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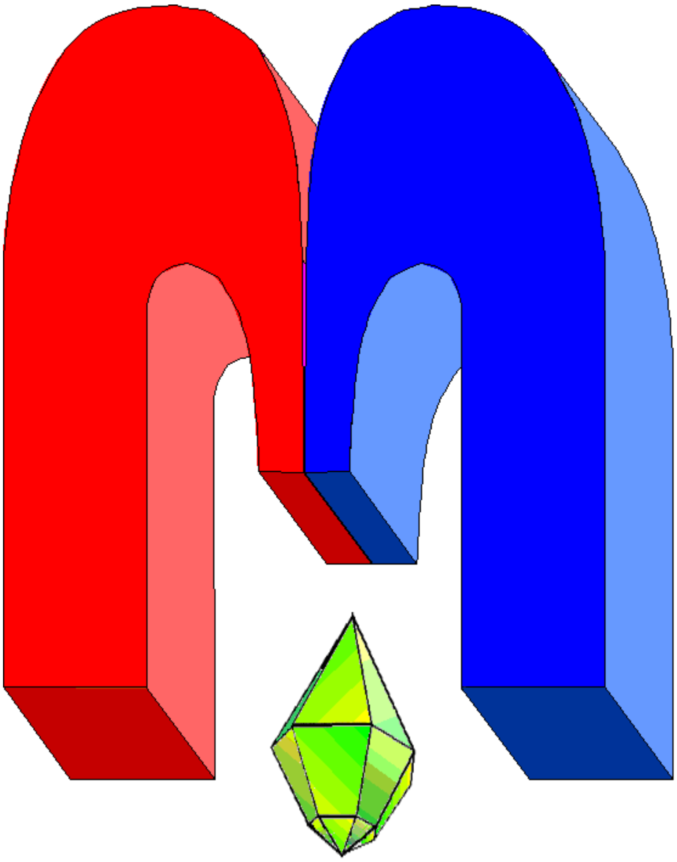

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* In Kazan State University the Electron Paramagnetic Resonance (EPR) was discovered by Zavosky E.K. in 1944.

# The Coulomb interaction between an s-orbital electron and ionic crystal lattice

*O.A. Anikeenok*

*Kazan State University, Kremlevskaya, 18, Kazan 420008, Russia*
*E-mail*: Oleg.Anikeenok@ksu.ru

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# The Coulomb interaction between an *s*-orbital electron and ionic crystal lattice

O.A. Anikeenok
*Kazan State University, Kremlevskaya, 18, Kazan 420008, Russian Federation*
*E-mail: Oleg.Anikeenok@ksu.ru*

Analytical expressions for the Coulomb interaction between an *s*-orbital electron and the surroundings, infinite ionic crystal lattice are derived. The *s*-orbital wave functions are presented in the form of a Gaussian expansion. As a test, Madelung constants and interaction energy for NaCl, $KMgF_3$, $CaF_2$ are calculated using a single Gaussian exponent. The calculated values are coincided with known literature data with a high degree of accuracy.

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**Keywords:** localized orbitals, Madelung energy, orbital energy.

## 1. Introduction

The calculation of energy of Coulomb interaction of orbital with infinite crystal lattice is one of the most important problems in the ion crystals theory. The value of this interaction is estimated by the electrostatic potential calculation at the lattice site [1-3]. In this paper, the expressions for the calculations of the interaction energy of the *s*-orbital electron with infinite crystal lattice are derived. The *s*-orbital is taken in the Gaussian expansion form. The expressions are absolutely convergent series, which do not require additional parameter for convergence of series as in [1] and which do not contain the sum taken over direct lattice. This series can be calculated with pinpoint accuracy. One exponent orbital is used for test calculations of NaCl, $KMgF_3$ and $CaF_2$ crystals.

## 2. General part

Let the ion is situated at the origin of coordinate system and the radial part of its *s*-orbital is described by the Gaussian Type Orbital (GTO) function. Then an *s*- electron wave function is

$$\psi_{ns} = \sqrt{\frac{1}{4\pi}} \sum a_i \exp\left( -\alpha_i r^2 \right), \tag{1}$$

where *n* is the main quantum number, *s* is the angular-momentum quantum number.

