Separating the powers of **Q** and **u** in (1.9.2.2) and (1.9.2.3), one may obtain expressions involving moments μ and cumulants k explicitly as

$$M(\mathbf{Q}) = \sum_{N=0}^{\infty} (i^N/N!) Q_i Q_j Q_k \ldots Q_n \mu^{ijk\ldots n} \qquad (1.9.2.4)$$

and the cumulant-generating function $K(\mathbf{Q})$ as

$$K(\mathbf{Q}) = \exp[M(\mathbf{Q})] = \sum_{N=1}^{\infty} (I^N/N!) Q_i Q_j Q_k \ldots Q_n k^{ijk\ldots n}. \qquad (1.9.2.5)$$

The indices $i, j, k, \ldots, n$ run in three-dimensional space from 1 to 3 and refer to the crystallographic basis system. Moments may be expressed in terms of cumulants (and *vice versa*); the transformation laws are given in *IT* B (2001), equation (1.2.12.9) and more completely in Kuhs (1988, 1992). The moment- and cumulant-generating functions are two ways of expressing the Fourier transform of the atomic probability density function (p.d.f.). If all terms up to infinity are taken into account, $M(\mathbf{Q})$ and $K(\mathbf{Q})$ are [by virtue of the identity $\exp(i\mathbf{Q}) = \sum (i\mathbf{Q})^N/N!$] identical. For a finite series, however, the cumulants of order N carry implicit information on contributions of order N^2, N^3 *etc.* in contrast to the moments. Equations (1.9.2.4) and (1.9.2.5) are useful, as they can be entered directly in a structure-factor equation (see Chapter 1.2 in *IT* B); however, the moments (and thus the cumulants) may also be calculated directly from the atomic p.d.f. as

$$\mu^{ijk\ldots n} = \int u^i u^j u^k \ldots u^n \,\text{p.d.f.}(\mathbf{u})\, \mathrm{d}\mathbf{u}. \qquad (1.9.2.6)$$

The real-space expression of the p.d.f. obtained from a Fourier transform of (1.9.2.5) is called an *Edgeworth series* expansion. If one assumes that the underlying atomic p.d.f. is close to a Gaussian distribution, one may separate out the Gaussian contributions to the moment-generating function as suggested by Kuznetsov *et al.* (1960) and formulate a generating function for quasimoments as

$$\tilde{M}(\mathbf{Q}) = \exp[(1/2)\langle(\mathbf{Qu})^2\rangle] \sum_{N=3}^{\infty} (i^N/N!) Q_i Q_j Q_k \ldots Q_n \tilde{\mu}^{ijk\ldots n}. \qquad (1.9.2.7)$$

These quasimoments are especially useful in crystallographic structure-factor equations, as they just modify the harmonic case. The real-space expression of the p.d.f. obtained from a Fourier transformation of (1.9.2.7) is called a *Gram–Charlier* series expansion. Discussions of its merits as compared to the Edgeworth series are given in Zucker & Schulz (1982*a*,*b*), Kuhs (1983, 1988, 1992) and Scheringer (1985).

1.9.2.1. *Tensorial properties of (quasi)moments and cumulants*

By separating the powers of **Q** and **u**, one obtains in equations (1.9.2.4), (1.9.2.5) and (1.9.2.7) the higher-order displacement tensors in the form of moments, cumulants or quasimoments, which we shall denote in a general way as $b^{ijk\cdots}$; note that b^{ij} is identical to β^{ij}. They transform on a change of the direct-lattice base according to

$$b^{pqr\cdots} = A_{pi} A_{qj} A_{rk} \ldots b^{ijk\cdots}. \qquad (1.9.2.8)$$

The higher-order displacement tensors are fully symmetric with respect to the interchange of any of their indices; in the nomenclature of Jahn (1949), their tensor symmetry thus is $[b^N]$. The number of independent tensor coefficients depends on the site symmetry of the atom and is tabulated in Sirotin (1960) as well as in Tables 1.9.3.1–1.9.3.6. For triclinic site symmetry, the numbers of independent tensor coefficients are 1, 3, 6, 10, 15, 21 and 28 for the zeroth to sixth order. Symmetry may further reduce the number of independent coefficients, as discussed in Section 1.9.3.

