An Alternative to Ewald Sums part I: Identities for Sums

R. Sperb[a]

[a] Seminar für Angewandte Mathematik, Eidgenössische Technische Hochschule, Zürich, Switzerland

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AN ALTERNATIVE TO EWALD SUMS
PART I: IDENTITIES FOR SUMS

R. SPERB

Seminar für Angewandte Mathematik, Eidgenössische Technische Hochschule, CH-8092 Zürich, Switzerland

In this paper identities are derived which allow the computation of the Coulomb energy associated with N charges in a central cell and all their periodic images. These identities are all consequences of one basic identity which is obtained in a simple and straightforward way. It is possible to extend the results to other types of potentials as well.

1. INTRODUCTION

The calculation of the Coulomb energy of an infinite periodic system is an important part of the numerical work in many applications. These systems are usually obtained by considering N charges in a central box and all their periodic images. One of the main problems is the acceleration of the slow convergence of the occurring sums. One of the first paper dealing with this problem was by Madelung 1918 [7] who was mainly concerned with Coulomb forces. In fact a new derivation of some of his central identities will be given here. Madelung's reasoning is restricted to the Coulomb case, whereas the present derivation works for a general class of potentials (including all power potentials). Madelung did not calculate the associated Coulomb energy, which is the hardest problem. Ewald [4] developed a method to calculate the Coulomb energy which is still widely used. His paper is rather difficult to read, but his method of derivation has influenced many researchers for decades. In 1991 Lekner [6] rederived some of the

central identities which are in essence contained in [7]. But Lekner made an elegant application of some powerful identities of Euler and Jacobi which were partly used by Ewald already. Lekner first calculated the Coulomb forces and then determined the Coulomb potential from there. Since the Coulomb potential becomes singular at a charge point, this procedure would actually require a delicate study of the limiting behaviour.

In this paper the derivation of the central identities for the associated sums is based on a simple basic lemma and ultimately leads to an equivalent formula for the Coulomb energy as Lekner's. For Coulomb forces it was given in [8].

The most important aspect of this formula will however be discussed in Part II, where we consider the situation that there are many charges in the central cell (say $> 10^2$). Then the amount of work required for N charges is proportional to N^2 since $(1/2)N(N-1)$ pairs have to be calculated for the Coulomb energy or the Coulomb forces. It is an important feature of our central result that it allows us to reduce drastically the CPU time required for many charges as compared to Ewald's method. Since the discussion is rather delicate and lengthy it will be postponed to a separate part. Numerical examples in practical applications will follow in separate works as well.

2. BASIC IDENTITIES

All the summation formulae to follow are consequences of a basic identity for sums of the general form

$$S(x,r) = \sum_{k=-\infty}^{\infty} p(x+k,r). \tag{2.1}$$

Here $x \in (0,1)$, $r > 0$ and p is an arbitrary function such that the series converges for $x \in (0,1)$ and $r > 0$.

It is easy to see that $S(x,r)$ is a periodic function in x (with period 1) for any $r > 0$. Therefore an obvious way to handle $S(x,r)$ is to expand it in a Fourier series with respect to x. This leads to

LEMMA 1   *Suppose that $p(s,r)$ is such that*

$$a_0(r) \equiv \int_{-\infty}^{\infty} p(s,r)ds$$

$$
\left.
\begin{aligned}
a_l(r) &\equiv \int_{-\infty}^{\infty} p(s,r)\cos(2\pi ls)ds \\[2em]
b_l(r) &\equiv \int_{-\infty}^{\infty} p(s,r)\sin(2\pi ls)ds
\end{aligned}
\right\} \ l = 1,2,3,\ldots
$$

all exist.

Then the following identity holds

$$
S(x,r) = a_0(r) + 2\sum_{l=1}^{\infty}[a_l(r)\cos(2\pi lx) + b_l(r)\sin(2\pi lx)]. \tag{2.2}
$$

Proof We use the complete orthonormal set of functions for the interval $(0,1)$, given by

$$
\{1, \sqrt{2}\cos(2\pi lx), \sqrt{2}\sin(2\pi lx)\}, \ l = 1,2,3,\ldots
$$

The Fourier coefficients of $S(x,r)$ are

$$
a_l = \sqrt{2}\int_0^1 \sum_{k=-\infty}^{\infty} p(s+k,r)\cos(2\pi ls)ds.
$$

Interchanging summation and integration and choosing the new integration variable $t = s + k$ we have

$$
a_l = \sqrt{2}\sum_{k=-\infty}^{\infty}\int_k^{k+1} p(t,r)\cos(2\pi lt)dt = \sqrt{2}\int_{-\infty}^{\infty} p(t,r)\cos(2\pi lt)dt,
$$

and the same reasoning holds for a_0 and b_l. This leads to identity (2.2).

Remark Two special cases are of importance.

