Any attempt to employ mathematical methods in the study of chemical questions must be considered profoundly irrational and contrary to the Spirit of Chemistry.
If Mathematical Analysis should ever hold a prominent place in chemistry – an aberration which is happily almost impossible – it would occasion a rapid and widespread degeneration of that science.

Auguste Comte
Philosophie Positive (1830)

1.1 Introduction
It has been more than 100 years since Appell [2] introduced lattice sums into physics, yet the article on which this chapter is based is apparently the first devoted entirely to the subject. We are, of course, aware that parts of other reviews (such as those by Born and Göppert-Mayer [21], Waddington [135], Tosi [133], and Sherman [125]) have dealt with Coulomb sums in ionic crystals, as a casual reading of this chapter will demonstrate. In the perusal of 100 years of literature, we will inevitably have missed or ignored relevant papers and their authors are urged to communicate with us directly.

The organization of this review is as follows. In Section 1.2 we present a historical survey, picking out and describing in detail some of the more important methods for calculation. Section 1.3 deals with the representation of lattice sums as Mellin-transformed products of theta functions. In Section 1.4 we discuss the evaluation of two-dimensional lattice sums by number-theoretic means, and in Section 1.5 we examine a promising new application of contour integration. Two brief appendices are concerned with connections among lattice sums, elliptic integrals, and lattice Green’s functions.
Lattice sums

1.2 Historical survey

Lattice sums are expressions of the form

$$\sum_{\mathbf{l}} F(\mathbf{l})$$

(1.2.1)

where the vector \(\mathbf{l}\) ranges over a \(d\)-dimensional lattice. In this review we shall be concerned primarily with the sums for which

$$F(\mathbf{l}) = (\exp b \cdot \mathbf{l})|1 + \mathbf{g}|^{-s}.$$  

(1.2.2)

We shall not indicate the value of \(d\) explicitly (although the cases \(d = 2, 3\) will be our main concern) nor shall we dwell on questions of convergence; these details should be clear from the context.

Apparently, lattice sums were first considered in physics by Appell [2–4], who examined the form of the solutions to Laplace’s equation for periodic sources. His procedure was to Fourier-transform the potentials and solve the resulting algebraic equations for the coefficients. He obtained an analytical expression for the potential of a line of point charges and derived a variant of the so-called Ewald method for higher-dimensional arrays, but his work appears not to have reached the notice of subsequent workers.

In 1902 Epstein [47] reported on efforts to find the most general function satisfying a functional equation similar to that for the Riemann zeta function,

$$\zeta(s) = \sum_{n=1}^{\infty} \frac{1}{n^s}.$$  

(1.2.3)

We describe what we feel are his most important findings.

Let \(q(\mathbf{l})\) be a positive definite quadratic form in the components of \(\mathbf{l}\):

$$q(\mathbf{l}) = a_{11}l_1^2 + \cdots + a_{dd}l_d^2 + 2(a_{12}l_1l_2 + \cdots),$$

where \(A = (a_{ij})\), \(i, j = 1, \ldots, d\) is a symmetric matrix. We shall denote by \(D\) the determinant of \(A\) and by \(\overline{q}(\mathbf{l})\) the quadratic form defined by the adjoint matrix

$$\overline{A} = (\overline{a}_{ij}), \quad \overline{a}_{ij} = \frac{1}{D} \frac{\partial D}{\partial a_{ij}}.$$  

(1.2.4)

Epstein found that the desired functions were\(^1\)

$$Z \left|_{\mathbf{g}}^{\mathbf{h}} \right. \frac{(q; s)}{\mathbf{l}} = \sum_{\mathbf{l}} \frac{e^{-2\pi i \mathbf{h} \cdot \mathbf{l}}}{[q(\mathbf{l} + \mathbf{g})]^{s/2}},$$  

(1.2.5)

where \(\mathbf{g}\) and \(\mathbf{h}\) are arbitrary vectors and the sum runs over the \(d\)-dimensional integer lattice. The sum is assumed to omit \(\mathbf{l} = -\mathbf{g}\) if \(\mathbf{g}\) is a lattice vector. This

\(^1\) The verticals indicate that the Epstein Zeta function \(Z\) depends on the vectors \(\mathbf{g}\) and \(\mathbf{h}\) as well as on the scalars \(q\) and \(s\).
class of *Epstein zeta functions* includes the solutions obtained by Appell and the lattice sums which later became important in crystal physics.

