Madelung constants and lattice sums for invariant cubic lattice complexes and certain tetragonal structures

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Abstract. A method is given of evaluating Madelung constants for invariant cubic lattice complexes. It is shown that a linear combination of at most 8 lattice sums is sufficient to give the Madelung constant of all such lattices. In many cases this reduces to just 3 sums. The 8 sums suffice also to determine the Madelung constant for tetragonal lattices with axial ratio $\sqrt{2}$ or 2 and for orthorhombic lattices with lattice parameters in the ratio $1:\sqrt{2}:2$. The method developed here is also applied to the evaluation of lattice sums arising from particles interacting with a general r^{-s} potential.

1. Introduction

The evaluation of Madelung constants α has been the subject of many studies. The names of Born (1921), Emersleben (1923) and Hund (1925, 1935) are associated with certain general approaches to this problem. Review articles by Waddington (1959) and Tosi (1964) give many references. Recently Sakamoto in a considerable amount of published and unpublished work from 1953 onwards, eg Sakamoto (1953, 1974), has presented a comprehensive study of electrostatic energies in lattices. Unfortunately much that he has published as well as his unpublished work is not easily accessible and whether some results given here are to be found in his work is not easy to discover. All these investigations refer to electrostatic interactions between particles. The purpose of this work is to systematize Hund's (1935) basic potential approach to the calculation of α and to generalize it to particles interacting with an r^{-s} potential. In particular a prescription will be given for evaluating α and other lattice sums for all structures forming invariant cubic lattice complexes (ICLC). Naor (1958), in discussing α for ICLC, showed that 17 lattice sums of which only 9 were independent, were sufficient to calculate α for *all* ICLC. He conjectured that these 9 sums were not only sufficient but necessary. Here it will be shown that only 8 of these 9 sums are independent. In most cases only 5 of these sums are required and indeed for many cubic crystals found in nature just 3 numbers in various linear combinations are sufficient to give α. The method used here will also enable α to be evaluated for certain tetragonal crystals.

2. The basic cubic potential of Hund and its generalization

Cubic structures are composed of interpenetrating simple cubic lattices (SC), generally of different lattice constant. For ICLC these lattice constants will be the same. In an ICLC any lattice site may be taken as a fundamental origin $(0, 0, 0)$. The particle at

this site will interact with particles on the various SC sites whose origin lattice point with respect to $(0, 0, 0)$ has coordinates (x, y, z) where $x, y, z \leqslant \frac{1}{2}$. Such a lattice is said to be based on (x, y, z) and designated $SC(x, y, z)$. If the particles interact with an r^{-s} potential, the generalized Hund potential $\psi(x, y, z : 2s)$ is defined as the lattice sum obtained by summing the interaction of the fundamental origin particle with the particles on the SC based on (x, y, z). Thus

$$\psi = \psi(x, y, z) = \psi(x, y, z : 2s) = \sum_{m, n, p = -\infty}^{\infty} [(n-x)^2 + (m-y)^2 + (p-z)^2]^{-s}. \qquad (2.1)$$

The sums are over all integer values of m, n, p. $\psi(0, 0, 0)$ is known as the self-potential and in its evaluation the interaction of the $(0, 0, 0)$ particle with itself is excluded, ie in (2.1) we exclude the term $m = n = p = 0$. Hund (1935) and Sakamoto (unpublished) discovered identities amongst $\psi(x, y, z)$ for varying x, y, z and $s = \frac{1}{2}$. Here general relations for arbitrary s will be obtained.

For ICLC, (x, y, z) can only take values which are multiples of $\frac{1}{8}$, and they must occur in certain combinations. Naor (1958) found these 17 possible combinations for cubic lattices and the related combination of Hund potentials. They are given in table 1.

3. The representation of ψ by θ-functions

The modified Mellin transform M_s is defined as follows:

$$\Gamma(s) M_s[f] = \int_0^\infty t^{s-1} f \, dt. \qquad (3.1)$$

It immediately follows that

$$\psi(x, y, z : 2s) = M_s \left(\sum_{-\infty}^{\infty} q^{(n-x)^2} \sum_{-\infty}^{\infty} q^{(n-y)^2} \sum_{-\infty}^{\infty} q^{(p-z)^2} \right), \qquad q = e^{-t}. \quad (3.2)$$

The transformed function is much simpler to handle since the triple sum in (2.1) is split into the product of three single sums. If (x, y, z) are all multiples of $\frac{1}{4}$, $\psi(x, y, z)$ may be expressed in terms of well known Jacobian θ-functions. These, as defined by Whittaker and Watson (1958), are

$$\theta_2 = \sum_{-\infty}^{\infty} q^{(n-1/2)^2} = 2q^{1/4}(1 + q^2 + q^6 + q^{12} + q^{20} + q^{30} \ldots)$$

$$\theta_3 = \sum_{-\infty}^{\infty} q^{n^2} = 1 + 2q + 2q^4 + 2q^9 \ldots$$

$$\theta_4 = \sum_{-\infty}^{\infty} (-1)^n q^{n^2} = 1 - 2q + 2q^4 - 2q^9 \ldots$$

$$\theta_1' = 2 \sum_0^{\infty} (-1)^n (2n+1) q^{(n+1/2)^2} = 2q^{1/4}(1 - 3q^2 + 5q^6 \ldots).$$

