Efficient calculation of Madelung constants for cubic crystals

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(Received 17 October 2008; published 9 January 2009)

A very simple and efficient numerical method for evaluating the Madelung constants for cubic crystals, using cubes of increasing size, is proposed. The results of successful applications to the NaCl and CsCl ionic crystals, representative perovskite cubic lattices, and to a simple cubic metal are reported.

DOI: 10.1103/PhysRevB.79.012102 PACS number(s): 61.50.Ah

The calculation of Madelung constants is a classical solid-state problem and allows one to evaluate the electrostatic energy of ionic crystal structures, such as the NaCl lattice, which is characterized by alternate point positive and negative charges, $Z_i = \pm 1$, with nearest-neighbor distance d. In this case the electrostatic potential acting on the ith ion, due to the charges on all other sites, can be written as

$$V_i = -Z_i \alpha e/d, \tag{1}$$

where e is the absolute value of the electronic charge and α is the Madelung constant, which is defined as ($r_{ij} = |\mathbf{r_j} - \mathbf{r_i}|$ is the distance between the ions located in the lattice sites i and j)

$$\alpha = d \sum_{j \neq i} (-Z_j)/r_{ij}. \tag{2}$$

As it is well known, the calculation of the above sum, in three-dimensional crystals, is not trivial because the series is only *conditionally convergent* due to the long-range decay of the Coulomb potential. Nowadays, the standard method for calculating α is represented by the method of Ewald,[1] which consists of placing neutralizing Gaussian charge distributions on each site, making the sum in real space rapidly convergent, and then separately calculating and subtracting the potential from the Gaussian caps, which can be done with a rapidly converging sum in reciprocal space. However, the problem of lattice summation remains the subject of active interest (see, for instance, Ref. 2, and references quoted therein) and many other schemes for evaluating the Madelung constants have been proposed (a few examples are listed in Ref. 3) although, similar to the scheme of Ewald,[1] they are relatively complex.

Interestingly, Harrison[4] recently provided an alternative, very simple, and elegant method for evaluating Madelung sums using a laptop computer. The basic idea is the following: if the Madelung sum is directly performed by summing the electrostatic q/r contributions for all the ions within a sphere of radius R, even considering a huge number of ions, the resulting potential at the central ions fluctuates in sign as well as magnitude with increasing R, this behavior being due to the fact that the net charge Q within the sphere also fluctuates. Hence, the difficulty can be easily fixed by correcting the potential at the center by a term $-Q/R$. Using such a simple correction, the improvement is dramatic so that the corrected result fluctuates only by 1% even for relatively small R values ($R \sim 50d$). Since for practical applications, a much higher precision is not physically meaningful, this means that the evaluation of the electrostatic energy of ionic crystals can be rapidly performed with a common laptop computer, by writing a trivial and very short code. The method has been successfully applied[4] not only to the prototypical NaCl-lattice case but also to the CsCl structure, complex compounds in the cubic perovskite structure and even bcc metals. In this last case the metal is modeled as a system of positive charges embedded in a compensating uniform negative background and the method described above is still applicable by lowering the potential at the center of the sphere by the electrostatic potential at the center of a uniform negative charge.[4]

We here propose another direct method, applicable to cubic crystals, which has some similarities to that of Harrison[4] and is characterized by an even faster convergence of the Madelung constant, as a function of the number of charged particles included in the sum. Basically, in our method, instead of considering spheres of increasing radius R, we use *cubes* of increasing size. In practice, this means that we carry out the sum of Eq. (2) by performing three nested loops (over the x, y, and z coordinates) and without the control statement which selects only the contributions coming from the ions inside the sphere of radius R. The advantage of this simple modification is that, if one considers a cube of linear size $L = 2nd$, it is easy to show that, i.e., for the NaCl lattice, the net charge included within this cube is simply given by

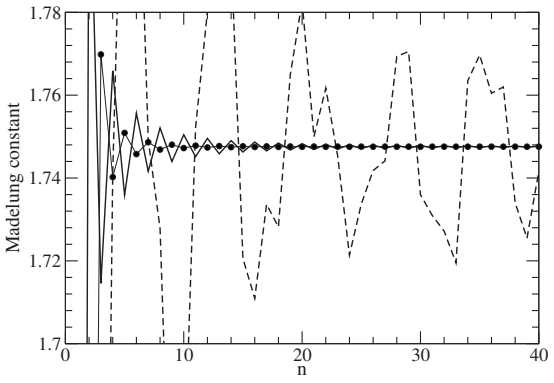

FIG. 1. Estimate of the Madelung constant α as a function of the cubic side, for the NaCl lattice, using the present method (solid line; the circles denote results obtained by averaging over subsequent estimates) and the scheme of Harrison (Ref. 4) (dashed line).

