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COULOMB FORCES AND POTENTIALS IN SYSTEMS WITH AN ORTHORHOMBIC UNIT CELL

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R. Sperb's development of the author's earlier work on summation of Coulomb fields in periodically repeated systems with a cubic unit cell is extended to systems with an orthorhombic unit cell. This permits rapid evaluation of Coulomb forces and potentials in systems other than those with a cubic unit cell. A general formula enables the Madelung constant to be calculated, as a function of the cell dimensions a, b and c.

Keywords: Coulomb forces; orthorhombic unit cell

1. INTRODUCTION

The author has derived formulae for the rapid evaluation of sums, over periodically repeated cells containing charges, of Coulomb forces and potentials [1]. In the two-dimensional case the cells had equal dimension in the repeated directions; in the three-dimensional case the cells were assumed to be cubes. Clark, Madden and Warren [2] have generalized the formulae for the two-dimensional repetition of the central cell to an arbitrary orthorhombic cell. Sperb [3] has given an elegant rederivation of the author's formulae, based on Fourier analysis of the periodic fields, and also showed how the restriction to cubic cells may be removed. This note gives explicit formulae for the Coulomb forces and potentials in a system of periodically repeated rectangular cells. The immediate motivation is the author's investigation of the dependence of the Coulomb energy in ice on proton order or disorder; a byproduct of the general formulae is that the

Madelung constants of orthorhombic systems can be written down analytically.

2. FORCE COMPONENTS, AND THE LAPLACIAN

We use the notation of reference [1]: the force exerted on particle i by the particle j, and by all the repetitions of particle j in the periodic system, is

$$\mathbf{F}_i = q_i q_j \sum_{\text{all cells}} \frac{\mathbf{r}_i - \mathbf{r}_j}{|\mathbf{r}_i - \mathbf{r}_j|^3} \tag{1}$$

where q_i and q_j are the charges on particles i and j. (Note that the periodic repetitions of particle i give zero force on the charge i in the central cell.) Let the cell whose repetition forms the system be rectangular, with x, y and z dimensions a, b and c, and let the central-cell components of the j to i displacement vector $\mathbf{r}_i - \mathbf{r}_j$ be defined in terms of dimensionless coordinates ξ, η and ζ as

$$x_i - x_j = \xi a, \quad y_i - y_j = \eta b, \quad z_i - z_j = \zeta c \tag{2}$$

Then we can write $\mathbf{F}_i$ in terms of dimensionless components as

$$\mathbf{F}_i = \frac{q_i q_j}{a^2} \, (X, \, Y, \, Z) \tag{3}$$

where X, Y and Z are functions of the normalized displacement components ξ, η and ζ, and of the cell dimension ratios b/a and c/a:

$$X = \sum_{l,}^{\infty} \sum_{m,}^{\infty} \sum_{n=-\infty}^{\infty} \frac{\xi + l}{[(\xi + l)^2 + (\frac{b}{a})^2(\eta + m)^2 + (\frac{c}{a})^2(\zeta + n)^2]^{3/2}}$$

$$Y = \left(\frac{a}{b}\right)^2 \sum_{l,}^{\infty} \sum_{m,}^{\infty} \sum_{n=-\infty}^{\infty} \frac{\eta + m}{[(\eta + m)^2 + (\frac{c}{b})^2(\zeta + n)^2 + (\frac{a}{b})^2(\xi + l)^2]^{3/2}} \tag{4}$$

$$Z = \left(\frac{a}{c}\right)^2 \sum_{l,}^{\infty} \sum_{m,}^{\infty} \sum_{n=-\infty}^{\infty} \frac{\zeta + n}{[(\zeta + n)^2 + (\frac{a}{c})^2(\xi + l)^2 + (\frac{b}{c})^2 (\eta + m)^2]^{3/2}}$$

Note that a, the x dimension of the unit cell, has been chosen to play a special role.

