

1.2. THE STRUCTURE FACTOR

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

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

k	N							
	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				$\frac{48K^3}{(K^2 + Z^2)^3}$	$\frac{384K^3Z}{(K^2 + Z^2)^5}$	$\frac{384K^3(9Z^2 - K^2)}{(K^2 + Z^2)^6}$	$\frac{11520K^3Z(3Z^2 - K^2)}{(K^2 + Z^2)^7}$	$\frac{11520K^3(33Z^4 - 22K^2Z^2 + K^4)}{(K^2 + Z^2)^8}$
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								$\frac{645120K^7}{(K^2 + Z^2)^8}$

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

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

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

where the superscript T indicates the transpose.

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

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

or

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

With the change of variable $b^{jk} = 2\pi^2 \sigma^{jk}$, (1.2.10.3a) 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 (1970b) 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 $\boldsymbol{\lambda}$ ($\lambda_1, \lambda_2, \lambda_3$), with length corresponding to the magnitude of the rotation, results in a displacement $\delta\mathbf{r}$, such that

$$\delta\mathbf{r} = (\boldsymbol{\lambda} \times \mathbf{r}) = \mathbf{Dr} \quad (1.2.11.1)$$

with

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

or in tensor notation, assuming summation over repeated indices,

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

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

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

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_{ij}^n , are given by

$$\begin{aligned} U_{11}^n &= +L_{22}r_3^2 + L_{33}r_2^2 - 2L_{23}r_2 r_3 + T_{11} \\ U_{22}^n &= +L_{33}r_1^2 + L_{11}r_3^2 - 2L_{13}r_1 r_3 + T_{22} \\ U_{33}^n &= +L_{11}r_2^2 + L_{22}r_1^2 - 2L_{12}r_1 r_2 + T_{33} \\ U_{12}^n &= -L_{33}r_1 r_2 - L_{12}r_2^2 + L_{13}r_2 r_3 + L_{23}r_1 r_3 + T_{12} \\ U_{13}^n &= -L_{22}r_1 r_3 + L_{12}r_2 r_3 - L_{13}r_2^2 + L_{23}r_1 r_2 + T_{13} \\ U_{23}^n &= -L_{11}r_2 r_3 + L_{12}r_1 r_3 - L_{13}r_1 r_2 - L_{23}r_1^2 + T_{23}, \end{aligned} \quad (1.2.11.5)$$

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} ,