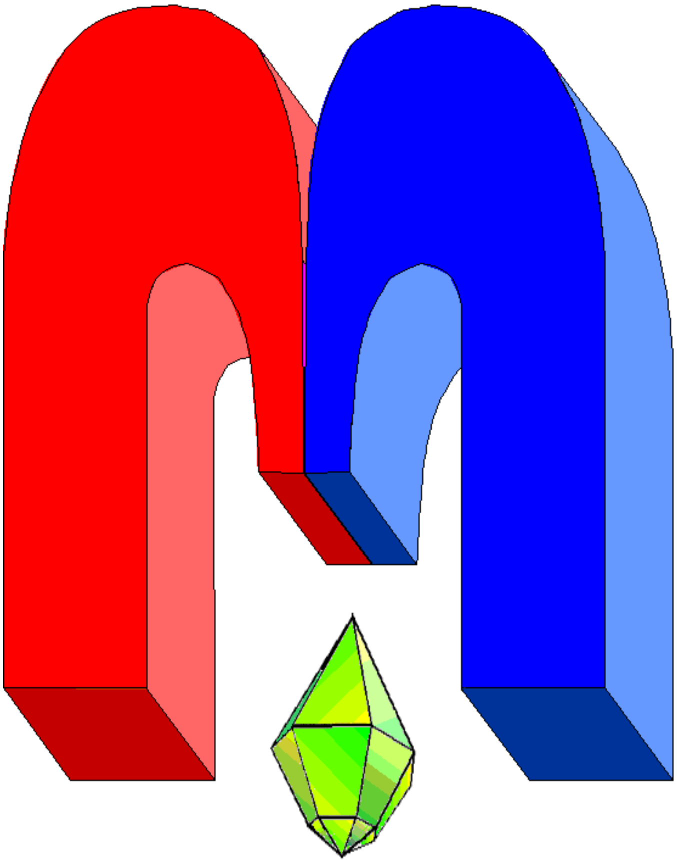
ISSN 2072-5981



agnetic
Resonance
in Solids

Electronic Journal

Volume **13,** *No.* **2**
pages **27-35**
2011

http://mrsej.ksu.ru

Established and published by Kazan University
Sponsored by International Society of Magnetic Resonance (ISMAR)
Registered by Russian Federation Committee on Press, August 2, 1996
First Issue was appeared at July 25, 1997

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[*] In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Approach to calculation of long-range Coulomb interaction matrix elements in ion crystals

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(Received November 18, 2011; revised December 22, 2011; accepted December 25, 2011)

Expressions for the calculation of matrix elements of the Coulomb interaction of the electron with an infinite crystal lattice in ion crystals have been obtained. In the general case, matrix elements are calculated on the orbitals belonging to ions of different sites. Gaussian-type orbitals are used in the calculations. All expressions are absolutely and rather rapidly converging series in the space of the inverse lattice vectors. At present the value of this interaction being only one-center is estimated by the Madelung constant, in other words, by calculating the electrostatic potential in the lattice site, i.e., in a point.

PACS: 61.50.Ah, 61.72.S

Keywords: localized orbitals, infinite crystal lattice, Madelung energy, orbital energy

1. Introduction

The method of secondary quantization with a partly nonorthogonal one-particle basis was developed in [1-4]. Its application to admixture centers [4], when the overlap integrals of ion orbitals are sufficiently small, allows one to build mathematically correct expressions for the perturbation-theory series within virtual and real charge transfer processes. To calculate physical characteristics of an admixture center ab initio, it is necessary to separate an U-region around the admixture ion where all interactions should be written exactly and the other part of the crystal, which is taken into account in the ion approximation. It is convenient to present the charge of nuclei Z of ions in the U-region as $Z = q + n + m$ [2], where q is the charge of the ion in the host crystal, n is the number of electrons in ions in the considered configuration, m is the deviation of the ion charge in the host crystal for the considered configuration. Such a partition allows one to rather simply group all interactions in the U-region, at least in ion crystals, with respect to their order of magnitude, e.g., when calculating the crystal field parameters or amplitudes of the transition of electrons between ions [2-4]. Note that the value of the ion charge – q in the U-region is a definite number and not a fitting parameter. In this approach it is necessary to calculate two-center matrix elements (TME) and one-center matrix elements (OME) of the long-range (LR) Coulomb interaction of an electron with an infinite crystal lattice.

At present the value of this interaction being only one-center is estimated by the Madelung constant, in other words, by calculating the electrostatic potential in the lattice site, i.e., in a point [5-8]. The exclusion is [9], where the energy of the Coulomb interaction of the *s*-electron with the infinite crystal lattice was calculated.

The article below is arranged as follows. General expressions for the calculation of TME of the LR Coulomb interaction of the electron with the infinite crystal lattice are derived in the second section. Formulas necessary for the calculation of matrix elements on s, p, d, f orbitals of ions are given as well. On the basis of the expressions for TME of the LR Coulomb interaction, the expressions for OME of the LR Coulomb interaction are presented and particular cases are considered.