In many least-squares programs for structure refinement, the atomic displacement parameters are used in a dimensionless form [as given in (1.9.1.4) for the harmonic case]. These dimensionless quantities may be transformed according to

$$U^{ijk\ldots n} = [N!/(2\pi)^N] b^{ijk\ldots n} |\mathbf{a}^i||\mathbf{a}^j||\mathbf{a}^k| \ldots |\mathbf{a}^n| \qquad (1.9.2.9)$$

(no summation) into quantities of units Å^N (or pm^N); $\mathbf{a}^i$ *etc.* are reciprocal-lattice vectors. Nowadays, the published structural results usually quote U^{ij} for the second-order terms; it would be good practice to publish only dimensioned atomic displacements for the higher-order terms as well.

1.9.2.2. *Contraction, expansion and invariants of atomic displacement tensors*

Anisotropic or higher-order atomic displacement tensors may contain a wealth of information. However, this information content is not always worth publishing in full, either because the physical meaning is not of importance or the significance is only marginal. Quantities of higher significance or better clarity are obtained by an operation known as tensor contraction. Likewise, lower-order terms may be expanded to higher order to impose certain (chemically implied) symmetries on the displacement tensors or to provide initial parameters for least-squares refinements. A contraction is obtained by multiplying the contravariant tensor components (referring to the real-space basis vectors) with the covariant components of the real-space metric tensor g_{ij}; for further details on tensor contraction, see Section 1.1.3.3.3. In the general case of atomic displacement tensors of (even) rank N, one obtains

$${}^N I_0 = g_{ij} g_{kl} \ldots g_{mn} b^{ijkl\ldots mn}. \qquad (1.9.2.10)$$

${}^N I_0$ is called the trace of a tensor of rank N and is a scalar invariant; it is given in units of length^N and provides an easily interpretable quantity: In the case of ${}^4 I_0$, a positive sign indicates that the corresponding (real-space) p.d.f. is peaked, a negative sign indicates flatness of the p.d.f. The larger ${}^N I_0$, the stronger the deviation from a Gaussian p.d.f. provoked by the atomic displacements of order N. The frequently quoted isotropic equivalent U value U_{eq} is also obtained by this contraction process. Noting that U^{ij} may be expressed in terms of b^{ij} ($= \beta^{ij}$) according to (1.9.2.9) and that the trace of the matrix **U** is given as $\text{Tr}(\mathbf{U}) = (2\pi^2)^{-1.2} I_0$, one obtains

$$U_{\text{eq}} = (1/3)(2\pi^2)^{-1} g_{ij} b^{ij}. \qquad (1.9.2.11)$$

Note that in all non-orthogonal bases, $\text{Tr}(\mathbf{U}) \neq U^{11} + U^{22} + U^{33}$. In older literature, the isotropic equivalent displacement parameter is often quoted as B_{eq}, which is related to U_{eq} through the identity $B_{\text{eq}} = 8\pi^2 U_{\text{eq}}$. The use of B_{eq} is now discouraged (Trueblood *et al.*, 1996). Higher atomic displacement tensors of odd rank N may be reduced to simple vectors **v** by the following contraction:

$${}^N v^i = g_{jk} g_{lm} \ldots g_{np} b^{ijklm\ldots np}. \qquad (1.9.2.12)$$

where v^1 is the 23 trace *etc.* ${}^N v^i$ is sometimes called a vector invariant, as it can be uniquely assigned to the tensor in question (Pach & Frey, 1964) and its units are length^{N-1}. The vector **v** is oriented along the line of maximum projected asymmetry for a given atom and vanishes for atoms with positional parameters fixed by symmetry; Johnson (1970) has named a vector closely related to ${}^3\mathbf{v}$ the vector of skew divergence. The calculation of **v** is useful as it gives the direction of the largest antisymmetric displacements contained in odd-rank higher-order thermal-motion tensors.