TABLE I. Estimate of the Madelung constant α as a function of the cubic side, $L=2nd$, for the NaCl and CsCl lattices, compared to the reference data (Ref. 8); in parentheses, the corresponding values, obtained using the method of Harrison (Ref. 4), are reported.

n	α_{NaCl}	α_{CsCl}
10	1.7505 (1.6650)	1.7654 (1.7958)
20	1.7483 (1.7826)	1.7634 (1.7513)
50	1.7477 (1.7525)	1.7628 (1.7610)
100	1.7476 (1.7400)	1.7627 (1.7631)
300	1.7476 (1.7457)	1.7627 (1.7613)
Ref.	1.7476	1.7627

$$Q(n) = -1^n, \tag{3}$$

and hence it exhibits regular oscillations from −1 to +1. By extending the above algorithm, by considering multiple, differently centered cubic cells, one finds that a similar behavior also applies to more complex ionic structures: for instance, in the case of the CsCl lattice, the charge oscillates again from −1 to +1, while in the WO_3 structure described below, one finds that the charge oscillations go from −6 to +6. From these observations it is very natural to propose that a good estimate of the Madelung constant, relative to a given n value, is obtained by taking the arithmetic average with the estimate corresponding to $n-1$,

$$\bar{\alpha}(n) = [\alpha(n) + \alpha(n-1)]/2. \tag{4}$$

As can be seen, looking at Fig. 1, relative to the NaCl case, the improvement obtained by using this recipe, with respect to the scheme of Harrison,[4] is evident; in fact one achieves a reasonably converged result (with an error of about 1%) for n as small as 6. Moreover, an even faster convergence can be obtained by observing that $\bar{\alpha}(n)$ itself exhibits regular oscillations; therefore, if one averages over subsequent $\bar{\alpha}(n)$ values, a 1% accuracy is already achieved for $n=3$ (see Fig. 1).

Clearly this improvement more than offsets the larger number of terms which must be explicitly summed, for a given n value, when a cube is used instead of a sphere: $(2L)^3/(4\pi L^3/3)=6/\pi\sim 1.9$. This behavior is also confirmed in the other ionic crystal structures investigated in the paper of Harrison,[4] namely, the CsCl lattice, two representative perovskite structures, and in a simple cubic metal (see Tables I–IV).

TABLE II. Electrostatic potential coefficients (to be multiplied by e/d), as a function of the cubic side, for the WO_3 perovskite lattice ($Z_O=-2$, $Z_A=+6$); in parentheses, the corresponding values, obtained using the method of Harrison (Ref. 4), are reported.

n	ϕ_A	ϕ_B	ϕ_O
10	−0.6505 (−0.6915)	−8.2164 (−8.2585)	3.7052 (3.6800)
20	−0.6561 (−0.7793)	−8.2220 (−8.3453)	3.7122 (3.5933)
50	−0.6579 (−0.7048)	−8.2237 (−8.2707)	3.7142 (3.6680)
100	−0.6581 (−0.6377)	−8.2240 (−8.2036)	3.7146 (3.7351)
200	−0.6582 (−0.6664)	−8.2241 (−8.2322)	3.7146 (3.7064)
300	−0.6582 (−0.6631)	−8.2241 (−8.2290)	3.7146 (3.7097)
600	−0.6582 (−0.6570)	−8.2241 (−8.2229)	3.7146 (3.7158)

TABLE III. Electrostatic potential coefficients (to be multiplied by e/d), as a function of the cubic side, for the AB perovskite lattice ($Z_B=-1$, $Z_A=+1$); in parentheses, the corresponding values, obtained using the method of Harrison (Ref. 4), are reported.

