Table 1.2.7.4. *Closed-form expressions for Fourier transform of Slater-type functions (Avery & Watson, 1977; Su & Coppens, 1990)*

$\langle j_k \rangle \equiv \int_0^\infty r^N \exp(-Zr) j_k(Kr)\, \mathrm{d}r, K = 4\pi \sin\theta/\lambda.$

	N							
k	1	2	3	4	5	6	7	8
0	$\frac{1}{K^2+Z^2}$	$\frac{2Z}{(K^2+Z^2)^2}$	$\frac{2(3Z^2-K^2)}{(K^2+Z^2)^3}$	$\frac{24Z(Z^2-K^2)}{(K^2+Z^2)^4}$	$\frac{24(5Z^2-10K^2Z^2+K^4)}{(K^2+Z^2)^5}$	$\frac{240Z(K^2-3Z^2)(3K^2-Z^2)}{(K^2+Z^2)^6}$	$\frac{720(7Z^6-35K^2Z^4+21K^4Z^2-K^6)}{(K^2+Z^2)^7}$	$\frac{40320(Z^7-7K^2Z^5+7K^4Z^3-K^6Z)}{(K^2+Z^2)^8}$
1		$\frac{2K}{(K^2+Z^2)^2}$	$\frac{8KZ}{(K^2+Z^2)^3}$	$\frac{8K(5Z^2-K^2)}{(K^2+Z^2)^4}$	$\frac{48KZ(5Z^2-3K^2)}{(K^2+Z^2)^5}$	$\frac{48K(35Z^4-42K^2Z^2+3K^4)}{(K^2+Z^2)^6}$	$\frac{1920KZ(7Z^4-14K^2Z^2+3K^4)}{(K^2+Z^2)^7}$	$\frac{5760K(21Z^6-63K^2Z^4+27K^4Z^2-K^6)}{(K^2+Z^2)^8}$
2			$\frac{8K^2}{(K^2+Z^2)^3}$	$\frac{48K^2Z}{(K^2+Z^2)^4}$	$\frac{48K^2(7Z^2-K^2)}{(K^2+Z^2)^5}$	$\frac{384K^2Z(7Z^2-3K^2)}{(K^2+Z^2)^6}$	$\frac{1152K^2(21Z^4-18K^2Z^2+K^4)}{(K^2+Z^2)^7}$	$\frac{11520K^2Z(21Z^4-30K^2Z^2+5K^4)}{(K^2+Z^2)^8}$
3				$\frac{48K^3}{(K^2+Z^2)^4}$	$\frac{384K^3Z}{(K^2+Z^2)^5}$	$\frac{384K^3(9Z^2-K^2)}{(K^2+Z^2)^6}$	$\frac{11520K^3Z(3Z^2-K^2)}{(K^2+Z^2)^7}$	$\frac{11520K^3(33Z^4-22K^2Z^2+K^4)}{(K^2+Z^2)^8}$
4					$\frac{384K^4}{(K^2+Z^2)^5}$	$\frac{3840K^4Z}{(K^2+Z^2)^6}$	$\frac{3840K^4(11Z^2-K^2)}{(K^2+Z^2)^7}$	$\frac{46080K^4Z(11Z^2-3K^2)}{(K^2+Z^2)^8}$
5						$\frac{3840K^5}{(K^2+Z^2)^6}$	$\frac{46080K^5Z}{(K^2+Z^2)^7}$	$\frac{40680K^5(13Z^2-K^2)}{(K^2+Z^2)^8}$
6							$\frac{46080K^6}{(K^2+Z^2)^7}$	$\frac{645120K^6Z}{(K^2+Z^2)^8}$
7								$\frac{645120K^7}{(K^2+Z^2)^8}$

$$P(\mathbf{u}) = \frac{|\boldsymbol{\sigma}^{-1}|^{1/2}}{(2\pi)^{3/2}} \exp\{-\tfrac{1}{2}\boldsymbol{\sigma}^{-1}_{jk}(u^j u^k)\}. \qquad (1.2.10.2a)$$

Here σ is the variance–covariance matrix, with covariant components, and $|\boldsymbol{\sigma}^{-1}|$ is the determinant of the inverse of σ. Summation over repeated indices has been assumed. The corresponding equation in matrix notation is

$$P(\mathbf{u}) = \frac{|\boldsymbol{\sigma}^{-1}|^{1/2}}{(2\pi)^{3/2}} \exp\{-\tfrac{1}{2}(\mathbf{u})^T \boldsymbol{\sigma}^{-1}(\mathbf{u})\}, \qquad (1.2.10.2b)$$

where the superscript T indicates the transpose.

