<center>1. GENERAL RELATIONSHIPS AND TECHNIQUES</center>

orbital product density functions $\phi_\mu(\mathbf{r})\varphi_\nu(\mathbf{r})$ and are given by

$$P_{\mu\nu} = \sum_i n_i c_{i\mu} c_{i\nu}. \qquad (1.2.8.2)$$

For a multi-Slater determinant wavefunction the electron density is expressed in terms of the occupied natural spin orbitals, leading again to (1.2.8.2) but with non-integer values for the coefficients n_i.

The summation (1.2.8.1) consists of one- and two-centre terms for which φ_μ and φ_ν are centred on the same or on different nuclei, respectively. The latter represent the overlap density, which is only significant if $\varphi_\mu(\mathbf{r})$ and $\varphi_\nu(\mathbf{r})$ have an appreciable value in the same region of space.

1.2.8.1. *One-centre orbital products*

If the atomic basis consists of hydrogenic type s, p, d, f, ... orbitals, the basis functions may be written as

$$\varphi(r, \theta, \varphi) = R_l(r) Y_{lm}(\theta, \varphi) \qquad (1.2.8.3a)$$

or

$$\varphi(r, \theta, \varphi) = R_l(r) y_{lmp}(\theta, \varphi), \qquad (1.2.8.3b)$$

which gives for corresponding values of the orbital products

$$\varphi_\mu(\mathbf{r})\varphi_\nu(\mathbf{r}) = R_l(r) R_{l'}(r) Y_{lm}(\theta, \varphi) Y_{l'm'}(\theta, \varphi) \qquad (1.2.8.4a)$$

and

$$\varphi_\mu(\mathbf{r})\varphi_\nu(\mathbf{r}) = R_l(r) R_{l'}(r) y_{lmp}(\theta, \varphi) y_{l'm'p'}(\theta, \varphi), \qquad (1.2.8.4b)$$

respectively, where it has been assumed that the radial function depends only on l.

Because the spherical harmonic functions form a complete set, their products can be expressed as a linear combination of spherical harmonics. The coefficients in this expansion are the *Clebsch–Gordan coefficients* (Condon & Shortley, 1957), defined by

$$Y_{lm}(\theta, \varphi) Y_{l'm'}(\theta, \varphi) = \sum_L \sum_M C_{Lll'}^{Mmm'} Y_{LM}(\theta, \varphi) \qquad (1.2.8.5a)$$

or the equivalent definition

$$C_{Lll'}^{Mmm'} = \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\varphi Y_{LM}^*(\theta, \varphi) Y_{lm}(\theta, \varphi) Y_{l'm'}(\theta, \varphi). \qquad (1.2.8.5b)$$

The $C_{Lll'}^{Mmm'}$ vanish, unless $L + l + l'$ is even, $|l - l'| < L < l + l'$ and $M = m + m'$.

The corresponding expression for y_{lmp} is

$$y_{lmp}(\theta, \varphi) y_{l'm'p'}(\theta, \varphi) = \sum_L \sum_M C_{Lll'}'^{Mmm'} y_{LMP}(\theta, \varphi), \qquad (1.2.8.5c)$$

with $M = |m + m'|$ and $|m - m'|$ for $p = p'$, and $M = -|m + m'|$ and $-|m - m'|$ for $p = -p'$ and $P = p \times p'$.

Values of C and C' for $l \leq 2$ are given in Tables 1.2.8.1 and 1.2.8.2. They are valid for the functions Y_{lm} and y_{lmp} with normalization $\int |Y_{lm}|^2 \, d\Omega = 1$ and $\int y_{lmp}^2 \, d\Omega = 1$.