Epstein showed that the functions (1.2.5) have the following properties:

(i) \[
Z\left|\begin{array}{l}
-g \\
h
\end{array}\right| (q; s) = Z\left|\begin{array}{l}
g \\
-h
\end{array}\right| (q; s). \tag{1.2.6}
\]

(ii) \[
Z\left|\begin{array}{l}
-g \\
-h
\end{array}\right| (q; s) = Z\left|\begin{array}{l}
g \\
-h
\end{array}\right| (q; s). \tag{1.2.7}
\]

(iii) If any component of \(h\) is increased by an integer, the right-hand side of (1.2.5) is unaffected.

(iv) If \(g_j\) is increased by unity, (1.2.5) is multiplied by \(\exp(-2\pi i h_j)\).

(v) The Epstein zeta functions may be continued analytically beyond their domain of absolute convergence with respect to \(s\) (which is \(\Re s > d\)) by means of the integral representation

\[
\pi^{-s/2} \Gamma\left(\frac{1}{2} s\right) Z\left|\begin{array}{l}
g \\
h
\end{array}\right| (q; s) = \int_1^\infty \int_0^\infty e^{\tau} \prod_{l=1}^D \prod_{k=1}^D \exp[-\pi zq(l + g) + 2\pi i l \cdot h] \frac{dz}{z^{s/2}} [\sum_{l=1}^D \sum_{k=1}^D \exp\left(-\pi zq(l + g) + 2\pi i l \cdot h\right)] \tag{1.2.8}
\]

The sums which occur in (1.2.8) are the generalized theta functions studied extensively by Krazer and Prym [96]. The two sums are related by the analogue of the Jacobi transformation for ordinary theta functions (see below). The lattice of the \(k\) vectors is, strictly speaking, the reciprocal lattice for the \(l\) vectors, but in the present case these are identical. Equation (1.2.8) is obtained by using the representation

\[
x^{-s} = \frac{1}{\Gamma(s)} \int_0^\infty x^{s-1} e^{-xz} dz \tag{1.2.9}
\]

and breaking up the range of integration. This simple device, due to Riemann, with minor modifications is the underlying motif in most of the practical work on lattice sums to be discussed below.

(vi) The Epstein zeta function obeys the functional equation

\[
\pi^{-s/2} \Gamma\left(\frac{1}{2} s\right) Z\left|\begin{array}{l}
g \\
h
\end{array}\right| (q; s) \left(\frac{d - s}{2}\right)^{d-1/2} \Gamma\left(\frac{d - s}{2}\right) \frac{e^{-2\pi i h \cdot \bar{g}}}{\sqrt{D}} \left|\begin{array}{l}
g \\
-h
\end{array}\right| (q; d-s). \tag{1.2.10}
\]
Equation (1.2.10) is valid for all sets of parameters, whereas (1.2.8) is non-trivial only when \( g \neq 0, h \neq 0 \). However, if this is not the case, (1.2.8) can be modified and becomes

\[
\pi^{-s/2} \Gamma(\frac{s}{2}) \left| \begin{array}{c} 0 \\ 0 \end{array} \right| (q; s) = \frac{2}{(s - d) \sqrt{D}} - \frac{2}{s} + \int_1^\infty dz \frac{z^{(s/2) - 1}}{\sqrt{D}} e^{-\pi z q(0)} dz + \frac{1}{\sqrt{D}} \int_1^\infty dz \frac{z^{(d-s)/2 - 1}}{\sqrt{D}} e^{-\pi z q(l)}.
\]

\[
(1.2.11)
\]

(vii) When \( h \) is not an integer vector, (1.2.5) is an entire function of \( s \); when \( h \) is integral, (1.2.5) has a simple pole at \( s = d \):

\[
\left| \begin{array}{c} g \\ h \end{array} \right| (q; s) = \frac{2\pi^{d/2}}{\sqrt{D} \Gamma(d/2)(s - d)} + C_0 + O(s - d).
\]

\[
(1.2.12)
\]

Epstein gave expressions for \( C_0 \), but these are quite complicated except for the case \( d = 2 \), where the result was already known from earlier work by Kronecker and Hurwitz (see Bellman [6]).