Table 1. Simple cubic potentials: $k = 2^{2s-3}$

Naor symbol	Hund potential	θ-function representation	Value for general s	Value for $s = \tfrac{1}{2}$
A	$\psi(0, 0, 0)$	$\theta_3^3 - 1 = k[(\theta_3 + \theta_4)^3 - 8]$	$a = k(a + 3b + 3c + d)$	$a(1) = b(1) + c(1) + d(1)/3$
B	$\psi(0, \tfrac{1}{2}, \tfrac{1}{2})$	$\theta_3\theta_4^2 = k[(\theta_3 + \theta_4)(\theta_3 - \theta_4)^2]$	$k(a - b - c + d)$	$d(1)/3$
G	$\psi(0, 0, \tfrac{1}{2})$	$\theta_3^2\theta_4 = k[(\theta_3 + \theta_4)^2(\theta_3 - \theta_4)]$	$k(a + b - c - d)$	$(3b(1) - d(1))/6$
D	$\psi(\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2})$	$\theta_2^3 = k(\theta_3 - \theta_4)^3$	$k(a - 3b + 3c - d)$	$(3c(1) - a(1))/2$
E	$\psi(\tfrac{1}{4}, \tfrac{1}{4}, \tfrac{1}{4})$	$2^{-3}\theta_2^3(q^{1/4}) = k^2(\theta_3 - \theta_4)^3$	$k^2(a - 3b + 3c - d)$	$(3c(1) - a(1))/8$
J	$\psi(\tfrac{1}{4}, \tfrac{1}{4}, \tfrac{1}{2})$	$k[\theta_2^2(\theta_3 - \theta_4)]$	$k^2(a - b - c + d) - ke$	$(d(1) - 3e(1))/12$
K	$\tfrac{1}{2}(\psi(0, 0, \tfrac{1}{4}) + \psi(\tfrac{1}{4}, \tfrac{1}{2}, \tfrac{1}{2}))$	$k[\theta_2(\theta_3^2 + \theta_4^2)]$	$k^2(a + b - c - d) + kf$	$(3b(1) - d(1) + 6f(1))/24$
Y	$\psi(0, \tfrac{1}{4}, \tfrac{1}{4})$	$k[\theta_2^2(\theta_3 + \theta_4)]$	$k^2(a - b - c + d) + ke$	$(d(1) + 3e(1))/12$
Z	$\psi(0, \tfrac{1}{4}, \tfrac{1}{2})$	$k[\theta_2(\theta_3^2 - \theta_4^2)]$	$k^2(a + b - c - d) - kf$	$(3b(1) - d(1) - 6f(1))/24$
L	$\tfrac{1}{4}(\psi(\tfrac{1}{8}, \tfrac{1}{8}, \tfrac{1}{8}) + 3\psi(\tfrac{1}{8}, \tfrac{3}{8}, \tfrac{3}{8}))$	$k^2(\theta_3^3 + \theta_4^3)$	$k^3(a - 3b + 3c - d) + k^2g$	$(3c(1) - a(1) + 2g(1))/32$
M	$\tfrac{1}{4}(\psi(\tfrac{3}{8}, \tfrac{3}{8}, \tfrac{3}{8}) + 3\psi(\tfrac{1}{8}, \tfrac{1}{8}, \tfrac{3}{8}))$	$k^2(\theta_3^3 - \theta_4^3)$	$k^3(a - 3b + 3c - d) - k^2g$	$(3c(1) - a(1) - 2g(1))/32$
N	$\tfrac{3}{4}(\psi(0, \tfrac{1}{8}, \tfrac{1}{8}) + \psi(\tfrac{1}{2}, \tfrac{3}{8}, \tfrac{3}{8}))$	$k^2[(\theta_3 + \theta_4)(\theta_3^2 + \theta_4^2)] + 2^4k(\theta_2\theta_3\theta_4)$	$k^3(a - b - c + d) + k^2(e + h + j) + 2^{5s-2}\beta(2s - 1)$	$(a(1) + 3e(1) + 3h(1) + 3j(1))/48 + 2^{-1/2}$
P	$\tfrac{1}{2}(\psi(\tfrac{1}{2}, \tfrac{1}{8}, \tfrac{1}{8}) + \psi(0, \tfrac{3}{8}, \tfrac{3}{8}))$	$k^2[(\theta_3 + \theta_4)(\theta_3^2 + \theta_4^2)] - 2^4k(\theta_2\theta_3\theta_4)$	$k^3(a - b - c + d) + k^2(e + h + j) - 2^{5s-2}\beta(2s - 1)$	$(a(1) + 3e(1) + 3h(1) + 3j(1))/48 - 2^{-1/2}$
R	$\tfrac{1}{2}(\psi(\tfrac{1}{4}, \tfrac{1}{8}, \tfrac{3}{8}) + \psi(\tfrac{1}{4}, \tfrac{1}{8}, \tfrac{3}{8}))$	$k^2[(\theta_3 - \theta_4)(\theta_3^2 + \theta_4^2)]$	$k^3(a - b - c + d) + k^2(-e + h - j)$	$(a(1) - 3e(1) + 3h(1) - 3j(1))/48$
S	$\tfrac{1}{2}(\psi(0, \tfrac{1}{8}, \tfrac{3}{8}) + \psi(\tfrac{1}{2}, \tfrac{1}{8}, \tfrac{3}{8}))$	$k^2[(\theta_3 + \theta_4)(\theta_3^2 - \theta_4^2)]$	$k^3(a - b - c + d) + k^2(e - h - j)$	$(a(1) + 3e(1) - 3h(1) - 3j(1))/48$
X	$\psi(\tfrac{1}{8}, \tfrac{1}{4}, \tfrac{3}{8})$	$k^2[(\theta_3 - \theta_4)(\theta_3^2 - \theta_4^2)]$	$k^3(a - b - c + d) + k^2(-e - h + j)$	$(a(1) - 3e(1) - 3h(1) + 3j(1))/48$
T	$\tfrac{1}{4}(\psi(0, \tfrac{1}{8}, \tfrac{1}{4}) + \psi(0, \tfrac{1}{4}, \tfrac{3}{8}) + \psi(\tfrac{1}{8}, \tfrac{1}{4}, \tfrac{1}{8}) + \psi(\tfrac{3}{8}, \tfrac{1}{4}, \tfrac{3}{8}))$	$k^2[\theta_2(\theta_3^2 - \theta_4^2)]$	$k^3(a + b - c - d) - k^2f$	$(3b(1) - d(1) - 6f(1))/96$