We define $\rho_{mn}(\eta, \zeta)$ by

$$\rho_{mn}^2 = \left(\frac{b}{a}\right)^2 (\eta + m)^2 + \left(\frac{c}{a}\right)^2 (\zeta + n)^2 \tag{5}$$

and use identities (5), (13) and (7) of [1] to reduce X to a rapidly convergent series over modified Bessel functions:

$$\begin{aligned} X &= \frac{2}{\sqrt{\pi}} \sum_{l,}^{\infty} \sum_{m,}^{\infty} \sum_{n=-\infty}^{\infty} (\xi + l) \int_0^{\infty} dt\, t^{1/2}\, e^{-[(\xi+l)^2 + \rho_{mn}^2]t} \\ &= 2\pi \sum_{l,}^{\infty} \sum_{m,}^{\infty} \sum_{n=-\infty}^{\infty} l \sin(2\pi l \xi) \int_0^{\infty} dt\, t^{-1}\, e^{-\pi^2 l^2/t - \rho_{mn}^2 t} \\ &= 8\pi \sum_{l=1}^{\infty} l \sin(2\pi l \xi) \sum_{m,}^{\infty} \sum_{n=-\infty}^{\infty} K_0(2\pi l \rho_{mn}) \end{aligned} \tag{6}$$

A generalization of this formula to arbitrary power laws has already been given by Sperb ([3], equation 11). Similar expressions can be written down for the Y and Z components of the force:

$$\begin{aligned} Y &= \left(\frac{a}{b}\right)^2 8\pi \sum_{m=1}^{\infty} m \sin(2\pi m \eta) \\ &\quad \sum_{n,}^{\infty} \sum_{l=-\infty}^{\infty} K_0\left(2\pi m \left[\left(\frac{c}{b}\right)^2 (\zeta + n)^2 + \left(\frac{a}{b}\right)^2 (\xi + l)^2\right]^{1/2}\right) \\ Z &= \left(\frac{a}{c}\right)^2 8\pi \sum_{n=1}^{\infty} n \sin(2\pi n \zeta) \\ &\quad \sum_{l,}^{\infty} \sum_{m=-\infty}^{\infty} K_0\left(2\pi n \left[\left(\frac{a}{c}\right)^2 (\xi + l)^2 + \left(\frac{b}{c}\right)^2 (\eta + m)^2\right]^{1/2}\right) \end{aligned} \tag{7}$$

Let us suppose that there exists a pair potential U_{ij} such that $\mathbf{F}_i = -\nabla_i U_{ij}$. The Laplacian of such a potential would then be

$$\nabla_i^2 U_{ij} = -\nabla_i \cdot \mathbf{F}_i = -\frac{q_i q_j}{a^2} \left(\frac{1}{a}\frac{\partial X}{\partial \xi} + \frac{1}{b}\frac{\partial Y}{\partial \eta} + \frac{1}{c}\frac{\partial Z}{\partial \zeta}\right) \tag{8}$$

In the cubic case we found ([1], end of section 4) that the Laplacian is a constant, taking the value which corresponds to a uniform neutralizing background charge in the Poisson equation. Here the volume of the cell is *abc*, and the Laplacian takes the value corresponding to a uniform neutralizing background because the following equality holds:

$$\begin{aligned}
&\frac{bc}{a^2}\sum_{l=1}^{\infty} l^2\cos(2\pi l\xi)\sum_{m,}^{\infty}\sum_{n=-\infty}^{\infty} K_0(2\pi l[b^2(\eta+m)^2 + c^2(\zeta+n)^2]^{1/2}/a)\\
&+\frac{ca}{b^2}\sum_{m=1}^{\infty} m^2\cos(2\pi m\eta)\sum_{n,}^{\infty}\sum_{l=-\infty}^{\infty} K_0(2\pi m[c^2(\zeta+n)^2 + a^2(\xi+l)^2]^{1/2}/b)\\
&\frac{ab}{c^2}\sum_{n=1}^{\infty} n^2\cos(2\pi n\zeta)\sum_{l,}^{\infty}\sum_{m=-\infty}^{\infty} K_0(2\pi n[a^2(\xi+l)^2 + b^2(\eta+m)^2]^{1/2}/c)\\
&= -(4\pi)^{-1}
\end{aligned} \tag{9}$$

3. THE POTENTIAL ENERGY PER UNIT CELL

While the periodic self-replication of a particle gives zero force on that particle, the Coulomb energy due to these repetitions is infinite in a system where the unit cell is repeated to infinity. To find the potential energy per unit cell we shall follow the elegant methods of R. Sperb [4], in which the cancellation of the infinite self-energies in a neutral system is made explicit.