(viii) The zeta function vanishes for \( s = -2, -4, -6, \ldots \) and for \( s = 0 \), unless \( g \) is integral. In this case

\[
\left| \begin{array}{c} g \\ h \end{array} \right| (q; 0) = -\exp(-2\pi i g \cdot h).
\]

\[
(1.2.13)
\]

(ix) If the components of \( g \) and \( h \) are 0 or 1/2 and 4\( g \cdot h \) is odd, then (1.2.5) is identically zero for all \( s \) and \( q \).

The numerical evaluation of lattice sums became an important topic in the first two decades of the twentieth century, when X-ray studies, and particularly the work of W. H. and W. L. Bragg, showed that ionic salts consist not of molecules but of interpenetrating lattices of the corresponding ions. The formal aspects and the role of lattice sums in crystal binding and lattice vibration studies were developed extensively by Born [17] and by his students, but the first accurate numerical result pertaining to a three-dimensional crystal – rock salt – was obtained by Madelung [103]. In view of its historical interest, we shall describe his calculation in some detail.

Madelung considered the problem of calculating the potential at the origin of an extended array of charges \( \pm E \) arranged on a rock salt lattice, a portion of which is displayed in Fig. 1.1. The lattice is considered to be composed of vertical planes \( \pi_0 \) (through the origin), \( \pi_{\pm 1}, \pi_{\pm 2}, \ldots \), and the plane \( \pi_0 \) is considered to be
1.2 Historical survey

Figure 1.1 (a) The rock salt structure decomposed into planes and lines of charges. (b) Unit cell of the rock salt lattice.

formed from vertical lines $L_0$ (through the origin), $L_{±1}, \ldots$ Hence, by symmetry, the potential at $O$ is

$$V(O) = V'_{L_0}(O) + 2 \sum_{n=1}^{\infty} [V_{L_n}(O) + V_{\pi_n}(O)].$$

(1.2.14)

Thus the problem reduces to calculating the potential due to a line of alternating charges and a centred square planar array of alternating charges. (The prime indicates that the charge $E$ is absent from the origin on the line $L_0$.) Although unaware, apparently, of the earlier work by Appell, Madelung used precisely the same method. Consider first the potential due to the array of charges shown in Fig. 1.2a. An arbitrary linear periodic charge density can be written

$$\rho(x) = \sum_{-\infty}^{\infty} \rho_0 e^{2\pi ilx/a}.$$  

(1.2.15)
Accordingly, we look for the potential at \((x, r)\) in the form

\[
v_1(x, r) = \sum_{-\infty}^{\infty} F_l(r) e^{2\pi i l x/a}.
\]  

(1.2.16)

By inserting (1.2.16) into Laplace’s equation, we find

\[
d^2 F_l \over dr^2 + \frac{1}{r} \frac{d F_l}{dr} - \frac{4\pi l^2}{a^2} F_l(r) = 0.
\]  

(1.2.17)

The solution to (1.2.17) which vanishes as \(r \to \infty\) \((l \neq 0)\) is

\[
F_l(r) = \begin{cases} 
C_l K_0(2\pi l r/a), & l \neq 0, \\
C_0 \ln (2a/r), & l = 0,
\end{cases}
\]  

(1.2.18)

where \(K_0\) denotes the modified Bessel function. However, from Poisson’s equation we have

\[
\rho(x) = -\frac{1}{2} \left. \frac{\partial v_1}{\partial r} \right|_{r=0},
\]  

