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# Madelung constants and lattice sums for hexagonal crystals

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**Abstract.** A method is given for the rapid evaluation of the Madelung constants for ionic compounds having hexagonal structures.

## 1. Introduction

In two previous communications (Zucker 1975, 1976), henceforth referred to as I and II, a systematic way of determining the Madelung constants,  $\alpha$ , of cubic lattices was described. The method employed was to systematize Hund's (1935) basic potential approach, and to represent these potentials as Mellin transforms of  $\theta$ -functions. A full description of this process has been given by Glasser and Zucker (1980), hereafter referred to as III. The purpose of this paper is to extend the method to crystals having hexagonal structures.

## 2. Basic hexagonal potentials

Just as in I where complex cubic structures were decomposed into interpenetrating simple cubic lattices, so hexagonal structures can be represented by interpenetrating orthorhombic lattices (o). Thus a simple hexagonal lattice (H) is formed by stacking planes of two-dimensional equilateral triangular lattices directly above each other. The direction of stacking is known as the  $c$ -axis and the separation of planes in terms of the nearest-neighbour distance,  $R$ , of the triangular lattice is known as the axial ratio,  $c$ . Any two-dimensional equilateral triangular lattice may be considered as being made up of two interpenetrating rectangular lattices of sides  $R$  and  $\sqrt{3}R$ . So the hexagonal lattice itself can be considered as being made up of two interpenetrating orthorhombic lattices, each lattice having orthogonal basic vectors of length  $R$ ,  $\sqrt{3}R$  and  $cR$ . A hexagonal close-packed structure (HCP) is made up of two interpenetrating hexagonal lattices which is thus four interpenetrating orthorhombic lattices. Hence, just as basic cubic Hund potentials were evaluated in I and II, so here we shall evaluate basic orthorhombic potentials. The situation is more complex than in the cubic case since the lattice points of an orthorhombic lattice from a fundamental origin are given by  $mi + \sqrt{3}nj + cpk$ , where  $m$ ,  $n$  and  $p$  are integers, and not simply  $mi + nj + pk$  as for cubic lattices.

As in I any lattice site may be taken as a fundamental origin  $(0, 0, 0)$ . The particle on this site will interact with particles on various o sites whose origin with respect to  $(0, 0, 0)$  has coordinates  $(x, y, z)$  where  $x, y, z \leq \frac{1}{2}$ . Such a lattice is said to be based on

$(x, y, z)$  and is designated  $o(x, y, z)$ . If the particles interact with an  $r^{-s}$  potential, the generalized Hund potential,  $o(x, y, z; 2s)$  is defined as the lattice sum obtained by summing the interaction of the fundamental origin particle with the particles on the  $o$  lattice based on  $(x, y, z)$ . Thus

$$o := o(x, y, z) = o(x, y, z; 2s) = \sum_{m,n,p=-\infty}^{\infty} [(m-x)^2 + 3(n-y)^2 + c^2(p-z)^2]^{-s}. \tag{2.1}$$

The sums are over all integer values of  $m, n, p$ .  $o(0, 0, 0)$  is known as the self-potential and in its evaluation the interaction of the origin particle with itself is excluded, i.e. in (2.1) we omit the term when  $m, n, p$  are simultaneously zero. As in the cubic case it may be seen from (2.1) that  $o$  is unaltered when  $x, y, z$  are replaced by  $1-x, 1-y, 1-z$  respectively, or displaced by any integer.

As in I the Mellin transform  $M_s$  is defined as

$$\Gamma(s)M_s[f] = \int_0^{\infty} t^{s-1}f dt \tag{2.2}$$

and it immediately follows that

$$o(x, y, z; 2s) = M_s \left( \sum_{m=-\infty}^{\infty} q^{(m-x)^2} \sum_{n=-\infty}^{\infty} q^{3(n-y)^2} \sum_{p=-\infty}^{\infty} q^{c^2(p-z)^2} \right) \quad q = e^{-t}. \tag{2.3}$$

For hexagonal structures  $x$  and  $y$  usually take values of  $\frac{1}{6}, \frac{1}{3}$  or  $\frac{1}{2}$ , while  $z$  will often be multiples of  $\frac{1}{16}$ . Apart from when  $z$  is an odd multiple of  $\frac{1}{16}$ , all the sums in (2.3) may be expressed in terms of Jacobian  $\theta$ -functions plus a further function,  $\theta_5$ . These are

$$\begin{aligned} \theta_2 &= \sum_{-\infty}^{\infty} q^{(n-1/2)^2} & \theta_3 &= \sum_{-\infty}^{\infty} q^{n^2} \\ \theta_4 &= \sum_{-\infty}^{\infty} (-1)^n q^{n^2} & \theta_5 &= \sum_{-\infty}^{\infty} (-1)^n q^{(2n-1/2)^2}. \end{aligned}$$