In fact only θ_2 and θ_3 are required since

$$x = 0: \quad \sum_{-\infty}^{\infty} q^{n^2} = \theta_3; \qquad x = \tfrac{1}{2}: \quad \sum_{-\infty}^{\infty} q^{(n-1/2)^2} = \theta_2;$$

$$x = \tfrac{1}{4}: \quad \sum_{-\infty}^{\infty} q^{(n-1/4)^2} = \tfrac{1}{2}\theta_2(q^{1/4}). \tag{3.3}$$

To handle multiples of $\tfrac{1}{8}$, an additional function θ_5 is required. This is given by

$$\theta_5 = 2\sum_{-\infty}^{\infty}(-1)^n q^{(2n-1/2)^2} = 2q^{1/4}(1 - q^2 - q^6 + q^{12} + q^{20} - q^{30} - q^{42}\ldots), \tag{3.4}$$

whence

$$x = \tfrac{1}{8}, \quad \sum_{-\infty}^{\infty} q^{(n-1/8)^2} = \tfrac{1}{4}(\theta_2(q^{1/16}) + \theta_5(q^{1/16}))$$

$$x = \tfrac{3}{8}, \quad \sum_{-\infty}^{\infty} q^{(n-3/8)^2} = \tfrac{1}{4}(\theta_2(q^{1/16}) - \theta_5(q^{1/16})). \tag{3.5}$$

(3.3) and (3.5) together with the following property of Mellin transforms,

$$M_s f[q^k] = k^{-s} M_s f[q], \tag{3.6}$$

allow all of Naor's combinations of ψ to be written in the forms given in table 1.

Now many identities hold amongst combinations of θ_2–θ_5. Ones used here and found in standard textbooks are

$$\theta_3 + \theta_4 = 2\theta_3(q^4); \qquad \theta_3 - \theta_4 = 2\theta_2(q^4); \qquad \theta_3 = \theta_3(q^4) + \theta_2(q^4);$$

$$\theta_3\theta_4 = \theta_4^2(q^2); \qquad 2\theta_2\theta_3 = \theta_2^2(q^{1/2}); \qquad \theta_1' = \theta_2\theta_3\theta_4. \tag{3.7a–f}$$

To these are added

$$\theta_5^2 = 2\theta_2(q^2)\theta_4(q^2); \qquad \theta_2\theta_5 = 2\theta_2(q^2)\theta_4(q^4). \tag{3.8a, b}$$

In appendix 1 some properties of θ_5 are given and the results (3.8) deduced. The manipulation of these identities enables us to find relations amongst the $\psi(x, y, z)$. For example, $\psi(0, 0, 0) = M_s[\theta_3^3 - 1]$, but since

$$\theta_3 = \theta_3(q^4) + \theta_2(q^4),$$

$$\psi(0, 0, 0) = M_s[(\theta_3(q^4) + \theta_2(q^4))^3 - 1]$$

$$= 2^{-2s}(\psi(0, 0, 0) + 3\psi(0, 0, \tfrac{1}{2}) + 3\psi(0, \tfrac{1}{2}, \tfrac{1}{2}) + \psi(\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}))$$

or when $s = \tfrac{1}{2}$,

$$\psi(0, 0, 0 : 1) = 3\psi(0, 0, \tfrac{1}{2} : 1) + 3\psi(0, \tfrac{1}{2}, \tfrac{1}{2} : 1) + \psi(\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2} : 1) \tag{3.9}$$

which is one of Hund's identities. Eventually all of Naor's (1958) 17 combinations can be reduced to combinations of the following 8 lattice sums. These are

$$b = b(2s) = \sum{}'(-1)^m(m^2 + n^2 + p^2)^{-s} = M_s[\theta_3^2\theta_4 - 1]$$

$$c = c(2s) = \sum{}'(-1)^{m+n}(m^2 + n^2 + p^2)^{-s} = M_s[\theta_3\theta_4^2 - 1]$$

$$d = d(2s) = \sum{}'(-1)^{m+n+p}(m^2 + n^2 + p^2)^{-s} = M_s[\theta_4^3 - 1]$$

$$e = e(2s) = \sum(-1)^m[m^2 + (n-\tfrac{1}{2})^2 + (p-\tfrac{1}{2})^2]^{-s} = M_s[\theta_4\theta_2^2]$$

$$f = f(2s) = \sum (-1)^{m+n}[m^2+n^2+(p-\tfrac{1}{2})^2]^{-s} = M_s[\theta_4^2\theta_2] \qquad (3.10b-j)$$

$$g = g(2s) = 8\sum (-1)^{m+n+p}[(2m-\tfrac{1}{2})^2+(2n-\tfrac{1}{2})^2+(2p-\tfrac{1}{2})^2]^{-s} = M_s[\theta_5^3]$$

$$h = h(2s) = 4\sum (-1)^{n+p}[m^2+(2m-\tfrac{1}{2})^2+(2p-\tfrac{1}{2})^2]^{-s} = M_s[\theta_3\theta_5^2]$$

$$j = j(2s) = 4\sum (-1)^{m+n+p}[m^2+(2n-\tfrac{1}{2})^2+(2p-\tfrac{1}{2})^2]^{-s} = M_s[\theta_4\theta_5^2].$$