2. General part

Let the radial part R_{nl} ion orbital $\left|\psi_{nlm}(\mathbf{r})\right\rangle$ where the electron is located has the form of the Gaussian basis expansion (GTO)

$$R_{nl} = \sum_i a_i r^l \exp\left(-\alpha_i r^2\right). \tag{1}$$

Let the first ion be located at the site with the radius-vector $\mathbf{R}_0 + \mathbf{r}_j, \mathbf{R}_0 = 0$. The second ion is in the site with the radius-vector $\mathbf{r}_b$. The charge q_p is in the site with the radius-vector $\mathbf{R}_n + \mathbf{r}_p$. Let us denote $\mathbf{r}_0 = \mathbf{r}_b - \mathbf{r}_j$, $\mathbf{R} = \mathbf{R}_n - \left(\mathbf{r}_j - \mathbf{r}_p\right)$, where $\mathbf{R}_n$ is the vector of the $n-$th crystal unit cell, $\mathbf{r}_j$ and $\mathbf{r}_p$ are the vectors of the ions of the unit cell, ξ, ξ' are the quantum numbers of ion orbitals.

The matrix element of the Coulomb interaction between the electron and the charge q_p calculated on the wave functions of the first and second ions has the form

$$\left\langle \psi_\xi\left(\mathbf{r}-\mathbf{r}_j\right)\right| - \frac{q_p}{\left|\mathbf{r}-\left(\mathbf{R}_n+\mathbf{r}_p\right)\right|}\left|\psi_{\xi'}\left(\mathbf{r}-\mathbf{r}_b\right)\right\rangle = \left\langle \psi_\xi(\mathbf{r})\right| - \frac{q_p}{\left|\mathbf{r}-\left[\mathbf{R}_n-\left(\mathbf{r}_j-\mathbf{r}_p\right)\right]\right|}\left|\psi_{\xi'}\left[\mathbf{r}-\left(\mathbf{r}_b-\mathbf{r}_j\right)\right]\right\rangle. \tag{2}$$

We define the $F\left(n_1 n_2 n_3\right)$ functions as follows

$$2\pi\, F\left(n_1 n_2 n_3\right) = -q_p \sum_{i,k} a_i b_k \int \exp\left(-\alpha_i \mathbf{r}^2\right) x^{n_1} y^{n_2} z^{n_3} \left|\mathbf{r}-\mathbf{R}\right|^{-1} \exp\left[-\beta_k \left(\mathbf{r}-\mathbf{r}_0\right)^2\right] dxdydz. \tag{3}$$

For example, the matrix element calculated on the $\left|p_z(\mathbf{r})\right\rangle$ functions has the form

$$\left\langle p_z(\mathbf{r})\right| - \frac{q_p}{\left|\mathbf{r}-\mathbf{R}\right|}\left|p_z\left(\mathbf{r}-\mathbf{r}_0\right)\right\rangle = \frac{3}{2}\left[F(002) - z_0 F(001)\right]. \tag{4}$$

Let us further present the $F\left(n_1 n_2 n_3\right)$ functions in a form convenient for calculations. To this end, we perform transformations used in [2]

$$\frac{1}{|\,\mathbf{r}-\mathbf{R}\,|} = \frac{2}{\sqrt{\pi}} \int_0^\infty dv \exp\left[-\left(\mathbf{r}-\mathbf{R}\right)^2 v^2\right], \tag{5}$$

$$v^2 = \frac{\alpha_{ik} u^2}{1-u^2}, \quad \left(\frac{1}{\alpha_{ik}+v^2}\right)^{\frac{3}{2}} dv = \frac{du}{\alpha_{ik}}, \tag{6}$$

where $\alpha_{ik} = \alpha_i + \alpha_k$. After transformations (5) and (6), the integration over *x*, *y*, *z* in (3) is reduced to table integrals [10] and the following expression is obtained for the $F\left(n_1 n_2 n_3\right)$ functions

$$F\left(n_1 n_2 n_3\right) = -q_p \sum_{i,k} a_i b_k \left(\frac{1}{\alpha_{ik}}\right) \int_0^1 du \prod_{s=1}^{3} \left\{ n_s! \sum_{m_s=0}^{\left[\frac{n_s}{2}\right]} \frac{\left(1-u^2\right)^{m_s}}{\left(4\alpha_{ik}\right)^{m_s} m_s!} \sum_{w_s=0}^{n_s-2m_s} \frac{\left[\left(R_s-c_s\right)u^2\right]^{n_s-2m_s-w_s}}{w_s!\left(n_s-2m_s-w_s\right)!} c_s^{w_s} \right\}$$
$$\times \exp\left[-\alpha_{ik}\left(\mathbf{R}-\mathbf{c}\right)^2 u^2\right] \exp\left(-\frac{\alpha_i \beta_k}{\alpha_{ik}} \mathbf{r}_0^2\right), \tag{7}$$