Hence all the  $o$ s considered here except those for which  $z$  is an odd multiple of  $\frac{1}{16}$  may be expressed in terms of  $\theta$ -functions.<sup>1</sup>

As a model example of how to calculate a typical  $o$  a detailed description of how  $o(\frac{1}{2}, \frac{1}{2}, 0)$  is evaluated is now given. It is easily shown that

$$o(\frac{1}{2}, \frac{1}{2}, 0) = M_s(\theta_2\theta_2(q^3)\theta_3(q^{c^2})). \tag{2.4}$$

By using the Poisson transformation formula as described in III, this can be written as

$$M_s(\theta_2\theta_2(q^3)\theta_3(q^{c^2})) = KM_{3/2-s}(\theta_4\theta_4(q^{1/3})\theta_3(q^{1/c^2})) \tag{2.5}$$

where

$$K = \frac{\pi^{2s-3/2}\Gamma(3/2-s)}{\Gamma(s)c\sqrt{3}}.$$

Since to evaluate Madelung constants we require the value of  $o$  when  $s = \frac{1}{2}$  we have

$$o(\frac{1}{2}, \frac{1}{2}, 0; 1) = (\pi c\sqrt{3})^{-1} M_1(\theta_4\theta_4(q^{1/3})\theta_3(q^{1/c^2})). \tag{2.6}$$

This transformation when written out in full is

$$\sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \frac{1}{[(m-\frac{1}{2})^2 + 3(n-\frac{1}{2})^2 + c^2p^2]^{1/2}} = \frac{\sqrt{3}}{\pi c} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \frac{(-1)^{m+n}}{m^2 + 3n^2 + 3p^2/c^2}. \tag{2.7}$$

The ' in the RHS of (2.7) excludes the term when  $m$ ,  $n$  and  $p$  are simultaneously zero. It should be pointed out that the LHS of (2.7) does not converge, but the RHS provides an analytic continuation of the LHS as described in II. For the purposes of calculation the RHS of (2.7) is very slowly convergent, but by making use of the identity

$$\sum_{-\infty}^{\infty} (-1)^m (m^2 + b^2)^{-1} = \frac{\pi \operatorname{cosech}(\pi b)}{b} \quad (2.8)$$

the RHS of (2.7) becomes

$$\frac{\sqrt{3}}{c} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \frac{(-1)^n \operatorname{cosech}[\pi(3n^2 + 3p^2/c^2)^{1/2}]}{(3n^2 + 3p^2/c^2)^{1/2}}. \quad (2.9)$$

The cosech sums are very rapidly convergent and for any given value of  $c$  (2.9) may be quickly evaluated. Similar processes are applied to evaluate all the  $O_s$  given in the tables. When  $z$  is an odd multiple of  $\frac{1}{6}$  further  $\theta$ -type functions and their Poisson transforms other than those given above are used (Zucker 1990). Together with the more general summation formula

$$\sum_{-\infty}^{\infty} \frac{(-1)^n}{(kn + l)^2 + b^2} = \frac{\pi \sinh(\pi b/k) \cos(\pi l/k)}{kb \cosh^2(\pi b/k) - \cos^2(\pi l/k)} \quad (2.10)$$

of which (2.8) is a special case obtained when  $k = 1$ , and  $l = 0$ , all the  $O_s$  were evaluated.

Calculations are carried out for two values of  $c$ , namely  $\sqrt{\frac{8}{3}}$  and 2. The former value is called the ideal ratio, and the orthorhombic potentials for such  $c$  will be designated  $O_1$ . Those for  $c = 2$  are shown as  $O_2$ . Simple hexagonal potentials are obtained by adding two orthorhombic potentials in which both  $x$  and  $y$  have been displaced by  $\frac{1}{2}$ , i.e.

$$H(x, y, z) = O(x, y, z) + O(x + \frac{1}{2}, y + \frac{1}{2}, z). \quad (2.11)$$

Similarly we can evaluate HCP potentials as

$$\text{HCP}(x, y, z) = H(x, y, z) + H(x + \frac{1}{2}, y + \frac{1}{6}, z + \frac{1}{2}). \quad (2.12)$$