The characteristic function, or Fourier transform, of $P(\mathbf{u})$ is

$$T(\mathbf{H}) = \exp\{-2\pi^2 \sigma^{jk} h_j h_k\} \qquad (1.2.10.3a)$$

or

$$T(\mathbf{H}) = \exp\{-2\pi^2 \mathbf{H}^T \boldsymbol{\sigma} \mathbf{H}\}. \qquad (1.2.10.3b)$$

With the change of variable $b^{jk} = 2\pi^2 \sigma^{jk}$, (1.2.10.3$a$) becomes

$$T(\mathbf{H}) = \exp\{-b^{jk} h_j h_k\}.$$

1.2.11. Rigid-body analysis

The treatment of rigid-body motion of molecules or molecular fragments was developed by Cruickshank (1956) and expanded into a general theory by Schomaker & Trueblood (1968). The theory has been described by Johnson (1970*b*) and by Dunitz (1979). The latter reference forms the basis for the following treatment.

The most general motions of a rigid body consist of rotations about three axes, coupled with translations parallel to each of the axes. Such motions correspond to screw rotations. A libration around a vector $\boldsymbol{\lambda}$ (λ_1, λ_2, λ_3), with length corresponding to the magnitude of the rotation, results in a displacement $\delta\mathbf{r}$, such that

$$\delta\mathbf{r} = (\boldsymbol{\lambda} \times \mathbf{r}) = \mathbf{D}\mathbf{r} \qquad (1.2.11.1)$$

with

$$\mathbf{D} = \begin{bmatrix} 0 & -\lambda_3 & \lambda_2 \\ \lambda_3 & 0 & -\lambda_1 \\ -\lambda_2 & \lambda_1 & 0 \end{bmatrix}, \qquad (1.2.11.2)$$

or in tensor notation, assuming summation over repeated indices,

$$\delta r_i = D_{ij} r_j = -\varepsilon_{ijk} \lambda_k r_j \qquad (1.2.11.3)$$

where the permutation operator ε_{ijk} equals +1 for i, j, k a cyclic permutation of the indices 1, 2, 3, or −1 for a non-cyclic permutation, and zero if two or more indices are equal. For $i = 1$, for example, only the ε_{123} and ε_{132} terms occur. Addition of a translational displacement gives

$$\delta r_i = D_{ij} r_j + t_i. \qquad (1.2.11.4)$$

When a rigid body undergoes vibrations the displacements vary with time, so suitable averages must be taken to derive the mean-square displacements. If the librational and translational motions are independent, the cross products between the two terms in (1.2.11.4) average to zero and the elements of the mean-square displacement tensor of atom n, U^n_{ij}, are given by

$$\begin{aligned}
U^n_{11} &= +L_{22}r_3^2 + L_{33}r_2^2 - 2L_{23}r_2r_3 + T_{11} \\
U^n_{22} &= +L_{33}r_1^2 + L_{11}r_3^2 - 2L_{13}r_1r_3 + T_{22} \\
U^n_{33} &= +L_{11}r_2^2 + L_{22}r_1^2 - 2L_{12}r_1r_2 + T_{33} \\
U^n_{12} &= -L_{33}r_1r_2 - L_{12}r_3^2 + L_{13}r_2r_3 + L_{23}r_1r_3 + T_{12} \\
U^n_{13} &= -L_{22}r_1r_3 + L_{12}r_2r_3 - L_{13}r_2^2 + L_{23}r_1r_2 + T_{13} \\
U^n_{23} &= -L_{11}r_2r_3 + L_{12}r_1r_3 - L_{13}r_1r_2 - L_{23}r_1^2 + T_{23},
\end{aligned} \qquad (1.2.11.5)$$

where the coefficients $L_{ij} = \langle \lambda_i \lambda_j \rangle$ and $T_{ij} = \langle t_i t_j \rangle$ are the elements of the 3×3 libration tensor $\mathbf{L}$ and the 3×3 translation tensor $\mathbf{T}$,

Table 1.2.8.1. *Products of complex spherical harmonics as defined by equation (1.2.7.2a)*

