The first term immediately gives

$$\frac{2\pi KZ_i}{a_i^2}\sum_{\Gamma} x_{\gamma ip}\varrho_{0\gamma}G(a_i,r_{\gamma i}) \qquad \text{(E6)}$$

whilst the third is

$$-\frac{1}{v}\int\frac{2\pi KZ_i}{a_i^2}x_{0ip}G(a_i,r_{0i}) \times\left[\sum_j KZ_jG(a_j,r_{0j})+d\right]\mathrm{d}v \qquad \text{(E7)}$$

in which the term involving d vanishes and the other part gives

$$\frac{2\pi K^2Z_i}{v}\sum_j Z_j\frac{x_{ijp}}{a_{ij}^2}G(a_{ij},r_{ij}) \qquad \text{(E8)}$$

by (B2) and (B13).
The Fourier correction is the transform of

$$\frac{2\pi KZ_ix_{0ip}}{a_i^2}G(a_i,r_{0i})[KZ_iG(a_i,r_{0i})+d] \qquad \text{(E9)}$$

in which the first part is

$$\frac{2\pi K^2Z_i^2}{a_i^2}T[x_{0ip}\,G^2(a_i,r_{0i})] \qquad \text{(E10)}$$

which is

$$\frac{2\pi K^2Z_i^2}{a_i^2}G(a_{ii},0)\ is_p\frac{\sqrt{2}}{a_i}G(\sqrt{2}/a_i,s) \qquad \text{(E11)}$$

by (B2), (B6), B(22) and (B23), so that the required transform is

$$\pi K^2Z_i^2\,G(a_{ii},0) \times\sum_{\text{whole space}} is_p\exp\{-\pi a_i^2\,s^2/2\}\exp\{-2\pi i\mathbf{r}_i\,.\,\mathbf{s}\} \qquad \text{(E12)}$$

$$=2\pi K^2Z_i^2\,G(a_{ii},0) \times\sum_{1/2\text{ space}} s_p\exp\{-\pi a_i^2s^2/2\}\sin 2\pi\mathbf{r}_i\,.\,\mathbf{s} \qquad \text{(E13)}$$

which enters (E5) with a sign reversal, to give (37), because (8) involves $F(\mathbf{r}_{0i})$, not $F(\mathbf{r}_{i0})$. The second part of (E9) similarly gives

$$4\pi KdZ_i\sum_{1/2\text{ space}} s_p\exp\{-\pi a_i^2\,s^2\}\sin 2\pi\mathbf{r}_i\,.\,\mathbf{s}\,. \qquad \text{(E14)}$$

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Accelerated Convergence of Crystal-Lattice Potential Sums*

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A method for increasing the rate of convergence of general crystal lattice sums of the type $\sum'_{j\neq k} q_jq_kr_{jk}^{-n}$ is described. The method is applicable for $n>3$, or for $n>0$ if $\sum_{\text{cell}} q_j=0$. A numerical example is given for the London dispersion energy ($n=6$) of the benzene crystal. The calculation effort required to obtain the lattice sum was reduced at least tenfold.

Introduction

We consider here crystal lattice pairwise sums of the type

$$S_n=\tfrac{1}{2}\sum_{j\neq k}{}' q_jq_kr_{jk}^{-n}\,,$$

for a general composite lattice. The subscript j runs over one unit cell, while the subscript k runs over the entire lattice, excepting $j=k$. The constants q_j are as-

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sociated with atom j and r_{jk} is an interatomic distance. The case $n=1$ is the familiar expression for the electrostatic energy of a crystal, where the q_j are the electrostatic charges on the atoms.

The series for the electrostatic energy converges quite slowly. In fact, it does not converge at all unless the condition of overall electrical neutrality is met: $\sum_{\text{cell}} q_j=0$. Ewald (1921) presented an alternative expression for the electrostatic energy which converges very rapidly; in this treatment a portion of the sum is evaluated in reciprocal space.

Bertaut (1952) has derived very general equations for the electrostatic energy, similar in principle to the Ewald treatment, and has given a physical interpretation to the method. The Bertaut equations are now widely used to obtain rapidly the electrostatic energy or Madelung constants of crystals.