Consider first two charges q_i and q_j. The potential energy of their Coulomb interactions, with each other and with their own and each other's images, is as follows:

$$\begin{aligned}
&q_i \text{ with } q_j \text{ in central cell:} && \frac{q_i q_j}{a}[\xi_{ij}^2 + \rho_{00}^2(\eta_{ij}, \zeta_{ij})]^{-1/2}\\
&q_i \text{ with } q_j \text{ repetitions:} && \frac{q_i q_j}{a}\sum_{l,}^{\infty}\sum_{m,}^{\infty}\sum_{n=-\infty}^{\infty}{}' [(\xi_{ij}+l)^2 + \rho_{mn}^2(\eta_{ij}, \zeta_{ij})]^{-1/2}\\
&q_j \text{ with } q_i \text{ repetitions:} && \frac{q_i q_j}{a}\sum_{l,}^{\infty}\sum_{m,}^{\infty}\sum_{n=-\infty}^{\infty}{}' [(\xi_{ij}+l)^2 + \rho_{mn}^2(\eta_{ij}, \zeta_{ij})]^{-1/2}
\end{aligned} \tag{10}$$

q_i with self-images: $$\frac{q_i^2}{a}\sum_{l,}^{\infty}\sum_{m,}^{\infty}\sum_{n=-\infty}^{\infty}{}' \left[l^2+\left(\frac{b}{a}\right)^2 m^2+\left(\frac{c}{a}\right)^2 n^2\right]^{-1/2}$$

q_j with self-images: $$\frac{q_j^2}{a}\sum_{l,}^{\infty}\sum_{m,}^{\infty}\sum_{n=-\infty}^{\infty}{}' \left[l^2+\left(\frac{b}{a}\right)^2 m^2+\left(\frac{c}{a}\right)^2 n^2\right]^{-1/2}$$

(The prime on the summations means that the term with l, m, n all zero is to be omitted; $\rho_{mn}(\eta, \zeta)$ is defined in (5).) We note that the interactions with particles outside of the central cell should be counted as belonging half to the central cell and half to each other cell. The Coulomb energy per cell is thus

$$E=\sum_{i<j}\sum \frac{q_i q_j}{a} S(\xi_{ij}, \eta_{ij}, \zeta_{ij})+\frac{T}{2a}\sum_i q_i^2 \tag{11}$$

where the sums S and T are defined as

$$S(\xi, \eta, \zeta)=\sum_{l,}^{\infty}\sum_{m,}^{\infty}\sum_{n=-\infty}^{\infty}[(\xi+l)^2+\rho_{mn}^2(\eta, \zeta)]^{-1/2} \tag{12}$$

$$T=\sum_{l,}^{\infty}\sum_{m,}^{\infty}\sum_{n=-\infty}^{\infty}{}' \left[l^2+\left(\frac{b}{a}\right)^2 m^2+\left(\frac{c}{a}\right)^2 n^2\right]^{-1/2} \tag{13}$$

We will calculate T from S in the limit as the distance between the particles in the central cell, $r_0=[(a\xi)^2+(b\eta)^2+(c\zeta)^2]^{1/2}$, tends to zero:

$$T=\lim_{r_o\to 0}\left\{S(\xi, \eta, \zeta)-\left[\xi^2+\left(\frac{b}{c}\right)^2\eta^2+\left(\frac{c}{a}\right)^2\zeta^2\right]^{-1/2}\right\} \tag{14}$$

Following Sperb [4] we shall work with

$$S_\beta(\xi, \eta, \zeta)=\sum_{l,}^{\infty}\sum_{m,}^{\infty}\sum_{n=-\infty}^{\infty}[(\xi+l)^2+\rho_{mn}^2]^{-1/2}\exp\{-\beta[(\xi+l)^2+\rho_{mn}^2]^{1/2}\} \tag{15}$$

and later take the limit of $\beta\to 0$. The expression which follows is a generalization of Sperb results to a non-cubic unit cell; we assume for simplicity that the dimensionless z-displacement ζ is restricted to the range $|\zeta| \leq 1$. Then (see the Appendix)

