

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:

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

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

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

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 $|F(0)|^2 = \sum_j \sum_k q_j q_k$, 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

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

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 $T_0 = \sum Q_{jj} = \sum q_j^2$; $T_1 = \sum_j \sum_{k > j} Q_{jk} = T_0 + 2 \sum_j \sum_{k > j} Q_{jk}$. 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} .

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

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

3.4. ACCELERATED CONVERGENCE TREATMENT OF R^{-n} LATTICE SUMS

$$V(3, \mathbf{R}_j) = (1/2) \sum_j \sum_k \sum_{\mathbf{d}} Q_{jk} \sum_{\mathbf{d}} R_{jkd}^{-3} [\operatorname{erfc}(a) + 2a\pi^{-1/2} \exp(-a^2)] \\ + (\pi/V_d) \sum_{\mathbf{h} \neq 0} T_2(\mathbf{h}) E_1(b^2) - (2\pi/3) w^3 T_0$$

$$V(4, \mathbf{R}_j) = (1/2) \sum_j \sum_k \sum_{\mathbf{d}} Q_{jk} \sum_{\mathbf{d}} R_{jkd}^{-4} (1 + a^2) \exp(-a^2) \\ + (\pi^{5/2}/V_d) \sum_{\mathbf{h} \neq 0} T_2(\mathbf{h}) |\mathbf{H}(\mathbf{h})| \\ \times [-\pi^{1/2} \operatorname{erfc}(b) + b^{-1} \exp(-b^2)] \\ + (\pi^2/V_d) w T_1 - (\pi^2/4) w^4 T_0$$

$$V(5, \mathbf{R}_j) = (1/2) \sum_j \sum_k \sum_{\mathbf{d}} Q_{jk} \sum_{\mathbf{d}} R_{jkd}^{-5} \\ \times [\operatorname{erfc}(a) + 2\pi^{-1/2} a (1 + 2a^2/3) \exp(-a^2)] \\ + (2\pi^3/3V_d) \sum_{\mathbf{h} \neq 0} T_2(\mathbf{h}) |\mathbf{H}(\mathbf{h})|^2 \\ \times [b^{-2} \exp(-b^2) - E_1(b^2)] \\ + (2\pi^2/3V_d) w^2 T_1 - (4\pi^2/15) w^5 T_0$$

$$V(6, \mathbf{R}_j) = (1/2) \sum_j \sum_k \sum_{\mathbf{d}} Q_{jk} \sum_{\mathbf{d}} R_{jkd}^{-6} [1 + a^2 + (a^4/2)] \exp(-a^2) \\ + (\pi^{9/2}/3V_d) \sum_{\mathbf{h} \neq 0} T_2(\mathbf{h}) |\mathbf{H}(\mathbf{h})|^3 \\ \times [\pi^{1/2} \operatorname{erfc}(b) + [(1/2b^3) - (1/b)] \exp(-b^2)] \\ + (\pi^3/6V_d) w^3 T_1 - (\pi^3/12) w^6 T_0$$

$$V(7, \mathbf{R}_j) = (1/2) \sum_j \sum_k \sum_{\mathbf{d}} Q_{jk} \sum_{\mathbf{d}} R_{jkd}^{-7} \\ \times [\operatorname{erfc}(a) + 2\pi^{-1/2} a [1 + (2/3)a^2 + (4/15)a^4] \\ \times \exp(-a^2)] \\ + (2\pi^5/15V_d) \sum_{\mathbf{h} \neq 0} T_2(\mathbf{h}) |\mathbf{H}(\mathbf{h})|^4 \\ \times [(-b^{-2} + b^{-4}) \exp(-b^2) + E_1(b^2)] \\ + (2\pi^3/15V_d) w^4 T_1 - (8\pi^3/105) w^7 T_0$$

$$V(8, \mathbf{R}_j) = (1/2) \sum_j \sum_k \sum_{\mathbf{d}} Q_{jk} \sum_{\mathbf{d}} R_{jkd}^{-8} \\ \times [1 + a^2 + (a^4/2) + (a^6/6)] \exp(-a^2) \\ + (2\pi^{13/2}/45V_d) \sum_{\mathbf{h} \neq 0} T_2(\mathbf{h}) |\mathbf{H}(\mathbf{h})|^5 \\ \times [-\pi^{1/2} \operatorname{erfc}(b) + [(1/b) - (1/2b^3) + (3/4b^5)] \\ \times \exp(-b^2)] \\ + (\pi^4/30V_d) w^5 T_1 - (\pi^4/48) w^8 T_0$$