The method used by Bertaut to derive the rapidly converging expressions for S_1 appeared to be specific for the case $n=1$. We will give an alternate derivation of the Bertaut equations by a method which illustrates that the technique is not restricted to the electrostatic case. Further, we will show that the restriction $\sum_j q_j=0$ may be removed when $n>3$. In this event an additional constant term appears which depends on the value of $\sum_j q_j$.

Convergence functions

Nijboer & DeWette (1957) have shown how to improve the convergence rate of S_n ($n>3, q_j=1$) for the special case where the sum is over lattice points only. The mathematical method was originated by Epstein (1903) and is also described and discussed in a review by Tosi (1964). We wish to generalize Nijboer & DeWette's result to a composite lattice in which the q_j are not necessarily unity and for $n>0$.

The general plan is to multiply the terms of the series by a convergence function, $\varphi(r)$, where $\varphi(0)=1$ and $\varphi(r)$ decreases rapidly to zero as r increases. The Fourier transform of the remainder of the terms of the series is then found, and the transformed series summed in reciprocal space.

Thus the sum may be written

$$S_n=\tfrac{1}{2}\sum_{j\neq k} q_j q_k r_{jk}^{-n}\varphi(r_{jk})+\tfrac{1}{2}\sum_{j\neq k} q_j q_k r_{jk}^{-n}[1-\varphi(r_{jk})]\,.$$

To facilitate the Fourier transformation S_n may be written in integral notation as

$$S_n=\tfrac{1}{2}\int[P(\mathbf{r})-P(\mathbf{r})\delta(\mathbf{r})]\varphi(r)r^{-n}\mathrm{d}\mathbf{r}$$
$$+\tfrac{1}{2}\int[P(\mathbf{r})-P(\mathbf{r})\delta(\mathbf{r})]\,[1-\varphi(r)]r^{-n}\mathrm{d}\mathbf{r}\,.$$

Here $P(\mathbf{r})$ is the Patterson function, defined by

$$P(\mathbf{r})=V^{-1}\sum_{\mathbf{h}_\lambda}|F(\mathbf{h}_\lambda)|^2\exp(2\pi i\mathbf{h}\,.\,\mathbf{r})=\sum_{\text{cell}} q_j q_k \zeta(\mathbf{r}-\mathbf{r}_{jk})\,,$$

$\mathbf{h}$ is the reciprocal-space vector, with the subscript λ indicating the reciprocal-lattice points, $\delta(\mathbf{r})$ is the Dirac delta function, and $\zeta(\mathbf{r})$ is the Kronecker delta function. The structure factor, $F(\mathbf{h})$, is given by $F(\mathbf{h})=\sum_{\text{cell}} q_j\exp(-2\pi i\mathbf{h}\,.\,\mathbf{r}_j)$, where the $\mathbf{r}_j$ are the atomic coordinates expressed as fractions of the unit-cell edges, and V is the volume of the unit cell. As indicated by the sum of delta functions, the Patterson function is nonzero only at the interatomic vector points $\mathbf{r}_{jk}$.

The second integral in the equation for S_n may be evaluated through use of Parseval's integral theorem for real functions:

$$\int f(\mathbf{r})g(\mathbf{r})\mathrm{d}\mathbf{r}=\int \mathrm{FT}_3[f(\mathbf{r})]\mathrm{FT}_3[g(\mathbf{r})]\mathrm{d}\mathbf{h}\,,$$

where $\mathrm{FT}_3[f(r)]=\int f(\mathbf{r})\exp(2\pi i\mathbf{h}\,.\,\mathbf{r})\mathrm{d}\mathbf{r}$ is the three-dimensional Fourier transform of $f(\mathbf{r})$. Making use of the fact that the three-dimensional Fourier transform of the Patterson function is the amplitude of the structure factor squared divided by the unit-cell volume, and using Parseval's theorem, the second integral may be written

$$I_2=\frac{1}{2V}\int|F(\mathbf{h})|^2\mathrm{FT}_3\left[\frac{1-\varphi(r)}{r^n}\right]\mathrm{d}\mathbf{h}$$
$$-\tfrac{1}{2}\int P(\mathbf{r})\delta(\mathbf{r})\left[\frac{1-\varphi(r)}{r^n}\right]\mathrm{d}\mathbf{r}\,.$$

While the choice of the convergence function, $\varphi(r)$, is not uniquely determined, additional restrictions on it may be inferred from the above integrals. Each integral must be defined at the origin; that is, both of the following limits must exist:

$$\lim_{r\to 0}\left[\frac{1-\varphi(r)}{r^n}\right]\qquad \lim_{h\to 0}\left\{\mathrm{FT}_3\left[\frac{1-\varphi(r)}{r^n}\right]\right\}.$$