For convenience we append the self-potential sum

$$a = a(2s) = \sum{}' (m^2+n^2+p^2)^{-s} = M_s[\theta_3^3-1] \qquad (3.10a)$$

but this is expressible in terms of b, c and d. These sums have been tabulated in table 4 for $s = \tfrac{1}{2}(\tfrac{1}{2})$ 8 to 10 decimal places. In (3.10) all the sums are over all integer values of m, n, p, except (3.10a–d) in which the case $m = n = p = 0$ is excluded. All the sums except $a(2s)$ converge for $s > 0$. $a(2s)$ has a simple pole at $s = \tfrac{3}{2}$ but just as the function $\zeta(s)$ represented by the sum $\sum_1^\infty n^{-s}$ for $s > 0$ has a simple pole at $s = 0$, yet is easily defined for $s < 0$, so there is no difficulty in defining $a(2s)$ for $s < \tfrac{3}{2}$. For

$$a(2s) = M_s[\theta_3^3-1] = M_s[[\tfrac{1}{2}(\theta_3(q^{1/4})+\theta_4(q^{1/4}))]^3-1]$$
$$= 2^{2s-3}M_s[\theta_3^3+3\theta_3^2\theta_4+3\theta_3\theta_4+\theta_4^3-8].$$

Therefore

$$a(2s) = 2^{2s-3}(a(2s)+3b(2s)+3c(2s)+d(2s))$$

and in particular

$$a(1) = b(1)+c(1)+\tfrac{1}{3}d(1). \qquad (3.11)$$

Since all the sums on the right-hand side of (3.11) converge for $s > 0$, $a(1)$ may be evaluated. In a similar way all of Naor's (1958) grouping may be evaluated in terms of (3.10a–j). The results are given in table 1 for general s together with values for $s = \tfrac{1}{2}$ in terms of $b(1) - j(1)$. In appendix 2 we give in detail the evaluation of N and P. Naor (1958) thought them to be independent, but in appendix 2 it is shown that they differ by a constant which for $s = \tfrac{1}{2}$ is equal to $2^{1/2}$.

In many ICLC the SC based on $(x, y, z), (x, y+\tfrac{1}{2}, z+\tfrac{1}{2}), (x+\tfrac{1}{2}, y, z+\tfrac{1}{2})$ and $(x+\tfrac{1}{2}, y+\tfrac{1}{2}, z)$ are often simultaneously occupied by the same particle. These four SC form the face-centred cubic (FCC) structure, and when this occurs we have an FCC lattice based on (x, y, z) or FCC (x, y, z). Knowledge of the potentials for such groups facilitates many calculations, and in table 2 the potentials for FCC (x, y, z) based on a few selected lattice sites have been given. It will be observed in both tables 1 and 2 that if (x, y, z) are either

Table 2. FCC potentials.

Lattice base	Values for general s	Value for $s = \tfrac{1}{2}$
$(0, 0, 0)$	$2^{2s-1}(a+d)$	$a(1)+d(1)$
$(0, 0, \tfrac{1}{2})$	$2^{2s-1}(a-d)$	$a(1)-d(1)$
$(0, \tfrac{1}{2}, \tfrac{1}{2})$	$2^{2s-1}(a+d)$	$a(1)+d(1)$
$(\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2})$	$2^{2s-1}(a-d)$	$a(1)-d(1)$
$(\tfrac{1}{4}, \tfrac{1}{4}, \tfrac{1}{4})$	$2^{4s-4}(a-3b+3c-d)$	$(3c(1)-a(1))/2$

0 or $\frac{1}{2}$ or all $\frac{1}{4}$ then only three independent constants, which we will choose to be b, c and d, are required to specify lattice sums. The majority of ionic crystals usually met with fall into these categories.

4. Prescription for evaluating Madelung constants

To find α for a given crystal, the total Hund potential for every ion making up the neutral complex in the crystal must be evaluated. The number of charges and the sign of the ions interacting have to be taken into account. The sum of all the Hund potentials divided by 2 then gives α. The following examples of increasing complexity illustrate the method.

(i) Na^+Cl^-

$$Na^+ \text{ at } (0,0,0) \rightarrow Na^+ = \text{FCC}(0,0,0); \qquad Cl^- = \text{FCC}(\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}).$$

$$\psi(Na^+) = a(1) + d(1) - (a(1) - d(1)) = 2d(1)$$

$$Cl^- \text{ at } (0,0,0) \rightarrow Cl^- = \text{FCC}(0,0,0); \qquad Na^+ = \text{FCC}(\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}).$$

$$\psi(Cl^-) = a(1) + d(1) - (a(1) - d(1)) = 2d(1).$$

Therefore

$$\alpha(Na^+Cl^-) = \tfrac{1}{2}(\psi(Na^+) + \psi(Cl^-)) = 2d(1). \tag{4.1}$$

(ii) $Ca^{2+}F_2^-$

$$Ca^{2+} \text{ at } (0,0,0) \rightarrow Ca^{2+} = \text{FCC}(0,0,0); \qquad F^- = \text{FCC}(\tfrac{1}{4},\tfrac{1}{4},\tfrac{1}{4}); \qquad F^- = \text{FCC}(\tfrac{3}{4},\tfrac{3}{4},\tfrac{3}{4})$$

$$\psi(Ca^{2+}) = 4(a(1) + d(1)) - (3c(1) - a(1)) - (3c(1) - a(1))$$

$$F^- \text{ at } (0,0,0) \rightarrow F^- = \text{FCC}(0,0,0); \qquad F^- = \text{FCC}(\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}); \qquad Ca^{2+} = \text{FCC}(\tfrac{1}{4},\tfrac{1}{4},\tfrac{1}{4})$$

$$\psi(F^-) = a(1) + d(1) + a(1) - d(1) - (3c(1) - a(1)).$$

Therefore

$$\alpha(Ca^{2+}F_2^-) = \tfrac{1}{2}(\psi(Ca^{2+}) + 2\psi(F^-)) = 6a(1) - 6c(1) + 2d(1) = 6b(1) + 4d(1). \tag{4.2}$$