(a) If $p = p(|x+k|,r)$ then p is symmetric in its first variable and all coefficients b_l vanish. Then identity (2.2) reduces to

$$
S(x,r) = 2\int_0^{\infty} p(s,r)ds + 4\sum_{l=1}^{\infty}\int_0^{\infty} p(s,r)\cos(2\pi ls)ds \cdot \cos(2\pi lx). \tag{2.3}
$$

(b) If $p(x + k, r) = -\partial P/\partial x$ and $P = P(|x + k|, r)$, then $p(-s, r) = -p(s, r)$ and all coefficients a_l vanish. Furthermore

$$b_l = 2\sqrt{2} \int_0^\infty p(s, r) \sin(2\pi ls) ds = -2\sqrt{2} P(s, r) \sin(2\pi ls) \Big|_0^\infty$$

$$+ 2\sqrt{2} \cdot 2\pi l \int_0^\infty P(s, r) \cos(2\pi ls) ds.$$

Assuming that $\lim_{s \to \infty} P(s, r) = 0$ we thus arrive at the identity

$$S(x, r) = 8\pi \sum_{l=1}^\infty l \cdot \int_0^\infty P(s, r) \cos(2\pi ls) ds \cdot \sin(2\pi lx). \tag{2.4}$$

Examples

(a) For Coulomb forces we can apply identity (2.4) with $P(s, r) = (s^2 + r^2)^{-1/2}$. Consider now a cube of side 1 and a unit charge at the origin. Then the x-component of the Coulomb force at the point (x, y, z), due to the charge and all its periodic images, is given by

$$F_x = \sum_{k, j, m = -\infty}^\infty \frac{x + k}{[(x + k)^2 + (y + j)^2 + (z + m)^2]^{3/2}} \cdot$$

Setting $r_{jm} = ((y + j)^2 + (z + m)^2)^{1/2}$ and

$$S(x, r_{jm}) = \sum_{k = -\infty}^\infty \frac{x + k}{[(x + k)^2 + r_{jm}^2]^{3/2}}$$

we can apply identity (2.4) to obtain

$$S(x, r_{jm}) = 8\pi \sum_{l=1}^\infty l \cdot K_0(2\pi l r_{jm}) \sin(2\pi lx), \tag{2.5}$$

where K_0 denotes a modified Bessel function. Since K_0 decays exponentially for large argument the sum over j and m converges fast and we arrive at

$$F_x = 8\pi \sum_{l=1}^\infty l \cdot \sin(2\pi lx) \sum_{j, m = -\infty}^\infty K_0(2\pi l r_{jm}). \tag{2.6}$$

Identity (2.6) was derived by Lekner in [6] by different methods.

(b) For $p(s,r) = \exp(-\beta(s^2 + r^2)^{1/2}) \cdot (s^2 + r^2)^{-1/2}$ we can apply identity (2.3). The corresponding Fourier-transform (see e.g. [2], p. 17, #27) then yields

$$\sum_{k=-\infty}^{\infty} \exp(-\beta[(x+k)^2 + r^2]^{1/2}) \cdot [(x+k)^2 + r^2]^{-1/2}$$

$$= 2K_0(\beta r) + 4\sum_{l=1}^{\infty} K_0[r(\beta^2 + 4\pi^2 l^2)^{1/2}] \cdot \cos(2\pi l x). \qquad (2.7)$$

(c) For $p(s,r) = (s^2 + r^2)^{-(1/2)-\nu}$, $\nu > 0$, identity (2.3) and the table in [2], p. 11, #7, together with the asymptotic formula for K_ν ([1], p. 375, #9.69) lead to

$$\sum_{k=-\infty}^{\infty} \frac{1}{[(x+k)^2 + r^2]^{(1/2)+\nu}} = \frac{\pi^{1/2}}{\Gamma(\nu + \frac{1}{2})} \left\{ \frac{\Gamma(\nu)}{r^{2\nu}} + 4\left(\frac{\pi}{r}\right)^\nu \right.$$

$$\left. \cdot \sum_{l=1}^{\infty} l^\nu \cdot K_\nu(2\pi l r) \cdot \cos(2\pi l x) \right\}. \qquad (2.8)$$

The sum on the left in (2.8) diverges if $\nu \to 0$. However we may take a collection of charges q_i such that

$$\sum_{i=1}^{I} q_i = 0,$$

and consider instead the sum

$$S := \sum_{k=-\infty}^{\infty} \sum_{i=1}^{I} \frac{q_i}{[(x_i + k)^2 + r_i^2]^{1/2}}.$$

We can use the asymptotic formulae

$$\Gamma(\nu) = \frac{1}{\nu} + o(\nu)$$

and

$$r_i^{-2\nu} = 1 - \log r_i \cdot 2\nu + o(\nu^2)$$

to conclude from (2.8) letting $v \to 0$ that

$$\sum_{k=-\infty}^{\infty} \sum_{i=1}^{I} \frac{q_i}{[(x_i + k)^2 + r_i^2]^{1/2}}$$

$$= \sum_{i=1}^{I} q_i \left\{ -2 \cdot \log r_i + 4 \sum_{l=1}^{I} K_0(2\pi l r_i) \cos(2\pi l x_i) \right\}. \quad (2.9)$$

3. COULOMB POTENTIAL AND COULOMB ENERGY

The first goal of this section is to derive an expression for the potential

$$U(\vec{r}) = \sum_{\vec{n} \in Z^3}' \sum_{i=1}^{N} \frac{q_i}{|\vec{r} - \vec{r}_i + \vec{n}|}, \quad (3.0)$$

where the prime indicates as usual that the $|\vec{n}| = 0$ terms in the sum are to be omitted. Note that this is a "regularized potential" since it contains no singular terms for $\vec{r} = \vec{r}_i$, in contrast to Madelung's definition. It has the advantage that it leads directly to the energy as defined below.