where $\left[n_s/2\right]$ is the integer part of a number in brackets; $x_{01}=x_0,\ \ x_{02}=y_0,\ \ x_{03}=z_0$ denote the coordinates of the vector $\mathbf{r}_0$; $c_s=\beta_k x_{0s}/\alpha_{ik}$ denote the components of the vector $\mathbf{c}$; $R_1=R_x,\ R_2=R_y,\ R_3=R_z$ denote the coordinates of the vector $\mathbf{R}$. After multiplication of three curly brackets in (7), the multipliers of the form

$$\left(R_x-c_1\right)^{\tilde{n}_1}\left(R_y-c_2\right)^{\tilde{n}_2}\left(R_z-c_3\right)^{\tilde{n}_3}\exp\left[-\alpha_{ik}\left(\mathbf{R}-\mathbf{c}\right)^2u^2\right], \tag{8}$$

where $\tilde{n}_s=n_s-2m_s-w_s$, are presented in each term of the resulting sum. According to the above notation $\mathbf{R}=\mathbf{R}_n-\left(\mathbf{r}_j-\mathbf{r}_p\right)$. We introduce a vector $\mathbf{r}=\mathbf{r}_j-\mathbf{r}_p$. Since the ion positions in the unit cell are rather arbitrary, we consider that the vector $\mathbf{r}$ is defined in all points of the unit cell and let us introduce the $D\left(\mathbf{r},\tilde{n}_1,\tilde{n}_2,\tilde{n}_3\right)$ function whose domain is the unit cell

$$D\left(\mathbf{r},\tilde{n}_1,\tilde{n}_2,\tilde{n}_3\right)=\sum_{\mathbf{R}_n}\prod_{s=1}^{3}\left\{\left(R_{ns}-x_s-c_s\right)^{n_s-2m_s-w_s}\exp\left[-\alpha_{ik}\left(R_{ns}-x_s-c_s\right)^2u^2\right]\right\}, \tag{9}$$

where $x_1=x,\ x_2=y,\ x_3=z$ are the coordinates of the vector $\mathbf{r}$; $R_{n1}=R_{nx},\ \ R_{n2}=R_{ny},\ \ R_{n3}=R_{nz}$ denote the coordinates of the vector $\mathbf{R}_n$. The $D\left(\mathbf{r},\tilde{n}_1,\tilde{n}_2,\tilde{n}_3\right)$ function is a periodic function of $\mathbf{r}$ with the period of the crystal unit cell (see, e.g., [11]) and the same as in [11], when the Fourier coefficients $D\left(\mathbf{g},\tilde{n}_1,\tilde{n}_2,\tilde{n}_3\right)$ of the $D\left(\mathbf{r},\tilde{n}_1,\tilde{n}_2,\tilde{n}_3\right)$ functions are found, integration over the unit cell can be reduced to the integration over the whole space. Thus

$$D\left(\mathbf{r},\tilde{n}_1,\tilde{n}_2,\tilde{n}_3\right)=\sum_{\mathbf{g}}D\left(\mathbf{g},\tilde{n}_1,\tilde{n}_2,\tilde{n}_3\right)\exp\left[i\left(\mathbf{gr}\right)\right], \tag{10}$$

$$D\left(\mathbf{g},\tilde{n}_1,\tilde{n}_2,\tilde{n}_3\right)=\frac{1}{v_c}\int x^{\tilde{n}_1}y^{\tilde{n}_2}z^{\tilde{n}_3}\exp\left\{-\left[\alpha_{ik}\mathbf{r}^2u^2+i\left(\mathbf{gr}\right)\right]\right\}dxdydz\,\exp\left[-i\left(\mathbf{gc}\right)\right], \tag{11}$$

where v_c is the volume of the unit cell, $\mathbf{g}$ is the vector of the inverse lattice, i is the imaginary unit. By performing integration in (11), we obtain

$$\begin{gathered}D\left(\mathbf{g},\tilde{n}_1,\tilde{n}_2,\tilde{n}_3\right)=\frac{1}{v_c}\left(\frac{\pi}{\alpha_{ik}}\right)^{\frac{3}{2}}\prod_{s=1}^{3}\tilde{n}_s!\left(\frac{1}{2}\right)^{\tilde{n}_s}\left\{\sum_{h_s=0}^{\left[\frac{\tilde{n}_s}{2}\right]}\frac{\left(-ig_s\right)^{\tilde{n}_s-2h_s}}{h_s!\left(\tilde{n}_s-2h_s\right)!}\left(\frac{1}{\alpha_{ik}u^2}\right)^{\tilde{n}_s-h_s}\right\}\\ \times\left(\frac{1}{u^3}\right)\exp\left(-\frac{\mathbf{g}^2}{4\alpha_{ik}u^2}\right)\exp\left[-i\left(\mathbf{gc}\right)\right],\end{gathered} \tag{12}$$