$$
\begin{aligned}
Y_{00}\ Y_{00} &= 0.28209479 Y_{00}\\
Y_{10}\ Y_{00} &= 0.28209479 Y_{10}\\
Y_{10}\ Y_{10} &= 0.25231325 Y_{20} + 0.28209479 Y_{00}\\
Y_{11}\ Y_{00} &= 0.28209479 Y_{11}\\
Y_{11}\ Y_{10} &= 0.21850969 Y_{21}\\
Y_{11}\ Y_{11} &= 0.30901936 Y_{22}\\
Y_{11}\ Y_{11-} &= -0.12615663 Y_{20} + 0.28209479 Y_{00}\\
Y_{20}\ Y_{00} &= 0.28209479 Y_{20}\\
Y_{20}\ Y_{10} &= 0.24776669 Y_{30} + 0.25231325 Y_{10}\\
Y_{20}\ Y_{11} &= 0.20230066 Y_{31} - 0.12615663 Y_{11}\\
Y_{20}\ Y_{20} &= 0.24179554 Y_{40} + 0.18022375 Y_{20} + 0.28209479 Y_{00}\\
Y_{21}\ Y_{00} &= 0.28209479 Y_{21}\\
Y_{21}\ Y_{10} &= 0.23359668 Y_{31} + 0.21850969 Y_{11}\\
Y_{21}\ Y_{11} &= 0.26116903 Y_{32}\\
Y_{21}\ Y_{11-} &= -0.14304817 Y_{30} + 0.21850969 Y_{10}\\
Y_{21}\ Y_{20} &= 0.22072812 Y_{41} + 0.09011188 Y_{21}\\
Y_{21}\ Y_{21} &= 0.25489487 Y_{42} + 0.22072812 Y_{22}\\
Y_{21}\ Y_{21-} &= -0.16119702 Y_{40} + 0.09011188 Y_{20} + 0.28209479 Y_{00}\\
Y_{22}\ Y_{00} &= 0.28209479 Y_{22}\\
Y_{22}\ Y_{10} &= 0.18467439 Y_{32}\\
Y_{22}\ Y_{11} &= 0.31986543 Y_{33}\\
Y_{22}\ Y_{11-} &= -0.08258890 Y_{31} + 0.30901936 Y_{11}\\
Y_{22}\ Y_{20} &= 0.15607835 Y_{42} - 0.18022375 Y_{22}\\
Y_{22}\ Y_{21} &= 0.23841361 Y_{43}\\
Y_{22}\ Y_{21-} &= -0.09011188 Y_{41} + 0.22072812 Y_{21}\\
Y_{22}\ Y_{22} &= 0.33716777 Y_{44}\\
Y_{22}\ Y_{22-} &= 0.04029926 Y_{40} - 0.18022375 Y_{20} + 0.28209479 Y_{00}
\end{aligned}
$$

Table 1.2.8.2. *Products of real spherical harmonics as defined by equations (1.2.7.2b) and (1.2.7.2c)*

$$
\begin{aligned}
y_{00}\ y_{00} &= 0.28209479 y_{00}\\
y_{10}\ y_{00} &= 0.28209479 y_{10}\\
y_{10}\ y_{10} &= 0.25231325 y_{20} + 0.28209479 y_{00}\\
y_{11\pm}\ y_{00} &= 0.28209479 y_{11\pm}\\
y_{11\pm}\ y_{10} &= 0.21850969 y_{21\pm}\\
y_{11\pm}\ y_{11\pm} &= 0.21850969 y_{22+} - 0.12615663 y_{20} + 0.28209479 y_{00}\\
y_{11+}\ y_{11-} &= 0.21850969 y_{22-}\\
y_{20}\ y_{00} &= 0.28209479 y_{20}\\
y_{20}\ y_{10} &= 0.24776669 y_{30} + 0.25231325 y_{10}\\
y_{20}\ y_{11\pm} &= 0.20230066 y_{31\pm} - 0.12615663 y_{11\pm}\\
y_{20}\ y_{20} &= 0.24179554 y_{40} + 0.18022375 y_{20} + 0.28209479 y_{00}\\
y_{21\pm}\ y_{00} &= 0.28209479 y_{21\pm}\\
y_{21\pm}\ y_{10} &= 0.23359668 y_{31\pm} + 0.21850969 y_{11\pm}\\
y_{21\pm}\ y_{11\pm} &= \pm 0.18467439 y_{32+} - 0.14304817 y_{30} + 0.21850969 y_{10}\\
y_{21\pm}\ y_{11\mp} &= 0.18467469 y_{32-}\\
y_{21\pm}\ y_{20} &= 0.22072812 y_{41\pm} + 0.09011188 y_{21\pm}\\
y_{21\pm}\ y_{21\pm} &= \pm 0.18022375 y_{42+} \pm 0.15607835 y_{22+}\\
&\quad - 0.16119702 y_{40} + 0.09011188 y_{20} + 0.28209479 y_{00}\\
y_{21+}\ y_{21-} &= -0.18022375 y_{42-} + 0.15607835 y_{22-}\\
y_{22\pm}\ y_{00} &= 0.28209479 y_{22\pm}\\
y_{22\pm}\ y_{10} &= 0.18467439 y_{32\pm}\\
y_{22\pm}\ y_{11\pm} &= \pm 0.22617901 y_{33+} - 0.05839917 y_{31+} + 0.21850969 y_{11+}\\
y_{22\pm}\ y_{11\mp} &= 0.22617901 y_{33-} \pm 0.05839917 y_{31-} \mp 0.21850969 y_{11-}\\
y_{22\pm}\ y_{20} &= 0.15607835 y_{42\pm} - 0.18022375 y_{22\pm}\\
y_{22\pm}\ y_{21\pm} &= \pm 0.16858388 y_{43+} - 0.06371872 y_{41+} + 0.15607835 y_{21+}\\
y_{22\pm}\ y_{21\mp} &= 0.16858388 y_{43-} \pm 0.06371872 y_{41-} \mp 0.15607835 y_{21-}\\
y_{22\pm}\ y_{22\pm} &= \pm 0.23841361 y_{44+} + 0.04029926 y_{40} - 0.18022375 y_{20}\\
&\quad + 0.28209479 y_{00}\\
y_{22+}\ y_{22-} &= 0.23841361 y_{44-}
\end{aligned}
$$