In order to calculate $U(\vec{r})$ we write it out more explicitly. Using the abbreviation

$$r_i(k, l, m) = [(x - x_i + k)^2 + (y - y_i + l)^2 + (z - z_i + m)^2]^{1/2}$$

we have

$$U(x, y, z) = \underbrace{\sum_{m=1}^{\infty} \sum_{k,l=-\infty}^{\infty} \sum_{i=1}^{N} q_i \left\{ \frac{1}{r_i(k, l, m)} + \frac{1}{r_i(k, l, -m)} \right\}}_{U_3(x, y, z)}$$

$$+ \underbrace{\sum_{l=1}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{i=1}^{N} q_i \left\{ \frac{1}{r_i(k, l, 0)} + \frac{1}{r_i(k, -l, 0)} \right\}}_{U_2(x, z, y)}$$

$$+ \underbrace{\sum_{k=1}^{\infty} \sum_{i=1}^{N} q_i \left\{ \frac{1}{r_i(k, 0, 0)} + \frac{1}{r_i(-k, 0, 0)} \right\}}_{U_1(x, z, y)}. \quad (3.1)$$

Note that the Coulomb energy can then be written as

$$E = \frac{1}{2} \sum_{j=1}^{N} q_j U(x_j, y_j, z_j) + \frac{1}{2} \sum_{i \neq j=1}^{N} q_i q_j \frac{1}{|\vec{r}_i - \vec{r}_j|}. \tag{3.2}$$

In order to derive an alternative expression for E we first consider

$$S_3(x, y, z, \beta) := \sum_{k,l,m=-\infty}^{\infty} ((x+k)^2 + (y+l)^2 + (z+m)^2)^{-1/2}. \tag{3.3}$$

$$\times \exp(-\beta[(x+k)^2 + (y+l)^2 + (z+m)^2]^{1/2}).$$

We set

$$\rho_{lm} = ((y+l)^2 + (z+m)^2)^{1/2}.$$

and use identity (2.7) with r replaced by ρ_{lm} to find

$$\sum_{k=-\infty}^{\infty} ((x+k)^2 + r_{lm}^2)^{-1/2} \cdot \exp(-\beta[(x+k)^2 + \rho_{lm}^2)]^{1/2})$$

$$= 2K_0(\beta\rho_{lm}) + 4 \sum_{p=1}^{\infty} K_0[\rho_{lm}(\beta^2 + (2\pi p)^2)^{1/2}] \cdot \cos(2\pi p x). \tag{3.4}$$

In the sum (we denote it by $T_{lm}^1(x, \beta)$) on the right side of Eq. (3.4) the limit $\beta \to 0$ is well behaved, also when the summation over l and m is performed. Thus we have to deal with the term $K_0(\beta\rho_{lm})$ in more detail.

We now write $\rho_{lm} = ((y+l)^2 + r_m^2)^{1/2}$, $r_m = |z+m|$, and use (2.7) again with $p(s,r) = 2K_0[\beta(s^2+r^2)^{-1/2}]$. From the table [2], p. 56, #43, we get

$$\sum_{l=-\infty}^{\infty} K_0[\beta(((y+l)^2) + r_m^2)^{1/2}] = \frac{\pi}{\beta} \exp(-\beta r_m)$$

$$+ \underbrace{2\pi \sum_{p=1}^{\infty} \frac{1}{((2\pi p)^2 + \beta^2)^{1/2}} \exp[-r_m((2\pi p)^2 + \beta^2)^{1/2}] \cdot \cos(2\pi p y)}_{\frac{1}{2} T_m^2(\beta)} \tag{3.5}$$

Again, the term $T_m^2(\beta)$ makes no difficulties as $\beta \to 0$ and the summation over m is performed. It remains to analyse

$$T^3(\beta, z) := \frac{2\pi}{\beta} \sum_{m=1}^{\infty} \left(\exp(-\beta|z+m|) + \exp(-\beta|z-m|) \right)$$

which consists of two geometric series. A few routine steps yield

$$T^3(\beta, z) = \frac{2\pi}{\beta} \frac{\exp(-\beta(1+z)) + \exp(\beta(1-z))}{1 - \exp(-\beta)},$$

and an expansion with respect to β gives

$$T^3(\beta, z) = 2\pi \left[\frac{2}{\beta^2} - \frac{1}{\beta} + \frac{1}{6} + z^2 + O(\beta) \right]. \tag{3.6}$$

Hence, if we form

$$\sum_{i=1}^{N} q_i T^3(\beta, z - z_i),$$

and let $\beta \to 0$ we are left with the simple expression

$$T^3(0) := 2\pi \sum_{i=1}^{N} (z - z_i)^2 q_i. \tag{3.7}$$

This holds for any set of N charges with charge neutrality.

Next we analyze the term

$$V(y, z) := 2 \sum_{\substack{m=-\infty \\ m \neq 0}}^{\infty} T_m^2(0) = 2 \sum_{\substack{m=-\infty \\ m \neq 0}}^{\infty} \sum_{p=1}^{\infty} \frac{1}{p} \cdot \exp[-2\pi p|z+m|] \cos(2\pi p y), \tag{3.8}$$

stemming from the second term on the right of (3.5).