(iii) Perovskites: general formula $A^{m+}B^{3n-m}X_3^{n-}$

$$A^{m+} \text{ at } (0,0,0) \rightarrow A^{m+} = \text{SC}(0,0,0); \qquad B^{3n-m} = \text{SC}(\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2})$$

$$3X^{n-} = \text{SC}(\tfrac{1}{2},\tfrac{1}{2},0), (0,\tfrac{1}{2},\tfrac{1}{2}), (\tfrac{1}{2},0,\tfrac{1}{2}).$$

$$\psi(A^{m+}) = m^2a(1) + m(3n - m)(3c(1) - a(1))/2 - mnd(1).$$

$$B^{3n-m} \text{ at } (0,0,0) \rightarrow B^{3n-m} = \text{SC}(0,0,0)$$

$$3X^{n-} = \text{SC}(0,0,\tfrac{1}{2}), (0,\tfrac{1}{2},0), (\tfrac{1}{2},0,0)$$

$$A^{m+} = \text{SC}(\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}).$$

$$\psi(B^{3n-m}) = (3n - m)^2a(1) - n(3n - m)(3b(1) - d(1))/2 + m(3n - m)(3c(1) - a(1))/2.$$

$$X^{n-} \text{ at } (0,0,0) \rightarrow X^{n-} = \text{SC}(0,0,0); \qquad 2X^{n-} = \text{SC}(0,\tfrac{1}{2},\tfrac{1}{2}), (\tfrac{1}{2},0,\tfrac{1}{2})$$

$$A^{m+} = \text{SC}(\tfrac{1}{2},\tfrac{1}{2},0); \qquad B^{3n+m} = \text{SC}(0,0,\tfrac{1}{2}).$$

$$\psi(X^{n-}) = n^2a(1) + 2n^2d(1)/3 - mnd(1)/3 - n(3n - m)(3b(1) - c(1))/2.$$

$$\alpha(A^{m+}B^{3n-m}X_3^{n-}) = \tfrac{1}{2}(\psi(A^{m+}) + \psi(B^{3n-m}) + 3\psi(X^-)).$$

After some algebra we have

$$\alpha(A^{m+}B^{3n-m}X_3^{n-}) = \tfrac{1}{2}[3(n-m)^2b(1) + 12n^2c(1) + (3n-m)^2d(1)]. \tag{4.3}$$

For example, for

$$Ba^{2+}Ti^{4+}O_3^{2-}, n = m = 2.$$

Therefore

$$\alpha(BaTiO_3) = 24c(1) + 8d(1).$$

Sakamoto (1958) has given a formula similar to (4.3) but in terms of the Born (1921) potentials Π. In table 5 a short list is given of α for some ionic crystals in terms of $b(1)$, $c(1)$ and $d(1)$ only. The numerical values given are all in terms of the basic cube side. The various linear relations discovered amongst α for various ionic crystals by several authors such as Fumi and Tosi (1957), Benson and Zeggeren (1957), Templeton (1955) and several others are easily deduced from table 5. Sakamoto (1958) gives a similar tabulation but in terms of Born potentials. Takahasi and Sakamoto (1960) show how to convert from Π to ψ and vice versa. They also tabulate numerical values of $\psi(x, y, z : 1)$ accurate to at least four decimal places for all values of x, y, z in multiples of $\frac{1}{24}$ from zero to $\frac{1}{2}$. There are 455 such terms many of which will be interdependent, but no systematic study of these relations has been carried out. From their table, α for quasi-cubic lattices of moderate complexity may be evaluated.

5. Tetragonal structures and other lattice sums

Tetragonal structures have a square base but a variable third lattice parameter. The ratio of this to that of one of the base lattice parameters is called the axial ratio (AR). If AR takes either the value $\sqrt{2}$ or 2 the potentials involved in their θ-function representation will contain θ-functions of arguments q^2 and q^4. By manipulation of relations (3.7) and (3.8) all such potentials may be expressed in terms of $a(2s)-e(2s)$ if x, y, z are zero or $\frac{1}{2}$. All such tetragonal potentials have been listed in table 3. A calculation was carried

Table 3. Tetragonal potentials: $k = 2^{2s-3}$; $l = 2^{s-2}$

AR	Lattice base	θ-representation	Value for general s	Value for $s = \frac{1}{2}$
$\sqrt{2}$	$(0,0,0)$	$\theta_3^2\theta_3(q^2)$	$l(a+b+c+d)$	$2^{-1/2}(3b(1)+3c(1)+2d(1))/3$
	$(0,0,\frac{1}{2})$	$\theta_3^2\theta_2(q^2)$	$l(a-b+c-d)$	$2^{-1/2}(3c(1)-d(1))/3$
	$(0,\frac{1}{2},0)$	$\theta_3\theta_2\theta_3(q^2)$	$kl(a-b-c+d)+le$	$2^{-3/2}(d(1)+3e(1))/3$
	$(\frac{1}{2},\frac{1}{2},0)$	$\theta_2^2\theta_3(q^2)$	$l(a+b-c-d)$	$2^{-1/2}(3b(1)-d(1))/3$
	$(\frac{1}{2},0,\frac{1}{2})$	$\theta_2\theta_3\theta_2(q^2)$	$kl(a-b-c+d)-le$	$2^{-3/2}(d(1)-3e(1))/3$
	$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	$\theta_2^2\theta_2(q^2)$	$l(a-b-c+d)$	$2^{1/2}d(1)/3$
2	$(0,0,0)$	$\theta_3^2\theta_3(q^4)$	$(a+b)/2$	$(6b(1)+3c(1)+d(1))/6$
	$(0,0,\frac{1}{2})$	$\theta_3^2\theta_2(q^4)$	$(a-b)/2$	$(3c(1)+d(1))/6$
	$(0,\frac{1}{2},0)$	$\theta_3\theta_2\theta_3(q^4)$	$k(a+b-c-d)/2 + 2^{2s}\beta(2s-1)$	$(3b(1)-d(1)+12)/12$
	$(\frac{1}{2},\frac{1}{2},0)$	$\theta_2^2\theta_3(q^4)$	$[k(a-b-c+d)+e]/2$	$(d(1)+3e(1))/6$
	$(0,\frac{1}{2},\frac{1}{2})$	$\theta_3\theta_2\theta_2(q^4)$	$k(a+b-c-d)/2 - 2^{2s}\beta(2s-1)$	$(3b(1)-d(1)-12)/12$
	$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	$\theta_2^2\theta_2(q^4)$	$[k(a-b-c+d)-e]/2$	$(d(1)-3e(1))/6$

