3. DUAL BASES IN CRYSTALLOGRAPHIC COMPUTING

$$S_n = [1/2V_d\Gamma(n/2)] \int |\mathbf{X}|^{-n}$$
$$\times [P(\mathbf{X}) - P(\mathbf{X})\delta(\mathbf{X})]\Gamma(n/2, \pi w^2|\mathbf{X}|^2) \, d\mathbf{X}$$
$$+ [1/2V_d\Gamma(n/2)] \int |\mathbf{X}|^{-n}$$
$$\times [P(\mathbf{X}) - P(\mathbf{X})\delta(\mathbf{X})]\gamma(n/2, \pi w^2|\mathbf{X}|^2) \, d\mathbf{X}.$$

The first integral is shown only for a consistent representation; actually it will be reconverted to a sum and evaluated in direct space. The first part of the second integral will be evaluated with Parseval's theorem and the second part in the limit as $|\mathbf{X}|$ approaches zero:

$$[1/2V_d\Gamma(n/2)] \int FT_3[P(\mathbf{X})]$$
$$\times FT_3[|\mathbf{X}|^{-n}\gamma(n/2, \pi w^2|\mathbf{X}|^2)] \, d\mathbf{H}$$
$$- \lim_{\mathbf{X}\to 0}[1/2V_d\Gamma(n/2)][P(0)|\mathbf{X}|^{-n}\gamma(n/2, \pi w^2|\mathbf{X}|^2)].$$

The first Fourier transform (of the Patterson function) is the set of amplitudes of the structure factors and the second Fourier transform has already been discussed above; the method for obtaining the limit (for n equal to or greater than 1) was also discussed above. The result obtained is

$$[1/2V_d\Gamma(n/2)]\pi^{n-(3/2)} \int |F[\mathbf{H}(\mathbf{h})]|^2|\mathbf{H}|^{n-3}$$
$$\times \Gamma[(-n/2) + (3/2), \pi w^{-2}|\mathbf{H}|^2] \, d\mathbf{H}$$
$$- [1/2V_d\Gamma(n/2)]|F(0)|^2 2\pi^{n/2}w^n n^{-1}.$$

The integral can be converted into a sum, since $|F[\mathbf{H}(\mathbf{h})]|$ is nonzero only at the reciprocal-lattice points:

$$[1/2V_d\Gamma(n/2)]\pi^{n-(3/2)}\sum_{\mathbf{h}}|F[\mathbf{H}(\mathbf{h})]|^2|\mathbf{H}(\mathbf{h})|^{n-3}$$
$$\times \Gamma[(-n/2) + (3/2), \pi w^{-2}|\mathbf{H}(\mathbf{h})|^2].$$

The term with $\mathbf{H}(\mathbf{h}) = 0$ is evaluated in the limit, for n greater than 3, as

$$[\Gamma(n/2)]^{-1}V_d^{-1}\pi^{n/2}w^{n-3}(n-3)^{-1}|F(0)|^2.$$

Since $|F(0)|^2 = \sum\sum q_j q_k$, this term is identical with the third term of $V(n, \mathbf{R}_j)$ as derived earlier. The case of $n = 1$ is handled in the same way as previously discussed, where the limit of this term is zero provided the unit cell has no net charge or dipole moment.

3.4.9. Evaluation of the incomplete gamma function

The incomplete gamma function may be expressed in terms of commonly available functions such as the exponential integral and the complement of the error function. The definition of the exponential integral is

$$E_1(x^2) = \int_{x^2}^{\infty} t^{-1}\exp(-t) \, dt = \Gamma(0, x^2).$$

The definition of the complement of the error function is

$$\mathrm{erfc}(x) = \int_x^{\infty} \exp(-t^2) \, dt = \pi^{-1/2}\Gamma(1/2, x^2).$$

Numerical approximations to these functions are given, for example, by Hastings (1955). The recursion formula for the incomplete gamma function (Davis, 1972)

$$\Gamma(n+1, x^2) = n\Gamma(n, x^2) + x^{2n}\exp(-x^2)$$

may be used to obtain working formulae starting from the special values of $\Gamma(0, x^2)$ and $\Gamma(1/2, x^2)$ which are defined above. Also we note that $\Gamma(1, x^2) = \exp(-x^2)$.