By using (1.2.8.5a) or (1.2.8.5c), the one-centre orbital products are expressed as a sum of spherical harmonic functions. It follows that the one-centre orbital product density basis set is formally equivalent to the multipole description, both in real and in reciprocal space. To obtain the relation between orbital products and the charge-density functions, the right-hand side of (1.2.8.5c) has to be multiplied by the ratio of the normalization constants, as the wavefunctions y_{lmp} and charge-density functions d_{lmp} are normalized in a different way as described by (1.2.7.3a) and (1.2.7.3b). Thus

$$y_{lmp}(\theta, \varphi) y_{l'm'p'}(\theta, \varphi) = \sum_L \sum_M R_{LMP} C_{Lll'}'^{Mmm'} \sum_P d_{LMP}(\theta, \varphi), \qquad (1.2.8.6)$$

where $R_{LMP} = M_{LMP}$ (wavefunction)$/L_{LMP}$ (density function). The normalization constants M_{lmp} and L_{lmp} are given in Table 1.2.7.1, while the coefficients in the expressions (1.2.8.6) are listed in Table 1.2.8.3.

1.2.8.2. *Two-centre orbital products*

Fourier transform of the electron density as described by (1.2.8.1) requires explicit expressions for the two-centre orbital product scattering. Such expressions are described in the literature for both Gaussian (Stewart, 1969*b*) and Slater-type (Bentley & Stewart, 1973; Avery & Ørmen, 1979) atomic orbitals. The expressions can also be used for Hartree–Fock atomic functions, as expansions in terms of Gaussian- (Stewart, 1969*b*, 1970; Stewart & Hehre, 1970; Hehre *et al.*, 1970) and Slater-type (Clementi & Roetti, 1974) functions are available for many atoms.

1.2.9. The atomic temperature factor

Since the crystal is subject to vibrational oscillations, the observed elastic scattering intensity is an average over all normal modes of the crystal. Within the Born–Oppenheimer approximation, the theoretical electron density should be calculated for each set of nuclear coordinates. An average can be obtained by taking into account the statistical weight of each nuclear configuration, which may be expressed by the probability distribution function $P(\mathbf{u}_1, \ldots, \mathbf{u}_N)$ for a set of displacement coordinates $\mathbf{u}_1, \ldots, \mathbf{u}_N$.

In general, if $\rho(\mathbf{r}, \mathbf{u}_1, \ldots, \mathbf{u}_N)$ is the electron density corresponding to the geometry defined by $\mathbf{u}_1, \ldots, \mathbf{u}_N$, the time-averaged electron density is given by

$$\langle\rho(\mathbf{r})\rangle = \int \rho(\mathbf{r}, \mathbf{u}_1, \ldots, \mathbf{u}_N) P(\mathbf{u}_1, \ldots, \mathbf{u}_N) \, d\mathbf{u}_1 \ldots d\mathbf{u}_N. \qquad (1.2.9.1)$$

When the crystal can be considered as consisting of perfectly following rigid entities, which may be molecules or atoms, expression (1.2.9.1) simplifies:

$$\langle\rho_{\text{rigid group}}(\mathbf{r})\rangle = \int \rho_{\text{r.g., static}}(\mathbf{r} - \mathbf{u}) P(\mathbf{u}) \, d\mathbf{u} = \rho_{\text{r.g., static}} * P(\mathbf{u}). \qquad (1.2.9.2)$$

In the approximation that the atomic electrons perfectly follow the nuclear motion, one obtains

$$\langle\rho_{\text{atom}}(\mathbf{r})\rangle = \rho_{\text{atom, static}}(\mathbf{r}) * P(\mathbf{u}). \qquad (1.2.9.3)$$

The Fourier transform of this convolution is the product of the Fourier transforms of the individual functions:

$$\langle f(\mathbf{H})\rangle = f(\mathbf{H}) T(\mathbf{H}). \qquad (1.2.9.4)$$

Thus $T(\mathbf{H})$, the atomic temperature factor, is the Fourier transform of the probability distribution $P(\mathbf{u})$.

1.2.10. The vibrational probability distribution and its Fourier transform in the harmonic approximation

For a harmonic oscillator, the probability distribution averaged over all populated energy levels is a Gaussian, centred at the equilibrium position. For the three-dimensional isotropic harmonic oscillator, the distribution is

$$P(u) = (2\pi\langle u^2\rangle)^{-3/2} \exp\{-|u|^2/2\langle u^2\rangle\}, \qquad (1.2.10.1)$$

where $\langle u^2\rangle$ is the mean-square displacement in any direction.

The corresponding trivariate normal distribution to be used for anisotropic harmonic motion is, in tensor notation,

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