introduction	10
1.2.2. General scattering expression for X-rays	10
1.2.3. Scattering by a crystal: definition of a structure factor	10
1.2.4. The isolated-atom approximation in X-ray diffraction	10
1.2.5. Scattering of thermal neutrons	11
1.2.5.1. Nuclear scattering	11
1.2.5.2. Magnetic scattering	11
1.2.6. Effect of bonding on the atomic electron density within the spherical-atom approximation: the kappa formalism	12
1.2.7. Beyond the spherical-atom description: the atom-centred spherical harmonic expansion	12
1.2.7.1. Direct-space description of aspherical atoms	12
1.2.7.2. Reciprocal-space description of aspherical atoms	14
Table 1.2.7.1. <i>Real spherical harmonic functions</i> (x, y, z are direction cosines)	13
Table 1.2.7.2. <i>Index-picking rules of site-symmetric spherical harmonics</i> (Kara & Kurki-Suonio, 1981)	15
Table 1.2.7.3. <i>'Kubic Harmonic' functions</i>	15
Table 1.2.7.4. <i>Closed-form expressions for Fourier transform of Slater-type functions</i> (Avery & Watson, 1977)	16
1.2.8. Fourier transform of orbital products	17
1.2.8.1. One-centre orbital products	17
1.2.8.2. Two-centre orbital products	18
Table 1.2.8.1. <i>Products of complex spherical harmonics as defined by equation (1.2.7.2a)</i>	17
Table 1.2.8.2. <i>Products of real spherical harmonics as defined by equations (1.2.7.2b) and (1.2.7.2c)</i>	17
1.2.9. The atomic temperature factor	18
1.2.10. The vibrational probability distribution and its Fourier transform in the harmonic approximation	18
1.2.11. Treatment of anharmonicity	18
1.2.11.1. The Gram-Charlier expansion	18
1.2.11.2. The cumulant expansion	19
1.2.11.3. The one-particle potential (OPP) model	20
1.2.11.4. Relative merits of the three expansions	20
Table 1.2.11.1. <i>Some Hermite polynomials</i> (Johnson & Levy, 1974; Zucker & Schulz, 1982)	19
1.2.12. The generalized structure factor	20
1.2.13. Conclusion	20
References	21

CONTENTS

1.3. FOURIER TRANSFORMS IN CRYSTALLOGRAPHY: THEORY, ALGORITHMS, AND APPLICATIONS (G. Bricogne)	23
1.3.0. General introduction	23
1.3.1. The mathematical theory of the Fourier transformation	24
1.3.1.0. Introduction	24
1.3.1.1. Preliminary notions and notation	24
1.3.1.1.1. Metric and topological notions in \mathbb{R}^n	24
1.3.1.1.2. Functions over \mathbb{R}^n	25
1.3.1.1.3. Multi-index notation	25
1.3.1.1.4. Integration, L^p spaces	25
1.3.1.1.5. Tensor products. Fubini's theorem	26
1.3.1.1.6. Topology in function spaces	26
1.3.1.1.6.1. General topology	26
1.3.1.1.6.2. Topological vector spaces	26
1.3.1.2. Elements of the theory of distributions	27
1.3.1.2.1. Origins	27
1.3.1.2.2. Rationale	28
1.3.1.2.3. Test function spaces	28
1.3.1.2.3.1. Topology on $\mathcal{E}(\Omega)$	28
1.3.1.2.3.2. Topology on $\mathcal{D}_K(\Omega)$	28
1.3.1.2.3.3. Topology on $\mathcal{D}(\Omega)$	28
1.3.1.2.3.4. Topologies on $\mathcal{E}^{(m)}$, $\mathcal{D}_K^{(m)}$, $\mathcal{D}^{(m)}$	28
1.3.1.2.4. Definition of distributions	28
1.3.1.2.5. First examples of distributions	29
1.3.1.2.6. Distributions associated to locally integrable functions	29
1.3.1.2.7. Support of a distribution	29
1.3.1.2.8. Convergence of distributions	29
1.3.1.2.9. Operations on distributions	29
1.3.1.2.9.1. Differentiation	30
1.3.1.2.9.1.1. Definition and elementary properties	30
1.3.1.2.9.1.2. Differentiation under the duality bracket	30
1.3.1.2.9.1.3. Effects of discontinuities	30
1.3.1.2.9.2. Integration of distributions in dimension 1	30
1.3.1.2.9.3. Multiplication of distributions by functions	31
1.3.1.2.9.4. Division of distributions by functions	31
1.3.1.2.9.5. Transformation of coordinates	31
1.3.1.2.9.6. Tensor product of distributions	32
1.3.1.2.9.7. Convolution of distributions	32
1.3.1.3. Fourier transforms of functions	33
1.3.1.3.0. Introduction	33
1.3.1.3.1. Fourier transforms in L^1	33
1.3.1.3.1.1. Linearity	33
1.3.1.3.1.2. Effect of affine coordinate transformations	33
1.3.1.3.1.3. Conjugate symmetry	33
1.3.1.3.1.4. Tensor product property	33
1.3.1.3.1.5. Convolution property	33
1.3.1.3.1.6. Reciprocity property	34
1.3.1.3.1.7. Riemann–Lebesgue lemma	34
1.3.1.3.1.8. Differentiation	34
1.3.1.3.1.9. Decrease at infinity	34
1.3.1.3.1.10. The Paley–Wiener theorem	34
1.3.1.3.2. Fourier transforms in L^2	34
1.3.1.3.2.1. Invariance of L^2	34
1.3.1.3.2.2. Reciprocity	34
1.3.1.3.2.3. Isometry	35
1.3.1.3.2.4. Eigenspace decomposition of L^2	35
1.3.1.3.2.5. The convolution theorem and the isometry property	35
1.3.1.3.3. Fourier transforms in \mathcal{S}	35
1.3.1.3.3.1. Definition and properties of \mathcal{S}	35
1.3.1.3.3.2. Gaussian functions and Hermite functions	35

