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Non-scalar contribution of potential in crystals

H. Uchiyama

Japan Synchrotron Radiation Research Institute, Koto 1-1-1, Sayo, Hyogo 679-5198, Japan

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ABSTRACT

Ewald-parameter dependence of Coulomb interaction in ionic crystals was studied using a point-charge model. In the presence of the long-range interaction, the ion configuration breaks spherical symmetry of local potential and charge at each ion site, and gives non-scalar contributions to them. This non-scalar potential has similar effects to Heisenberg interaction, while is intrinsically distinct from conventional multipole expansions of the scalar potential. Symmetry and magnitude of the scalar and non-scalar potentials are similar for most materials despite the different definitions, but one exception can be seen in parent materials of hole-doped high-T_c cuprates.

1. Introduction

In crystal-field theory, anisotropic Coulomb potential causes deviation of wavefunctions from spherical symmetry around a site of an ionic crystal [1]. It is well known that d electrons in the octahedral field produced by six surrounding anions split into t_{2g} and e_g orbitals with different energies. The anisotropic potential is described as a multipole expansion, a scalar function of the position. The potential is originally composed of contributions from the nearest neighboring ions with high symmetry or cubic groups. More general consideration of the anisotropic potential, which includes contributions beyond the neighboring ions with lower symmetry, is discussed using the Ewald method [2–4]. However, Ref. [2] indicates that this method has conditional convergence for the multipole expansions. The treatment beyond the Ewald method is required for the absolute convergence, and this treatment for charge density is applied to the first principle calculations [5,6]. Some reports mention that the conditional convergence is caused by the shape of the crystal [7].

Classical Heisenberg interaction discusses another deviation from spherical symmetry. This interaction is controlled by spin orientations at the nearest neighboring sites, similar to the crystal field theory, but describes local rotational symmetry exactly at the site, in contrast to the anisotropy above. Given the fact that rotational symmetry at a certain point in general includes contributions from all ions in the crystal, there is some possibility of unknown interaction at the site, which is not described by the Heisenberg interaction only.

In this report, Coulomb interaction in crystals with infinite periodicity were reinvestigated in the point-charge model, based on the Ewald method. It turns out that, in the presence of the long-range interaction, the Coulomb potential has another, non-scalar, contribution, which breaks the spherical symmetry at the site, in addition to the scalar contribution. This dual aspects of the potential may cause the conditional convergence of the Ewald method. The non-scalar contribution, which has the same deviation of the spherical symmetry as the Heisenberg interaction, is caused by the ion configuration of the infinite lattice, and coexists with distortion of the charge from the original spherical symmetry. This non-scalar contributions neither violate Poisson's equation nor affect scalar potential and charge. Furthermore, it can be defined both at magnetic and non-magnetic ions, in contrast to the Heisenberg interaction, and be considered as anisotropy of local relative permittivity in the framework of the scalar-potential field.

As specific examples, anisotropic potentials and charges of a d-ion in a NaCl-type structure and ions in ZnO, ZnS (zinc blende), CaF_2, TiO_2 (rutile), $SrTiO_3$, La_2CuO_4, Nd_2CuO_4, and $HgBa_2CuO_4$ were calculated. Though these two (scalar and non-scalar) potentials are defined differently, they have the same symmetries and similar magnitudes at the ion sites in $SrTiO_3$ and the d-ion site in the NaCl-type structure. The similar features are also observed in more complicated materials, such as ZnO, ZnS, CaF_2, TiO_2, and Nd_2CuO_4. However, these potentials have completely different symmetries at the O sites in the CuO_2 planes of La_2CuO_4 and $HgBa_2CuO_4$, parent materials of hole-doped high-T_c cuprates. This difference may have some connection with the hole-doped superconductivity.

2. Method

In the Ewald method, the Coulomb potential induced by the surrounding point charges at an i-th ion site ($\mathbf{r}_i$) is expressed as

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follows, using a parameter ξ:

$$V(\mathbf{r}_i) = \sum_{j\neq i} f(\xi) + \sum_{j}\sum_{k\neq 0} g(\xi) - \frac{Z_i e}{2\pi^{3/2}\varepsilon_0}\xi, \tag{1}$$

when the crystal has charge neutrality. Here, ε_0 is the vacuum permittivity, $f(\xi)$ is the contribution from real space

$$f(\xi) = \frac{Z_j e}{4\pi\varepsilon_0 |\mathbf{r}_j - \mathbf{r}_i|}\,\mathrm{erfc}(|\mathbf{r}_j - \mathbf{r}_i|\xi), \tag{2}$$

and $g(\xi)$ is the contribution from reciprocal space

$$g(\xi) = \frac{Z_j e}{4\pi^2 k^2 \varepsilon_0 v} e^{-\pi^2 k^2/\xi^2} e^{2\pi i \mathbf{k}\cdot(\mathbf{r}_j - \mathbf{r}_i)}, \tag{3}$$

where v is the volume of the unit cell.