A first possibility is to sum over m first, which gives after some algebra:

$$\sum_{\substack{m=-\infty \\ m \neq 0}}^{\infty} \exp[-2\pi p|z+m|] = \frac{\exp(-\pi \cdot p)}{Sh(\pi p)} Ch(2\pi p z), \quad (0 \leqslant z \leqslant 1).$$

Thus, a first way to write $V(y,z)$ is

$$V(y,z) = 2 \sum_{p=1}^{\infty} \frac{1}{p} \frac{\exp(-\pi \cdot p)}{Sh(\pi p)} Ch(2\pi pz) \cdot \cos(2\pi py) \qquad (3.9)$$

A second possibility is to sum over p first. To do so we write the term as the real part of a complex function:

$$\frac{1}{p} \exp(-|z+m|2\pi p) \cos(2\pi py) = \frac{1}{p} Re[\exp(-\zeta \cdot p)]$$

with $\zeta = 2\pi(|z+m| - i \cdot y)$. Then, since $Re\,\zeta > 0$ we have

$$\sum_{p=1}^{\infty} \frac{1}{p} \exp(-p \cdot \zeta) = \int_{\zeta}^{\infty} \sum_{p=1}^{\infty} \exp(-p \cdot w)dw = \int_{\zeta}^{\infty} \frac{\exp(-w)}{1 - \exp(-w)} dw$$

$$= -\log(1 - \exp(-\zeta)).$$

Now

$$Re[\log(1 - \exp(-\zeta))] = \log|1 - \exp(-(|z+m| - i \cdot y)2\pi)|$$

$$= \frac{1}{2}\log\{1 - 2\exp(-|z+m|2\pi)\cos(2\pi y)$$

$$+ \exp(-|z+m|4\pi)\},$$

and therefore a second way to express $V(y,z)$ is

$$V(y,z) = -\sum_{\substack{m=-\infty \\ m \neq 0}}^{\infty} \log\{1 - 2\exp(-|z+m|2\pi)\cos(2\pi y) + \exp(-|z+m|4\pi)\}$$

$$= -\sum_{\substack{m=-\infty \\ m \neq 0}}^{\infty} L[y, z+m], \qquad (3.10)$$

with the obvious definition of $L[y, z+m]$.

Remark The sum in (3.10) converges very fast in the whole range $y, z \in (0,1)$, whereas the convergence becomes slow in (3.9) is z approaches 1.

We can now collect all terms which give a contribution to $U_3(x, y, z)$. As an abbreviation for later on we set, for $r > 0$ and any s,

$$Be[r, s] = 4 \sum_{p=1}^{\infty} K_0(2\pi pr) \cos(2\pi ps). \qquad (3.11)$$

Then from (3.4), (3.7) and (3.10) one finds

$$U_3(x, y, z) = \sum_{i=1}^{N} q_i \left\{ \sum_{m=1}^{\infty} \sum_{l=-\infty}^{\infty} (Be[\rho_i(l, m), x - x_i] + Be[\rho_i(l, -m), x - x_i]) \right.$$

$$\left. + V(y - y_i, z - z_i) + 2\pi(z - z_i)^2 \right\}, \qquad (3.12)$$

where $\rho_i(l, m) = ((y - y_i + l)^2 + (z - z_i + m)^2)^{1/2}$.

We now turn our attention to the term $U_2(x, y, z)$. Analogously as before we first consider the expression

$$S_2(x, y, z, \beta) = \sum_{l=1}^{\infty} \sum_{k=-\infty}^{\infty} \frac{\exp(-\beta[(x+k)^2 + (y+l)^2 + z^2]^{1/2})}{[(x+k)^2 + (y+l)^2 + z^2]^{1/2}}. \qquad (3.13)$$

Setting $\rho(l) = ((y+l)^2 + z^2)^{1/2}$ we can express the sum over k as in (3.4) in different form as

$$S_2(x, y, z, \beta) = 2 \sum_{l=1}^{\infty} \left\{ K_0(\beta \rho(l)) + 4 \sum_{p=1}^{\infty} K_0(\rho(l)[\beta^2 + (2\pi p)^2]^{1/2}) \cdot \cos(2\pi px) \right\}. \qquad (3.14)$$

The second sum in (3.14) is well defined for $\beta \to 0$. For $U_2(x, y, z)$ we will need the sum

$$S(\beta) := 2 \sum_{l=1}^{\infty} K_0(\beta \rho(l)) + K_0(\beta \rho(-l))$$

$$= 2 \sum_{l=-\infty}^{\infty} K_0(\beta \rho(l)) - 2K_0(\beta \rho(0)).$$

As in (3.5) we can transform the last sum to

$$\frac{2\pi}{\beta} \exp(-\beta|z|) + 4\pi \sum_{p=1}^{\infty} \frac{1}{[(2\pi p)^2 + \beta^2]^{1/2}} \exp(-|z|[(2\pi p)^2 + \beta^2]^{1/2}) \cdot \cos 2\pi py.$$

For $\beta \to 0$ we only have to look at the terms

$$\frac{2\pi}{\beta}\exp(-\beta|z|) = 2\pi\left(\frac{1}{\beta} - |z| + O(\beta)\right)$$

and

$$-2K_0(\beta\rho(0)) = 4\log\beta + \log(\rho^2(0)) + O(\beta)$$

with $\rho^2(0) = y^2 + z^2$.

If one now forms a sum $\Sigma_{i=1}^{N} q_i\{\ \}$ the remaining terms as $\beta \to 0$ lead to

$$U_2(x,y,z) = \sum_{i=1}^{N} q_i\left\{\sum_{l=1}^{\infty} (Be\,[\rho_i(l), x - x_i] + Be\,[\rho_i(-l), x - x_i])\right.$$

$$+ 2\sum_{p=1}^{\infty} \frac{1}{p}\exp(-2\pi p|z - z_i|)\cos(2\pi p(y - y_i))$$

$$\left. + \log(\rho_i^2(0)) - 2\pi|z - z_i|\right\}, \qquad (3.15)$$

with $\rho_i^2(l) = (y - y_i + l)^2 + (z - z_i)^2$.