respectively. Since pairs of terms such as $\langle t_i t_j\rangle$ and $\langle t_j t_i\rangle$ correspond to averages over the same two scalar quantities, the **T** and **L** tensors are symmetrical.

If a rotation axis is correctly oriented, but incorrectly positioned, an additional translation component perpendicular to the rotation axes is introduced. The rotation angle and the parallel component of the translation are invariant to the position of the axis, but the perpendicular component is not. This implies that the **L** tensor is unaffected by any assumptions about the position of the libration axes, whereas the **T** tensor depends on the assumptions made concerning the location of the axes.

The quadratic correlation between librational and translational motions can be allowed for by including in (1.2.11.5) cross terms of the type $\langle D_{ik} t_j\rangle$, or, with (1.2.11.3),

$$
\begin{aligned}
U_{ij} &= \langle D_{ik} D_{jl}\rangle r_k r_l + \langle D_{ik} t_j + D_{ji} t_i\rangle r_k + \langle t_i t_j\rangle\\
&= A_{ijkl} r_k r_l + B_{ijk} r_k + \langle t_i t_j\rangle,
\end{aligned}
\tag{1.2.11.6}
$$

which leads to the explicit expressions such as

$$
\begin{aligned}
U_{11} = \langle \delta r_1\rangle^2 &= \langle \lambda_3^2\rangle r_2^2 + \langle \lambda_2^2\rangle r_3^2 - 2\langle \lambda_2\lambda_3\rangle r_2 r_3\\
&\quad - 2\langle \lambda_3 t_1\rangle r_2 - 2\langle \lambda_2 t_1\rangle r_3 + \langle t_1^2\rangle,\\
U_{12} = \langle \delta r_1 \delta r_2\rangle &= -\langle \lambda_3^2\rangle r_1 r_2 + \langle \lambda_1\lambda_3\rangle r_2 r_3 + \langle \lambda_2\lambda_3\rangle r_1 r_3\\
&\quad - \langle \lambda_1\lambda_2\rangle r_3^2 + \langle \lambda_3 t_1\rangle r_1 - \langle \lambda_1 t_1\rangle r_3\\
&\quad - \langle \lambda_3 t_2\rangle + r_2\langle \lambda_2 t_2\rangle r_3 + \langle t_1 t_2\rangle.
\end{aligned}
\tag{1.2.11.7}
$$

The products of the type $\langle \lambda_i t_j\rangle$ are the components of an additional tensor, **S**, which unlike the tensors **T** and **L** is unsymmetrical, since $\langle \lambda_i t_j\rangle$ is different from $\langle \lambda_j t_i\rangle$. The terms involving elements of **S** may be grouped as

$$
\langle \lambda_3 t_1\rangle r_1 - \langle \lambda_3 t_2\rangle r_2 + (\langle \lambda_2 t_2\rangle - \langle \lambda_1 t_1\rangle) r_3 \tag{1.2.11.8}
$$

or

$$
S_{31} r_1 - S_{32} r_2 + (S_{22} - S_{11}) r_3.
$$

As the diagonal elements occur as differences in this expression, a constant may be added to each of the diagonal terms without changing the observational equations. In other words, the trace of **S** is indeterminate.

