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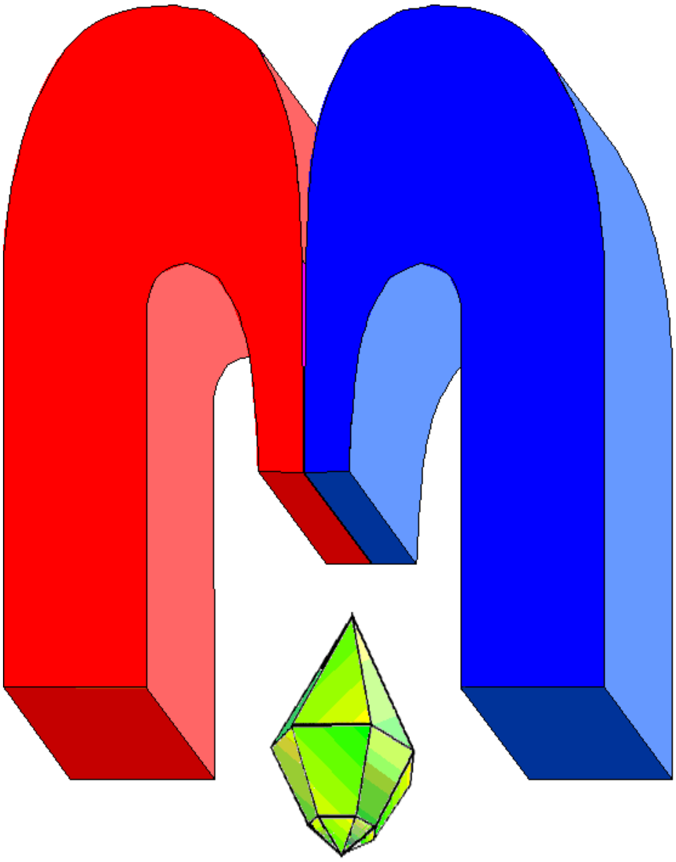

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* In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

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Calculation of the matrix elements of the long-range Coulomb interaction in low-symmetry crystals

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The expressions for calculating the matrix elements of the Coulomb interaction between an electron and a low-symmetry infinite crystal lattice have been obtained. One-center matrix elements are considered. The Gaussian type of orbitals (GTO) is used in calculations. All expressions are absolutely and rapidly converging series in the space of reciprocal lattice vectors.

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1. Introduction.

Currently, the value of the long-range Coulomb interaction (LRCI), i.e. Coulomb interaction between an electron and an infinite crystal lattice in the case of low symmetry is estimated using the Madelung constant, in other words, by calculating the electrostatic potential at the lattice site, i.e., a point [1-4]. The expressions for calculating the LRCI matrix elements in the case of orthorhombic lattices are given in [5]. Using the results [5], the expressions were obtained in [6] for calculating the LRCI matrix elements on *p* and *d*-orbitals and the crystal NaV_2O_5 was considered. For this crystal, in particular, the Madelung energies and diagonal matrix elements on *p* and *d* orbitals were calculated. If for vanadium ions the values of these quantities coincide well enough, they differ markedly for oxygen ions. For example, the following estimates were obtained for one of the oxygen ions: $E_M = -1.18856$ a.u., $E(p_z) = -0.96122$ a.u. The difference between these quantities is on the order of 6 eV. The energy of p_x, p_y orbitals is $E(p_x) = -1.02686$ a.u., $E(p_y) = -1.18351$ a.u, respectively. Thus, the splitting of the diagonal matrix elements is on the order of 2-6 eV.

The LRCI matrix elements enter, for example, the expressions for the ab initio calculations of the amplitudes of electron transfer between ions [7]. It can be seen that the LRCI estimates for the transition amplitudes in a given crystal by the methods [1-4] can lead to the incorrect interpretation of the experimental data. In [8], the expressions were obtained for calculating the LRCI matrix elements on *f*-orbitals. The expressions obtained were used in estimating the crystal field parameters for the impurity centers considered in [8]. The improvement in agreement with experiment was obtained in comparison with standard methods. In this paper we obtain expressions for the calculation of such matrix elements in the case of low symmetry.

2. General part

Let the radial part $R_{nl}(r)$ of the ionic orbital $\psi_{nlm}(\mathbf{r})$ on which the electron is located, have the Gaussian type of orbitals (GTO) form

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

Let the vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ are the vectors of the cell of the triclinic lattice. We denote by $\mathbf{R}_l = l_1\mathbf{a}_1 + l_2\mathbf{a}_2 + l_3\mathbf{a}_3$ the vector determining the position of the unit cell, a $\mathbf{r}_j$ and $\mathbf{r}_p$ are vectors of ions in the unit cell. We consider the isolated ion determined by the vectors $\mathbf{R}_0 + \mathbf{r}_j, \mathbf{R}_0 = 0.$ The charge q_p is in the site $\mathbf{R}_l + \mathbf{r}_p$. Then the matrix element of the Coulomb interaction of an electron with a charge

q_p defined on the wave functions of the isolated ion has the form (in a.u.) [5, 8]

$$\int \psi_\xi^*\left(\mathbf{r}-\mathbf{r}_j\right)\left(-q_p\left|\mathbf{r}-\left(\mathbf{R}_l+\mathbf{r}_p\right)\right|^{-1}\right)\psi_{\xi'}\left(\mathbf{r}-\mathbf{r}_j\right)dV=\int \psi_\xi^*\left(\mathbf{r}\right)\left(-q_p\left|\mathbf{r}-\left(\mathbf{R}_l+\mathbf{r}_p-\mathbf{r}_j\right)\right|^{-1}\right)\psi_{\xi'}\left(\mathbf{r}\right)dV. \tag{2}$$