where $g_1=g_x,\ \ g_2=g_y,\ \ g_3=g_z$ are the coordinates of the vector $\mathbf{g}$. Let us further introduce the $F_{jb}\left(n_1n_2n_3\right)$ functions. To this end, we substitute $\mathbf{R}=\mathbf{R}_n-\mathbf{r}$ into expression (7) and perform summation over vectors $\mathbf{R}_n$ with the use of expressions (9)-(12), then we substitute $\mathbf{r}=\mathbf{r}_j-\mathbf{r}_p$ into the obtained expression and perform summation over vectors $\mathbf{r}_p$ of the whole unit cell. These calculations are bulky but rather simple and as a result, we obtain

$$F_{jb}\left(n_1n_2n_3\right)=-\frac{\pi^{\frac{3}{2}}}{v_c}n_1!n_2!n_3!\sum_{i,k}a_ib_k\left(\frac{1}{\alpha_{ik}}\right)^{\frac{5}{2}}\exp\left(-\frac{\alpha_ib_k}{\alpha_{ik}}\mathbf{r}_0^2\right)\int_0^1du\left(\frac{1}{u}\right)^3$$
$$\times\sum_{\mathbf{g}}f_{jb}\left(n_1,g_x\right)f_{jb}\left(n_2,g_y\right)f_{jb}\left(n_3,g_z\right)\exp\left(-\frac{\mathbf{g}^2}{4\alpha_{ik}u^2}\right)\left(\sum_pq_p\exp\left[i\mathbf{g}\left(\mathbf{r}_j-\mathbf{r}_p\right)\right]\right)\exp[-i\mathbf{gc}], \tag{13}$$

where

$$f_{jb}\left(n,g_s\right)=\sum_{m=0}^{\left[\frac{n}{2}\right]}\frac{\left(1-u^2\right)^m}{\left(4\alpha_{ik}\right)^m m!}\sum_{w=0}^{n-2m}\frac{1}{w!}\left(\frac{-ig_s}{2\alpha_{ik}}\right)^{n-2m-w}c_s^w\sum_{h=0}^{\left[\frac{n-2m-w}{2}\right]}\frac{(-1)^h}{h!(n-2m-w-2h)!}\left(\frac{u\sqrt{\alpha_{ik}}}{g_s}\right)^{2h}. \tag{14}$$

Then we obtain the explicit expressions of the $f_{jb}\left(n,\,g_s\right)$ functions for the values $n=0,1,2,3,4$

$$Z_s=\frac{\beta_kx_{0s}}{\alpha_{ik}}-i\frac{g_s}{2\alpha_{ik}},\qquad f_{jb}\left(0,g_s\right)=1,\qquad f_{jb}\left(1,g_s\right)=Z_s,\qquad f_{jb}\left(2,g_s\right)=\frac{1}{2!}Z_s^2+\frac{1}{4\alpha_{ik}},$$
$$f_{jb}\left(3,g_s\right)=\frac{1}{3!}Z_s^3+\frac{1}{4\alpha_{ik}}Z_s,\qquad f_{jb}\left(4,g_s\right)=\frac{1}{4!}Z_s^4+\frac{1}{8\alpha_{ik}}Z_s^2+\frac{1}{32\alpha_{ik}^2}. \tag{15}$$

It is seen that the $f_{jb}\left(n,\,g_s\right)$ functions do not depend on the parameter u. Below we will call the sum over the index p in parentheses in (13) as a structural factor $G_j\left(\mathbf{g}\right)$. It is presented as follows

$$G_j\left(\mathbf{g}\right)=G_j^{(1)}\left(\mathbf{g}\right)+iG_j^{(2)}\left(\mathbf{g}\right)=\sum_pq_p\exp\left[i\mathbf{g}\left(\mathbf{r}_j-\mathbf{r}_p\right)\right],$$
$$G_j^{(1)}\left(\mathbf{g}\right)=\cos\left(\mathbf{gr}_j\right)F_1\left(\mathbf{g}\right)+\sin\left(\mathbf{gr}_j\right)F_2\left(\mathbf{g}\right),\qquad G_j^{(2)}\left(\mathbf{g}\right)=\sin\left(\mathbf{gr}_j\right)F_1\left(\mathbf{g}\right)-\cos\left(\mathbf{gr}_j\right)F_2\left(\mathbf{g}\right), \tag{16}$$
$$F_1\left(\mathbf{g}\right)=\sum_pq_p\cos\left(\mathbf{gr}_p\right),\qquad F_2\left(\mathbf{g}\right)=\sum_pq_p\sin\left(\mathbf{gr}_p\right).$$