In terms of the **L**, **T** and **S** tensors, the observational equations are

$$
U_{ij} = G_{ijkl} L_{kl} + H_{ijkl} S_{kl} + T_{ij}. \tag{1.2.11.9}
$$

The arrays G_{ijkl} and H_{ijkl} involve the atomic coordinates $(x,\ y,\ z) = (r_1,\ r_2,\ r_3)$, and are listed in Table 1.2.11.1. Equations (1.2.11.9) for each of the atoms in the rigid body form the observational equations, from which the elements of **T**, **L** and **S** can be derived by a linear least-squares procedure. One of the diagonal elements of **S** must be fixed in advance or some other suitable constraint applied because of the indeterminacy of Tr(**S**). It is common practice to set Tr(**S**) equal to zero. There are thus eight elements of **S** to be determined, as well as the six each of **L** and **T**, for a total of 20 variables. A shift of origin leaves **L** invariant, but it intermixes **T** and **S**.

If the origin is located at a centre of symmetry, for each atom at **r** with vibration tensor $\mathbf{U}^n$ there will be an equivalent atom at $-\mathbf{r}$ with

Table 1.2.8.3. *Products of two real spherical harmonic functions y_{lmp} in terms of the density functions d_{lmp} defined by equation (1.2.7.3b)*

$$
\begin{aligned}
y_{00}\, y_{00} &= 1.0000 d_{00} \\
y_{10}\, y_{00} &= 0.43301 d_{10} \\
y_{10}\, y_{10} &= 0.38490 d_{20} + 1.0 d_{00} \\
y_{11\pm}\, y_{00} &= 0.43302 d_{11\pm} \\
y_{11\pm}\, y_{10} &= 0.31831 d_{21\pm} \\
y_{11\pm}\, y_{11\pm} &= 0.31831 d_{22+} - 0.19425 d_{20} + 1.0 d_{00} \\
y_{11+}\, y_{11-} &= 0.31831 d_{22-} \\
y_{20}\, y_{00} &= 0.43033 d_{20} \\
y_{20}\, y_{10} &= 0.37762 d_{30} + 0.38730 d_{10} \\
y_{20}\, y_{11\pm} &= 0.28864 d_{31\pm} - 0.19365 d_{11\pm} \\
y_{20}\, y_{20} &= 0.36848 d_{40} + 0.27493 d_{20} + 1.0 d_{00} \\
y_{21\pm}\, y_{00} &= 0.41094 d_{21\pm} \\
y_{21\pm}\, y_{10} &= 0.33329 d_{31\pm} + 0.33541 d_{11\pm} \\
y_{21\pm}\, y_{11\pm} &= \pm 0.26691 d_{32+} - 0.21802 d_{30} + 0.33541 d_{10} \\
y_{21\pm}\, y_{11\mp} &= -0.26691 d_{32-} \\
y_{21\pm}\, y_{20} &= 0.31155 d_{41\pm} + 0.13127 d_{21\pm} \\
y_{21\pm}\, y_{21\pm} &= \pm 0.25791 d_{42+} \pm 0.22736 d_{22+} - 0.24565 d_{40} + 0.13747 d_{20} \\
&\quad + 1.0 d_{00} \\
y_{21+}\, y_{21-} &= 0.25790 d_{42-} + 0.22736 d_{22-} \\
y_{22\pm}\, y_{00} &= 0.41094 d_{22\pm} \\
y_{22\pm}\, y_{10} &= 0.26691 d_{32\pm} \\
y_{22\pm}\, y_{11\pm} &= \pm 0.31445 d_{33+} - 0.083323 d_{31+} + 0.33541 d_{11+} \\
y_{22\pm}\, y_{11\mp} &= 0.31445 d_{33-} \pm 0.083323 d_{31-} \mp 0.33541 d_{11-} \\
y_{22\pm}\, y_{20} &= 0.22335 d_{42\pm} - 0.26254 d_{22\pm} \\
y_{22\pm}\, y_{21\pm} &= \pm 0.23873 d_{43+} - 0.089938 d_{41+} + 0.22736 d_{21+} \\
y_{22\pm}\, y_{21\mp} &= 0.23873 d_{43-} \pm 0.089938 d_{41-} \mp 0.22736 d_{21-} \\
y_{22\pm}\, y_{22\pm} &= \pm 0.31831 d_{44+} + 0.061413 d_{40} - 0.27493 d_{20} + 1.0 d_{00} \\
y_{22+}\, y_{22-} &= 0.31831 d_{44-}
\end{aligned}
$$

the same vibration tensor. When the observational equations for these two atoms are added, the terms involving elements of **S** disappear since they are linear in the components of **r**. The other terms, involving elements of the **T** and **L** tensors, are simply doubled, like the $\mathbf{U}^n$ components.

The physical meaning of the **T** and **L** tensor elements is as follows. $T_{ij}l_il_j$ is the mean-square amplitude of translational vibration in the direction of the unit vector l with components l_1, l_2, l_3 along the Cartesian axes and $L_{ij}l_il_j$ is the mean-square amplitude of libration about an axis in this direction. The quantity $S_{ij}l_il_j$ represents the mean correlation between libration about the axis l and translation parallel to this axis. This quantity, like $T_{ij}l_il_j$, depends on the choice of origin, although the sum of the two quantities is independent of the origin.