$$\begin{aligned} S_\beta(\xi,\eta,\zeta) = {} & \frac{4\pi}{\beta^2}\left(\frac{a^2}{bc}\right) + \frac{2\pi c}{b}\left(\zeta^2 - |\zeta| + \frac{1}{6}\right) \\ & + 4\sum_{l=1}^{\infty} \cos(2\pi l \xi) \sum_{m,}^{\infty} \sum_{n=-\infty}^{\infty} K_0(2\pi l \rho_{mn}(\eta, \zeta)) \\ & - \sum_{n=-\infty}^{\infty} \log[1 - 2\cos(2\pi\eta)\exp(-2\pi|\zeta + n|c/b) \\ & + \exp(-4\pi|\zeta + n|c/b)] + O(\beta^2) \end{aligned} \tag{16}$$

To evaluate T we will use the result ([5], equation 8.526.1)

$$\begin{aligned} 4\sum_{l=1}^{\infty} \cos(2\pi l\xi) K_0(2\pi l \rho) = {} & 2[\gamma + \log(\rho/2)] + [\xi^2 + \rho^2]^{-1/2} \\ & + \sum_{l=1}^{\infty} \{[(l-\xi)^2 + \rho^2]^{-1/2} - l^{-1}\} \\ & + \sum_{l=1}^{\infty} \{[(l+\xi)^2 + \rho^2]^{-1/2} - l^{-1}\} \end{aligned} \tag{17}$$

(γ is Euler's constant, 0.5772 ...). Here and in the following we let ρ stand for $\rho_{00}(\eta, \zeta)$, i.e.

$$\rho^2 = \left(\frac{b}{a}\right)^2 \eta^2 + \left(\frac{c}{a}\right)^2 \zeta^2 \tag{18}$$

The logarithmic singularity as $\rho \to 0$ in the sum over the modified Bessel functions in (16), made explicit in (17), is cancelled by the $n = 0$ term of the sum over logarithms in (16), of which the leading terms as ρ tends to zero is $-2\log(2\pi\rho a/b)$. (An explicit formula for the η, $\zeta = 0$ case is given in the Appendix.) Thus T, defined in (14), reduces to

$$\begin{aligned} T = {} & \frac{4\pi}{\beta^2}\left(\frac{a^2}{bc}\right) + \frac{\pi}{3}\left(\frac{c}{b}\right) + 2\gamma - 2\log(4\pi a/b) \\ & - 4\sum_{n=1}^{\infty} \log(1 - e^{-2\pi nc/b}) + 4\sum_{l=1}^{\infty} \sum_{m,}^{\infty} \sum_{n=-\infty}^{\infty}{}' K_0(2\pi l [b^2m^2 + c^2n^2]^{1/2}/a) \\ & + O(\beta^2) \end{aligned} \tag{19}$$

where the prime on the summation indicates that the term with m and n both zero is to be omitted.

We are now in position to evaluate the Coulomb energy per cell, given in (11). The coefficient of the singular term $(4\pi/\beta^2)(a^2/bc)$ is

$$a^{-1} \sum_{i<j}\sum q_i q_j + (2a)^{-1} \sum_i q_i^2 = (2a)^{-1} \left(\sum_i q_i \right)^2 = 0 \qquad (20)$$

since the net charge in each cell is zero. Thus for neutral systems the Coulomb energy is well-defined in the limit of $\beta \to 0$. Note that the coefficient of $(\pi/3)\,(c/b)$ likewise cancels for any neutral system. The energy for an arbitrary number of particles is given by substituting (16) and (19) into (11). For two particles in the unit cell, with charges $+q$ and $-q$, the energy per cell is, with $\xi = \xi_{12}$, etc,

$$E_2(\xi, \eta, \zeta) = \frac{-q^2}{a} \{S(\xi, \eta, \zeta) - T\} \equiv \frac{-q^2}{a} V(\xi, \eta, \zeta) \qquad (21)$$

where V is a dimensionless potential function. From (6) and (16) we see that the x-component of the interparticle force is $X = -\partial V/\partial \xi$. Note that the x-dimension of the unit cell plays a special role: $Y = -(a/b)\,\partial V/\partial \eta$ and $Z = -(a/c)\,\partial V/\partial \zeta$.