When ξ is small enough ($\xi \to 0$), $g(\xi)$ approaches zero, and Eq. (1) becomes

$$V(\mathbf{r}_i) + \frac{Z_i e}{2\pi^{3/2}\varepsilon_0}\xi \sim \sum_{j\neq i} f. \tag{4}$$

This equation indicates that the potential and charge at the i-th site are determined by the surrounding ions ($j \neq i$) for small ξ. Furthermore, because the right side of Eq. (4) is not a summation of distribution with spherical symmetry, the left side is also expected to lose the symmetry and deviate from scalars.

When the spherical symmetry of the local potential and charge are broken at $\mathbf{r}_i$, Eq. (1) can be expanded using associated Legendre polynomials (P_l^m) in spherical polar coordinates (θ, φ):

$$V_i^{(n)}(\theta,\varphi) + \frac{Z_i^{(n)}(\theta,\varphi)e}{2\pi^{3/2}\varepsilon_0}\xi = \sum_{l=0}^{n} k_{nl} L_i^{(l)}(\xi,\theta,\varphi), \tag{5}$$

for the n-th order expansion. Here,

$$\begin{aligned} L_i^{(l)} &= a_i^{l0} P_l^0(\cos\theta) \\ &\quad + \sum_{m=1}^{l} [a_i^{lm} P_l^m(\cos\theta)\cos m\varphi + b_i^{lm} P_l^m(\cos\theta)\sin m\varphi], \\ a_i^{lm}(\xi) &= C_{lm}\sum_{j\neq i} f P_l^m(\cos\theta)\cos m\varphi \\ &\quad + C_{lm}\sum_{j}\sum_{k\neq 0} g P_l^m(\cos\theta)\cos m\varphi, \end{aligned}$$

and

$$\begin{aligned} b_i^{lm}(\xi) &= C_{lm}\sum_{j\neq i} f P_l^m(\cos\theta)\sin m\varphi \\ &\quad + C_{lm}\sum_{j}\sum_{k\neq 0} g P_l^m(\cos\theta)\sin m\varphi. \end{aligned} \tag{6}$$

The coefficient C_{lm} may be given as

$$\begin{aligned} C_{lm} &= (-1)^m \frac{2(l-m)!}{(l+m)!} C_{l0} \quad (m \geq 1), \\ C_{l0} &= \frac{l!}{(2l-1)!!}. \end{aligned} \tag{7}$$

The n-th order Legendre expansion of the anisotropic potential is alternatively expressed as the n-fold tensor product of the unit vector, $(\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta)$ [8], and hence the coefficient k_{nl} should satisfy the following equation:

$$\cos^n\theta + \cos^{n-1}\theta = \sum_{l=0}^{n} k_{nl} C_{l0} P_l^0(\cos\theta), \tag{8}$$

for even $n(\geq 2)$ ($k_{00} = 1$ for $n=0$). It should be noted that the charges in Eqs. (2) and (3) (Z_j) should also deviate from scalars, because Eq. (5) indicates deviation from the spherical (isotropic) charge at $\mathbf{r}_i$. However, this further deviation is not considered here for simplicity.

For instance, the Legendre expansions at Ti and O sites in a cubic perovskite, $SrTiO_3$ (a=3.905 Å) are considered (Fig. 1). In the crystal, scalar point charges (Sr^{2+}, Ti^{4+}, and O^{2-}) are assumed, which behave as ions. Fig. 1(a) and (c), respectively, shows $a_{\mathrm{Ti}}^{00}(\xi)$ and $a_{\mathrm{O}}^{00}(\xi)$, or ξ dependence of the scalar (isotropic) terms ($l=0$) at the Ti and O sites. Eq. (5) indicates that the isotropic potentials are given by the a_i^{00}-intercepts ($V_{\mathrm{O}}^{(0)}$ and $V_{\mathrm{Ti}}^{(0)}$), and that the isotropic charges are given by the slopes ($Z_{\mathrm{O}}^{(0)}$ and $Z_{\mathrm{Ti}}^{(0)}$). The former exactly corresponds to the conventional scalar potentials ($V_{\mathrm{O}}^{(0)} = 23.8$ eV and $V_{\mathrm{Ti}}^{(0)} = -45.6$ eV) and the latter gives the self charges at $\mathbf{r}_i$ ($Z_{\mathrm{O}}^{(0)} = -2$ and $Z_{\mathrm{Ti}}^{(0)} = +4$). These values are unchanged in an arbitrary region of ξ.