out for the structure A^+B^-, with $A^+ = SC(0, 0, 0)$ and $B^- = SC(\frac{1}{2}, \frac{1}{2}, 0)$ of which $CaWO_4$ is a physical example. This structure was considered by Hoppe (1956). For the three cases of AR $= 1$, $\sqrt{2}$ and 2, the results obtained here were

AR $= 1$ $\qquad \alpha(A^+B^-) = b(1) + c(1) = 2 \cdot 254776 \ (1 \cdot 594367)$

AR $= \sqrt{2}$ $\qquad \alpha(A^+B^-) = 2^{-1/2}(c(1) + d(1)) = 2 \cdot 282508 \ (1 \cdot 613977)$

AR $= 2$ $\qquad \alpha(A^+B^-) = (2b(1) + c(1) - e(1))/2 = 2 \cdot 284666 \ (1 \cdot 615503).$ $\qquad$ (5.1)

The figures in brackets are the values of α given in terms of the closest anion–cation distance. The first two agree with the values given by Hoppe (1956), but he estimated the value for AR $= 2$ by extrapolation to be approximately $1 \cdot 623$. It is seen here that it can be directly calculated and is smaller than Hoppe's value. Orthorhombic lattices with lattice parameters in the ratio $1 : \sqrt{2} : 2$ can also have all their potentials written in terms of $a(2s)$–$j(2s)$ for x, y, z either zero or $\frac{1}{2}$, but there appears to be no physical example of such an ionic crystal.

There is no difficulty in using table 1 to evaluate other lattice sums. For example the sums found by Lennard-Jones and Ingham (1925) for r^{-s} potentials for the SC, BCC and FCC lattices made up of one kind of particle, are easily expressed in terms of $a(2s)$ etc. Thus

$$SC(2s) = a(2s); \qquad BCC(2s) = 2^{2s-2}(a(2s) + 3c(2s)); \qquad FCC(2s) = 2^{2s-1}(a(2s) + d(2s)).$$

Other lattice sums may be written in terms of $a(2s)$–$j(2s)$ or in terms of the cubic lattice sums just given. For example, the diamond (D) lattice is represented by $FCC(0, 0, 0)$ plus $FCC(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. From table 2 it can immediately be shown that

$$D(2s) = 2^{2s-1}(a + d) + 2^{4s-4}(a - 3b + 3c - d).$$ $\qquad$ (5.2)

Table 4. Lattice sums: $N \times 10^n$ where n is figure in brackets

s	$a(2s)$	$b(2s)$	$c(2s)$
0·5	$-2\cdot83729\ 74794\ (0)$	$-7\cdot74386\ 14142\ (-1)$	$-1\cdot48038\ 98065\ (0)$
1·0	$-8\cdot91363\ 2917\ (0)$	$-3\cdot01380\ 2247\ (-1)$	$-1\cdot83004\ 53641\ (0)$
1·5	∞	$2\cdot22287\ 10876\ (-1)$	$-2\cdot04619\ 36439\ (0)$
2·0	$1\cdot65323\ 1596\ (1)$	$6\cdot89222\ 57409\ (-1)$	$-2\cdot15688\ 72986\ (0)$
2·5	$1\cdot03775\ 2483\ (1)$	$1\cdot06198\ 23625\ (0)$	$-2\cdot19682\ 98536\ (0)$
3·0	$8\cdot40192\ 0546\ (0)$	$1\cdot34110\ 86694\ (0)$	$-2\cdot19552\ 19241\ (0)$
3·5	$7\cdot46705\ 7780\ (0)$	$1\cdot54220\ 45834\ (0)$	$-2\cdot17385\ 03493\ (0)$
4·0	$6\cdot94580\ 7926\ (0)$	$1\cdot68375\ 14910\ (0)$	$-2\cdot14481\ 33764\ (0)$
4·5	$6\cdot62885\ 9200\ (0)$	$1\cdot78204\ 45621\ (0)$	$-2\cdot11558\ 44408\ (0)$
5·0	$6\cdot42611\ 9101\ (0)$	$1\cdot84981\ 05369\ (0)$	$-2\cdot08956\ 01364\ (0)$
5·5	$6\cdot29229\ 4498\ (0)$	$1\cdot89638\ 45503\ (0)$	$-2\cdot06792\ 79901\ (0)$
6·0	$6\cdot20214\ 9043\ (0)$	$1\cdot92837\ 73751\ (0)$	$-2\cdot05071\ 32697\ (0)$
6·5	$6\cdot14059\ 9581\ (0)$	$1\cdot95037\ 80885\ (0)$	$-2\cdot03741\ 37084\ (0)$
7·0	$6\cdot09818\ 4126\ (0)$	$1\cdot96553\ 80752\ (0)$	$-2\cdot02735\ 27819\ (0)$
7·5	$6\cdot06876\ 4295\ (0)$	$1\cdot97601\ 03762\ (0)$	$-2\cdot01985\ 80752\ (0)$
8·0	$6\cdot04826\ 3469\ (0)$	$1\cdot98326\ 37191\ (0)$	$-2\cdot01433\ 88512\ (0)$