CONTENTS

1.3.1.3.3.3. Heisenberg's inequality, Hardy's theorem	36
1.3.1.3.3.4. Symmetry property	36
1.3.1.3.4. Various writings of Fourier transforms	36
1.3.1.3.5. Tables of Fourier transforms	37
1.3.1.4. Fourier transforms of tempered distributions	37
1.3.1.4.0. Introduction	37
1.3.1.4.1. \mathcal{S} as a test function space	37
1.3.1.4.2. Definition and examples of tempered distributions	37
1.3.1.4.3. Fourier transforms of tempered distributions	37
1.3.1.4.4. Transposition of basic properties	37
1.3.1.4.5. Transforms of δ -functions	38
1.3.1.4.6. Reciprocity theorem	38
1.3.1.4.7. Multiplication and convolution	38
1.3.1.4.8. L^2 aspects, Sobolev spaces	39
1.3.1.5. Periodic distributions and Fourier series	39
1.3.1.5.0. Terminology	39
1.3.1.5.1. \mathbb{Z}^n -periodic distributions in \mathbb{R}^n	39
1.3.1.5.2. Identification with distributions over $\mathbb{R}^n/\mathbb{Z}^n$	39
1.3.1.5.3. Fourier transforms of periodic distributions	39
1.3.1.5.4. The case of non-standard period lattices	40
1.3.1.5.5. Duality between periodization and sampling	40
1.3.1.5.6. The Poisson summation formula	41
1.3.1.5.7. Convolution of Fourier series	41
1.3.1.5.8. Toeplitz forms, Szegő's theorem	41
1.3.1.5.8.1. Toeplitz forms	41
1.3.1.5.8.2. The Toeplitz–Carathéodory–Herzglotz theorem	41
1.3.1.5.8.3. Asymptotic distribution of eigenvalues of Toeplitz forms	42
1.3.1.5.8.4. Consequences of Szegő's theorem	42
1.3.1.5.9. Convergence of Fourier series	42
1.3.1.5.9.1. Classical L^1 theory	42
1.3.1.5.9.2. Classical L^2 theory	43
1.3.1.5.9.3. The viewpoint of distribution theory	43
1.3.1.6. The discrete Fourier transformation	44
1.3.1.6.1. Shannon's sampling theorem and interpolation formula	44
1.3.1.6.2. Duality between subdivision and decimation of period lattices	44
1.3.1.6.2.1. Geometric description of sublattices	44
1.3.1.6.2.2. Sublattice relations for reciprocal lattices	44
1.3.1.6.2.3. Relation between lattice distributions	44
1.3.1.6.2.4. Relation between Fourier transforms	45
1.3.1.6.2.5. Sublattice relations in terms of periodic distributions	45
1.3.1.6.3. Discretization of the Fourier transformation	46
1.3.1.6.4. Matrix representation of the discrete Fourier transform (DFT)	47
1.3.1.6.5. Properties of the discrete Fourier transform	47
1.3.2. Numerical computation of the discrete Fourier transform	47
1.3.2.0. Introduction	47
1.3.2.1. One-dimensional algorithms	48
1.3.2.1.1. The Cooley–Tukey algorithm	48
1.3.2.1.2. The Good (or prime factor) algorithm	49
1.3.2.1.2.1. Ring structure on $\mathbb{Z}/N\mathbb{Z}$	49
1.3.2.1.2.2. The Chinese remainder theorem	50
1.3.2.1.2.3. The prime factor algorithm	50
1.3.2.1.3. The Rader algorithm	51
1.3.2.1.3.1. N an odd prime	51
1.3.2.1.3.2. N a power of an odd prime	51
1.3.2.1.3.3. N a power of 2	52
1.3.2.1.4. The Winograd algorithms	52

CONTENTS

1.3.2.2. Multidimensional algorithms	53
1.3.2.2.1. The method of successive one-dimensional transforms	53
1.3.2.2.2. Multidimensional factorization	53
1.3.2.2.2.1. Multidimensional Cooley–Tukey factorization	53
1.3.2.2.2.2. Multidimensional prime factor algorithm	54
1.3.2.2.2.3. Nesting of Winograd small FFT’s	55
1.3.2.2.2.4. The Nussbaumer–Quandalle algorithm	55
1.3.2.2.3. Global algorithm design	56
1.3.2.2.3.1. From local pieces to global algorithms	56
1.3.2.2.3.2. Computer architecture considerations	56
1.3.2.2.3.3. The Johnson–Burrus family of algorithms	56
1.3.3. Crystallographic applications of Fourier transforms	57
1.3.3.0. Introduction	57
1.3.3.1. Crystallographic Fourier transform theory	57
1.3.3.1.1. Crystal periodicity	57
1.3.3.1.1.1. Period lattice, reciprocal lattice, and structure factors	57
1.3.3.1.1.2. Structure factors in terms of form factors	58
1.3.3.1.1.3. Fourier series for the electron density and its summation	58
1.3.3.1.1.4. Friedel’s law, anomalous scatterers	58
1.3.3.1.1.5. Parseval’s identity and other L^2 theorems	59
1.3.3.1.1.6. Convolution, correlation, and Patterson function	59
1.3.3.1.1.7. Sampling theorems, continuous transforms, interpolation	60
1.3.3.1.1.8. Sections and projections	60
1.3.3.1.1.9. Differential syntheses	61
1.3.3.1.1.10. Toeplitz forms, determinantal inequalities, and Szegő’s theorem	61
1.3.3.1.2. Crystal symmetry	62
1.3.3.1.2.1. Crystallographic groups	62
1.3.3.1.2.2. Groups and group actions	62
1.3.3.1.2.2.1. Left and right actions	62
1.3.3.1.2.2.2. Orbits and isotropy subgroups	62
1.3.3.1.2.2.3. Fundamental domain and orbit decomposition	63
1.3.3.1.2.2.4. Conjugation, normal subgroups, semi-direct products	63
1.3.3.1.2.2.5. Associated actions in function spaces	63
1.3.3.1.2.2.6. Orbit exchange	64
1.3.3.1.2.3. Classification of crystallographic groups	64
1.3.3.1.2.4. Crystallographic group action in real space	65
1.3.3.1.2.5. Crystallographic group action in reciprocal space	66
1.3.3.1.2.6. Structure factor calculation	66
1.3.3.1.2.7. Electron-density calculations	67
1.3.3.1.2.8. Parseval’s theorem with crystallographic symmetry	67
1.3.3.1.2.9. Convolution theorems with crystallographic symmetry	68
1.3.3.1.2.10. Correlation and Patterson functions	68
1.3.3.2. Crystallographic discrete Fourier transform algorithms	69
1.3.3.2.0. Historical introduction	69
1.3.3.2.1. Defining relations and symmetry considerations	70
1.3.3.2.2. Interaction between symmetry and decomposition	71
1.3.3.2.3. Interaction between symmetry and factorization	72
1.3.3.2.3.1. Multidimensional Cooley–Tukey factorization	72
1.3.3.2.3.2. Multidimensional Good factorization	74
1.3.3.2.3.3. Crystallographic extension of the Rader/Winograd factorization	74
1.3.3.2.4. Treatment of conjugate and parity-related symmetry properties	77
1.3.3.2.4.1. Hermitian-symmetric or real-valued transforms	77
1.3.3.2.4.1.1. Underlying group action	77