We have evaluated all the  $O_s$  required to give the potentials given by Hund (1935). He designates simple hexagonal potentials with ideal axial ratio as  $\phi$ , and those with  $c = 2$  as  $\chi$ . However, Hund does *not* consider the simple hexagonal lattice as two interpenetrating orthorhombic lattices, but rather as a single lattice based on the oblique axes which generate the two-dimensional triangular planes plus the  $c$ -axis. The relationship between Hund's notation and ours is thus

$$H_1(x, y, z) = \phi(x + 2y, y, z) \quad H_2(x, y, z) = \chi(x + 2y, y, z).$$

The results have been displayed in tables 1 and 2.

It should be noted here that Hund (1925, 1935) carried out all his calculations using the classical Ewald (1921) method. This has been described in many places, for example in III, and has been the most widely used way of evaluating Madelung constants. Hund's calculations were carried out in the pre-computer age and were of low accuracy. Though the Ewald approach may be used to evaluate lattice sums with high accuracy using computing facilities now available, the speed of computation is much slower than that of the methods described here. The evaluation of sums such as (2.9) may be carried out very rapidly even on a hand calculator. Also, Madelung sums are in general conditionally convergent, and it has been shown by Borwein *et al* (1985)

Table 1. Potentials for ideal ratio structures.

$(x, y, z)$	$O_1(x, y, z)$	$H_1(x, y, z)$	$HCPI(x, y, z)$
0, 0, 0	-1.810 788 568		
$\frac{1}{2}, \frac{1}{2}, 0$	-0.427 933 559	-2.238 722 127	
$\frac{1}{2}, \frac{1}{6}, \frac{1}{2}$	-0.411 075 032		-3.241 858 615
$0, \frac{1}{3}, \frac{1}{2}$	-0.592 061 457	-1.003 136 489	
$0, 0, \frac{3}{16}$	1.463 029 512		
$\frac{1}{2}, \frac{1}{2}, \frac{3}{16}$	-0.515 347 818	0.947 681 694	
$\frac{1}{2}, \frac{1}{6}, \frac{11}{16}$	-0.189 965 740		0.306 709 483
$0, \frac{2}{3}, \frac{11}{16}$	0.451 006 471	-0.640 972 211	
$0, 0, \frac{1}{4}$	0.663 007 203		
$\frac{1}{2}, \frac{1}{2}, \frac{1}{4}$	-0.567 940 485	0.095 066 718	
$\frac{1}{2}, \frac{1}{6}, \frac{3}{4}$	-0.033 148 156		-0.291 457 223
$0, \frac{2}{3}, \frac{3}{4}$	-0.353 375 784	-0.386 523 941	
$0, 0, \frac{3}{8}$	-0.063 832 645		
$\frac{1}{2}, \frac{1}{2}, \frac{3}{8}$	-0.662 091 054	-0.725 923 698	
$\frac{1}{2}, \frac{1}{6}, \frac{7}{8}$	0.309 974 907		-0.561 591 621
$0, \frac{2}{3}, \frac{7}{8}$	-0.145 642 830	0.164 332 077	
$0, 0, \frac{1}{2}$	-0.254 929 338		
$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	-0.699 992 112	-0.954 921 450	
$\frac{1}{2}, \frac{1}{6}, 0$	0.478 496 161		-0.522 569 455
$0, \frac{2}{3}, 0$	-0.046 144 166	0.432 351 995	
$0, \frac{1}{6}, \frac{1}{16}$	1.447 296 870		
$\frac{1}{2}, \frac{2}{3}, \frac{1}{16}$	-0.202 973 683	1.244 323 187	
$\frac{1}{2}, \frac{2}{3}, \frac{7}{16}$	-0.593 471 399		0.309 974 907
$0, \frac{1}{6}, \frac{7}{16}$	-0.340 876 881	-0.934 348 280	
$0, \frac{1}{6}, \frac{1}{4}$	0.204 770 760		
$\frac{1}{2}, \frac{2}{3}, \frac{1}{4}$	-0.410 308 276	-0.205 537 516	
$0, \frac{1}{3}, \frac{3}{8}$	-0.527 398 285		
$\frac{1}{2}, \frac{2}{6}, \frac{3}{8}$	-0.310 537 205	-0.837 935 490	

that certain methods of summation do not actually converge. Typically, the Ewald method avoids the technical difficulties attendant on this fact by rendering the sums involved absolutely convergent by the inclusion of a convergence factor which is an added complication. Again Borwein *et al* note that defining Madelung sums by Mellin transforms of  $\theta$ -functions avoids all ambiguities, and that analytic continuation provides a unique result for such lattice sums.