Nijboer & DeWette suggest as a choice for the convergence function

$$\varphi(r)=\frac{\Gamma(n/2,K^2\pi r^2)}{\Gamma(n/2)}=\frac{1}{\Gamma(n/2)}\int_{K^2\pi r^2}^{\infty}t^{n/2-1}e^{-t}\mathrm{d}t\,,$$

where $\Gamma(m)$ and $\Gamma(m,x)$ are the gamma function and the incomplete gamma function, respectively. They show that the three-dimensional Fourier transform of $[1-\varphi(r)]/r^n$ is

$$\mathrm{FT}_3\left[\frac{1-\varphi(r)}{r^n}\right]$$
$$=\pi^{n-3/2}h^{n-3}\Gamma\left(-\frac{n}{2}+\frac{3}{2},\frac{\pi h^2}{K^2}\right)\Big/\Gamma\left(\frac{n}{2}\right).$$

Inserting the limiting values of $[1-\varphi(r)]/r^n$ and $P(\mathbf{r})$, we have

$$I_2=\tfrac{1}{2}\pi^{n-3/2}V^{-1}[\Gamma(n/2)]^{-1}\int|F(\mathbf{h})|^2h^{n-3}\Gamma\left(-\frac{n}{2}+\frac{3}{2},\right.$$
$$\left.\frac{\pi h^2}{K^2}\right)\mathrm{d}\mathbf{h}-\tfrac{1}{2}\left[\Gamma\left(\frac{n}{2}\right)\right]^{-1}P(0)\left[\frac{2K^n\pi^{n/2}}{n}\right].$$

The limit as $h \rightarrow 0$ of the integrand is evaluated as

$$|F(0)|^2 \pi^{3/2-n/2} K^{n-3} \left[\frac{2}{n-3}\right], \quad (n>3) .$$

Making use of the fact that the structure factor, $F(\mathbf{h})$, is nonzero only at the reciprocal-lattice points, $\mathbf{h}_\lambda$, the final result may be written again in the form of a sum:

$$S_n = \frac{1}{2\Gamma(n/2)} \Big[\sum_{j \neq k} q_j q_k r_{jk}^{-n} \Gamma\left(\frac{n}{2}, a^2\right) + V^{-1} \pi^{n-3/2} \times \sum_{\mathbf{h}_\lambda \neq 0} |F(\mathbf{h}_\lambda)|^2 h_\lambda^{n-3} \Gamma\left(-\frac{n}{2}+\frac{3}{2}, b^2\right) + V^{-1} \pi^{n/2} K^{n-3} \times \left[\frac{2}{n-3}\right] \Big[\sum_{\text{cell}} q_j \Big]^2 - 2n^{-1} \pi^{n/2} K^n \Big\{ \sum_{\text{cell}} q_j^2 \Big\} \Big] ,$$

where $a^2 = \pi K^2 r_{jk}^2$ and $b^2 = \pi h_\lambda^2 / K^2$. The sum converges for $n>3$; note that n is not necessarily an integer. If $\sum_{\text{cell}} q_j = 0$, then the formula for S_n converges for all $n>0$.

For the electrostatic case, $n=1$ and $\sum_{\text{cell}} q_j = 0$, we have

$$S_1 = \frac{1}{2\Gamma(\frac{1}{2})} \Big[\sum_{j \neq k} q_j q_k r_{jk}^{-1} \Gamma(\tfrac{1}{2}, a^2) + V^{-1} \pi^{-1/2} \sum_{\mathbf{h}_\lambda \neq 0} |F(\mathbf{h}_\lambda)|^2 h_\lambda^{-2} \Gamma(1, b^2) - 2\pi^{1/2} K \sum_{\text{cell}} q_j^2 \Big] .$$

Since

$$\Gamma(\tfrac{1}{2}) = \pi^{1/2}, \Gamma(1, b^2) = \exp(-b^2), \text{ and } \Gamma(\tfrac{1}{2}, a^2) = \pi^{1/2} \int_a^\infty \exp(-t^2) \mathrm{d}t = \pi^{1/2} \mathrm{ERFC}(a),$$

$$S_1 = \tfrac{1}{2} \sum_{j \neq k} q_j q_k r_{jk}^{-1} \mathrm{ERFC}(a) + \frac{1}{2\pi V} \sum_{\mathbf{h}_\lambda \neq 0} \times |F(\mathbf{h}_\lambda)|^2 h_\lambda^{-2} \exp(-b^2) - K \sum_{\text{cell}} q_j^2 .$$

The last equation is identical to that given by Bertaut (1952).