The calculations leading to (3.10) now show that

$$-2\sum_{p=1}^{\infty} \frac{1}{p}\exp(-2\pi p|z - z_i|)\cos 2\pi p(y - y_i) = L[y - y_i, z - z_i] \quad (3.16)$$

where $L[\,,\,]$ is defined in (3.10).

The last term to study is

$$U_1(x,y,z) = \sum_{k=1}^{\infty} \sum_{i=1}^{N} q_i\left\{\frac{1}{r_i(k,0,0)} + \frac{1}{r_i(-k,0,0)}\right\}$$

$$= \sum_{k=-\infty}^{\infty} \sum_{i=1}^{N} \frac{q_i}{r_i(k,0,0)} - \sum_{i=1}^{N} \frac{q_i}{r_i(0,0,0)}.$$

We can apply now identity (2.9) which in the present case gives

$$U_1(x,y,z) = \sum_{i=1}^{N} q_i\left\{Be\,[\rho_i(0), x - x_i] - 2\log\rho_i(0) - \frac{1}{r_i(0,0,0)}\right\}. \quad (3.17)$$

In order to find the expression for the Coulomb energy as given by (3.2) we collect the terms with $\vec{r} \neq \vec{r}_j(E_1)$ and look at the limit as $\vec{r} \to \vec{r}_j(E_2)$. The combination of (3.12), (3.15) and (3.17) shows that the $i \neq j$ part of the Coulomb energy can be written as

$$E_1 = \frac{1}{2} \sum_{\substack{i \neq j = 1}}^{N} q_i q_j \left\{ \sum_{m, l = -\infty}^{\infty} Be[\rho_{ij}(l, m), x_i - x_j] + W(y_i - y_j, z_i - z_j) \right.$$

$$\left. + 2\pi((z_i - z_j)^2 - |z_i - z_j|) \right\}, \tag{3.18}$$

where we have set

$$\rho_{ij}(l, m) = [(y_i - y_j + l)^2 + (z_i - z_j + m^2)]^{1/2}$$

and

$$W(y, z) := -\sum_{m = -\infty}^{\infty} L[y, z + m]. \tag{3.19}$$

The "self energy" E_2 containing the $i = j$ terms needs some separate analysis which now follows.

We start with term $U_3(x, y, z)$ given by (3.12).

For the Coulomb energy one has to form

$$C_3 := \sum_{j=1}^{N} q_j U_3(x_j, y_j, z_j).$$

This expression is well defined and one finds

$$C_3 = \sum_{i=1}^{N} q_i^2 \left\{ 8 \sum_{m=1}^{\infty} \sum_{l=-\infty}^{\infty} \sum_{p=1}^{\infty} K_0[2\pi p \sqrt{l^2 + m^2}] - 4 \sum_{n=1}^{\infty} \log(1 - e^{-2\pi n}) \right\}. \tag{3.20}$$

Next we look at the term $U_2(x, y, z)$ which because of (3.16) can be written as

$$U_2(x, y, z) = \sum_{i=1}^{N} q_i \left\{ \sum_{l=1}^{\infty} (Be[\rho_i(l), x - x_i] + Be[\rho_i(-l), x - x_i]) \right.$$

$$\left. + \log((y - y_i)^2 + (z - z_i)^2) - L[y - y_i, z - z_i] - 2\pi|z - z_i| \right\}. \tag{3.21}$$

The only terms that become singular as $y \to y_i$, $z \to z_i$ are the two terms involving the logarithms. A straightforward series expansion shows that the two log-terms have the limit $-\log(4\pi^2)$ as $y \to y_i$, $z \to z_i$. Hence the contribution to the Coulomb energy stemming from $U_2(x, y, z)$ is

$$C_2 := \sum_{i=1}^{N} q_i^2 \left\{ 8 \sum_{l,p=1}^{\infty} K_0(2\pi p \cdot l) - \log(4\pi^2) \right\}. \qquad (3.22)$$

The last and hardest term to analyze stems from $U_1(x, y, z)$ given by (3.17). If we take $x = x_i$ and $\rho = \sqrt{y^2 + z^2}$ there in the place of $\rho_i(0)$ the expression to study is

$$f(\rho) := Be[\rho, 0] - 2 \cdot \log \rho - \frac{1}{\rho} = 4 \sum_{p=1}^{\infty} K_0(2\pi p \rho) - 2 \log \rho - \frac{1}{\rho}. \qquad (3.23)$$

We state the result in the form of

LEMMA 2

> *For $0 < \rho < 1$ one has*
>
> $$f(\rho) = 2 \sum_{p=1}^{\infty} \binom{-\frac{1}{2}}{p} \zeta(2p+1)\rho^{2p} + c_0 = 2 \sum_{l=1}^{\infty} \left(\frac{1}{l} - \frac{1}{\sqrt{l^2 + \rho^2}} \right) + c_0$$
>
> *with $\zeta = $ Riemann Zeta function and*
>
> $$c_0 = -2(\log 2 - \gamma) \cong -0.231863. \qquad (3.24)$$

Proof   We consider the function

$$g(\rho) := \sum_{l=1}^{\infty} \left(\frac{1}{l} - \frac{1}{\sqrt{l^2 + \rho^2}} \right). \qquad (3.25)$$

Then

$$g'(\rho) = \rho \sum_{l=1}^{\infty} \frac{1}{(l^2 + \rho^2)^{3/2}}.$$

We can now apply identity (2.8) with $v = 1$, $x = 0$ yielding after some rearrangement

$$g'(\rho) = \frac{1}{\rho} - \frac{1}{2\rho^2} + 4\pi \sum_{p=1}^{\infty} p K_1(2\pi p \rho).$$