CONTENTS

1.3.3.2.4.1.2. Calculation of structure factors	77
1.3.3.2.4.1.3. Calculation of electron densities	78
1.3.3.2.4.2. Hermitian-antisymmetric or pure imaginary transforms	78
1.3.3.2.4.3. Complex symmetric and antisymmetric transforms	78
1.3.3.2.4.4. Real symmetric transforms	79
1.3.3.2.4.5. Real antisymmetric transforms	80
1.3.3.2.4.6. Generalized multiplexing	80
1.3.3.2.5. Global crystallographic algorithms	80
1.3.3.2.5.1. Triclinic groups	80
1.3.3.2.5.2. Monoclinic groups	80
1.3.3.2.5.3. Orthorhombic groups	81
1.3.3.2.5.4. Trigonal, tetragonal, and hexagonal groups	81
1.3.3.2.5.5. Cubic groups	81
1.3.3.2.5.6. Treatment of centred lattices	81
1.3.3.2.5.7. Programming considerations	81
1.3.3.3. Basic crystallographic computations	82
1.3.3.3.0. Introduction	82
1.3.3.3.1. Fourier synthesis of electron-density maps	82
1.3.3.3.2. Fourier analysis of modified electron-density maps	82
1.3.3.3.2.1. Squaring	82
1.3.3.3.2.2. Other non-linear operations	82
1.3.3.3.2.3. Solvent flattening	83
1.3.3.3.2.4. Molecular averaging by non-crystallographic symmetries	83
1.3.3.3.2.5. Molecular envelope transforms <i>via</i> Green's theorem	84
1.3.3.3.3. Structure factors from model atomic parameters	84
1.3.3.3.4. Structure factors <i>via</i> model electron-density maps	85
1.3.3.3.5. Derivatives for variational phasing techniques	86
1.3.3.3.6. Derivatives for model refinement	86
1.3.3.3.6.1. The method of least squares	86
1.3.3.3.6.2. Booth's differential Fourier syntheses	87
1.3.3.3.6.3. Booth's method of steepest descents	87
1.3.3.3.6.4. Cochran's Fourier method	87
1.3.3.3.6.5. Cruickshank's modified Fourier method	88
1.3.3.3.6.6. Agarwal's FFT implementation of the Fourier method	89
1.3.3.3.6.7. Lifchitz's reformulation	89
1.3.3.3.6.8. A simplified derivation	89
1.3.3.3.6.9. Discussion of macromolecular refinement techniques	90
1.3.3.3.6.10. Sampling considerations	90
1.3.3.3.7. Miscellaneous correlation functions	90
1.3.3.4. Related applications	91
1.3.3.4.1. Helical diffraction	91
1.3.3.4.1.1. Circular harmonic expansions in polar coordinates	91
1.3.3.4.1.2. The Fourier transform in polar coordinates	91
1.3.3.4.1.3. The transform of an axially periodic fibre	92
1.3.3.4.1.4. Helical symmetry and associated selection rules	92
1.3.3.4.2. Application to probability theory and direct methods	92
1.3.3.4.2.1. Analytical methods of probability theory	93
1.3.3.4.2.1.1. Convolution of probability densities	93
1.3.3.4.2.1.2. Characteristic functions	93
1.3.3.4.2.1.3. Moment-generating functions	93
1.3.3.4.2.1.4. Cumulant-generating functions	93
1.3.3.4.2.1.5. Asymptotic expansions and limit theorems	93
1.3.3.4.2.1.6. The saddlepoint approximation	94
1.3.3.4.2.2. The statistical theory of phase determination	94
1.3.3.4.2.2.0. Definitions and conventions	95