The position of the charge $q$ is determined by the vector $\mathbf{R} = \left( R_x, R_y, R_z \right)$. The Coulomb interaction of such *s*-electron with the charge $q$ may be written [4]

$$\left\langle \psi_{ns} \right| \left( -\frac{q}{|\mathbf{r} - \mathbf{R}|} \right) \left| \psi_{ns} \right\rangle = -\frac{1}{2} q \sum a_i a_k \left( \frac{1}{\alpha_{ik}} \right) \int_0^1 \exp\left[ -\alpha_{ik} \mathbf{R}^2 x^2 \right] dx, \tag{2}$$

where $\alpha_{ik} = \alpha_i + \alpha_k$.

The Coulomb interaction of the ion *s*-electron at the site $\mathbf{r}_j$ with the crystal lattice is the sum of functions (2). Then the electron - lattice interaction, including the ion of the site $\mathbf{r}_j$, is energy $E_j$. It may be written as follows

$$\begin{aligned} E_j &= \left\langle \psi_{ns} \right| \left( -\sum_{\mathbf{R}_m} \sum_p \frac{q_p}{|\mathbf{r} - [\mathbf{R}_m - (\mathbf{r}_j - \mathbf{r}_p)]|} \right) \left| \psi_{ns} \right\rangle = \\ &= -\frac{1}{2} \sum_{\mathbf{R}_m} \sum_p q_p \sum a_i a_k \left( \frac{1}{\alpha_{ik}} \right) \int_0^1 \exp\left[ -\alpha_{ik} [\mathbf{R}_m - (\mathbf{r}_j - \mathbf{r}_p)]^2 x^2 \right] dx = , \\ &= -\frac{1}{2} \sum a_i a_k \left( \frac{1}{\alpha_{ik}} \right) \int_0^1 dx \sum_{\mathbf{R}_m} \left( \sum_p q_p \exp[-\alpha_{ik} [\mathbf{R}_m - (\mathbf{r}_j - \mathbf{r}_p)]^2 x^2] \right) \end{aligned} \tag{3}$$

where $\mathbf{R}_m$ is the radius vector of unit cell, $\mathbf{r}_j$ is the radius vector of ion unit cell, $q_p$ is the charge of ion with the radius vector $\mathbf{r}_p$. According to (2) an interaction energy $E_0$ between the *s*-electron at the site $\mathbf{r}_j$ and the single unit positive charge at the same site $\mathbf{r}_j$ ($\mathbf{R} = 0$) may be written as

$$E_0 = -\frac{1}{2} \sum a_i a_k \left( \frac{1}{\alpha_{ik}} \right).$$

The interaction energy $E_{or}^j$ of *s*-orbital and crystal lattice is

$$E_{or}^j = E_j - q_j E_0, \tag{4}$$

where $q_j$ is the charge of the site $\mathbf{r}_j$ ion.

The expressions (3) and (4) are the functions of the lattice variables. Using transformation [5], the expression (4) may be displayed in the term of reciprocal lattice variable

$$\frac{2}{\sqrt{\pi}} \sum_{\mathbf{R}_m} \exp\left[ -[\mathbf{R}_m - (\mathbf{r}_j - \mathbf{r}_p)]^2 x^2 \right] = \frac{2\pi}{v_c} \sum_{\mathbf{g}} \frac{1}{x^3} \exp\left( -\frac{\mathbf{g}^2}{4x^2} \right) \exp\left[ i(\mathbf{g} \cdot (\mathbf{r}_j - \mathbf{r}_p)) \right], \tag{5}$$

where $\mathbf{g}$ is the vector of reciprocal lattice, $v_c$ is the volume of unit cell.