But since for Bessel functions one has $K_1(s) = -(dK_0/ds)$ we are led to

$$g(\rho) = \log \rho + \frac{1}{2\rho} - 2 \sum_{p=1}^{\infty} K_0(2\pi p \rho) + \text{const.}. \qquad (3.26)$$

We can now apply an identity given in [5] (I am indebted to Prof. J. Lekner for pointing this out):

$$4 \sum_{p=1}^{\infty} K_0(2\pi p \rho) \cdot \cos(2\pi p x) = 2\left[\gamma + \log\left(\frac{\rho}{2}\right) \right] + \frac{1}{\sqrt{\rho^2 + x^2}}$$

$$+ \sum_{l=1}^{\infty} \left\{ \frac{1}{\sqrt{(1-x)^2 + \rho^2}} - \frac{1}{l} \right\}$$

$$+ \sum_{l=1}^{\infty} \left\{ \frac{1}{\sqrt{(l+x)^2 + \rho^2}} - \frac{1}{l} \right\}. \qquad (3.27)$$

With $x = 0$ a simple combination of (3.23), (3.26) and (3.27) shows that c_0 has the value given in equation (3.24), with $\gamma = $ Euler constant. This proves Lemma 2. The contribution to the Coulomb energy stemming from $U_1(x, y, z)$ is thus

$$C_1 := \sum_{i=1}^{N} q_i^2 \cdot c_0. \qquad (3.28)$$

Finally we can collect all terms contributing to the self energy E_2. The numerical evaluation of the sums in (3.20), (3.22) and the expression (3.28) lead to

$$E_2 = Q_0 \sum_{i=1}^{N} q_i^2, \qquad (3.29)$$

with

$$Q_0 = 2 \sum_{p=1}^{\infty} \sum_{m,n=-\infty}^{\infty}{}' K_0(2\pi p(m^2 + n^2)^{1/2}) - 2 \sum_{l=1}^{\infty} \log(1 - e^{-2\pi \cdot l}) + \gamma - \log(4\pi)$$

$$\cong -1.942248.$$

Remark The constant Q_0 is in accordance with the corresponding constant given by Lekner in [6], p. 495. Lekner derived it by completely different arguments.

We sum up our calculations in the form of a

THEOREM   *The Coulomb energy as defined by (3.2) can be expressed as*

$$E = \frac{1}{2} \sum_{i \neq j = 1}^{N} q_i q_j \left\{ \sum_{m,l=-\infty}^{\infty} Be[\rho_{ij}(l,m), x_i - x_j] \right.$$

$$- \sum_{m=-\infty}^{\infty} L[y_i - y_j, z_i - z_j + m]$$

$$\left. + 2\pi((z_i - z_j)^2 - |z_i - z_j|) \right\} + Q_0 \cdot \sum_{i=1}^{N} q_i^2 \qquad (3.30)$$

where

$$\rho_{ij}^2(l,m) := (y_i - y_j + l)^2 + (z_i - z_j + m)^2,$$

$$Be[\rho, x] := 4 \sum_{p=1}^{\infty} K_0(2\pi p \rho)\cos(2\pi p x),$$

$$L[y, z] := \log\{1 - 2\cos(2\pi y)e^{-2\pi|z|} + e^{-4\pi|z|}\},$$

$$Q_0 \cong -1.942248.$$

Remarks

1. In some applications one considers a two dimensional layer of cells of some finite height extending to infinity only in two dimensions. This means that the potential as defined in (3.1) contains only the terms $U_2(x, y, z)$ and $U_1(x, y, z)$. It is then easy to verify that the associated Coulomb energy is given by terms described in the following

COROLLARY   *The Coulomb energy of a two-dimensional layer of finite
height h, i.e.* $0 \leqslant z \leqslant h$, *with associated Coulomb potential*

$$U(x,y,z) = \sum_{l=1}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{i=1}^{N} q_i \left\{ \frac{1}{r_i(k,l)} + \frac{1}{r_i(k,-l)} \right\}$$

$$+ \sum_{k=1}^{\infty} \sum_{i=1}^{N} q_i \left\{ \frac{1}{r_i(k,0)} + \frac{1}{r_i(-k,0)} \right\}$$

where $r_i^2(k,l) = (x - x_i + k)^2 + (y - y_i + l)^2 + (z - z_i)^2$, *can be expressed as*

$$E = \frac{1}{2} \sum_{i \neq j = 1}^{N} q_i q_j \left\{ \sum_{l=-\infty}^{\infty} Be[\rho_{ij}(l), x_i - x_j] \right.$$

$$\left. - L[y_i - y_j, z_i - z_j] - 2\pi |z_i - z_j| \right\} + \hat{Q}_0 \cdot \sum_{i=1}^{N} q_i^2 \qquad (3.31)$$

with $\rho_{ij}^2(l) := (y_i - y_j + l)^2 + (z_i - z_j)^2$ *and*

$$\hat{Q}_0 = 4 \sum_{l,p=1}^{\infty} K_0(2\pi p \cdot l) + \gamma - \log(4\pi) \cong -1.955013.$$

2. Both expression (3.30) and (3.31) coincide with the formulae (28), (34) and
(43) of Lekner [6] as some simple algebra reveals. An important differ-
ence in the derivation is that the constants Q_0, $\hat{Q}_0$ were not found a
posteriori by comparison with a special case as in [6]. They follow from
the definition of the Coulomb energy.

