

A few remarks on the Coulomb potential of the ionic lattices

M. Apostol

Department of Theoretical Physics,
 Institute of Atomic Physics, Magurele-Bucharest MG-6,
 POBox MG-35, Romania

Abstract

The Coulomb potential at an arbitrary point in an ionic lattice is related to the Coulomb potential generated at that point by one ion, or a few ions, of the lattice.

Suppose that we are interested in the Coulomb potential of the crystalline field of an ionic lattice at an arbitrary point; we denote this point by 0 and take it as the origin of the reference frame. Let us chose an ion of the lattice, whose charge is taken as equal to unity, placed at the position \mathbf{R} ; it may appear as being the most convenient to chose this ion as close as possible to 0. We denote the Coulomb potential $V(|\mathbf{r} - \mathbf{R}|)$ produced by this ion at the point \mathbf{r} by $v(\mathbf{r})$, *i.e.*

$$v(\mathbf{r}) = V(|\mathbf{r} - \mathbf{R}|) . \quad (1)$$

The total Coulomb potential produced by the lattice at \mathbf{r} may be written as

$$\mathcal{V}(\mathbf{r}) = v(\mathbf{r}) + \sum_i q_i V(|\mathbf{r} - \mathbf{R}_i|) , \quad (2)$$

where the summation extends over all the remaining ions in the lattice and q_i denotes the charge of the i -th ion.

The ions can be classified according to their distance R_n to the point \mathbf{r} , and we label by m the m -th ion in each class n ; *i.e.*, for any i in (2) there is a couple nm , such that $\mathbf{R}_i = \mathbf{R}_{nm}$. Further on, for any ion nm there is a rotation $\mathcal{R}^{-1}(nm)$ which brings \mathbf{R}_{nm} parallel to \mathbf{R} ; if we denote this rotated vector by \mathbf{R}_n and by α_n the ratio of its modulus to R , we may write

$$\mathbf{R}_{nm} = \mathcal{R}(nm)\mathbf{R}_n = \alpha_n \mathcal{R}(nm)\mathbf{R} . \quad (3)$$

It follows that the potential (2) may be written as

$$\begin{aligned} \mathcal{V}(\mathbf{r}) &= v(\mathbf{r}) + \sum_{nm} \frac{q_{nm}}{\alpha_n} \mathcal{R}(nm) V(|\mathbf{r}/\alpha_n - \mathbf{R}|) = v(\mathbf{r}) + \sum_{nm} \frac{q_{nm}}{\alpha_n} \mathcal{R}(nm) v(\mathbf{r}/\alpha_n) = \\ &= \sum_{nm} \frac{q_{nm}}{\alpha_n} \mathcal{R}(nm) v(\mathbf{r}/\alpha_n) , \end{aligned} \quad (4)$$

where the homogeneity of the Coulomb potential has been used and we have extended the summation to including $\alpha_n = 1$, too. This is the basic relationship of the present remarks.

The total Coulomb potential at the point we are interested in is obtained from (4) as

$$\mathcal{V}(0) = \sum_{nm} \frac{q_{nm}}{\alpha_n} v(0) , \quad (5)$$

i.e., it is given by the ion we have chosen with an effective charge. If we denote by $x_i, i = 1, 2, 3$, the components of the vector \mathbf{r} we may write the derivatives of $\mathcal{V}(\mathbf{r})$ given by (4) as

$$\frac{\partial \mathcal{V}(\mathbf{r})}{\partial x_i} \Big|_0 = \left[\sum_{nm} \frac{q_{nm}}{\alpha_n^2} \mathcal{R}(nm) \right] \left\{ \frac{\partial v(\mathbf{r})}{\partial x_i} \right\}_0 = \left[\sum_{nm} \frac{q_{nm}}{\alpha_n^2} \mathcal{R}_{ij}(nm) \right] \frac{\partial v(\mathbf{r})}{\partial x_j} \Big|_0 \quad , \quad (6)$$

which shows that an effective-charge matrix gives the first-order derivatives of the potential. Similarly, a second-rank tensor expresses the second-order derivatives by

$$\frac{\partial^2 \mathcal{V}(\mathbf{r})}{\partial x_i \partial x_j} \Big|_0 = \left[\sum_{nm} \frac{q_{nm}}{\alpha_n^3} \mathcal{R}_{ik}(nm) \mathcal{R}_{jl}(nm) \right] \frac{\partial^2 v(\mathbf{r})}{\partial x_k \partial x_l} \Big|_0 \quad . \quad (7)$$