By substituting (16) in (13) we obtain for the $F_{jb}\left(n_1n_2n_3\right)$ functions

$$F_{jb}\left(n_1n_2n_3\right)=-\frac{\pi^{\frac{3}{2}}}{v_c}n_1!n_2!n_3!\sum_{i.k}a_ib_k\left(\frac{1}{\alpha_{ik}}\right)^{\frac{5}{2}}\exp\left(-\frac{\alpha_ib_k}{\alpha_{ik}}\mathbf{r}_0^2\right)\int_0^1du\left(\frac{1}{u}\right)^3$$
$$\times\sum_{\mathbf{g}}f_{jb}\left(n_1,g_x\right)f_{jb}\left(n_2,g_y\right)f_{jb}\left(n_3,g_z\right)\exp\left(-\frac{\mathbf{g}^2}{4\alpha_{ik}u^2}\right)G_j\left(\mathbf{g}\right)\exp\left[-i\left(\mathbf{gc}\right)\right]. \tag{17}$$

By performing integration over the parameter u in (17) we obtain the final expression for the $F_{jb}\left(n_1n_2n_3\right)$ functions

$$F_{jb}\left(n_1n_2n_3\right)=-\frac{2\pi^{\frac{3}{2}}}{v_c}n_1!n_2!n_3!\sum_{i,k}a_ib_k\left(\frac{1}{\alpha_{ik}}\right)^{\frac{3}{2}}\exp\left(-\frac{\alpha_ib_k}{\alpha_{ik}}\mathbf{r}_0^2\right)$$
$$\times\sum_{\mathbf{g}}f_{jb}\left(n_1,g_x\right)f_{jb}\left(n_2,g_y\right)f_{jb}\left(n_3,g_z\right)\exp\left(-\frac{\mathbf{g}^2}{4\alpha_{ik}}\right)\frac{G_j\left(\mathbf{g}\right)}{\mathbf{g}^2}\exp\left[-i\left(\mathbf{gc}\right)\right]. \tag{18}$$

Now we introduce the operator H_{LR} of the Coulomb interaction between the electron and the infinite crystal lattice

$$\left\langle \psi_{\xi}\left(\mathbf{r}-\mathbf{r}_{j}\right)\right| H_{LR}\left|\psi_{\xi'}\left(\mathbf{r}-\mathbf{r}_{b}\right)\right\rangle = \left\langle \psi_{\xi}\left(\mathbf{r}-\mathbf{r}_{j}\right)\right| - \sum_{n,p}\frac{q_{p}}{\left|\mathbf{r}-\left(\mathbf{R}_{n}+\mathbf{r}_{p}\right)\right|}\left|\psi_{\xi'}\left(\mathbf{r}-\mathbf{r}_{b}\right)\right\rangle .$$

Thus, the matrix elements of the operator H_{LR} calculated on the orbitals of the lattice ions are expressed in terms of the $F_{jb}\left(n_1 n_2 n_3\right)$ functions. For example, we obtain for the $\left|p_z\left(\mathbf{r}\right)\right\rangle$ and $\left|p_z\left(\mathbf{r}-\mathbf{r}_0\right)\right\rangle$ orbitals

$$\left\langle p_z\left(\mathbf{r}\right)\right| H_{LR}\left|p_z\left(\mathbf{r}-\mathbf{r}_0\right)\right\rangle = \frac{3}{2}\left[F_{jb}\left(002\right)-z_0 F_{jb}\left(001\right)\right]. \tag{19}$$

One-center matrix elements

One-center matrix elements can be expressed in terms of the $F_j\left(n_1 n_2 n_3\right)$ functions. To find these functions, it is sufficient to take $\mathbf{r}_0 = 0$ in (18) and we obtain

$$F_j\left(n_1 n_2 n_3\right) = -\frac{2\pi^{\frac{3}{2}}}{v_c} n_1! n_2! n_3! \sum_{i,k} a_i b_k \left(\frac{1}{\alpha_{ik}}\right)^{\frac{3}{2}} \sum_{\mathbf{g}} f\left(n_1, g_x\right) f\left(n_2, g_y\right) f\left(n_3, g_z\right) \frac{G_j\left(\mathbf{g}\right)}{\mathbf{g}^2} \exp\left(-\frac{\mathbf{g}^2}{4\alpha_{ik}}\right). \tag{20}$$

The $f\left(n, g_s\right)$ functions are obtained from expressions (14) for the $f_{jb}\left(n, g_s\right)$ functions, if only the terms with the index $w = 0$ are kept there. To obtain the $f\left(n, g_s\right)$ functions for the values $n = 0,1,2,3,4$, it is necessary to assume $x_{0s} = 0$ in the expression Z_s in formulas (15). The $f\left(n, g_s\right)$ functions for the values $n = 5,6$ are given below

$$\begin{gathered} z_s = -i\frac{g_s}{2\alpha_{ik}}, \qquad f\left(5, g_s\right) = \frac{1}{5!} z_s^5 + \frac{1}{24\alpha_{ik}} z_s^3 + \frac{1}{32\alpha_{ik}^2} z_s, \\ f\left(6, g_s\right) = \frac{1}{6!} z_s^6 + \frac{1}{96\alpha_{ik}} z_s^4 + \frac{1}{64\alpha_{ik}^2} z_s^2 + \frac{1}{384\alpha_{ik}^3}. \end{gathered} \tag{21}$$

Thus, all matrix elements for the s, p, d, f orbitals of ions are determined.