(1.2.19)

which gives \(C_l = 2\rho_l\). Hence the desired potential is

\[
v_1(x, r) = 2\rho_0 \ln \left(\frac{2a}{r}\right) + 2 \sum_{-\infty}^{\infty} \rho_l K_0 \left(\frac{2\pi l r}{a}\right) e^{2\pi i l x/a}.
\]  

(1.2.20a)

(Note that we have adjusted the potential by an additive constant such that as \(r \to \infty\) it gives the potential of a uniform line charge of density \(\rho_0\).) For the
1.2 Historical survey

linear array in Fig. 1.2a Madelung’s result is

\[ v_1(x, r) \equiv \sum_{-\infty}^{\infty} \frac{E}{[(x-a)^2 + r^2]^{1/2}} \]

\[ = \frac{2E}{a} \left[ \ln \left( \frac{2a}{r} \right) + 2 \sum_{l=1}^{\infty} \rho_l K_0 \left( \frac{2\pi lr}{a} \right) \cos \frac{2\pi lx}{a} \right]. \] (1.2.20b)

Mathematically, this procedure is equivalent to using the Poisson summation formula, by which the slowly convergent first series in (1.2.20b) is replaced by the rapidly convergent second series. The potential for the alternating array in Fig. 1.2b is

\[ v_L(x, r) = v_1(x, r) - v_1(x + a/2, r) \]

\[ = \frac{8E}{a} \sum_{l=1}^{\infty} K_0 \left( \frac{2\pi(2l-1)r}{a} \right) \cos \left( \frac{2\pi(2l-1)x}{a} \right). \] (1.2.21)

The potential at \( O \) due to all the other charges is most easily obtained by direct summation:

\[ v'_L(O) = \frac{4E}{a} \left( 1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \cdots \right) = \frac{4E}{a} \ln 2. \] (1.2.22)

In the case of the plane rectangular lattice shown in Fig. 1.3 we begin by looking for a potential having the form

\[ V = \sum_l F_l \cos \frac{2\pi l_1 x}{a} \cos \frac{2\pi l_2 y}{b} \] (1 = (l_1, l_2)). (1.2.23)

Substituting this into Laplace’s equation yields

\[ \frac{d^2 F_l}{d z^2} - 4\pi^2 k_l^2 F_l = 0, \quad k_l^2 = \frac{l_1^2}{a^2} + \frac{l_2^2}{b^2}, n \] (1.2.24)
which has the solution (vanishing as \( z \to \infty \) for \( k_1^2 \neq 0 \))

\[
F_1 = \begin{cases} 
C_1 e^{-2\pi k_1 z}, & k_1 \neq 0, \\
C_0 + C_1 z, & k_1 = 0.
\end{cases} \tag{1.2.25}
\]

This corresponds to the periodic charge density

\[
\rho(x, y) = \sum_l \rho_l \cos \frac{2\pi l_1 x}{a} \cos \frac{2\pi l_2 y}{b}. \tag{1.2.26}
\]

Proceeding from Poisson’s equation, just as for the linear case, we find

\[
v_2(x, y, z) = \frac{4E}{ab} \sum_{l_1, l_2=1}^{\infty} \frac{e^{-2\pi l_1 z/k_1}}{k_1} \cos \frac{2\pi l_1 x}{a} \cos \frac{2\pi l_2 y}{b} \\
+ \frac{2E}{b} \sum_{l_1}^{\infty} \left( \frac{e^{-2\pi l_1 z/a}}{\cos \frac{2\pi l_1 x}{a} + e^{-2\pi l_1 z/b} \cos \frac{2\pi l_1 y}{b}} \right) \\
- \frac{2\pi E z}{ab} + \text{const.} \tag{1.2.27}
\]

For a centred square alternating array, corresponding to the planes \( \pi \) in Fig. 1.1, we obtain easily

\[
V_\pi = \frac{16E}{ab} \sum_{l_1=1}^{\infty} \sum_{l_2=1}^{\infty} \frac{e^{-2\pi l_1 z/k_1}}{k_1} \cos \frac{2\pi l_1 x}{a} \cos \frac{2\pi l_2 y}{a}. \tag{1.2.28}
\]

In addition to those above, Madelung’s paper contains a number of other calculations relating to two- and three-dimensional periodic arrays.