3.4.10. Summation over the asymmetric unit and elimination of intramolecular energy terms

Let us consider the case where the unit cell contains Z molecules which are related by Z symmetry operations, and it is desired to include only intermolecular distances in the summation. In the direct sum (1) the indices j and k will then run only over the asymmetric unit, and all terms with $\mathbf{d} = 0$ are eliminated. The calculated energy refers then to one molecule (or mole) rather than to one unit cell. The correction term (2) also refers to one molecule according to the range of j and k. Since the reciprocal-lattice sum refers to the entire unit cell, terms (3) and (4) need to be divided by Z to refer the energy to one molecule.

Both the direct and reciprocal sums must be corrected for the elimination of intramolecular terms. Using the convergence function $W(R)$, we have

$$V(n, \mathbf{R}_j) = \sum_{\text{inter}}|\mathbf{R}|^{-n}W(R) + \sum_{\text{intra}}|\mathbf{R}|^{-n}W(R)$$
$$+ \sum_{\text{inter}}|\mathbf{R}|^{-n}[1 - W(R)] + \sum_{\text{intra}}|\mathbf{R}|^{-n}[1 - W(R)].$$

As mentioned above, the second summation term, which is the intramolecular term in direct space, is simply left out of the calculation. When using the accelerated-convergence method the third and fourth summation terms are always obtained, evaluated in reciprocal space. The undesired inclusion of the intramolecular term (fourth term above) in the reciprocal-space sum may be compensated for by explicit subtraction of this term from the sum.

3.4.11. Reference formulae for particular values of n

In this section let $a^2 = \pi w^2|\mathbf{R}_k + \mathbf{X}(\mathbf{d}) - \mathbf{R}_j|^2$ and $b^2 = \pi w^{-2}|\mathbf{H}(\mathbf{h})|^2$. Let $T_0 = \sum Q_{jj} = \sum q_j^2$; $T_1 = \sum\sum Q_{jk} = T_0 + 2\sum\sum_{j>k}Q_{jk}$. If the geometric mean combining law holds, $T_1 = (\sum_j q_j)^2$; let

$$T_2(h) = \sum_j\sum_k Q_{jk}\exp[2\pi i\mathbf{H}(\mathbf{h})\cdot(\mathbf{R}_k - \mathbf{R}_j)]$$
$$= T_0 + 2\sum_{j>k}\sum Q_{jk}\cos[2\pi\mathbf{H}(\mathbf{h})\cdot(\mathbf{R}_k - \mathbf{R}_j)].$$

Then

$$T_2(\mathbf{h}) = |F(\mathbf{h})|^2 = |\sum_j q_j\exp[2\pi i\mathbf{H}(\mathbf{h})\cdot\mathbf{R}_j]|^2 = A(\mathbf{h})^2 + B(\mathbf{h})^2,$$

where

$$A(\mathbf{h}) = \sum_j q_j\cos[2\pi\mathbf{H}(\mathbf{h})\cdot\mathbf{R}_j]$$

and

$$B(\mathbf{h}) = \sum_j q_j\sin[2\pi\mathbf{H}(\mathbf{h})\cdot\mathbf{R}_j].$$

The formulae below describe $V(n, \mathbf{R}_j)$ in terms of T_0, T_1 and T_2; the distance $|\mathbf{R}_k + \mathbf{X}(\mathbf{d}) - \mathbf{R}_j|$ is simply represented by R_{jkd}.

$$V(1, \mathbf{R}_j) = (1/2)\sum_j\sum_k{}'\, q_j\, q_k\sum_{\mathbf{d}}R_{jkd}^{-1}\,\mathrm{erfc}(a)$$
$$+ (1/2\pi V_d)\sum_{\mathbf{h}\neq 0}T_2(\mathbf{h})|\mathbf{H}(\mathbf{h})|^{-2}\exp(-b^2) - wT_0$$

$$V(2, \mathbf{R}_j) = (1/2)\sum_j\sum_k{}'\, Q_{jk}\sum_{\mathbf{d}}R_{jkd}^{-2}\exp(-a^2)$$
$$+ (\pi/2V_d)\sum_{\mathbf{h}\neq 0}T_2(\mathbf{h})|\mathbf{H}(\mathbf{h})|^{-1}\mathrm{erfc}(b) - (\pi/2)w^2T_0$$

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