The non-symmetrical tensor **S** can be written as the sum of a symmetric tensor with elements $S^S_{ij} = (S_{ij} + S_{ji})/2$ and a skew-symmetric tensor with elements $S^A_{ij} = (S_{ij} - S_{ji})/2$. Expressed in terms of principal axes, $\mathbf{S}^S$ consists of three principal screw correlations $\langle \lambda_I t_I \rangle$. Positive and negative screw correlations correspond to opposite senses of helicity. Since an arbitrary constant may be added to all three correlation terms, only the differences between them can be determined from the data.

The skew-symmetric part $\mathbf{S}^A$ is equivalent to a vector $(\boldsymbol{\lambda} \times \mathbf{t})/2$ with components $(\boldsymbol{\lambda} \times \mathbf{t})_i/2 = (\lambda_j t_k - \lambda_k t_j)/2$, involving correlations between a libration and a perpendicular translation. The components of $\mathbf{S}^A$ can be reduced to zero, and **S** made symmetric, by a change of origin. It can be shown that the origin shift that

Table 1.2.11.1. *The arrays G_{ijkl} and H_{ijkl} to be used in the observational equations $U_{ij} = G_{ijkl}L_{kl} + H_{ijkl}S_{kl} + T_{ij}$ [equation (1.2.11.9)]*

G_{ijkl}

	kl					
ij	11	22	33	23	31	12
11	0	z^2	y^2	$-2yz$	0	0
22	z^2	0	x^2	0	$-2xz$	0
33	y^2	x^2	0	0	0	$-2xy$
23	$-yz$	0	0	$-x^2$	xy	xz
31	0	$-xz$	0	xy	$-y^2$	yz
12	0	0	$-xy$	xz	yz	$-z^2$

H_{ijkl}

	kl								
ij	11	22	33	23	31	12	32	13	21
11	0	0	0	0	$-2y$	0	0	0	$2z$
22	0	0	0	0	0	$-2z$	$2x$	0	0
33	0	0	0	$-2x$	0	0	0	$2y$	0
23	0	$-x$	x	0	0	y	0	$-z$	0
31	y	0	$-y$	z	0	0	0	0	$-x$
12	$-z$	z	0	0	x	0	$-y$	0	0

symmetrizes **S** also minimizes the trace of **T**. In terms of the coordinate system based on the principal axes of **L**, the required origin shifts $\widehat{\rho}_i$ are

$$\widehat{\rho}_1 = \frac{\widehat{S}_{23} - \widehat{S}_{32}}{\widehat{L}_{22} + \widehat{L}_{33}} \quad \widehat{\rho}_2 = \frac{\widehat{S}_{31} - \widehat{S}_{13}}{\widehat{L}_{11} + \widehat{L}_{33}} \quad \widehat{\rho}_3 = \frac{\widehat{S}_{12} - \widehat{S}_{21}}{\widehat{L}_{11} + \widehat{L}_{22}}, \quad (1.2.11.10)$$

in which the carets indicate quantities referred to the principal axis system.

The description of the averaged motion can be simplified further by shifting to three generally non-intersecting libration axes, one each for each principal axis of **L**. Shifts of the $\mathbf{L}_1$ axis in the $\mathbf{L}_2$ and $\mathbf{L}_3$ directions by

$${}^1\widehat{\rho}_2 = -\widehat{S}_{13}/\widehat{L}_{11} \text{ and } {}^1\widehat{\rho}_3 = \widehat{S}_{12}/\widehat{L}_{11}, \quad (1.2.11.11)$$

respectively, annihilate the S_{12} and S_{13} terms of the symmetrized **S** tensor and simultaneously effect a further reduction in Tr(**T**) (the presuperscript denotes the axis that is shifted, the subscript the direction of the shift component). Analogous equations for displacements of the $\mathbf{L}_2$ and $\mathbf{L}_3$ axes are obtained by permutation of the indices. If all three axes are appropriately displaced, only the diagonal terms of **S** remain. Referred to the principal axes of **L**, they represent screw correlations along these axes and are independent of origin shifts.