The form of (21) is that of a potential energy of one pair of particles, even though the interaction of an infinity of particles is involved. For a neutral cell with any number of charges, the Coulomb potential energy can be written as a sum over pairs: from (11) and (20) we have

$$E = a^{-1} \sum_{i<j}\sum q_i q_j (S_{ij} - T) \qquad (22)$$

where S_{ij} stands for $S(\xi_{ij}, \eta_{ij}, \zeta_{ij})$. The dimensionless potential function for each pair i, j is thus $V_{ij} = S_{ij} - T$. Note that it is noncentral:

$$\begin{aligned} V(a, b, c; \xi, \eta, \zeta) = {} & 4 \sum_{l=1}^{\infty} \cos(2\pi l \xi) \sum_{m,}^{\infty} \sum_{n=-\infty}^{\infty} K_0(2\pi l \rho_{mn}(\eta, \zeta)) \\ & - \sum_{n=-\infty}^{\infty} \log[1 - 2\cos(2\pi\eta)\exp(-2\pi|\zeta + n|c/b) + \exp(-4\pi|\zeta + n|c/b)] \\ & + 2\pi \left(\frac{c}{b} \right) [\zeta^2 - |\zeta|] + C(a, b, c) \end{aligned} \qquad (23)$$

where

$$
\begin{aligned}
C(a,b,c) &= 2\log(4\pi a/b) - 2\gamma + 4\sum_{n=1}^{\infty}\log[1-\exp(-2\pi nc/b)] \\
&\quad - 4\sum_{l=1}^{\infty}\sum_{m,}^{\infty}\sum_{n=-\infty}^{\infty}{}' K_0(2\pi l[(bm)^2+(cn)^2]^{1/2}/a)
\end{aligned}
\tag{24}
$$

These results are consistent with equation (43) of [1] because the expression

$$
\begin{aligned}
2\pi(\eta^2 - \zeta^2 + |\zeta|) + \sum_{n=-\infty}^{\infty}\log[1 - 2\cos(2\pi\eta)e^{-2\pi|\zeta+n|} + e^{-4\pi|\zeta+n|}] \\
-\log\lim_{M=-\infty}\prod_{-M}^{M}\frac{\cosh[2\pi(\eta+m)] - \cos(2\pi\zeta)}{\cosh(2\pi m)}
\end{aligned}
\tag{25}
$$

is identically a constant, independent of η and ζ for $|\eta| < 1$, $|\zeta| < 1$. The value of this constant is

$$
\Lambda = \log(2) + 2\sum_{m=1}^{\infty}\log(1+e^{-4\pi m}) = 0.693\,154\,155\ldots \tag{26}
$$

and the constant C_3 defined by (44) of [1] is also given by $C_3 = C(a, a, a) - \Lambda$.

For N charges per unit cell there are $N(N-1)/2$ pairs, and it appears that computational work must increase quadratically with N, but Sperb [4] has shown that the Coulomb energy per cell can be reformulated so as to increase linearly with N.

4. MADELUNG CONSTANTS OF IONIC CRYSTALS

Our formulae can be used to calculate the Madelung constants for ionic crystals with an arbitrary number of charges in a neutral orthorhombic cell. For example, in the case of charges $+q$ and $-q$ in the unit cell, in a *CsCl* structure deformed so that the dimensions a, b and c of the unit cell are not all equal, the Madelung constant defined in terms of the lattice dimension a is, from (16), (19) and (21),

$$
\begin{aligned}
M(a,b,c) &= S\left(a,b,c;\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}\right) - T(a,b,c) = V\left(a,b,c;\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}\right) \\
&= 2\log(4\pi a/b) - 2\gamma + 4\sum_{n=1}^{\infty}\log[(1-e^{-2\pi nc/b})/(1-e^{-2\pi(n+\frac{1}{2})c/b})]
\end{aligned}
$$

$$
\begin{aligned}
&- 4\log(1 - e^{-\pi c/b}) \\
&+ 4\sum_{l=1}^{\infty}(-)^{l}\sum_{m,n}^{\infty}\sum_{=-\infty}^{\infty} K_0\left(2\pi l\left[b^2\left(m+\tfrac{1}{2}\right)^2 + c^2\left(n+\tfrac{1}{2}\right)^2\right]^{1/2}\Big/ a\right) \\
&- 4\sum_{l=1}^{\infty}\sum_{m,}^{\infty}\sum_{n=-\infty}^{\infty}{}' K_0(2\pi l[b^2m^2 + c^2n^2]^{1/2}/a)
\end{aligned} \tag{27}
$$

(The two charges are at $(0, 0, 0)$ and $(a/2, b/2, c/2)$, so the nearest-neighbour distance is $d = (a^2 + b^2 + c^2)^{1/2}/2$; the Madelung constant defined in terms of d is Md/a.)