The generalization of the Bertaut equation to the range $0<n\leq 3$ was not immediately obvious. The reason for this is that his derivation makes use of a theorem which is uniquely true only for $n=1$. This theorem states that the energy of interaction of a point charge is identical to that of a corresponding spherically smeared charge distribution. As we have shown, this type of equation also holds for $n>3$ even if $\sum_{\text{cell}} q_j \neq 0$, in which case a term appears which depends on the value of $\sum_{\text{cell}} q_j$.

Application to the London dispersion energy

The leading term in an approximate expression for the London dispersion energy (Hirschfelder, Curtiss & Bird, 1954) between non-bonded atoms is proportional to the inverse sixth power of the interatomic distance, r_{jk}:

$$E_{jk} = -\frac{3}{2} \frac{I_j I_k}{(I_j + I_k)} \frac{\alpha_j \alpha_k}{r_{jk}^6} \simeq -\frac{q_j q_k}{r_{jk}^6}$$

where I is the ionization energy and α is the polarizability. The geometric mean combining law holds fairly well here for the coefficients q_j since the range of variation of the polarizabilities is larger than that of the ionization energies. If we further assume that the interactions are pairwise additive, the London dispersion energy of a crystal is identical to the negative of S_6, with appropriately chosen values of q_j. Values of q_j may be theoretically estimated or they may be derived from known crystal structures (Williams, 1966).

In terms of the complement of the error function, ERFC(x), which was defined above, S_6 may be written:

$$S_6 = \tfrac{1}{2} \sum_{j \neq k} q_j q_k r_{jk}^{-6} (1 + a^2 + \tfrac{1}{2} a^4) \exp(-a^2) + \left(\frac{\pi^{9/2}}{3V}\right) \sum_{\mathbf{h}_\lambda = 0} |F(\mathbf{h}_\lambda)|^2 h_\lambda^3 \Big[\pi^{1/2} \mathrm{ERFC}(b) + \left(\frac{1}{2b^3} - \frac{1}{b}\right) \times \exp(-b^2) \Big] + (1/6) \pi^3 K^3 V^{-1} \Big(\sum_{\text{cell}} q_j \Big)^2 - \left(\frac{1}{12}\right) \pi^3 K^6 \Big(\sum_{\text{cell}} q_j^2 \Big) .$$

Often one is interested only in the energy of interaction between groups of atoms (*e.g.* between molecules). In this case the intramolecular contribution to the sum can easily be evaluated term by term and subtracted from the total. Also, although the formula as written calls for summing j over one complete unit cell, it is easy to reduce the formula to sum only over one molecule, if the other molecules in the unit cell are related by symmetry. In this case the constant involving $\sum q_j^2$ needs to be multiplied by Z, and the $|F|^2$ terms need to be divided by Z, where Z is the number of molecules in the cell. The other two terms are unchanged, and the resulting energy is per molecule (or per mole) rather than per unit cell.

Numerical calculations

The crystal structure of benzene (Bacon, Curry & Wilson, 1964) at −55° was chosen to illustrate the convergence properties of S_6. The nonbonded potential parameters (Williams, 1966) were taken as $q_{\mathrm{C}}^2 = 535$ and $q_{\mathrm{H}}^2 = 36$. S_6 was evaluated for three values of K(0·2, 0·3, and 0·4) as −1052·61050 kcal.mole^{-1}. The intramolecular terms were summed directly to obtain −1035·37533 kcal.mole^{-1}. Thus the London energy is −17·23517 ± 0·00001 kcal.mole^{-1}. The error limit given refers to the termination error of the series; no estimates of the errors in q_{H} and q_{C} were included. The convergence method provides an alternative to termination error estimation by integration methods (Kihara & Koba, 1952).