CONTENTS

1.3.3.4.2.2.1. Vectors of trigonometric structure-factor expressions ..	95
1.3.3.4.2.2.2. Distributions of random atoms and moment-generating functions	95
1.3.3.4.2.2.3. The joint probability distribution of structure factors ..	95
1.3.3.4.2.2.4. Maximum-entropy distributions of atoms	96
1.3.3.4.2.2.5. Role of the Fourier transformation	96
References	97
1.4. SYMMETRY IN RECIPROCAL SPACE (U. Shmueli with Appendix B by U. Shmueli and S. R. Hall)	107
1.4.1. Introduction	107
1.4.2. Effects of symmetry on the Fourier image of the crystal	107
1.4.2.1. Point-group symmetry of the reciprocal lattice	107
1.4.2.2. Relationship between structure factors at symmetry-related points of the reciprocal lattice ..	108
1.4.2.3. Symmetry factors for space-group-specific Fourier summations	109
1.4.2.4. Symmetry factors for space-group-specific structure-factor formulae	110
1.4.3. Structure-factor tables	110
1.4.4. Symmetry in reciprocal space: space-group tables	112
Appendix A: Comments on the preparation and usage of the tables	114
Appendix B: Space-group symbols for numeric and symbolic computations	115
Table B.1. <i>Lattice symbol L</i>	117
Table B.2. <i>Translation symbol T</i>	117
Table B.3. <i>Rotation symbol N for principal axes</i>	118
Table B.4. <i>Rotation symbol N for face-diagonal axes</i>	118
Table B.5. <i>Rotation symbol N for body-diagonal axes</i>	118
Table B.6. <i>Computer-adapted space-group symbols</i>	118
References	126
TRIGONOMETRIC STRUCTURE FACTORS	
Table 1.4.3.A. <i>Plane groups</i>	128
Table 1.4.3.B. <i>Triclinic space groups</i>	128
Table 1.4.3.C. <i>Monoclinic space groups</i>	129
Table 1.4.3.D. <i>Orthorhombic space groups</i>	131
Table 1.4.3.E. <i>Tetragonal space groups</i>	134
Table 1.4.3.F. <i>Trigonal and hexagonal space groups</i>	142
Table 1.4.3.G. <i>Cubic space groups</i>	148
THREE-DIMENSIONAL SPACE GROUPS IN RECIPROCAL SPACE	
Table 1.4.4. <i>Crystallographic space groups in reciprocal space</i>	153
 PART 2: RECIPROCAL SPACE IN CRYSTAL-STRUCTURE DETERMINATION	 183
2.1. STATISTICAL PROPERTIES OF THE WEIGHTED RECIPROCAL LATTICE (U. Shmueli and A. J. C. Wilson) ..	184
2.1.1. Introduction	184
2.1.2. The average intensity of the general reflections	184
2.1.3. The average intensity of zones and rows	185
Table 2.1.3.1. <i>Intensity-distribution effects of symmetry elements causing systematic absences</i>	185
Table 2.1.3.2. <i>Intensity-distribution effects of symmetry elements not causing systematic absences</i>	186
Table 2.1.3.3. <i>Average multiples for the thirty-two point groups (modified from Rogers, 1950)</i>	186
2.1.4. Probability density distributions – mathematical preliminaries	187
2.1.4.1. Characteristic functions	187
2.1.4.2. The cumulant-generating function	187
2.1.4.3. The central-limit theorem	188
2.1.4.4. Conditions of validity	188
2.1.4.5. Non-independent variables	188

CONTENTS

2.1.5. Ideal probability density distributions	188
2.1.5.1. Acentric distributions	189
2.1.5.2. Centric distributions	189
2.1.5.3. Effect of other symmetry elements on the acentric and centric distributions	189
2.1.5.4. Other ideal distributions	189
2.1.5.5. Relation to the distributions of I	190
2.1.5.6. Cumulative distribution functions	190
Table 2.1.5.1. <i>Some properties of gamma and beta distributions</i>	191
2.1.6. Distributions of sums, averages, and ratios	190
2.1.6.1. Distributions of sums and averages	190
2.1.6.2. Distribution of ratios	191
2.1.6.3. Intensities scaled to the local average	192
2.1.6.4. The use of normal approximations	192
2.1.7. Non-ideal distributions	192
2.1.7.1. Introduction	192
2.1.7.2. The correction-factor approach	193
2.1.7.3. The Fourier method	196
2.1.7.4. Fourier-Bessel series	197
2.1.7.5. Other non-ideal distributions	197
2.1.7.6. Comparison of the correction-factor and Fourier approaches	198
Table 2.1.7.1. <i>Some even absolute moments of the trigonometric structure factor</i>	194
Table 2.1.7.2. <i>Closed expressions for γ_{2k} [equation (2.1.7.11)] for space groups of low symmetry</i>	196
Table 2.1.7.3. <i>Atomic contributions to the expansion coefficients of Fourier and Fourier-Bessel p.d.f.'s</i>	198
References	199
2.2. DIRECT METHODS (C. Giacovazzo)	201
2.2.1. Introduction	201
2.2.2. Origin specification	201
Table 2.2.2.1. <i>Allowed origin translations, semi-invariant moduli, and phases for centrosymmetric primitive space groups</i>	203
Table 2.2.2.2. <i>Allowed origin translations, semi-invariant moduli, and phases for noncentrosymmetric primitive space groups</i>	204
Table 2.2.2.3. <i>Allowed origin translations, semi-invariant moduli, and phases for centrosymmetric non-primitive space groups</i>	206
Table 2.2.2.4. <i>Allowed origin translations, semi-invariant moduli, and phases for noncentrosymmetric non-primitive space groups</i>	208
2.2.3. Normalized structure factors	206
Table 2.2.3.1. <i>Moments of the distributions (2.2.3.4) and (2.2.3.5)</i>	210
2.2.4. Phase-determining formulae	208
2.2.4.1. Inequalities among structure factors	208
2.2.4.2. Probabilistic phase relationships for structure invariants	210
2.2.4.3. Triplet relationships	211
2.2.4.4. Triplet relationships using structural information	212
2.2.4.5. Quartet phase relationships	213
2.2.4.6. Quintet phase relationships	214
2.2.4.7. Determinantal formulae	215
2.2.4.8. Algebraic relationships for structure seminvariants	216
2.2.4.9. Formulae estimating one-phase structure seminvariants of the first rank	216
2.2.4.10. Formulae estimating two-phase structure seminvariants of the first rank	217
Table 2.2.4.1. <i>List of quartets symmetry equivalent to $\Phi = \Phi_1$ in the class mmm</i>	214
2.2.5. Direct methods in real and reciprocal space: the Sayre's equation	218
2.2.6. Scheme of procedure for phase determination	219
2.2.7. Other multiresolution methods applied to small molecules	221
Table 2.2.7.1. <i>Magic-integer sequences for small numbers of phases (n) together with the number of sets produced and the root-mean-square error in the phases</i>	221
2.2.8. Some references to direct methods packages	223