In I several relations amongst the cubic potentials were discovered using various identities which exist between the  $\theta$ -functions. Undoubtedly relations exist amongst the  $o$  such as

$$H(0, \frac{1}{3}, \frac{1}{2}) = 3H(0, \frac{1}{6}, \frac{1}{4}) + H(0, \frac{1}{3}, \frac{1}{4}) \quad (2.13)$$

but here these have not been investigated as fully as was done in the cubic case considered in I.

Table 2. Potentials for  $c = 2$ .

$(x, y, z)$	$O_2(x, y, z)$	$H_2(x, y, z)$
0, 0, 0	-1.596 909 816	
$\frac{1}{2}, \frac{1}{2}, 0$	-0.198 107 679	-1.795 017 494
0, 0, $\frac{1}{4}$	0.335 718 524	
$\frac{1}{2}, \frac{1}{2}, \frac{1}{4}$	-0.469 477 797	-0.133 759 273
0, 0, $\frac{1}{2}$	-0.489 404 337	
$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	-0.711 290 122	-1.200 694 459
0, $\frac{1}{6}, \frac{1}{4}$	0.069 393 760	
$\frac{1}{2}, \frac{2}{3}, \frac{1}{4}$	-0.348 265 388	-0.278 871 629
0, $\frac{1}{3}, 0$	0.179 645 660	
$\frac{1}{2}, \frac{5}{6}, 0$	0.696 530 776	0.876 176 436
0, $\frac{1}{3}, \frac{1}{8}$	0.013 386 840	
$\frac{1}{2}, \frac{5}{6}, \frac{1}{8}$	0.428 995 199	0.442 382 039
0, $\frac{1}{3}, \frac{1}{4}$	-0.309 996 217	
$\frac{1}{2}, \frac{5}{6}, \frac{1}{4}$	-0.066 804 790	-0.376 801 007
0, $\frac{1}{3}, \frac{3}{8}$	-0.563 988 121	
$\frac{1}{2}, \frac{5}{6}, \frac{3}{8}$	-0.431 581 563	-0.995 569 684
0, $\frac{1}{3}, \frac{1}{2}$	-0.655 672 635	
$\frac{1}{2}, \frac{5}{6}, \frac{1}{2}$	-0.557 743 256	-1.213 415 891

### 3. Evaluation of some Madelung constants

To find  $\alpha$  for a given crystal the total Hund potential of every ion making up the neutral complex in the crystal must be evaluated, taking into account both the number and sign of the charges on the ions. Half the sum of the Hund potentials then gives  $\alpha$ . Two examples are now illustrated. Zinc sulphide (ZnS) occurs as two crystalline forms. One of these, the zinc blende structure, is made up of interpenetrating cubic lattices and has been treated by many authors. The other form is the wurzite structure which consists of two interpenetrating HCPI structures. If we take the  $Zn^{2+}$  as based on HCPI(0, 0, 0) then the  $S^{2-}$  is based on HCPI(0, 0,  $\frac{3}{8}$ ). Thus

$$POT(Zn^{2+}) = 4HCPI(0, 0, 0) - 4HCPI(0, 0, \frac{3}{8})$$

$$POT(S^{2-}) = 4HCPI(0, 0, 0) - 4HCPI(0, 0, \frac{3}{8}).$$

Thus  $\alpha(\text{wurzite}) = \frac{1}{2}[POT(Zn^{2+}) + POT(S^{2-})] = 4[HCPI(0, 0, 0) - HCPI(0, 0, \frac{3}{8})]$ . From table 1 this gives  $\alpha(\text{wurzite}) = 10.721\ 067\ 98$  in terms of  $R$ . In terms of the nearest anion-cation distance,  $D$ , this has to be multiplied by  $\sqrt{\frac{3}{8}}$  giving 6.565 286 512. However, when Hund (1925) first evaluated  $\alpha(\text{wurzite})$  along with other simple AB structures in which A obviously has the same number of positive charges,  $Z$ , as B has negative charges, he gave the value of  $\alpha$  in terms of  $Z^2$ . It has thus become common in the literature to give  $\alpha$  in this case as the values given above divided by four, since  $Z$  for ZnS is two. Thus in terms of  $D$ ,  $\alpha(\text{wurzite}) = 1.641\ 321\ 627 \dots$ , which agrees with the only other value calculated to this accuracy (Sakamoto 1958). The actual details of Sakamoto's calculation are unpublished.