Particular cases

The matrix element of the operator H_{LR} on the $\left|p_z\left(\mathbf{r}\right)\right\rangle$ wave functions and at $F_2(\mathbf{g}) = 0,\ \mathbf{r}_0 = (x_0, 0, 0)$ according to (18) and (19) is expressed in terms of the function

$$\begin{gathered} F_{jb}\left(002\right) = \frac{1}{2v_c \pi^{1/2}} \sum_{i,k} a_i b_k \left(\frac{1}{\alpha_{ik}}\right)^{\frac{5}{2}} \exp\left(-\frac{\alpha_i \beta_k}{\alpha_{ik}} x_0^2\right) \sum_{n_x, n_y, n_z} \left[\frac{\pi^2}{\alpha_{ik}}\left(\frac{n_z}{c}\right)^2 - \frac{1}{2}\right] \\ \times \cos\left\{2\pi\left[\left(x_j - \frac{x_0 \beta_k}{\alpha_{ik}}\right) n_x + y_j n_y + z_j n_z\right]\right\} \frac{F_1\left(n_x, n_y, n_z\right)}{\left[\left(\frac{n_x}{a}\right)^2 + \left(\frac{n_y}{b}\right)^2 + \left(\frac{n_z}{c}\right)^2\right]} \\ \times \exp\left\{-\frac{\pi^2}{\alpha_{ik}}\left[\left(\frac{n_x}{a}\right)^2 + \left(\frac{n_y}{b}\right)^2 + \left(\frac{n_z}{c}\right)^2\right]\right\}, \end{gathered} \tag{22}$$

where $F_1(\mathbf{g}) \equiv F_1\left(n_x, n_y, n_z\right)$, $\mathbf{g} = \left(2\pi\, n_x / a, 2\pi\, n_y / b, 2\pi\, n_z / c\right)$, a,b,c are the lattice constants. The quantities x_j, y_j, z_j, x_0 in the argument of the cosine are given in relative units.

The one-center diagonal matrix elements calculated with the help of (20) are the energy E_j of the Coulomb interaction between the orbital electron located in the site $\mathbf{r}_j$ and the crystal lattice, including the interaction with the charge q_j located in the same site. At the same time, it is natural to refer the interaction between this electron and its nucleus to the Hartree-Fock energy [2-4]. In this case it is necessary to exclude the interaction between the considered electron and the charge q_j from the energy E_j, i.e., to introduce the quantity $E_j(\psi)$ defined as follows (in [9] it is denoted as E_{or}^{j})

$$E_j(\psi) = E_j - q_j E_0, \tag{23}$$

where E_0 is the interaction between the considered electron and the unit positive charge at the same site, ψ is the orbital. The energy E_0 can be expressed in terms of the $F_0\left(n_1 n_2 n_3\right)$ functions, which are determined by formula (3), if $\mathbf{r}_0 = 0$, $\mathbf{R} = 0$, $q_p = 1$. If it is taken into account that $F_0\left(n_1 n_2 n_3\right) \neq 0$ only when n_1, n_2, n_3 are even numbers, then, according to (7), we obtain

$$F_0\left(n_1 n_2 n_3\right) = -\frac{n_1! n_2! n_3!}{m_1! m_2! m_3!} \frac{m!}{2^m (2m+1)!!} \sum_{i,k} a_i a_k \left(\frac{1}{\alpha_{ik}}\right)^{1+m}, \tag{24}$$

where $n_1 = 2m_1, n_2 = 2m_2, n_3 = 2m_3$, $m = m_1 + m_2 + m_3$.

We write below the expressions $F_0\left(n_1 n_2 n_3\right)$, which are used further

$$\begin{gathered}
F_0(000) = -\sum_{i,k} a_i a_k \left(\frac{1}{\alpha_{ik}}\right), \qquad F_0(200) = F_0(020) = F_0(002) = -\frac{1}{3}\sum_{i,k} a_i a_k \left(\frac{1}{\alpha_{ik}}\right)^2, \\
F_0(220) = -\frac{2}{15}\sum_{i,k} a_i a_k \left(\frac{1}{\alpha_{ik}}\right)^3, \qquad F_0(400) = F_0(040) = -\frac{2}{5}\sum_{i,k} a_i a_k \left(\frac{1}{\alpha_{ik}}\right)^3.
\end{gathered} \tag{25}$$