Then the interaction energy $E_j$ may be written as follows

$$E_j = -\frac{\pi^{\frac{3}{2}}}{v_c}\sum a_i a_k \left(\frac{1}{\alpha_{ik}}\right)^{\frac{3}{2}} \sum_{\mathbf{g}} G_j(\mathbf{g})\frac{1}{\mathbf{g}^2}\exp\left(-\frac{\mathbf{g}^2}{4\alpha_{ik}}\right), \tag{6}$$

$$G_j(\mathbf{g}) = \cos\left(\mathbf{g}\mathbf{r}_j\right)F_1(\mathbf{g}) + \sin\left(\mathbf{g}\mathbf{r}_j\right)F_2(\mathbf{g}), \tag{7}$$

$$F_1(\mathbf{g}) = \sum_p q_p \cos\left(\mathbf{g}\mathbf{r}_p\right), \quad F_2(\mathbf{g}) = \sum_p q_p \sin\left(\mathbf{g}\mathbf{r}_p\right). \tag{8}$$

The function (7) is named as a structure factor of the crystal.

### 3. Calculation

Let us take one exponent orbital

$$\psi_{1s} = \sqrt{\frac{1}{4\pi}}a\exp\left(-\alpha r^2\right), \qquad a = 2\left(\frac{8\alpha^3}{\pi}\right)^{\frac{1}{4}}. \tag{9}$$

Hereinafter all quantities are given in atomic units (au). According to equations (6) and (9)

$$E_j = -\frac{4\pi}{v_c}\sum_{\mathbf{g}} G_j(\mathbf{g})\frac{1}{\mathbf{g}^2}\exp\left(-\frac{\mathbf{g}^2}{8\alpha}\right) \tag{10}$$

$$E_0 = -2\left(\frac{2\alpha}{\pi}\right)^{\frac{1}{2}}. \tag{11}$$

Let us examine NaCl crystal. The unit cell is defined as

$$\text{Na: } \mathbf{r}_1 = (0,0,0), \quad \mathbf{r}_3 = (0.5a, 0.5a, 0.5b). \quad \text{Cl: } \mathbf{r}_2 = (0.5a, 0.5a, 0), \quad \mathbf{r}_4 = (0,0,0.5b). \tag{12}$$

where $b = \sqrt{2}a$, $b = 5.63$ Å or $b = 10.63916232186962$ .

The energy $E_j$ for NaCl according to (10) is written as follows

$$E_{Na} = -\frac{2}{b\pi}\sum_{n_x,n_y,n_z}\frac{G_{Na}(\mathbf{n})}{2n_x^2 + 2n_y^2 + n_z^2}\exp\left[-\frac{\pi^2}{2\alpha b^2}\left(2n_x^2 + 2n_y^2 + n_z^2\right)\right], \tag{13}$$

where $G_{Na}(\mathbf{n})$ is the structure factor, $b$ is the absolute value of the unite cell vector along the axis $z$ .The structure factor $G_{Na} \equiv G_{Na}(\mathbf{n})$ for NaCl is defined as

$$G_{Na} = 1 - (-1)^{n_x+n_y} - (-1)^{n_z} + (-1)^{n_x+n_y+n_z} .$$

The value $\alpha_{or}^{Na}$ is defined by formula

$$\alpha_{or}^{Na} = \frac{b}{2}\left(E_{Na} - q_{Na}E_0\right) \tag{14}$$

Below we use the calculation accuracy up to 25 decimal places. According to equation (14) one can obtain

$\alpha = 0.01$, $\alpha_{or}^{Na} = 0{,}84887524443760629933366228$;

$\alpha = 0.1$, $\alpha_{or}^{Na} = 1.74297851983335938881232629$;

$\alpha = 1$, $\alpha_{or}^{Na} = 1.74756459463318219063362119$;

$\alpha = 10$, $\alpha_{or}^{Na} = 1.74756459463318219063362120$;

$\alpha = 100$, $\alpha_{or}^{Na} = 1.74756459463318219063362120$.

Another test is the lattice constant variation. Consider $\alpha = 0.1$. Let $b'$ is a new lattice constant and $b$ is the lattice constant we used before. So, we are obtained

$b' = 3b$, $\alpha_{or}^{Na} = 1.74756459463318219063361765$ ;

$b' = 6b$, $\alpha_{or}^{Na} = 1.74756459463318219063362120$.