3. In (3.30) and (3.31) the sums involving the Bessel functions may require
many terms if the arguments $\rho_{ij}(l,m)$ or $\rho_{ij}(l)$ become small (say $<10^{-2}$)
for a particular pair i,j. This situation was already recognized by
Madelung [7]. In fact, we have to study the behaviour of the two singu-
lar terms $Be[,]$ and $L[,]$ as the arguments tend to zero. This is done in
the following.

In order to derive an alternative expression which converges fast for small
r let us first consider

$$F(x,r,p) = \sum_{k=-\infty}^{\infty} [(x+k)^2 + r^2]^{-(1/2)-p}, \qquad (3.32)$$

where we assume $p > 0$ and $0 \leqslant r < 1$, $0 \leqslant x < 1$.

Since

$$[(x + k)^2 + r^2]^{-(1/2)-p} = |x + k|^{-1-2p} \cdot \left[1 + \left(\frac{r}{x+k} \right)^2 \right]^{-(1/2)-p}$$

we find by expansion that

$$[(x + k)^2 + r^2]^{-(1/2)-p} = \sum_{l=0}^{\infty} \binom{-p - \frac{1}{2}}{l} r^{2l} \frac{1}{|x + k|^{2l+2p+1}}.$$

The generalized Zeta-function (Hurwitz Zeta-function) is defined for arbitrary $m \neq 0, -1, -2, \ldots$ and $x \in \mathbb{C}$ by

$$\zeta(m, x) = \sum_{k=0}^{\infty} \frac{1}{(k + x)^m}. \tag{3.33}$$

We may write $F(x, r, p)$ in the form

$$F(x, r, p) = \sum_{k=0}^{\infty} [(1 + x + k)^2 + r^2]^{-(1/2)-p}$$

$$+ \sum_{k=0}^{\infty} [(1 - x + k)^2 + r^2]^{-(1/2)-p} + [x^2 + r^2]^{-(1/2)-p}$$

and then use the definition (3.33) to find

$$F(x, r, p) = \sum_{l=0}^{\infty} \binom{-p - \frac{1}{2}}{l} r^{2l} \{ \zeta(2l + 1 + 2p, 1 + x)$$

$$+ \zeta(2l + 1 + 2p, 1 - x) \} + [x^2 + r^2]^{-(1/2)-p}. \tag{3.34}$$

The only term in (3.34) which needs special attention when $p \rightarrow 0$ is the one with $l = 0$. The asymptotic behavior of $\zeta(m, x)$ is given by (see [3], p. 26)

$$\zeta(m, x) = \frac{1}{m - 1} - \psi(x) + o(m - 1), \tag{3.35}$$

where $\psi(x)$ is the Digamma-function.

Hence for any collection of M charges q_i for which

$$\sum_{i=1}^{M} q_i = 0$$

we have

$$\sum_{i=1}^{M} q_i F(x_i, r_i, 0) = \sum_{i=1}^{M} q_i G(r_i, x_i), \qquad (3.36)$$

where $G(r, x)$ is defined by

$$G(r, x) = \sum_{l=1}^{x} \binom{-\frac{1}{2}}{l} r^{2l} \{\zeta(2l + 1, 1 + x) + \zeta(2l + 1, 1 - x)\}$$

$$- \psi(1 + x) - \psi(1 - x) + \frac{1}{\sqrt{x^2 + r^2}} \qquad (3.37)$$

The function $G(r, x)$ is defined for $0 \leqslant r < 1$ and $0 \leqslant x < 1$. One can check however that the series converges only for $|x + r| < 1$. It is not hard to check that the following relations hold

$$\begin{cases} G(r, x) & = G(r, -x) \\ G(r, 1 - x) & = G(r, x) \end{cases} \qquad (3.38)$$

It follows from (3.38) that we can always restrict x to the interval $[-\frac{1}{2}, \frac{1}{2}]$ and r may be restricted e.g. to the interval $(0, \frac{1}{4})$, since $G(r, x)$ will only be used for small values of r.

Since (3.36) holds for any collection of charges with charge neutrality and we have a different expression for the same quantity in the form of identity (2.9), we may conclude the following identity: For $0 \leqslant r < 0.5$ and $|x| \leqslant 0.5$ one has

$$G(r, x) = Be[r, x] - 2\log r + \text{const.}. \qquad (3.39)$$

Evaluation of both sides at a convenient value of r and x give const. $\cong 1.386294$. Identity (3.39) allows then to replace the terms $Be[,]$ in our Theorem or Corollary by $G(r, x)$ which is more advantageous to use for small values of r.

Note that the function $Be[r, x]$ becomes singular for $r \to 0$. However there is another singular term in (3.30) of opposite sign:

$L[y_i - y_j, z_i - z_j + m] = L[y_i - y_j + l, z_i - z_j + m]$ (for any $l \in \mathbb{Z}$). This term has a logarithmic singularity as well for $r = [(y_i - y_j + l)^2 + (z_i - z_j + m)^2]^{1/2} \to 0$, which is possible for $-1 \leqslant l, m \leqslant 1$.