According to (20) and (25), the energy of the interaction between the arbitrary *s*-orbital $E_j(s)$ and the lattice determined by (23) can be written as

$$E_j(s) = \frac{\pi^{\frac{1}{2}}}{4} \sum_{i,k} a_i a_k \left(\frac{1}{\alpha_{ik}}\right)^{\frac{3}{2}} \left[-\frac{4\pi}{v_c} \sum_{\mathbf{g}} \frac{G_j(\mathbf{g})}{\mathbf{g}^2} \exp\left(-\frac{\mathbf{g}^2}{4\alpha_{ik}}\right) + 2q_j \left(\frac{\alpha_{ik}}{\pi}\right)^{\frac{1}{2}} \right]. \tag{26}$$

Let us denote the expression in square brackets in (26) as $E_j^{(1)}(s)$ and assume $\alpha_{ik} = 2\alpha$ then

$$E_j^{(1)}(s) = -\frac{4\pi}{v_c} \sum_{\mathbf{g}} \frac{G_j(\mathbf{g})}{\mathbf{g}^2} \exp\left(-\frac{\mathbf{g}^2}{8\alpha}\right) + 2q_j \left(\frac{2\alpha}{\pi}\right)^{\frac{1}{2}}. \tag{27}$$

The expression (27) is the energy $E_j(s)$ for the *s*-orbital composed of an exponent with the index α [9]. The α_{or}^{j} value is determined in [9] analogous to the Madelung constant α_M. The constant α_{or}^{Na} for the NaCl crystal was calculated in [9] for different α values with the accuracy of up to 25 digits after the decimal point. For example,

$$\alpha = 0.1, \qquad \alpha_{or}^{Na} = 1.742978519833359388123262 9,$$

$$\alpha = 1, \qquad \alpha_{or}^{Na} = 1.7475645946331821906362119,$$

$$\alpha = 10 \text{ and } \alpha = 100, \qquad \alpha_{or}^{Na} = 1.7475645946331821906362120.$$

The Madelung constant α_M for NaCl calculated by direct summing in [12] with the accuracy of up to 25 digits after the decimal point is

$$\alpha_M = 1.7475645946331821906362120.$$

It is seen that one and the same number (with given accuracy) is in the expression (26) for the arbitrary *s*-orbital in square brackets if $\alpha_{ik} \geq 4$ ($\alpha \geq 2$) by the order of magnitude. In the case of NaCl, for such α_{ik} the energy $E_{Na}^{(1)}(s) = 0.32851544$ a.u. given with the accuracy of up to 8 digits after the decimal point coincides with the Madelung energy. The explanation of this fact is obvious. According to the Gauss theorem, if a spherically symmetric charge distribution does not overlap with a point charge, this charge distribution can be considered as the point charge as well.

Below we consider *p*-orbitals. According to (20), (23) and (25), the energy of the interaction between the p_x-orbital $E_j(p_x)$ with the crystal lattice can be written as

$$E_j(p_x) = \frac{3\pi^{\frac{1}{2}}}{8} \sum_{i,k} a_i a_k \left(\frac{1}{\alpha_{ik}}\right)^{\frac{5}{2}} \left[\frac{4\pi}{v_c} \sum_{\mathbf{g}} \left(\frac{g_x^2}{2\alpha_{ik}} - 1 \right) \frac{G_j(\mathbf{g})}{\mathbf{g}^2} \exp\left(-\frac{\mathbf{g}^2}{4\alpha_{ik}} \right) + \frac{4}{3} q_j \left(\frac{\alpha_{ik}}{\pi} \right)^{\frac{1}{2}} \right]. \tag{28}$$

The expression in square brackets in (28) is denoted as $E_j^{(1)}(p_x)$ and we assume $\alpha_{ik} = 2\alpha$ then

$$E_j^{(1)}(p_x) = \frac{4\pi}{v_c} \sum_{\mathbf{g}} \left(\frac{g_x^2}{4\alpha} - 1 \right) \frac{G_j(\mathbf{g})}{\mathbf{g}^2} \exp\left(-\frac{\mathbf{g}^2}{8\alpha} \right) + \frac{4}{3} q_j \left(\frac{2\alpha}{\pi} \right)^{\frac{1}{2}}. \tag{29}$$

The expression (29) is the energy $E_j(p_x)$ for the p_x-orbital composed of an exponent with the index α. Structural factors $G_j(\mathbf{g})$ for the NaCl and KMgF$_3$ crystals are given in [9]. The calculations according to the formula (29) for the Na ion in the case of the NaCl crystal for the values $\alpha = 1, 2, 5$ give the value $E_{Na}^{(1)}(p_x) = 0.32851544$ a.u., i.e., the Madelung energy. The calculations according to the formula (29) for the Mg ion in the case of the KMgF$_3$ crystal for the values $\alpha = 1, 2, 5$ give the value $E_{Mg}^{(1)}(p_x) = 0.82429794$ a.u., i.e., the Madelung energy [9]. The explanation of this fact is also obvious. The crystals are cubic and the quadrupole interaction for the p orbitals is zero. To calculate the energies of the p_y, p_z-orbitals, it is necessary to substitute the explicit variable g_x in (28) for the variables g_y, g_z, respectively.