Table 4.—continued

s	$d(2s)$	$e(2s)$	$f(2s)$
0·5	− 1·74756 45946 (0)	1·54017 09012 (0)	1·31967 05870 (0)
1·0	− 2·51935 61521 (0)	4·14586 74219 (0)	4·83858 95905 (0)
1·5	− 3·23862 47661 (0)	7·89370 4872 (0)	1·25682 51129 (1)
2·0	− 3·86316 38072 (0)	1·30547 52185 (1)	2·84777 47226 (1)
2·5	− 4·37860 11499 (0)	2·01326 91063 (1)	6·05220 64903 (1)
3·0	− 4·78844 37139 (0)	2·99064 94892 (1)	1·24657 84291 (2)
3·5	− 5·10542 93720 (0)	4·35078 44901 (1)	2·52849 72479 (2)
4·0	− 5·34556 57733 (0)	6·25476 65025 (1)	5·09071 47682 (2)
4·5	− 5·52466 36380 (0)	8·93057 52590 (1)	1·02130 48420 (3)
5·0	− 5·65666 62484 (0)	1·27004 38916 (2)	2·04553 77585 (3)
5·5	− 5·75308 49044 (0)	1·80197 68497 (2)	4·09376 26666 (3)
6·0	− 5·82302 77889 (0)	2·55323 13378 (2)	8·18997 51417 (3)
6·5	− 5·87349 60409 (0)	3·61481 94853 (2)	1·63821 72875 (4)
7·0	− 5·90976 23766 (0)	5·11542 70695 (2)	3·27663 54948 (4)
7·5	− 5·93573 95661 (0)	7·23702 14795 (2)	6·55345 21329 (4)
8·0	− 5·95429 97599 (0)	1·02369 24529 (3)	1·31070 67253 (5)

s	$g(2s)$	$h(2s)$	$j(2s)$
0·5	2·53355 74044 (0)	3·63498 9014 (0)	1·28584 65498 (0)
1·0	5·62814 94825 (0)	7·72948 90464 (0)	3·68988 29776 (0)
1·5	8·78504 00797 (0)	1·21638 47976 (1)	7·34798 76218 (0)
2·0	1·18570 62518 (1)	1·74144 40838 (1)	1·25172 26760 (1)
2·5	1·48859 26393 (1)	2·42350 87473 (1)	1·96621 59451 (1)
3·0	1·79851 64284 (1)	3·35884 28415 (1)	2·95258 97876 (1)
3·5	2·12830 71340 (1)	4·67175 92062 (1)	4·32167 38240 (1)
4·0	2·49028 98412 (1)	6·52937 08145 (1)	6·23339 52840 (1)
4·5	2·89604 08839 (1)	9·16256 07686 (1)	8·91536 18774 (1)
5·0	3·35677 95759 (1)	1·28947 06095 (2)	1·26898 61363 (2)
5·5	3·88391 24460 (1)	1·81814 30446 (2)	1·80125 47440 (2)
6·0	4·48956 02845 (1)	2·56662 25287 (2)	2·55274 54010 (2)
6·5	5·18703 17651 (1)	3·62587 41613 (2)	3·61449 61780 (2)
7·0	5·99125 50183 (1)	5·12452 94757 (2)	5·11521 39126 (2)
7·5	6·91919 09161 (1)	7·24450 17880 (2)	7·23688 19704 (2)
8·0	7·99025 18812 (1)	1·02430 62668 (3)	1·02368 33762 (3)

Table 5. α for some ionic crystals

Crystal	$b(1)$	$c(1)$	$d(1)$	α
NaCl			2	3·49512 919
CsCl	$\frac{3}{2}$		$\frac{1}{2}$	2·03536 151
ZnS	$\frac{3}{2}$		$\frac{3}{2}$	3·78292 6104
CaF_2	6		4	11·63657 5227
Cu_2O	3	3	2	10·25945 7033
$KZnF_3$		6	2	12·37746 803
$LaAlO_3$	$\frac{3}{2}$	24	$\frac{9}{2}$	44·55497 524
ReO_3	6	24	18	71·63183 526
$BaTiO_3$		24	8	49·50987 213
$NaTaO_3$	$\frac{3}{2}$	24	$\frac{25}{2}$	58·53549 203
ScF_3	$\frac{3}{2}$	6	$\frac{9}{2}$	17·90795 873
YOF	$\frac{27}{2}$		$\frac{19}{2}$	27·05607 657
BiF_3	6		10	22·12196 279
$BaLiF_3$	$\frac{3}{2}$	6	$\frac{1}{2}$	10·91770 0035

Using the result that $a(2s) = 2^{2s-3}(a+3b+3c+d)$, (5.2) may be rewritten in a number of ways of which the following are particularly simple:

$$D(2s) = \text{FCC}(2s) + 2^{2s-1}(\text{BCC}(2s) - \text{SC}(2s)) = 2^{2s-1}(\text{BCC}(2s) + d(2s)). \quad (5.3)$$

Similar formulae can be obtained for other lattices.