Setting $\eta = \pi \cdot y$, $\zeta = \pi \cdot z$ a series expansion gives

$$\log(y^2 + z^2) - L[y, z] = -\log(4\pi^2) + 2 \cdot \zeta + \frac{1}{3}(\eta^2 - \zeta^2)$$

$$+ \frac{1}{90}(\eta^4 - 6\eta^2 \zeta^2 + \zeta^4) + \frac{2}{2835}(\eta^6 - 15\eta^4 \cdot \zeta^2$$

$$+ 15\eta^2 \cdot \zeta^4 - \zeta^6) + \text{higher order terms}$$

$$=: La[y, z] - \log(4\pi^2) \qquad (3.40)$$

with the obvious definition of the approximation $La[y, z]$. Combining now (3.39) and (3.40) we arrive at the following result:

If $\rho_{ij}(l, m) = ((y_i - y_j + l)^2 + (z_i - z_j + m)^2)^{1/2}$ becomes small (say < 0.1), then we can replace the combination

$$Be[\rho_{ij}(l, m), x_i - x_j] - L[y_i - y_j, z_i - z_j + m]$$

$$= Be[\rho_{ij}(l, m), x_i - x_j] - L[y_i - y_j + l, z_i - z_j + m] \qquad (3.41)$$

in (3.30) by

$$G[\rho_{ij}(l, m), x_i - x_j] + La[y_i - y_j + l, z_i - z_j + m] - 5.0620485 \qquad (3.42)$$

where $G[\,,\,]$ is defined in (3.37) and $La[\,,\,]$ in (3.40).

Numerical Example As an illustration we consider two charges ± 1 and compare

$$Sd[x_1, x_2, r] = \sum_{k=-\infty}^{\infty} \left\{ \frac{1}{\sqrt{(x_1 + k)^2 + r^2}} - \frac{1}{\sqrt{(x_2 + k)^2 + r^2}} \right\}$$

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with the expression from (2.9), namely

$$S[x_1, x_2, r] = 4 \sum_{l=1}^{\infty} K_0(2\pi l r) \{\cos(2\pi l x_1) - \cos(2\pi l x_2)\},$$

as well as the formula following from (3.36) which is

$$H[x_1, x_2, r] = G(r, x_1) - G(r, x_2).$$

We choose $x_1 = 0.2$, $x_2 = 0.3$ and $r = 0.5$

$$Sd = 0.0727395 \qquad k = -500 \text{ to } 500$$

$$S = 0.0727393 \qquad l = 1 \text{ to } 5$$

$$H = 0.07274 \qquad l = 1 \text{ to } 15$$

Now if r becomes smaller the sum in (3.37) converges much faster. With the same values of x_1, x_2 and $r = 0.01$:

$$Sd = 1.5271559 \qquad k = -600 \text{ to } 600$$

$$S = 1.5271557 \qquad l = 1 \text{ to } 200$$

$$H = 1.5271558 \qquad l = 1 \text{ to } 2$$

4. In formula (3.30) the coordinates x, y, z seem to be treated in a unsymmetric way. It was shown by Lekner [6] that indeed (3.30) is symmetric in x, y, z, as it should be.
5. There are many interesting special cases for the identity (2.9). In particular we can get quickly convergent series for Madelung constants. To this end consider the sum

$$S(r) := \sum_{l=-\infty}^{\infty} \frac{(-1)^l}{\sqrt{l^2 + r^2}}, \quad r > 0. \tag{3.43}$$

We rewrite (3.43) in the form

$$S(r) = \sum_{k=-\infty}^{\infty} \left(\frac{1}{\sqrt{(2k)^2 + r^2}} - \frac{1}{\sqrt{(2k+1)^2 + r^2}} \right)$$

$$= \frac{1}{2} \sum_{k=-\infty}^{\infty} \left(\frac{1}{\sqrt{k^2 + (\frac{r}{2})^2}} - \frac{1}{\sqrt{(k + \frac{1}{2})^2 + (\frac{r}{2})^2}} \right).$$

By identity (2.9) it follows that

$$S(r) = 2 \sum_{p=1}^{\infty} (K_0(\pi \cdot p \cdot r) - (-1)^p K_0(\pi \cdot p \cdot r)) = 4 \sum_{p=1}^{\infty} K_0((2p-1)\pi \cdot r). \quad (3.44)$$

Identity (3.44) now serves to find an alternative expression for the Madelung constant of a square of side 1, namely

$$M_S := \sum_{k,l=-\infty}^{\infty}{}' \frac{(-1)^{k+l+1}}{\sqrt{k^2 + l^2}}. \quad (3.45)$$

Writing (3.45) out in more explicit form as

$$M_S = 2 \sum_{k=-\infty}^{\infty} \sum_{l=1}^{\infty} \frac{(-1)^{k+l+1}}{\sqrt{k^2 + l^2}} + 2 \sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k} \quad (3.46)$$

one readily checks that

$$M_S = 8 \sum_{l=1}^{\infty} (-1)^{l+1} \sum_{k=1}^{\infty} K_0((2k-1)\pi l) + \log 4$$

$$\cong 1.6155426. \quad (3.47)$$

With little extra work we can get the corresponding expression for the Madelung contant of a unit cube, i.e.

$$M_C := \sum_{k,l,m=-\infty}^{\infty}{}' \frac{(-1)^{k+l+m+1}}{\sqrt{k^2 + l^2 + m^2}}. \quad (3.48)$$

If we write

$$M_C = 2 \sum_{k,l=-\infty}^{\infty} \sum_{m=1}^{\infty} \frac{(-1)^{k+l+m+1}}{\sqrt{k^2 + l^2 + m^2}} + M_S$$

and use (3.44) we see that

$$M_C = 8 \sum_{p,k=1}^{\infty} \sum_{l=-\infty}^{\infty} (-1)^{k+l+1} K_0[(2p-1)\pi\sqrt{k^2+l^2}] + M_S$$

$$\cong 1.747565. \tag{3.49}$$

A completely different, but more complicated derivation of (3.46), (3.49) and similar types of sums was given in [9].

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