A simple check on our formulae is provided by considering a cubic lattice of the *CsCl* type to be made up from orthorhombic cells. For example in a unit cell of dimensions $(a, 2a, a)$, charges of one sign are at $(\xi, \eta, \zeta) = (0, 0, 0)$ and $(0, 1/2, 0)$, while charges of the opposite sign are at $(1/2, 1/4, 1/2)$ and $(1/2, 3/4, 1/2)$. The Coulomb interactions are q^2/a times $2V(0, 1/2, 0)$ $-4V(1/2, 1/4, 1/2)$, and there are two $\pm q$ pairs in the enlarged unit cell, so that

$$
M(a, 2a, a) = 2V\left(a, 2a, a; \tfrac{1}{2}, \tfrac{1}{4}, \tfrac{1}{2}\right) - V\left(a, 2a, a; 0, \tfrac{1}{2}, 0\right) \tag{28}
$$

The fact that $M(a,\ 2a,\ a) = M(a,\ a,\ a)$ implies an identify between three dimensionless potentials $V = S - T$. (Numerically, both Madelung constants evaluate to 2.0353615..., in agreement with the quoted nearest-neighbour value [7] 1.76267477...). An infinity of such identities can be derived, since the Madelung constants $M(la,\ ma,\ na)$ are all equal to $M(a,\ a,\ a)$ for positive integer l, m and n.

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APPENDIX

We consider the sum S_β defined in (15). From [6] p. 17 #27 and equation (2.3) of [4] we have

$$\begin{aligned}\sum_{l=-\infty}^{\infty}[(\xi+l)^2+r^2]^{-1/2}\exp\{-\beta[(\xi+l)^2+r^2]^{1/2}\} \\ = 2K_0(\beta r)+4\sum_{l=1}^{\infty}\cos(2\pi l\xi)K_0\{r[\beta^2+(2\pi l)^2]^{1/2}\}\end{aligned} \tag{A1}$$

Both sides of this equation, with $r=\rho_{mn}(\eta,\zeta)$, are to be summed over m and n as in (15). The second term on the right is non-singular as β tends to zero, with a contribution to $S_{\beta\to 0}$ equal to

$$4\sum_{l=1}^{\infty}\cos(2\pi l\xi)\sum_{m,}^{\infty}\sum_{n=-\infty}^{\infty}K_0[2\pi l\rho_{mn}(\eta,\zeta)]\equiv K(\xi,\eta,\zeta) \tag{A2}$$

The first term diverges as β tends to zero; we will calculate the leading terms in

$$J_\beta(\eta,\zeta)\equiv 2\sum_{m,}^{\infty}\sum_{n=-\infty}^{\infty}K_0[\beta\rho_{mn}(\eta,\zeta)] \tag{A3}$$

From [6], p. 56 # 43 and (2.3) of [4] we find, setting $\beta'=\beta b/a$, that

$$\sum_{m=-\infty}^{\infty}K_0\{\beta'[(\eta+m)^2+r_n^2]^{1/2}\}=\frac{\pi}{\beta'}e^{-\beta' r_n}+2\pi\sum_{m=1}^{\infty}\frac{\cos(2\pi m\eta)}{R_m}e^{-r_nR_m} \tag{A4}$$

where $R_m^2\equiv(2\pi m)^2+(\beta')^2$. Again the second term on the right has a finite limit as $\beta\to 0$, and gives a contribution to J_β of

$$L(\eta,\zeta)=2\sum_{m=1}^{\infty}\frac{\cos(2\pi m\eta)}{m}\sum_{n=-\infty}^{\infty}e^{-2\pi m r_n} \tag{A5}$$

where $r_n \equiv |\zeta + n|c/b$. The sum over m in (A5) can be written as the real part of

$$\sum_{m=1}^{\infty} \frac{1}{m} e^{-mu} = -\log(1 - e^{-u}), \quad u = 2\pi[|\zeta + n|c/b + i\eta] \tag{A6}$$