CONTENTS

2.2.9. Direct methods in macromolecular crystallography	223
2.2.9.1. Introduction	223
2.2.9.2. Integration of direct methods with isomorphous replacement techniques	223
2.2.9.3. Integration of anomalous-dispersion techniques with direct methods	224
References	225
2.3. PATTERSON AND MOLECULAR-REPLACEMENT TECHNIQUES (M. G. Rossmann and E. Arnold)	230
2.3.1. Introduction	230
2.3.1.1. Background	230
2.3.1.2. Limits to the number of resolved vectors	231
2.3.1.3. Modifications: origin removal, sharpening, etc.	231
2.3.1.4. Homometric structures and the uniqueness of structure solutions; enantiomorphic solutions	232
2.3.1.5. The Patterson synthesis of the second kind	233
2.3.2. Interpretation of Patterson maps	233
2.3.2.1. Simple solutions in the triclinic cell. Selection of the origin	233
2.3.2.2. Harker sections	234
2.3.2.3. Finding heavy atoms	235
2.3.2.4. Superposition methods. Image detection	236
2.3.2.5. Systematic computerized Patterson vector-search procedures. Looking for rigid bodies	237
Table 2.3.2.1. <i>Coordinates of Patterson peaks for C₂H₆Cl₂Cu₂N₂ projection</i>	234
Table 2.3.2.2. <i>Square matrix representation of vector interactions in a Patterson of a crystal with M crystallographic asymmetric units each containing N atoms</i>	234
Table 2.3.2.3. <i>Position of Harker sections within a Patterson</i>	235
2.3.3. Isomorphous replacement difference Pattersons	237
2.3.3.1. Introduction	237
2.3.3.2. Finding heavy atoms with centrosymmetric projections	237
2.3.3.3. Finding heavy atoms with three-dimensional methods	238
2.3.3.4. Correlation functions	239
2.3.3.5. Interpretation of isomorphous difference Pattersons	239
2.3.3.6. Direct structure determination from difference Pattersons	240
2.3.3.7. Isomorphism and size of the heavy-atom substitution	241
2.3.4. Anomalous dispersion	241
2.3.4.1. Introduction	241
2.3.4.2. The $P_s(\mathbf{u})$ function	242
2.3.4.3. The position of anomalous scatterers	243
2.3.5. Noncrystallographic symmetry	243
2.3.5.1. Definitions	243
2.3.5.2. Interpretation of Pattersons in the presence of noncrystallographic symmetry	245
Table 2.3.5.1. <i>Possible types of vector searches</i>	245
Table 2.3.5.2. <i>Orientation of the glyceraldehyde-3-phosphate dehydrogenase molecular twofold axis in the orthorhombic cell</i>	245
2.3.6. Rotation functions	246
2.3.6.1. Introduction	246
2.3.6.2. Matrix algebra	248
2.3.6.3. Symmetry	249
2.3.6.4. Sampling, background, and interpretation	250
2.3.6.5. The fast rotation function	253
Table 2.3.6.1. <i>Different types of uses for the rotation function</i>	246
Table 2.3.6.2. <i>Eulerian symmetry elements for all possible types of space-group rotations</i>	250
Table 2.3.6.3. <i>Numbering of the rotation function space groups</i>	250
Table 2.3.6.4. <i>Rotation function Eulerian space groups</i>	251
2.3.7. Translation functions	254
2.3.7.1. Introduction	254
2.3.7.2. Position of a noncrystallographic element relating two unknown structures	254
2.3.7.3. Position of a known molecular structure in an unknown unit cell	255
2.3.7.4. Position of a noncrystallographic symmetry element in a poorly defined electron-density map	255