In the past a common choice for the summation limit in practice has been around 6 to 8 Å, resulting in a termination error of 14 to 6%. Kitaigorodskii (1968) found a 15 Å limit was necessary to achieve 1% accuracy; this limit requires evaluation of about 9×10^3

terms for benzene. Fig. 1 illustrates the convergence properties of the direct space series for various values of K. The Figure shows a dramatic increase in the convergence rate as K is increased. The relative errors shown in the figures refer to the London energy only, not the entire S_6.

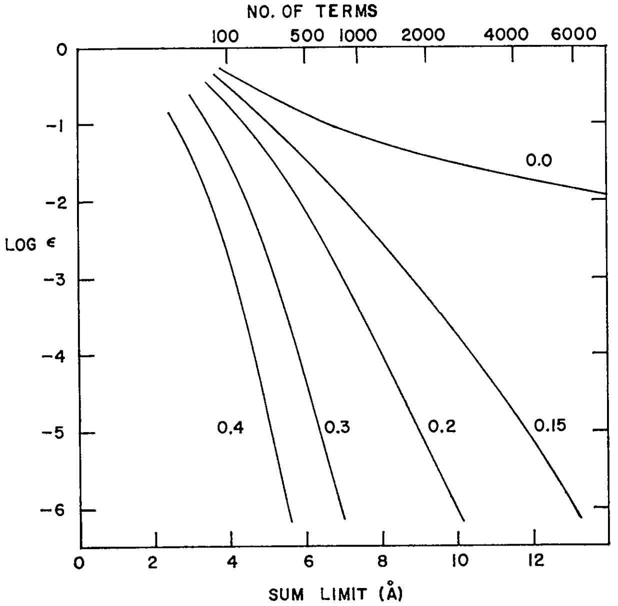

Fig. 1. The relative error, ε, which results from neglect of direct space terms with r greater than the sum limit. The benzene S_6 example is shown for various values of the convergence constant, K.

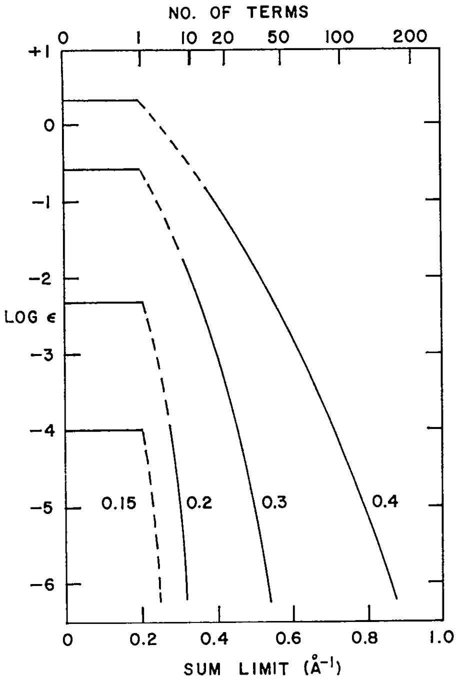

Fig. 2. The relative error, ε, which results from neglect of reciprocal space terms with h greater than the sum limit. The benzene S_6 example is shown for various values of the convergence constant, K.

Fig. 2 shows the convergence behavior of the reciprocal space series. Although only a few terms yield rapid convergence, it should be remembered that each term requires an ancillary sum over the molecule to obtain the structure factor. The number of terms refers only to the asymmetric portion of the reciprocal lattice, one octant in this case. Note that the error at low h values is constant, since for benzene the first term of the series occurs at $h = 0{\cdot}2094\text{A}^{-1}$.

The optimum value of K will depend on the characteristics of the particular computer and program which are used, but a value of 0·3 may often be satisfactory. At a relative error level of 0·01, the convergence modified series reduced the number of terms which needed to be considered from over 7000 to 150, with 10 reciprocal space terms being required. Even larger savings are achieved at higher accuracy levels.

If K is small it may be possible to neglect entirely the reciprocal space series while still retaining considerable convergence benefit in direct space. At a relative error level of 0·01, Fig. 2 shows that the reciprocal series may be neglected entirely if $K = 0{\cdot}2$. The direct series needs to be summed only to 6 Å to obtain the desired 1% accuracy. (500 terms.)

This feature is of benefit in applying the convergence method where relatively low accuracy is required or where computer limitations or programming problems make evaluation of the structure factors difficult. Thus only a small modification is necessary to incorporate the convergence technique into exisitng direct space summation programs. At the 6 Å summation limit, termination error is decreased from 14% to less than 1%.

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