The elements of the reduced **T** are

$$\begin{aligned} {}^r\widehat{T}_{II} &= \widehat{T}_{II} - \sum_{K \neq I} (\widehat{S}_{KI})^2/\widehat{L}_{KK} \\ {}^r\widehat{T}_{IJ} &= \widehat{T}_{IJ} - \sum_K \widehat{S}_{KI}\widehat{S}_{KJ}/\widehat{L}_{KK}, \quad J \neq I. \end{aligned} \quad (1.2.11.12)$$

The resulting description of the average rigid-body motion is in terms of six independently distributed instantaneous motions – three screw librations about non-intersecting axes (with screw pitches given by $\widehat{S}_{11}/\widehat{L}_{11}$ *etc.*) and three translations. The parameter set consists of three libration and three translation amplitudes, six

Table 1.2.12.1. *Some Hermite polynomials (Johnson & Levy, 1974; Zucker & Schulz, 1982)*

$$
\begin{aligned}
H(\mathbf{u}) &= 1\\
H_j(\mathbf{u}) &= w_j\\
H_{jk}(\mathbf{u}) &= w_jw_k - p_{jk}\\
H_{jkl}(\mathbf{u}) &= w_jw_kw_l - (w_jp_{kl} + w_kp_{lj} + w_lp_{jk}) = w_jw_kw_l - 3w(_jp_{kl})\\
H_{jklm}(\mathbf{u}) &= w_jw_kw_lw_m - 6w(_jw_kp_{lm}) + 3p_j(_kp_{lm})\\
H_{jklmn}(\mathbf{u}) &= w_jw_kw_lw_mw_n - 10w(_lw_mw_np_{jk}) + 15w(_np_{jk}p_{lm})\\
H_{jklmnp}(\mathbf{u}) &= w_jw_kw_lw_mw_nw_p - 15w(_jw_kw_lw_mp_{jk}) + 45w(_jw_kp_{lm}p_{np})\\
&\quad - 15p_j(_kp_{lm}p_{np})
\end{aligned}
$$

where $w_j \equiv p_{jk}u^k$ and p_{jk} are the elements of σ^{-1}, defined in expression (1.2.10.2). Indices between brackets indicate that the term is to be averaged over all permutations which produce distinct terms, keeping in mind that $p_{jk} = p_{kj}$ and $w_jw_k = w_kw_j$ as illustrated for H_{jkl}.

angles of orientation for the principal axes of **L** and **T**, six coordinates of axis displacement, and three screw pitches, one of which has to be chosen arbitrarily, again for a total of 20 variables.

Since diagonal elements of **S** enter into the expression for ${}^rT_{IJ}$, the indeterminacy of Tr(**S**) introduces a corresponding indeterminacy in ${}^r\mathbf{T}$. The constraint Tr(**S**) = 0 is unaffected by the various rotations and translations of the coordinate systems used in the course of the analysis.

1.2.12. Treatment of anharmonicity

The probability distribution (1.2.10.2) is valid in the case of rectilinear harmonic motion. If the deviations from Gaussian shape are not too large, distributions may be used which are expansions with the Gaussian distribution as the leading term. Three such distributions are discussed in the following sections.

1.2.12.1. *The Gram–Charlier expansion*

The three-dimensional Gram–Charlier expansion, introduced into thermal-motion treatment by Johnson & Levy (1974), is an expansion of a function in terms of the zero and higher derivatives of a normal distribution (Kendall & Stuart, 1958). If D_j is the operator $\mathrm{d}/\mathrm{d}u^j$,

$$
\begin{aligned}
P(\mathbf{u}) = [1 - c^jD_j + \frac{1}{2!}c^{jk}D_jD_k - \frac{1}{3!}c^{jkl}D_jD_kD_l + \ldots\\
+ (-1)^r\frac{c^{\alpha_1}\ldots c^{\alpha_r}}{r!}D_{\alpha_1}D_{\alpha_r}]P_0(\mathbf{u}),
\end{aligned}
\tag{1.2.12.1}
$$

where $P_0(\mathbf{u})$ is the harmonic distribution, $\alpha_1 = 1, 2$ or 3, and the operator $D_{\alpha_1}\ldots D_{\alpha_r}$ is the rth partial derivative $\partial^r/(\partial u^{\alpha 1}\ldots\partial u^{\alpha r})$. Summation is again implied over repeated indices.

The differential operators D may be eliminated by the use of three-dimensional Hermite polynomials $H_{\alpha_1\ldots\alpha_2}$ defined, by analogy with the one-dimensional Hermite polynomials, by the expression

$$
D_{\alpha_1}\ldots D_{\alpha_r}\exp(-\tfrac{1}{2}\sigma^{-1}_{jk}u^ju^k) = (-1)^rH_{\alpha_1\ldots\alpha_r}(\mathbf{u})\exp(-\tfrac{1}{2}\sigma^{-1}_{jk}u^ju^k),
\tag{1.2.12.2}
$$

which gives

$$
\begin{aligned}
P(\mathbf{u}) = \Big[1 + \frac{1}{3!}c^{jkl}H_{jkl}(\mathbf{u}) + \frac{1}{4!}c^{jklm}H_{jklm}(\mathbf{u}) + \frac{1}{5!}c^{jklmn}H_{jklmn}(\mathbf{u})\\
+ \frac{1}{6!}c^{jklmnp}H_{jklmnp}(\mathbf{u}) + \ldots\Big]P_0(\mathbf{u}),
\end{aligned}
\tag{1.2.12.3}
$$

where the first and second terms have been omitted since they are equivalent to a shift of the mean and a modification of the harmonic term only. The permutations of $j, k, l\ldots$ here, and in the following sections, include all combinations which produce different terms.