CONTENTS

2.3.8. Molecular replacement	256
2.3.8.1. Using a known molecular fragment	256
2.3.8.2. Using noncrystallographic symmetry for phase improvement	256
2.3.8.3. Equivalence of real- and reciprocal-space molecular replacement	257
Table 2.3.8.1. <i>Molecular replacement: phase refinement as an iterative process</i>	257
2.3.9. Conclusions	258
2.3.10. Acknowledgements	258
References	258
2.4. ISOMORPHOUS REPLACEMENT AND ANOMALOUS SCATTERING (M. Vijayan and S. Ramaseshan)	264
2.4.1. Introduction	264
2.4.2. Isomorphous replacement method	264
2.4.2.1. Isomorphous replacement and isomorphous addition	264
2.4.2.2. Single isomorphous replacement method	265
2.4.2.3. Multiple isomorphous replacement method	265
2.4.3. Anomalous-scattering method	266
2.4.3.1. Dispersion correction	266
2.4.3.2. Violation of Friedel's law	266
2.4.3.3. Friedel and Bijvoet pairs	267
2.4.3.4. Determination of absolute configuration	268
2.4.3.5. Determination of phase angles	268
2.4.3.6. Anomalous scattering without phase change	268
2.4.3.7. Treatment of anomalous scattering in structure refinement	269
Table 2.4.3.1. <i>Phase angles of different components of the structure factor in space group P222</i>	267
2.4.4. Isomorphous replacement and anomalous scattering in protein crystallography	269
2.4.4.1. Protein heavy-atom derivatives	269
2.4.4.2. Determination of heavy-atom parameters	269
2.4.4.3. Refinement of heavy-atom parameters	271
2.4.4.4. Treatment of errors in phase evaluation: Blow and Crick formulation	272
2.4.4.5. Use of anomalous scattering in phase evaluation	273
2.4.4.6. Estimation of r.m.s. error	273
2.4.4.7. Suggested modifications to Blow and Crick formulation and the inclusion of phase information from other sources	274
2.4.4.8. Fourier representation of anomalous scatterers	275
2.4.5. Anomalous scattering of neutrons and synchrotron radiation. The multiwavelength method	275
2.4.5.1. Neutron anomalous scattering	275
2.4.5.2. Anomalous scattering of synchrotron radiation	276
References	276
2.5. ELECTRON DIFFRACTION AND ELECTRON MICROSCOPY IN STRUCTURE DETERMINATION	280
FOREWORD (J. M. Cowley)	280
2.5.1. Electron diffraction and electron microscopy (J. M. Cowley)	281
2.5.1.1. Introduction	281
2.5.1.2. The interactions of electrons with matter	282
2.5.1.3. Recommended sign conventions	283
2.5.1.4. Scattering of electrons by crystals; approximations	284
2.5.1.5. Kinematical diffraction formulae	285
2.5.1.6. Imaging with electrons	286
2.5.1.7. Imaging of very thin and weakly scattering objects	287
2.5.1.8. Crystal structure imaging	288
2.5.1.9. Image resolution	289
2.5.1.10. Electron diffraction in electron microscopes	289
Table 2.5.1.1. <i>Standard crystallographic and alternative crystallographic sign conventions for electron diffraction</i>	284

CONTENTS

2.5.2. Space-group determination by convergent-beam electron diffraction (P. Goodman)	290
2.5.2.1. Introduction	290
2.5.2.2. Background theory and analytical approach	291
2.5.2.2.1. Direct and reciprocity symmetries: Types I and II	291
2.5.2.2.2. Reciprocity and Friedel's law	292
2.5.2.2.3. Internal disc symmetries	292
2.5.2.2.4. Zero-layer absences	292
2.5.2.3. Pattern observation of individual symmetry elements	293
2.5.2.4. Auxiliary tables	294
2.5.2.5. Space-group analyses of single crystals; experimental procedure and published examples	306
2.5.2.5.1. Stages of procedure	306
2.5.2.5.2. Examples	306
2.5.2.6. Use of CBED in study of crystal defects, twins, and polytypes	309
2.5.2.7. Present limitations and general conclusions	309
2.5.2.8. Computer programs available	310
Table 2.5.2.1. <i>Listing of the symmetry elements relating to CBED patterns under the classifications of 'vertical' (I), 'horizontal' (II), and combined or roto-inversionary axes</i>	291
Table 2.5.2.2. <i>Diagrammatic illustrations of the actions of five types of symmetry elements on an asymmetric pattern component</i>	293
Table 2.5.2.3. <i>Diffraction point-group tables, giving whole-pattern and central-beam pattern symmetries in terms of BESR diffraction-group symbols and diperiodic-group symbols</i>	294
Table 2.5.2.4. <i>Tabulation of principal-axis CBED pattern symmetries against relevant space groups given as Volume A numbers</i>	295
Table 2.5.2.5. <i>Conditions for observations of GS bands for the 137 space groups exhibiting these extinctions</i>	296
2.5.3. Electron-diffraction structure analysis (EDSA) (B. K. Vainshtein and B. B. Zvyagin)	310
2.5.4. Image reconstruction (B. K. Vainshtein)	314
2.5.5. Three-dimensional reconstruction (B. K. Vainshtein)	320
2.5.5.1. The object and its projection	320
2.5.5.2. Orthoaxial projection	321
2.5.5.3. Discretization	321
2.5.5.4. Methods of direct reconstruction	322
2.5.5.5. The method of back-projection	322
2.5.5.6. The algebraic and iteration methods	323
2.5.5.7. Reconstruction using Fourier transformation	323
2.5.5.8. Three-dimensional reconstruction in the general case	323
References	325

PART 3: DUAL BASES IN CRYSTALLOGRAPHIC COMPUTING 331

3.1. DISTANCES, ANGLES, AND THEIR STANDARD DEVIATIONS (D. E. Sands)	332
3.1.1. Scalar product	332
3.1.2. Length of a vector	332
3.1.3. Angle between two vectors	332
3.1.4. Vector product	333
3.1.5. Permutation tensors	333
3.1.6. Components of vector product	333
3.1.7. Some vector relationships	333
3.1.8. Planes	333
3.1.9. Variance-covariance matrices	334
3.1.10. Mean values	335
3.1.11. Computation	336
References	336