Using formulas (1.2.21), (1.2.22), and (1.2.28), it is simple to calculate the potential at the reference site \( O \) for the rock salt structure. On the basis of (1.2.14), for three-decimal place accuracy Madelung found it sufficient to keep the following contributions to \( \psi(O) = (E/a)\mu \).

1. The line \( L_0, \mu_0 = 4 \ln 2 \).
2. The lines \( L_{\pm 1} (x = 0, r = a/2), \mu_1 \approx 16K_0(\pi) + K_0(3\pi) \);
3. The lines \( L_{\pm 2} (x = 0, r = a), \mu_2 \approx -16K_0(2\pi) \).
4. The lines \( L_{\pm 3} (x = 0, r = 3a/2), \mu_3 \approx 16K_0(3\pi) \).
5. The planes \( \pi_{\pm 1} (x, y, z) = (0, 0, \pm a/2), \mu_4 \approx 32 \left[ \frac{\exp(-\pi \sqrt{2})}{\sqrt{2}} + 2 \frac{\exp(-\pi \sqrt{10})}{\sqrt{10}} \right] \).
6. The planes \( \pi_{\pm 2} (x, y, z) = (0, 0, \pm a), \mu_5 \approx -32 \frac{\exp(-\pi \sqrt{2})}{\sqrt{2}} \).

Thus Madelung obtained \( \mu \approx 3.487 \).
1.2 Historical survey

Although very expedient in this case, Madelung’s procedure is not generally applicable, owing to the complicated geometrical considerations needed to decompose more complex lattice structures. Indeed, Landé [98] overlooked a line of charges in decomposing the fluorite lattice. Madelung’s method was later applied by Bethe [14], Jones and Dent [84], and others to obtain field distributions in NaCl and other ionic crystals. It is interesting that, by summing directly over the first nine shells of ions surrounding a sodium ion, Kendall [94] was able to obtain Madelung’s result to within 10%. In this review we shall not consider such direct summation procedures. Curiously, almost exactly when Madelung was doing his work, Ornstein and Zernicke [112] independently used precisely the same method in three dimensions to re-sum similar series occurring in a study of the magnetic properties of cubic lattices.

The need for a more flexible summation procedure applicable to an arbitrary crystal structure was met by P. Ewald [49]. The procedure is based on the rediscovery of the Riemann–Appell device expressed in Equation (1.2.11) and was formulated and developed for cubic crystals in terms of ordinary theta functions in Ewald’s 1912 thesis. He later published a generalized version, which, because of its usefulness and wide application, we shall describe in detail. (For an exposition relating to \( d = 2 \), see Fetter [50].) Consider a crystal lattice described by the vectors

\[
\mathbf{R}_p = \mathbf{R}_l + \mathbf{r}_t \quad p = (l, t), \quad t = 1, \ldots, \nu \quad (d = 3). \tag{1.2.29}
\]

Here \( \mathbf{l} \) is an integer vector which labels the Bravais lattice vectors \( \mathbf{R}_l \); the vectors \( \mathbf{r}_t \) lie in the unit cell and are associated with electric charges \( \varepsilon_t \). We shall denote by \( \mathbf{K}_l \) the reciprocal lattice vectors corresponding to the \( \mathbf{R}_l \); i.e., if

\[
\mathbf{R}_l = l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 + l_3 \mathbf{a}_3
\]

then

\[
\mathbf{K}_l = l_1 \mathbf{b}_1 + l_2 \mathbf{b}_2 + l_3 \mathbf{b}_3,
\]

where

\[
\mathbf{a}_i \cdot \mathbf{b}_j = \delta_{ij}, \quad V_0 = \mathbf{a}_1 \times \mathbf{a}_2 \cdot \mathbf{a}_3.
\]

We shall illustrate the procedure for the electrostatic sum

\[
\Phi'(p) = \sum_{p' \neq p} \left( \frac{\varepsilon_{p'}}{R_{pp'}} \right) \exp (i K_0 R_{pp'}) \exp (i \mathbf{k} \cdot \mathbf{R}_{p'}), \tag{1.2.30}
\]

where \( R_{pp'} = |\mathbf{R}_p - \mathbf{R}_{p'}| \).