Acknowledgments

Appendix 1. Some properties of θ_5

Though the θ-functions have been most useful here expressed as infinite series it is often simpler to find many of their interrelated properties by using their representations as infinite products. If in the usual notation

$$Q_0 = \prod_1^\infty (1 - q^{2n}); \qquad Q_1 = \prod_1^\infty (1 + q^{2n}); \qquad Q_2 = \prod_1^\infty (1 + q^{2n-1});$$

$$Q_3 = \prod_1^\infty (1 - q^{2n-1})$$

then the following relations hold (Whittaker and Watson 1958):

$$\theta_2 = 2q^{1/4}Q_0Q_1^2; \qquad \theta_3 = Q_0Q_2^2; \qquad \theta_4 = Q_0Q_3^2; \qquad \theta_1' = 2q^{1/4}Q_0^3. \quad (A.1.1a\text{–}d)$$

It is elementary to show that

$$Q_1Q_2Q_3 = 1; \qquad Q_0Q_3 = Q_0(q^{1/2}); \qquad Q_1Q_2 = Q_1(q^{1/2}):$$
$$Q_2Q_3 = Q_3(q^2); \qquad Q_0Q_1 = Q_0(q^2). \quad (A.1.2a\text{–}e)$$

With these relations the identities (3.7) are easily verified. Properties of θ_5 may be deduced from another identity, namely

$$Q_0/Q_3 = 1 + q + q^3 + q^6 + q^{10} \ldots + q^{n(n+1)/2} \ldots. \quad (A.1.3)$$

Put $-q^2$ for q in this series and multiply by $2q^{1/4}$. Now since $Q_0(-q^2) = Q_0(q^2)$ and $Q_3(-q^2) = Q_2(q^2)$ we have

$$2q^{1/4}Q_0(q^2)/Q_2(q^2) = 2q^{1/4}(1 - q^2 - q^6 + q^{12} + q^{20} \ldots) = \theta_5. \quad (A.1.4)$$

Now from (A.1.1), $\theta_2\theta_4 = 2q^{1/4}Q_0^2Q_1^2Q_3^2$ which, by multiplying top and bottom by Q_2^2, yields $\theta_2\theta_4 = 2q^{1/4}Q_0^2/Q_2^2$. Putting q^2 for q in this and multiplying by 2 we have

$$2\theta_2(q^2)\theta_4(q^2) = 4q^{1/2}Q_0^2(q^2)/Q_2^2(q^2) = \theta_5^2 \quad (A.1.5)$$

thus verifying (3.8a).

Again from (3.7e) we may write $\theta_2 = \sqrt{2\theta_2(q^2)\theta_3(q^2)}$, and since it has been shown that $\theta_5 = \sqrt{2\theta_2(q^2)\theta_4(q^2)}$ we have $\theta_2\theta_5 = 2\theta_2(q^2)\sqrt{\theta_3(q^2)\theta_4(q^2)}$ which from (3.7d) gives

$$\theta_2\theta_5 = 2\theta_2(q^2)\theta_4(q^4). \quad (A.1.6)$$

Appendix 2. The evaluation of $N(2s)-P(2s)$

$$N(2s) = \tfrac{1}{2}(\psi(0,\tfrac{1}{8},\tfrac{1}{8}:2s)+\psi(\tfrac{1}{2},\tfrac{3}{8},\tfrac{3}{8}:2s)). \tag{A.2.1}$$

Writing this as Mellin-transformed θ-functions, this becomes

$$
\begin{aligned}
N(2s) &= \tfrac{1}{2}M_s[\theta_3[\tfrac{1}{4}(\theta_2(q^{1/16})+\theta_5(q^{1/16}))]^2 + \theta_2[\tfrac{1}{4}(\theta_2(q^{1/16})-\theta_5(q^{1/16}))]^2] \\
&= 2^{4s-5}M_s[\theta_3(q^{16})\{\theta_2+\theta_5\}^2 + \theta_2(q^{16})\{\theta_2-\theta_5\}^2] \\
&= 2^{4s-5}M_s[\{\theta_3(q^{16})+\theta_2(q^{16})\}\{\theta_2^2+\theta_5^2\} + 2\theta_2\theta_5\{\theta_3(q^{16})-\theta_2(q^{16})\}].
\end{aligned}
$$

Using (3.7) we have

$$\theta_3(q^{16})+\theta_2(q^{16}) = \theta_3(q^4) = (\theta_3+\theta_4)/2 \qquad \text{and} \qquad \theta_3(q^{16})-\theta_2(q^{16}) = \theta_4(q^4);$$

hence

$$N(2s) = 2^{4s-6}M_s[(\theta_3+\theta_4)(\theta_2^2+\theta_5^2)] + 2^{4s-4}M_s[\theta_2\theta_5\theta_4(q^4)]. \tag{A.2.2}$$

Now $\theta_2\theta_5\theta_4(q^4) = 2\theta_2(q^2)\theta_4(q^4)\theta_4(q^4)$ and since $\theta_4^2(q^2) = \theta_3\theta_4$ this becomes $2\theta_2(q^2)$ $\theta_3(q^2)\theta_4(q^2)$; thus

$$2^{4s-4}M_s[\theta_2\theta_5\theta_4(q^4)] = 2^{4s-4}M_s 2\theta_2(q^2)\theta_3(q^2)\theta_4(q^2) = 2^{3s-3}M_s[\theta_2\theta_3\theta_4].$$

But $\theta_2\theta_3\theta_4 = \theta_1'$ and $M_s[\theta_1'] = 2^{2s+1}\beta(2s-1)$ (Zucker 1974), where

$$\beta(s) = \sum_0^\infty (-1)^n(2n+1)^{-s}.$$

Thus finally

$$N(2s) = 2^{4s-6}M_s[(\theta_3+\theta_4)(\theta_2^2+\theta_5^2)] + 2^{5s-2}\beta(2s-1). \tag{A.2.3}$$

A similar analysis for $P(2s)$ yields

$$P(2s) = 2^{4s-6}M_s[(\theta_3+\theta_4)(\theta_2^2+\theta_5^2)] - 2^{5s-2}\beta(2s-1). \tag{A.2.4}$$

Therefore

$$N(2s)-P(2s) = 2^{5s-1}\beta(2s-1). \tag{A.2.5}$$

For $s=\tfrac{1}{2}$, $N(1)-P(1) = 2^{3/2}\beta(0)$ and since $\beta(0) = \tfrac{1}{2}$ (see Glasser 1973) it immediately follows that $N(1)-P(1) = 2^{1/2}$. Sakamoto (1974) says he has proved this result but it is unpublished.

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