CONTENTS

3.2. THE LEAST-SQUARES PLANE (R. E. Marsh and V. Schomaker)	337
3.2.1. Least-squares plane based on uncorrelated, isotropic weights	337
3.2.2. The proper least-squares plane, with Gaussian weights	340
References	344
3.3. MOLECULAR MODELLING AND GRAPHICS (R. Diamond)	345
3.3.1. Graphics	345
3.3.1.1. Coordinate systems, notation, and standards	345
3.3.1.1.1. Cartesian and crystallographic coordinates	345
3.3.1.1.2. Homogeneous coordinates	345
3.3.1.1.3. Notation	346
3.3.1.1.4. Standards	346
3.3.1.2. Orthogonal (or rotation) matrices	346
3.3.1.2.1. General form	346
3.3.1.2.2. Measurement of rotations and strains from coordinates	349
3.3.1.2.3. Orthogonalization of impure rotations	352
3.3.1.2.4. Eigenvalues and eigenvectors of orthogonal matrices	352
3.3.1.3. Projection transformations and spaces	353
3.3.1.3.1. Definitions	353
3.3.1.3.2. Translation	353
3.3.1.3.3. Rotation	353
3.3.1.3.4. Scale	353
3.3.1.3.5. Windowing and perspective	353
3.3.1.3.6. Stereoviews	355
3.3.1.3.7. Viewports	356
3.3.1.3.8. Compound transformations	356
3.3.1.3.9. Inverse transformations	357
3.3.1.3.10. The three-axis joystick	357
3.3.1.3.11. Other useful rotations	358
3.3.1.3.12. Symmetry	358
3.3.1.4. Modelling transformations	358
3.3.1.4.1. Rotation about a bond	358
3.3.1.4.2. Stacked transformations	358
3.3.1.5. Drawing techniques	359
3.3.1.5.1. Types of hardware	359
3.3.1.5.2. Optimization of line drawings	360
3.3.1.5.3. Representation of surfaces by lines	360
3.3.1.5.4. Representation of surfaces by dots	360
3.3.1.5.5. Representation of surfaces by shading	361
3.3.1.5.6. Advanced hidden-line and hidden-surface algorithms	361
3.3.2. Molecular modelling, problems and approaches	362
3.3.2.1. Connectivity	362
3.3.2.1.1. Connectivity tables	362
3.3.2.1.2. Implied connectivity	362
3.3.2.2. Modelling methods	363
3.3.2.2.1. Methods based on conformational variables	363
3.3.2.2.2. Methods based on positional coordinates	364
3.3.2.2.3. Approaches to the problem of multiple minima	365
3.3.3. Implementations	365
3.3.3.1. Systems for the display and modification of retrieved data	366
3.3.3.1.1. <i>ORTEP</i>	366
3.3.3.1.2. Feldmann's system	366
3.3.3.1.3. Lesk & Hardman software	366
3.3.3.1.4. <i>GRAMPS</i>	366
3.3.3.1.5. Takenaka & Sasada's system	366
3.3.3.1.6. <i>MIDAS</i>	366

CONTENTS

3.3.3.1.7. <i>Insight</i>	367
3.3.3.1.8. <i>HYDRA</i>	367
3.3.3.2. Molecular-modelling systems based on electron density	367
3.3.3.2.1. <i>CHEMGRAF</i>	367
3.3.3.2.2. <i>GRIP</i>	367
3.3.3.2.3. Barry & North's system	367
3.3.3.2.4. <i>MMS-X</i>	368
3.3.3.2.5. Texas A&M University system	368
3.3.3.2.6. <i>Bilder</i>	368
3.3.3.2.7. <i>Frodo</i>	368
3.3.3.2.8. <i>Guide</i>	369
3.3.3.3. Molecular-modelling systems based on other criteria	369
3.3.3.3.1. <i>Molbuild</i> , <i>Rings</i> , <i>PRXBLD</i> , and <i>MM2/MMP2</i>	369
3.3.3.3.2. <i>Script</i>	369
3.3.3.3.3. <i>CHARMM</i>	369
3.3.3.3.4. Commercial systems	370
References	370
3.4. ACCELERATED CONVERGENCE TREATMENT OF R^{-n} LATTICE SUMS (D. E. Williams)	374
3.4.1. Introduction	374
3.4.2. Definition and behaviour of the direct-space sum	374
Table 3.4.2.1. <i>Untreated lattice-sum results for the Coulombic energy ($n = 1$) of sodium chloride</i>	374
Table 3.4.2.2. <i>Untreated lattice-sum results for the dispersion energy ($n = 6$) of crystalline benzene</i>	375
3.4.3. Preliminary description of the method	375
3.4.4. Preliminary derivation to obtain a formula which accelerates the convergence of an R^{-n} sum over lattice points $X(d)$	375
3.4.5. Extension of the method to a composite lattice	377
3.4.6. The case of $n = 1$ (Coulombic lattice energy)	378
3.4.7. The cases of $n = 2$ and $n = 3$	378
3.4.8. Derivation of the accelerated convergence formula <i>via</i> the Patterson function	378
3.4.9. Evaluation of the incomplete gamma function	379
3.4.10. Summation over the asymmetric unit and elimination of intramolecular energy terms	379
3.4.11. Reference formulae for particular values of n	379
3.4.12. Numerical illustrations	380
Table 3.4.12.1 <i>Accelerated-convergence results for the Coulombic sum ($n = 1$) of sodium chloride: the direct sum plus the constant term</i>	380
Table 3.4.12.2 <i>The reciprocal-lattice results for the Coulombic sum ($n = 1$) of sodium chloride</i>	381
Table 3.4.12.3. <i>Accelerated-convergence results for the dispersion sum ($n = 6$) of crystalline benzene: the figures shown are the direct-lattice sum plus the two constant terms</i>	381
Table 3.4.12.4. <i>The reciprocal-lattice results for the dispersion sum ($n = 6$) of crystalline benzene</i>	381
Table 3.4.12.5. <i>Approximate time required to evaluate the dispersion sum ($n = 6$) for crystalline benzene within 0.001 kJ mol⁻¹ truncation error</i>	381
References	381
PART 4: DIFFUSE SCATTERING AND RELATED TOPICS	383
4.1. THERMAL DIFFUSE SCATTERING OF X-RAYS AND NEUTRONS (B. T. M. Willis)	384
4.1.1. Introduction	384
4.1.2. Dynamics of three-dimensional crystals	384
4.1.3. Scattering of X-rays by thermal vibrations	387
4.1.4. Scattering of neutrons by thermal vibrations	388
4.1.5. Phonon dispersion relations	389