Thus the regular part of J_β can be expressed as a sum over logarithms:

$$\begin{aligned} L(\eta, \zeta) = -\sum_{n=-\infty}^{\infty} &\log[1 - 2\cos(2\pi\eta)\exp(-2\pi|\zeta + n|c/b) \\ &+ \exp(-4\pi|\zeta + n|c/b)] \end{aligned} \tag{A7}$$

Finally, it remains to consider the singular contribution to J_β, namely

$$I_\beta(\zeta) \equiv \frac{2\pi}{\beta'} \sum_{n=-\infty}^{\infty} e^{-\beta' r_n} = \frac{2\pi}{\beta}\left(\frac{a}{b}\right) \sum_{n=-\infty}^{\infty} e^{-\alpha|\zeta+n|} \tag{A8}$$

where $\alpha = \beta c/a$. The sum over n is periodic in ζ and even in ζ, and by result (2.3) of [4] can be expressed as a cosine series:

$$\begin{aligned} \sum_{n=-\infty}^{\infty} e^{-\alpha|\zeta+n|} &= \frac{2}{\alpha} + 4\alpha \sum_{n=1}^{\infty} \frac{\cos(2\pi n\zeta)}{\alpha^2 + (2\pi n)^2} \\ &= \frac{2}{\alpha} + \frac{\alpha}{\pi^2} \sum_{n=1}^{\infty} \frac{\cos(2\pi n\zeta)}{n^2} + O(\alpha^3) \end{aligned} \tag{A9}$$

The periodic function $\sum_1^\infty \cos(2\pi n\zeta)/n^2 = \pi^2(\frac{1}{6} - |\zeta| + \zeta^2)$ for $|\zeta| \leq 1$, so in this range of ζ we have

$$I_\beta(\zeta) = \frac{4\pi}{\beta^2}\left(\frac{a^2}{bc}\right) + 2\pi\left(\frac{c}{b}\right)\left(\frac{1}{6} - |\zeta| + \zeta^2\right) + O(\beta^2) \tag{A10}$$

Finally, the sum $I_\beta(\zeta) + L(\eta, \zeta) + K(\xi, \eta, \zeta)$ gives (16).

The potential function (16) appears to be singular when both the y and z displacements are zero. There is no physical reason for such a divergence, and in fact the potential function takes a regular form, derived below. We first consider the singular parts of $S_\beta(\xi, \eta, \zeta)$ as $\rho = \sqrt{(b/a)^2\eta^2 + (c/a)^2\zeta^2}$ tends to zero. These are

$$4\sum_{l=1}^{\infty} \cos(2\pi l\xi) K_0(2\pi l\rho) - 2\log(2\pi\rho a/b) \tag{A11}$$

From (17) we see that the log ρ terms cancel, and what remains is

$$|\xi|^{-1}+\sum_{l=1}^{\infty}\{(l-\xi)^{-1}-l^{-1}\}+\sum_{l=1}^{\infty}\{(l+\xi)^{-1}-l^{-1}\}+2\gamma-2\log(2\pi a/b)$$
$$=|\xi|^{-1}-\psi(1-\xi)-\psi(1+\xi)-2\log(2\pi a/b) \tag{A12}$$

where ψ is the logarithmic derivative of the Γ function. Thus the potential function $V=S-T$ takes the form (for zero η, ζ and $|\xi|<1$)

$$V=|\xi|^{-1}-2\gamma-\psi(1-\xi)-\psi(1+\xi)$$
$$+4\sum_{l=1}^{\infty}[\cos(2\pi l\xi)-1]\sum_{m,n}^{\infty}\sum_{=-\infty}^{\infty}{}' K_0(2\pi l[b^2m^2+c^2n^2]^{1/2}/a) \tag{A13}$$

The behaviour at small $|\xi|$ is $V(a,b,c;\xi,0,0)=|\xi|^{-1}+O(\xi^2)$. In general, as $\xi^2+\rho^2$ tends to zero, the potential function has the leading term $[\xi^2+\rho^2]^{-1/2}$, in accord with the expected dominant term in the potential energy of two charges in close approach, namely q_iq_j/r_{ij}.