A first remark would be that the series in (5) – (7) are alternate, so that it is relatively easy to estimate the error in truncating them; which would provide an estimation of how many ions contribute significantly to the Coulomb potential and to its derivatives at a given, position. Secondly, it appears preferable to chose not a single ion placed at \mathbf{R} , but a few equivalent ions surrounding the position 0; by equivalent ions we mean here those ions connected by lattice translations, and we may chose, for example, the nearest-neighbours of 0. We get in this case another potential $v(\mathbf{r})$, and the relationships (5) – (7) hold also for this potential; in the case of a lattice with basis we may have several types of $v(\mathbf{r})$ -potentials, for each type relations similar with (5) – (7) holding. For special 0-points the derivatives of $v(\mathbf{r})$ may vanish, and even the second-order derivatives may do so (as, for example, for points of cubic symmetry); in which case, from (6) and (7), the derivatives of the total potential $\mathcal{V}(\mathbf{r})$ vanish; which means that the equilibrium position of an ion, established with the short-range inter-molecular potentials, would not be changed by the Coulomb potential.

Turning now to (4) we may define

$$\frac{1}{\alpha_n} \sum_m q_{nm} \mathcal{R}(nm) = \cos(\beta(\alpha_n)) M(\alpha_n) \quad , \quad (8)$$

where β is such as to reproduce the oscillations of the lhs of (8) and the matrix $M(\alpha_n)$ is no longer a rotation. The initializations in (8) are $n = 1, \alpha = 1, \beta = 0$ and $M = 1$. Since α_n is a slowly varying function (providing, of course, that 0 be not too close of an ion) we may pass to integral in (4),

$$\mathcal{V}(\mathbf{r}) = \int_1^\infty d\alpha \cdot \cos \beta \cdot G(\alpha) \quad , \quad (9)$$

where $G(\alpha) = M(\alpha)v(\mathbf{r}/\alpha)n'(\alpha)$, and further on

$$\mathcal{V}(\mathbf{r}) = \int_0^\infty d\beta \cdot \cos \beta \cdot F(\beta) \quad , \quad (10)$$

where $F(\beta) = G(\alpha)\alpha'(\beta)$. The integral in (10) may not converge; for example, one can see easily from (8) that $M(\alpha)$ goes like α for large α (for a three-dimensional lattice). This situation is specific to the long-range Coulomb potential, and we assume that it is regularized by suitable exponentially-decreasing factors. Then, the estimation of (10) proceeds by integrating by parts; we have successively

$$\begin{aligned} \mathcal{V}(\mathbf{r}) &= \sin 0 \cdot [F(\infty) - F(0)] + \cos 0 \cdot [F^{(1)}(\infty) - F^{(1)}(0)] - \\ &- \sin 0 \cdot [F^{(2)}(\infty) - F^{(2)}(0)] - \cos 0 \cdot [F^{(3)}(\infty) - F^{(3)}(0)] + \dots = \\ &= -F^{(1)}(0) + F^{(3)}(0) - \dots \quad . \end{aligned} \quad (11)$$

Since α varies slowly we may limit ourselves to the first term in (11), which is given by

$$F^{(1)}(0) = \left[M'(1)v(\mathbf{r})n'(1) + M(1)v'_\alpha(\mathbf{r})n'(1) + M(1)v(\mathbf{r})n''(1) \right] \cdot \alpha'^2(1) + \\ + M(1)v(\mathbf{r})n'(1) \cdot \alpha''(1) . \quad (12)$$

It is easy to check that the second term in (12) is proportional to $-\mathbf{r} \cdot \text{grad}v(\mathbf{r})$, so that the potential $\mathcal{V}(\mathbf{r})$ can be represented from (12) as

$$\mathcal{V}(\mathbf{r}) = M \cdot v(\mathbf{r}) - \text{const} \cdot \mathbf{r} \cdot \text{grad}v(\mathbf{r}) , \quad (13)$$

where M denotes an undetermined matrix. One may also check easily that the representation (13) is consistent with the series expansion given by (5) – (7).

The matrix M in (13) contains factors comparable with the magnitude of the *const* factor in (13); from (12) one can see that, allowing for one-order of magnitude reduction due to $n'(1)$, these factors are proportional to the first derivative of the distance ratio of the ions; as the lattice is uniformly packed this derivative is small, and the relative high Coulomb potential is greatly reduced, as is well known (and as one might have expected). One can easily check that the order of magnitude of this reduction is $\sim \delta/a$, where δ is the distance of the point 0 from the centre of the unit cell and a is the lattice constant. There are positions in the lattice where the Coulomb potential does not experience such a reduction, but their spatial extent is of the order of the atomic size.

Finally we remark that if \mathbf{R} defines a reflection axis the rotation matrices involved above reduce to the unit matrix and (13) tells, in this case, that $\mathcal{V}(\mathbf{r})$ is close to a flat potential.