CONTENTS

4.1.6. Measurement of elastic constants	390
References	391
4.2. DISORDER DIFFUSE SCATTERING OF X-RAYS AND NEUTRONS (H. Jagodzinski and F. Frey)	392
4.2.1. Scope of this chapter	392
4.2.2. Summary of basic scattering theory	393
4.2.3. General treatment	395
4.2.3.1. Qualitative interpretation of diffuse scattering	395
4.2.3.2. Guideline to solve a disorder problem	404
4.2.4. Quantitative interpretation	406
4.2.4.1. Introduction	406
4.2.4.2. One-dimensional disorder of ordered layers	406
4.2.4.3. Two-dimensional disorder of chains	411
4.2.4.4. Disorder with three-dimensional correlations (defects, local ordering, and clustering)	415
4.2.4.5. Orientational disorder	422
4.2.5. Measurement of diffuse scattering	424
References	429
4.3. DIFFUSE SCATTERING IN ELECTRON DIFFRACTION (J. M. Cowley and J. Gjønnes)	434
4.3.1. Introduction	434
4.3.2. Inelastic scattering	435
4.3.3. Kinematical and pseudo-kinematical scattering	436
4.3.4. Dynamical scattering: Bragg scattering effects	436
4.3.5. Multislice calculations for diffraction and imaging	438
4.3.6. Qualitative interpretation of diffuse scattering of electrons	438
References	439
4.4. SCATTERING FROM MESOMORPHIC STRUCTURES (P. S. Pershan)	441
4.4.1. Introduction	441
Table 4.4.1.1. <i>Some of the symmetry properties of the series of three-dimensional phases described in Fig. 4.4.1.1.</i>	441
Table 4.4.1.2. <i>The symmetry properties of the two-dimensional hexatic and crystalline phases</i>	442
4.4.2. The nematic phase	443
Table 4.4.2.1. <i>Summary of critical exponents from X-ray scattering studies of the nematic to smectic-A phase transition</i>	445
4.4.3. Smectic-A and smectic-C phases	445
4.4.3.1. Homogeneous smectic-A and smectic-C phases	445
4.4.3.2. Modulated smectic-A and smectic-C phases	447
4.4.3.3. Surface effects	448
4.4.4. Phases with in-plane order	449
4.4.4.1. Hexatic phases in two dimensions	450
4.4.4.2. Hexatic phases in three dimensions	451
4.4.4.2.1. Hexatic-B	451
4.4.4.2.2. Smectic-F, smectic-I	451
4.4.4.3. Crystalline phases with molecular rotation	453
4.4.4.3.1. Crystal-B	453
4.4.4.3.2. Crystal-G, crystal-J	455
4.4.4.4. Crystalline phases with herringbone packing	455
4.4.4.4.1. Crystal-E	455
4.4.4.4.2. Crystal-H, crystal-K	456
4.4.5. Discotic phases	456

CONTENTS

4.4.6. Other phases	457
References	458
PART 5: DYNAMICAL THEORY AND ITS APPLICATIONS	
5.1. DYNAMICAL THEORY OF X-RAY DIFFRACTION (A. Authier)	464
5.1.1. Introduction	464
5.1.2. Fundamentals of plane-wave dynamical theory	464
5.1.2.1. Propagation equation	464
5.1.2.2. Wavefields	465
5.1.2.3. Boundary conditions at the entrance surface	465
5.1.2.4. Fundamental equations of dynamical theory	466
5.1.2.5. Dispersion surface	466
5.1.2.6. Polarization	467
5.1.2.7. Propagation direction	467
5.1.3. Solutions of plane-wave dynamical theory	467
5.1.3.1. Departure from Bragg's law of the incident wave	467
5.1.3.2. Transmission and reflection geometries	468
5.1.3.3. Middle of the reflection domain	468
5.1.3.4. Deviation parameter	469
5.1.3.5. <i>Pendellösung</i> and extinction distance	469
5.1.3.6. Solution of the dynamical theory	470
5.1.3.7. Geometrical interpretation of the solution in the zero absorption case	470
5.1.4. Standing waves	470
5.1.5. Anomalous absorption	471
5.1.6. Intensities of plane waves in the transmission geometry	471
5.1.6.1. Absorption coefficient	471
5.1.6.2. Boundary conditions for the amplitudes at the entrance surface - intensities of the reflected and refracted waves	471
5.1.6.3. Boundary conditions at the exit surface	472
5.1.6.4. Reflecting power	473
5.1.6.5. Integrated intensity	474
5.1.6.6. Thin crystals - comparison with the geometrical theory	474
5.1.7. Intensity of plane waves in the reflection geometry	474
5.1.7.1. Thick crystals	474
5.1.7.2. Thin crystals	475
5.1.8. Real waves	477
5.1.8.1. Introduction	477
5.1.8.2. Borrmann effect	477
5.1.8.3. Spherical-wave <i>Pendellösung</i>	478
APPENDIX	478
References	479
5.2. DYNAMICAL THEORY OF ELECTRON DIFFRACTION (A. F. Moodie, J. M. Cowley, and P. Goodman)	481
5.2.1. Introduction	481
5.2.2. The defining equations	481
5.2.3. Forward scattering	481
5.2.4. Solution by integration	482
5.2.5. Projection approximation - real-space solution	482
5.2.6. Semi-reciprocal space	482
5.2.7. Two-beam derivation	483
5.2.8. Eigenvalue approach	483

CONTENTS

5.2.9. Translational invariance	483
5.2.10. Bloch-wave formulations	484
5.2.11. Dispersion surfaces	484
5.2.12. Physical optics approach	484
5.2.13. Born-series evaluation	485
5.2.14. Approximations	485
References	485
AUTHOR INDEX	487
SUBJECT INDEX	495