The coefficients c, defined by (1.2.12.1) and (1.2.12.2), are known as the *quasimoments* of the frequency function $P(\mathbf{u})$ (Kutznetsov *et al.*, 1960). They are related in a simple manner to the moments of the function (Kendall & Stuart, 1958) and are invariant to permutation of indices. There are 10, 15, 21 and 28 components of c for orders 3, 4, 5 and 6, respectively. The multivariate Hermite polynomials are functions of the elements of σ^{-1}_{jk} and of u^k, and are given in Table 1.2.12.1 for orders ≤ 6 (*IT* IV, 1974; Zucker & Schulz, 1982).

The Fourier transform of (1.2.12.3) is given by

$$
\begin{aligned}
T(\mathbf{H}) = \Big[1 - \frac{4}{3}\pi^3ic^{jkl}h_jh_kh_l + \frac{2}{3}\pi^4c^{jklm}h_jh_kh_lh_m\\
+ \frac{4}{15}\pi^5ic^{jklmn}h_jh_kh_lh_mh_n\\
- \frac{4}{45}\pi^6c^{jklmnp}h_jh_kh_lh_mh_nh_p + \ldots\Big]T_0(\mathbf{H}),
\end{aligned}
\tag{1.2.12.4}
$$

where $T_0(\mathbf{H})$ is the harmonic temperature factor. $T(\mathbf{H})$ is a power-series expansion about the harmonic temperature factor, with even and odd terms, respectively, real and imaginary.

1.2.12.2. *The cumulant expansion*

A second statistical expansion which has been used to describe the atomic probability distribution is that of Edgeworth (Kendall & Stuart, 1958; Johnson, 1969). It expresses the function $P(\mathbf{u})$ as

$$
\begin{aligned}
P(\mathbf{u}) = \exp\Big(\kappa^jD_j + \frac{1}{2!}\kappa^{jk}D_jD_k - \frac{1}{3!}\kappa^{jkl}D_jD_kD_l\\
+ \frac{1}{4!}\kappa^{jklm}D_jD_kD_lD_m - \ldots\Big)P_0(\mathbf{u}).
\end{aligned}
\tag{1.2.12.5a}
$$

Like the moments μ of a distribution, the cumulants κ are descriptive constants. They are related to each other (in the one-dimensional case) by the identity

$$
\exp\Big\{\kappa_1t + \frac{\kappa_2t^2}{2!} + \ldots\frac{\kappa_rt^r}{r!} + \ldots\Big\} = 1 + \mu_1t + \frac{\mu_2t^2}{2!} + \ldots + \frac{\mu_rt^r}{r!}.
\tag{1.2.12.5b}
$$

When it is substituted for t, (1.2.12.5b) is the characteristic function, or Fourier transform of $P(t)$ (Kendall & Stuart, 1958).

The first two terms in the exponent of (1.2.12.5a) can be omitted if the expansion is around the equilibrium position and the harmonic term is properly described by $P_0(\mathbf{u})$.

The Fourier transform of (1.2.12.5a) is, by analogy with the left-hand part of (1.2.12.5b) (with t replaced by $2\pi ih$),

$$
\begin{aligned}
T(\mathbf{H}) &= \exp\Big[\frac{(2\pi i)^3}{3!}\kappa^{jkl}h_jh_kh_l + \frac{(2\pi i)^4}{4!}\kappa^{jklm}h_jh_kh_lh_m + \ldots\Big]T_0(\mathbf{H})\\
&= \exp\Big[-\frac{4}{3}\pi^3i\kappa^{jkl}h_jh_kh_l + \frac{2}{3}\pi^4\kappa^{jklm}h_jh_kh_lh_m + \ldots\Big]T_0(\mathbf{H}),
\end{aligned}
\tag{1.2.12.6}
$$

where the first two terms have been omitted. Expression (1.2.12.6) is similar to (1.2.12.4) except that the entire series is in the exponent. Following Schwarzenbach (1986), (1.2.12.6) can be developed in a Taylor series, which gives

references