We have

\[
\Phi'(p) = \lim_{r \to \mathbf{R}_p} \left\{ \sum_{t' = 1}^{\nu} \varepsilon_{t'} \exp (i \mathbf{k} \cdot \mathbf{r}_{t'}) \left[ \pi (\mathbf{r} - \mathbf{r}_{t'}) - \delta_{tt'} F_1 (\mathbf{r} - \mathbf{r}_{t'}) \right] \right\}, \tag{1.2.31}
\]
Lattice sums

where

\[ \pi(r) = \sum_{l'} \exp(iK_0|\mathbf{R}_{l'} - r| + i\mathbf{k} \cdot \mathbf{R}_{l'}) \left| \mathbf{R}_{l'} - r \right| \]  \hspace{1cm} (1.2.32)

and

\[ F_l(r) = \exp(iK_0|\mathbf{R}_l - r| + i\mathbf{k} \cdot \mathbf{R}_l) \left| \mathbf{R}_l - r \right|. \]  \hspace{1cm} (1.2.33)

Hence, the problem reduces to calculating the slowly convergent sum (1.2.32) and taking the limit in (1.2.31).

Precisely as Epstein [47] did, Ewald used the following basic theorem from Krazer and Prym [96]:

**Theorem 1.2.1** Let \( \mathbf{d}_1, \mathbf{d}_2, \mathbf{d}_3 \) generate a Bravais lattice, let \( \mathbf{A} \) and \( \mathbf{v} \) be arbitrary vectors and let \( V_0 = \mathbf{d}_1 \times \mathbf{d}_2 \cdot \mathbf{d}_3 \). Let \( \mathbf{c}_1, \mathbf{c}_2, \mathbf{c}_3 \) be the corresponding unit vectors for the reciprocal lattice and let

\[ q_l = \sum_i l_i \mathbf{d}_i + \mathbf{v}, \quad p_l = \pi \sum_i l_i \mathbf{c}_i. \]  \hspace{1cm} (1.2.34)

Then

\[ \sum_l \exp(-q_l^2 + i\mathbf{q}_l \cdot \mathbf{A}) = \frac{\pi^{3/2}}{V_0} \sum_l \exp[-(p_l - \frac{1}{2} \mathbf{v})^2 + 2i(p_l \cdot \mathbf{A})], \]  \hspace{1cm} (1.2.35)

where the sum is over the integer \( l \) lattice.

The sum in (1.2.32) is only conditionally convergent. To avoid technical difficulties attendant on this fact, it is advisable to render the series absolutely convergent by including a convergence factor. This is done most simply by assuming that \( K_0 \) has an imaginary part that is small and positive. To transform (1.2.32) we take note of the integral representation (1.2.10), for \( \alpha \geq 0, \)

\[ e^{-\alpha R} = \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-R^2 t^2} e^{-\alpha^2/4t^2} dt. \]  \hspace{1cm} (1.2.36)

We can replace \( \alpha \) by \(-iK_0\) if the path of integration is deformed in such a way that \( K_0^2/4t^2 \) becomes purely imaginary as \( t \) approaches zero. Thus we have

\[ \frac{\exp(iK_0 R)}{R} = \frac{2}{\sqrt{\pi}} \int_{(0)}^\infty \exp\left(-R^2 t^2 + \frac{K_0^2}{4t^2}\right) dt, \]  \hspace{1cm} (1.2.37)

where the path of integration leaves the origin along the ray \( \arg t = \arg K_0 - \pi/4 \) and then returns to the real axis. From (1.2.32) and (1.2.37) we have

\[ \pi(r) = \frac{2}{\sqrt{\pi}} \int_{(0)}^\infty \sum_l \exp\left[-(\mathbf{R}_l - r)^2/4t^2 + i\mathbf{k} \cdot \mathbf{R}_l + \frac{K_0^2}{4t^2}\right] dt. \]  \hspace{1cm} (1.2.38)