As a second example cadmium iodide,  $CdI_2$ , will be discussed.  $CdI_2$  may be considered as interpenetrating simple hexagonal lattices with  $Cd^{2+}$  based on HI(0, 0, 0)

Table 3. Madelung constants of some hexagonal structures.

Structure	$D/R$	$\alpha(R)$	$\alpha(D)$
Wurzite	$\sqrt{\frac{8}{3}}$	2.680 266 994	1.641 321 627
NiAs type	$\sqrt{\frac{1}{2}}$	4.889 406 510	3.457 332 500
BN type	$\sqrt{\frac{1}{3}}$	2.646 966 603	1.528 226 880
Ice type	$\sqrt{\frac{3}{32}}$	7.270 377 298	2.226 089 327
$\text{CdI}_2$	$\sqrt{\frac{1}{2}}$	6.173 207 106	4.365 116 607

with  $\text{I}_I^-$  on  $\text{HI}(-1, \frac{2}{3}, \gamma)$  and  $\text{I}_{II}^-$  on  $\text{HI}(0, \frac{1}{3}, -\gamma)$ . Thus

$$\text{POT}(\text{Cd}^{2+}) = 4\text{HI}(0, 0, 0) - 2\text{HI}(0, \frac{1}{3}, \gamma) - 2\text{HI}(0, \frac{1}{3}, -\gamma)$$

$$\text{POT}(\text{I}_I^-) = \text{HI}(0, 0, 0) + \text{HI}(0, \frac{1}{3}, 2\gamma) - 2\text{HI}(0, \frac{1}{3}, \gamma)$$

$$\text{POT}(\text{I}_{II}^-) = \text{HI}(0, 0, 0) + \text{HI}(0, \frac{1}{3}, 2\gamma) - 2\text{HI}(0, \frac{1}{3}, -\gamma).$$

Hence

$$\begin{aligned} \alpha(\text{CdI}_2) &= \frac{1}{3}[\text{POT}(\text{Cd}^{2+}) + \text{POT}(\text{I}_I^-) + \text{POT}(\text{I}_{II}^-)] \\ &= 3\text{HI}(0, 0, 0) + \text{HI}(0, \frac{1}{3}, 2\gamma) - 4\text{HI}(0, \frac{1}{3}, \gamma). \end{aligned}$$

Hund (1925) has evaluated these potentials for several values of  $\gamma$  and for several values of  $c$ . The value usually required is for  $\gamma = \frac{1}{4}$  and  $c$  equal to the ideal ratio. Hund (1925) gives this value as 4.71 (in terms of  $D$  which is  $R/\sqrt{2}$ ) and this is the value often quoted in the literature, e.g. Sherman (1932), Hoppe (1956) and Waddington (1959). However, this is incorrect, since if we calculate  $\alpha(\text{CdI}_2)$  using the potential values given in Hund's (1925) own tables the value found is 4.40. All the other values of  $\alpha$  given by Hund for varying  $\gamma$  and  $c$  are correct and it is strange that this one error has perpetuated itself in much published work. Using the more accurate values found here  $\alpha(\text{CdI}_2) = 4.365 116 607$ . Johnson and Templeton (1961) give the value  $\alpha(\text{CdI}_2) = 4.384 09$  which has been calculated for a  $c$ -value of 1.617 which is slightly different from the ideal ratio of  $\sqrt{\frac{8}{3}} = 1.633$ . In table 3 a few accurate values for  $\alpha$  of some hexagonal structures have been listed. (A full description of all these structures together with relevant diagrams may be found in Megaw (1973).) The  $\alpha$ -values have been given both in terms of  $D$  and in terms of  $R$ . It seems apposite here to correct a small numerical error appearing in a paper by Borwein *et al* (1988) concerning the energy of static electron lattices. The results for the HCP structure were evaluated by the methods used here and a slight error was made. In that paper a result given as

$$U_{(\text{HCP})} = -3.241 858 662 e^2/R = -1.791 676 267 e^2/r,$$

should read

$$U_{(\text{HCP})} = -3.241 858 615 e^2/R = -1.791 676 241 e^2/r.$$

The conclusions of that paper are unaffected.

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