For example, the interaction between the crystal lattice and the $\left| d_{xy}(\mathbf{r}) \right\rangle$ and $\left| d_{x^2-y^2}(\mathbf{r}) \right\rangle$ orbitals is determined following $F_j(n_1 n_2 n_3)$ functions:

$$F_j(400) = -\frac{3\pi^{\frac{3}{2}}}{v_c} \sum_{i,k} a_i a_k \left(\frac{1}{\alpha_{ik}}\right)^{\frac{7}{2}} \sum_{\mathbf{g}} \left(\frac{g_x^4}{24\alpha_{ik}^2} - \frac{g_x^2}{2\alpha_{ik}} + \frac{1}{2} \right) \frac{G_j(\mathbf{g})}{\mathbf{g}^2} \exp\left(-\frac{\mathbf{g}^2}{4\alpha_{ik}} \right). \tag{30}$$

The $F_j\left(040\right)$ function is obtained by substituting the explicit variable g_x in (30) for the variable g_y.

$$F_j\left(220\right)=-\frac{\pi^{\frac{3}{2}}}{2v_c}\sum_{i,k}a_i a_k\left(\frac{1}{\alpha_{ik}}\right)^{\frac{7}{2}}\sum_{\mathbf{g}}\left(\frac{g_x^2}{2\alpha_{ik}}-1\right)\left(\frac{g_y^2}{2\alpha_{ik}}-1\right)\frac{G_j\left(\mathbf{g}\right)}{\mathbf{g}^2}\exp\left(-\frac{\mathbf{g}^2}{4\alpha_{ik}}\right). \qquad (31)$$

In conclusion of this section, we present the expression for the $F_j\left(n_1n_2n_3\right)$ functions in which numerical integration is used. It can be useful when the α_{ik} values are rather large

$$\begin{gathered}F_j\left(n_1n_2n_3\right)=-\frac{\pi^{\frac{3}{2}}}{v_c}n_1!n_2!n_3!\sum_p q_p\sum_{i,k}a_i b_k\left(\frac{1}{\alpha_{ik}}\right)^{\frac{5}{2}}\int_0^1 du\left(\frac{1}{u}\right)^3 \\ \times\left\{\prod_{s=1}^{3}\left[\sum_{g_s}f\left(n_s,g_s\right)\exp\left(-\frac{g_s^2}{4\alpha_{ik}u^2}+ig_s\left(x_{js}-x_{ps}\right)\right)\right]-f\left(n_1,0\right)f\left(n_2,0\right)f\left(n_3,0\right)\right\},\end{gathered} \qquad (32)$$

where $x_{j1}=x_j, x_{j2}=y_j, x_{j3}=z_j$ are the coordinates of the vector $\mathbf{r}_j$ and analogously x_{ps} are the coordinates of the vector $\mathbf{r}_p$. The second term in the formula (32) eliminates the divergence at $\mathbf{g}=0$. If the expression (20) is called the “exact value”, then the formula (32) gives the values which in the most cases coincide with this “exact value” to 8-10 digits after the decimal point already in the calculations with the accuracy set in the programs by default.

3. Discussion

The above TME and OME of the LR Coulomb interaction between the electron and the infinite crystal lattice arise naturally within the approach of [1-4]. The comments about TME follow. For ion crystals or admixture centers in ion crystals, TME is small when the region of the overlap of anion and cation orbitals coincides with the region of the change of the electrostatic potential sign. However, if the average values $\langle r\rangle$ of the orbitals of ions considerably differ, the value of these matrix elements may be noticeable and they have to be taken into account in the ab initio calculations. In our opinion, the two-center matrix elements should be also estimated in the calculation of the amplitudes of the charge transfer over the anion or cation sublattice, since the overlap region fits the region of the constant electrostatic potential sign. For example, the amplitudes of the transition over the oxygen sublattice of La_2CuO_4 were calculated in [13]. The value of these amplitudes is within $0.4\div0.6\,\mathrm{eV}$ but only the short-range interaction in taken into account. At the same time, for α'-NaV_2O_5 according to (19) and (22) the value of the corrections from the long-range Coulomb interaction over the σ-bond $\approx-0.105\,\mathrm{eV}$, and that over the π-bond $\approx 0.174\,\mathrm{eV}$. Thus, in the general case the long-range Coulomb interaction should be estimated when such amplitudes are calculated.

Conclusions

In the general case, the U-region around the admixture ion or the unit cell determined above is several coordination spheres, where the short-range interactions can be written exactly. Formulas obtained in this work allow one to rather exactly take into account the long-range Coulomb interaction as well. Hence, we obtained a method for the ab initio calculation of physical quantities in the U-region, at least at rather small overlap integrals needing no introduction of any parameters.

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