n	ϕ_A	ϕ_B	ϕ_O
10	−1.0161 (−0.9986)	1.0193 (1.0368)	−0.2417 (−0.2242)
20	−1.0173 (−1.0243)	1.0181 (1.0111)	−0.2429 (−0.2499)
50	−1.0176 (−1.0187)	1.0177 (1.0167)	−0.2432 (−0.2443)
100	−1.0177 (−1.0174)	1.0177 (1.0180)	−0.2433 (−0.2430)
200	−1.0177 (−1.0169)	1.0177 (1.0185)	−0.2433 (−0.2425)
300	−1.0177 (−1.0185)	1.0177 (1.0169)	−0.2433 (−0.2441)
600	−1.0177 (−1.0178)	1.0177 (1.0176)	−0.2433 (−0.2434)

Clearly, the usefulness of such a method is not particularly apparent in the prototypical NaCl and CsCl ionic lattices, where literature reference data are available since a long time ago, but instead in applications to more complex compound such as the cubic perovskite structures. Following the notation of Ref. 4, these structures can be denoted by ABO_3, where the A atoms are located in the body-center position of the reference cube, the atoms B are at the corners, and the O atoms are at the cube edges. Assuming that each atom type has a well-defined charge (typically $Z_O=-2$ and $Z_A+Z_B+3Z_O=0$, due to charge neutrality), the basic ingredient for evaluating the electrostatic energy of the structure is represented by the values of the electric potential on each site, ϕ_A, ϕ_B, and ϕ_O, due to all the ions except the reference one from that site. In fact, the electrostatic energy per formula unit is then given by[5]

$$E_{\mathrm{el}} = 1/2(Z_A e\phi_A + Z_B e\phi_B + 3Z_O e\phi_O). \tag{5}$$

In Tables II and III we have reported the electric poten-

TABLE IV. Electrostatic potential V_{sc} (to be multiplied by e/r_0, where r_0 is the atomic sphere radius) as a function of the cubic side, for a simple cubic metal, compared to the reference value (Ref. 7); in parentheses, the corresponding values, obtained using the method of Harrison (Ref. 4), are reported.

n	V_{sc}
10	−1.76015 (−1.78126)
20	−1.76013 (−1.76025)
50	−1.76012 (−1.75807)
100	−1.76012 (−1.76116)
200	−1.76012 (−1.75982)
300	−1.76012 (−1.75980)
600	−1.76012 (−1.75998)
800	−1.76012 (−1.76018)
Ref.	−1.76012

tials for the case of WO_3 (although ϕ_A can be calculated, there is no atom in the A site) and of AB (this compound, where the O site is empty, corresponds to a CsCl structure, differing from the standard one because of a different nearest-neighbor distance[4]), respectively. Combining these results, the Madelung potentials for other perovskites can be easily obtained, as described by Harrison;[4] moreover, effective, fractional charges could be adopted for more realistic descriptions.[4]

In the case of the simple cubic metal the average over subsequent n estimates is not very helpful since the charge does not fluctuate in sign, and the electrostatic potential V_{sc} must be lowered not by the potential at the center of a uniform, negatively charged sphere, $V_{sphere}=3/2Q/R'$ (R' is very close to R but does not coincide with it since it is defined in such a way that the charge density of Q in the sphere of radius R' is exactly the bulk value), as in the approach of Harrison,[4] but instead by the potential at the center of a uniform, negatively charged cube, which is given by[6]

$$V_{cube} = Q/L'[3\ \ln(3^{1/2}+2) - \pi/2] \sim 2.38Q/L'. \quad (6)$$

With our scheme, similar to what is done in the Harrison procedure, the length L' is defined in such a way that the charge density of Q in the cube of side L' coincides with the bulk value. Moreover, in order to obtain the correct electrostatic potential, using cubes instead of spheres, a constant correction term $[-\pi e/(12d)]$ must be added, as shown in detail by Nijboer and Ruijgrok.[9] As can be seen in Table IV, even in this last case the improvement is dramatic; in fact a good convergence is obtained using n as small as 5.

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