At the Ti site, though the anisotropic contributions of l=1, 2, and 3 are zero, non-zero contribution appears at the 4th order ($L_{\mathrm{Ti}}^{(4)} \neq 0$). When the Ti–O bonds are directed to the Cartesian coordinates, a_{Ti}^{40} and a_{Ti}^{44} become non-zero, as seen in Fig. 1(b). In contrast to the isotropic contribution (l=0, Fig. 1(a)), these coefficients have ξ dependence. For small ξ, we can estimate the non-scalar potential and charge using the intercepts and slopes of the dotted lines in Fig. 1(b). One of the inset figures (blue) in Fig. 1(b) suggests positive charge anisotropy determined by the slopes of a_{Ti}^{40} and a_{Ti}^{44}, and the other (red) suggests negative potential anisotropy obtained by the intercepts. Both the anisotropic potential and charge have O_h symmetry, but the signs are opposite. These features are similar to the isotropic contributions, where the isotropic (scalar) charge and potential ($Z_{\mathrm{Ti}}^{(0)}$ and $V_{\mathrm{Ti}}^{(0)}$) have the same (spherical) symmetry with the opposite signs, as seen in Fig. 1(a). This similarity validates the existence of the non-scalar (anisotropic) charge and potential at small ξ.

At the O site, non-zero contribution appears at the 2nd order ($L_{\mathrm{O}}^{(2)} \neq 0$); when the z-axis is taken along the Ti–O bond direction, a_{O}^{20} becomes non-zero as shown in Fig. 1(d). Similar to the Ti site, the anisotropic potential and charge at O can be defined (only) for small ξ; the slope and intercept of a_{O}^{20} give negative charge anisotropy (red) and positive potential anisotropy (blue), as shown in the insets of Fig. 1(d). Again, the potential and charge have the same symmetry with the opposite signs.

These non-scalar contributions of the potential and charge have several features. First, these do not violate the Poisson's equation around the i-th ion; only the scalar term of the charge ($Z_i^{(0)}$) at $\mathbf{r}_i$ contributes to the equation, because Eq. (5) satisfies the following equation:

$$(n+1)\iint \lim_{\xi\to 0} Z_i^{(n)} \sin\theta\, d\theta\, d\varphi = 4\pi Z_i^{(0)}, \tag{9}$$

for even n. Secondly, the non-scalar potential and charge reflect rotational symmetry at the i-th site, because the Legendre expansion in Eq. (5) is chiefly affected by the surrounding ions ($f(\xi)$) for small ξ. Finally, the non-scalar potential and charge for small ξ suggest some relation to the long-range Coulomb interaction, because ξ has the dimension of $1/r$. These features suggest spherical symmetry breaking of the potential and charge at $\mathbf{r}_i$, owing to the long-range Coulomb interaction.

In the conventional crystal-field theory, on the other hand, anisotropic Coulomb potential caused by the neighboring ions around $\mathbf{r}_i$ is expressed as a scalar function of the position. When contribution of the infinite periodicity (beyond the neighboring ions) is included in the theory, the scalar potential at $\mathbf{r}_s + \mathbf{r}_i$ is given by

$$V_i(\mathbf{r}_s) = \sum_{j\neq i} f(\xi, \mathbf{r}_s) + \sum_{j}\sum_{k\neq 0} g(\xi, \mathbf{r}_s) - \frac{Z_i e}{4\pi\varepsilon_0}\frac{\mathrm{erf}(\xi r_s)}{r_s}. \tag{10}$$

Here,

$$f(\xi, \mathbf{r}_s) = \frac{Z_j e}{4\pi\varepsilon_0 |\mathbf{r}_j - \mathbf{r}_i - \mathbf{r}_s|}\mathrm{erfc}(|\mathbf{r}_j - \mathbf{r}_i - \mathbf{r}_s|\xi),$$

and

$$g(\xi, \mathbf{r}_s) = \frac{Z_j e}{4\pi^2 k^2 \varepsilon_0 v} e^{-\pi^2 k^2/\xi^2} e^{2\pi i \mathbf{k}\cdot(\mathbf{r}_j - \mathbf{r}_i - \mathbf{r}_s)}. \tag{11}$$