$$V(9, \mathbf{R}_j) = (1/2) \sum_j \sum_k \sum_{\mathbf{d}} Q_{jk} \sum_{\mathbf{d}} R_{jkd}^{-9} \\ \times [\operatorname{erfc}(a) + 2\pi^{-1/2} a [1 + (2/3)a^2 + (4/15)a^4 \\ + (8/105)a^6] \exp(-a^2)] \\ + (4\pi^7/315V_d) \sum_{\mathbf{h} \neq 0} T_2(\mathbf{h}) |\mathbf{H}(\mathbf{h})|^6 \\ \times [(b^{-2} - b^{-4} + 2b^{-6}) \exp(-b^2) - E_1(b^2)] \\ + (8\pi^4/315V_d) w^6 T_1 - (16\pi^4/945) w^9 T_0$$

$$V(10, \mathbf{R}_j) = (1/2) \sum_j \sum_k \sum_{\mathbf{d}} Q_{jk} \sum_{\mathbf{d}} R_{jkd}^{-10} \\ \times [1 + a^2 + (a^4/2) + (a^6/6) + (a^8/24)] \exp(-a^2) \\ + (\pi^{17/2}/315V_d) \sum_{\mathbf{h} \neq 0} T_2(\mathbf{h}) |\mathbf{H}(\mathbf{h})|^7 \\ \times [\pi^{1/2} \operatorname{erfc}(b) + [(-1/b) + (1/2b^3) - (3/4b^5)] \\ + (15/8b^7)] \exp(-b^2) \\ + (\pi^5/168V_d) w^7 T_1 - (\pi^5/240) w^{10} T_0.$$

3.4.12. Numerical illustrations

Consider the case of the sodium chloride crystal structure (a face-centred cubic structure) as a simple example for evaluation of the Coulombic sum. The sodium ion can be taken at the origin, and the chloride ion halfway along an edge of the unit cell. The results can easily be generalized for this structure type by using the unit-cell edge length, a , as a scaling constant.

First, consider the nearest neighbours. Each sodium and each chloride ion is surrounded by six ions of opposite sign at a distance of $a/2$. The Coulombic energy for the first coordination sphere is $-(1/2)(12)(2/a)(1389.3654) = -16672.385/a \text{ kJ mol}^{-1}$. Table 3.4.2.1 shows that the converged value of the lattice energy is $-4855.979/a$. Thus the nearest-neighbour energy is over three times more negative than the total lattice energy. In the second coordination sphere each ion is surrounded by 12 similar ions at a distance of $a/2^{1/2}$. The energy contribution of the second sphere is $+(1/2)(24)(2^{1/2}/a)(1389.3654) = +23578.313/a$. Thus, major cancellation occurs and the net energy for the first two coordination spheres is $+6905.928/a$ which actually has the wrong sign for a stable crystal. The third coordination sphere again makes a negative contribution. Each ion is surrounded by eight ions of opposite sign at a distance of $a/3^{1/2}$. The energy contribution is $-(1/2)(16)(3^{1/2}/a)(1389.3654) = -19251.612/a$, now giving a total so far of $-12345.684/a$. In the fourth coordination sphere each ion is surrounded by six others of the same sign at a distance of a . The energy contribution is $+(1/2)(12)(1/a)(1389.3654) = +8336.19/a$ to yield a total of $-4009.491/a$.

It is seen immediately by examining the numbers that the Coulombic sum is converging very slowly in direct space. Madelung (1918) devised a method for accurate evaluation of the sodium chloride lattice sum. However, his method is not generally applicable for more complex lattice structures. Evjen (1932) emphasized the importance of summing over a neutral domain, and replaced the sum with an integral outside of the first few shells of nearest neighbours. But the method of Ewald remained as the

Table 3.4.12.1. Accelerated-convergence results for the Coulombic sum ($n = 1$) of sodium chloride ($\text{kJ mol}^{-1}, \text{\AA}$): the direct sum plus the constant term

Limit	$w = 0.1$	$w = 0.15$	$w = 0.2$	$w = 0.3$	$w = 0.4$
6.0	-779.087	-838.145	-860.393	-924.275	-1125.372
8.0	-818.549	-860.194	-863.764	-924.282	-1125.372
10.0	-865.323	-862.818	-863.811	-924.282	
12.0	-861.183	-862.824	-863.811		
14.0	-862.717	-862.828			
16.0	-862.792	-862.828			
18.0	-862.810				
20.0	-862.825				