The Madelung constant $\alpha_M$ for NaCl calculated by direct summation up to 25 decimal places was presented in work [6]

$$\alpha_M = 1.7475645946331821906362120 \tag{15}$$

The explanation of the coincidence of (15) with our calculations is evident. According to the Gauss theorem if the spherically symmetrical distribution of charge does not overlap with the point charge then this distribution for this point charge looks like the point charge.

Let us examine $KMgF_3$ and $CaF_2$ crystals. The energy $E_j$ for $KMgF_3$ and $CaF_2$ according to (10) is written as follows (for $\alpha = 1$)

$$E_j = -\frac{1}{a\pi} \sum_{n_x, n_y, n_z} \frac{G_j(\mathbf{n})}{n_x^2 + n_y^2 + n_z^2} \exp\left[ -\frac{\pi^2}{2a^2} \left( n_x^2 + n_y^2 + n_z^2 \right) \right], \tag{16}$$

The structure factors for $KMgF_3$ are defined as

$$G_K = 2(-1)^{n_x+n_y+n_z} - (-1)^{n_x+n_y} - (-1)^{n_x+n_z} - (-1)^{n_y+n_z} + 1 \tag{17}$$

$$G_{Mg} = 2 - (-1)^{n_x} - (-1)^{n_y} - (-1)^{n_z} + (-1)^{n_x+n_y+n_z} \tag{18}$$

$$G_F = 2(-1)^{n_z} - 1 - (-1)^{n_x+n_z} - (-1)^{n_y+n_z} + (-1)^{n_x+n_y}. \tag{19}$$

For the crystal $KMgF_3$ $a = 3.973$ Å or $a = 7.507884885397513$ . For simplicity we use below the accuracy of calculated values up to 8 decimal places. Then

$\alpha_{or}^{K} = 2.69360482$, $E_{or}^{K} = 0.35877013$, $\alpha_{or}^{Mg} = 6.18873401$, $E_{or}^{Mg} = 0.82429794$,

$\alpha_{or}^{F} = -3.22795440$, $E_{or}^{F} = -0.42994191$.

The Madelung constants $\alpha$ for $KMgF_3$ according to [7] are

$\alpha_{Mg} = 6.189$, $\alpha_F = -3.228$.

The structure factors for $CaF_2$ are defined as

$$G_{Ca} = 2\left[1 + (-1)^{n_x+n_y}\right]\left[1 + (-1)^{n_x+n_z}\right] - (-1)^{\frac{n_x+n_y+n_z}{2}} \left[1 + (-1)^{n_x}\right]\left[1 + (-1)^{n_y}\right]\left[1 + (-1)^{n_z}\right], \tag{20}$$

$$G_F = \left[1 + (-1)^{n_x}\right]\left[1 + (-1)^{n_y}\right]\left[1 + (-1)^{n_z}\right]\left[(-1)^{\frac{n_x+n_y+n_z}{2}} - 1\right]. \tag{21}$$

For $CaF_2$ $a = 5.462$ Å or $a = 10.321688206403527$ , then

$\alpha_{or}^{Ca} = 7.56585221$, $E_{or}^{Ca} = 0.73300530$, $\alpha_{or}^{F} = -4.07072302$, $E_{or}^{F} = -0.39438539$.

The Madelung constant $\alpha_M$ is defined in handbook [8] and for $CaF_2$ $\alpha_M = 2.51939$. Using $E_{or}^{Ca}$ and $E_{or}^{F}$ we can obtain the same result for $\alpha_M$ in the framework of proposed here approach.

So, we can conclude that our calculated values coincide with known values adduced in references. Equation (6) is absolutely convergent series, which continuous in $\alpha_i$. Therefore all the calculations are mathematically correct.

## Conclusions

The expressions for the calculations of the interaction energy of the *s*-orbital electron with infinite crystal lattice are derived. The equations can be used for the Madelung energy calculations in case of sufficiently localized orbitals. The Madelung energy for the NaCl, $KMgF_3$ and $CaF_2$ crustals are calculated.

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