Let us denote $\mathbf{R}=\mathbf{R}_l+\mathbf{r}_p-\mathbf{r}_j$. We define the functions $F_{p,j}^l\left(n_1n_2n_3\right)$ as

$$2\pi F_{p,j}^l\left(n_1n_2n_3\right)=-q_p\sum_{i,k}a_ib_k\int x^{n_1}y^{n_2}z^{n_3}\left|\mathbf{r}-\mathbf{R}\right|^{-1}\exp\left[-\left(\alpha_i+\beta_k\right)\mathbf{r}^2\right]dxdydz. \tag{3}$$

The matrix elements (2) on the orbitals of the isolated ion can be expressed in terms of the $F_{p,j}^l\left(n_1n_2n_3\right)$ functions. For example, the matrix element for the $\psi_{pz}\left(\mathbf{r}\right)=\left(3/4\pi\right)^{1/2}\sum a_iz\exp\left(-\alpha_ir^2\right)$ orbital has the form

$$\int \psi_{pz}^*\left(\mathbf{r}\right)\left(-q_p\left|\mathbf{r}-\mathbf{R}\right|^{-1}\right)\psi_{pz}\left(\mathbf{r}\right)dV=\frac{3}{2}F\left(002\right).$$

We write the unit vectors of the triclinic lattice with respect to the Cartesian coordinate system in the form

$$\mathbf{a}_1=a\mathbf{e}_1,\qquad \mathbf{a}_2=b\mathbf{e}_2,\qquad \mathbf{a}_3=c\mathbf{e}_3, \tag{4}$$

$$\mathbf{e}_1=\mathbf{i},\qquad \mathbf{e}_2=\cos\alpha\,\mathbf{i}+\sin\alpha\,\mathbf{j},\qquad \mathbf{e}_3=\sin\theta\cos\varphi\,\mathbf{i}+\sin\theta\sin\varphi\,\mathbf{j}+\cos\theta\,\mathbf{k}. \tag{5}$$

Then for the $\mathbf{R}_l$, $\mathbf{r}_p$, $\mathbf{r}_j$ vectors we obtain the expressions

$$\begin{aligned}\mathbf{R}_l&=l_1\mathbf{a}_1+l_2\mathbf{a}_2+l_3\mathbf{a}_3=\\&=\left(l_1a+l_2b\cos\alpha+l_3c\sin\theta\cos\varphi\right)\mathbf{i}+\left(l_2b\sin\alpha+l_3c\sin\theta\sin\varphi\right)\mathbf{j}+l_3c\cos\theta\,\mathbf{k},\end{aligned} \tag{6}$$

$$\begin{aligned}\mathbf{r}_p&=x_p\mathbf{a}_1+y_p\mathbf{a}_2+z_p\mathbf{a}_3=\\&=\left(x_pa+y_pb\cos\alpha+z_pc\sin\theta\cos\varphi\right)\mathbf{i}+\left(y_pb\sin\alpha+z_pc\sin\theta\sin\varphi\right)\mathbf{j}+z_pc\cos\theta\,\mathbf{k},\end{aligned} \tag{7}$$

$$\begin{aligned}\mathbf{r}_j&=x_j\mathbf{a}_1+y_j\mathbf{a}_2+z_j\mathbf{a}_3=\\&=\left(x_ja+y_jb\cos\alpha+z_jc\sin\theta\cos\varphi\right)\mathbf{i}+\left(y_jb\sin\alpha+z_jc\sin\theta\sin\varphi\right)\mathbf{j}+z_jc\cos\theta\,\mathbf{k}.\end{aligned} \tag{8}$$

The components of the $\left[\mathbf{r}-\left(\mathbf{R}_l+\mathbf{r}_p-\mathbf{r}_j\right)\right]$ vector in the Cartesian coordinate system according to (6)-(8) are written as

$$x-\left[\left(l_1+x_p-x_j\right)a+\left(l_2+y_p-y_j\right)b\cos\alpha+\left(l_3+z_p-z_j\right)c\sin\theta\cos\varphi\right]=x-A_1, \tag{9}$$

$$y-\left[\left(l_2+y_p-y_j\right)b\sin\alpha+\left(l_3+z_p-z_j\right)c\sin\theta\sin\varphi\right]=y-A_2, \tag{10}$$

$$z-\left(l_3+z_p-z_j\right)c\cos\theta=z-A_3. \tag{11}$$

Further we present the function $F_{p,j}^l\left(n_1n_2n_3\right)$ in the form convenient for calculations. To do this, we use the transformation

$$\frac{1}{\left|\mathbf{r}-\mathbf{R}\right|}=\frac{2}{\sqrt{\pi}}\int_0^\infty dv\exp\left[-\left(\mathbf{r}-\mathbf{R}\right)^2v^2\right]. \tag{12}$$

After the transformation (12) and integration with respect to x, y, z in (3), we obtain

$$\begin{aligned}F_{p,j}^l\left(n_1n_2n_3\right)=-q_p\sum_{i,k}a_ib_k\int_0^\infty\frac{dv}{\left(\alpha_{ik}+v^2\right)^{3/2}}\prod_{s=1}^{3}\left\{n_s!\sum_{m_s=0}^{\left[n_s/2\right]}\frac{\left(A_sv^2\right)^{n_s-2m_s}}{4^{m_s}m_s!\left(n_s-2m_s\right)!\left(\alpha_{ik}+v^2\right)^{n_s-m_s}}\right\}\\\times\exp\left[-\left(\sum_{w=1}^{3}A_w^2\right)\frac{\alpha_{ik}v^2}{\alpha_{ik}+v^2}\right],\end{aligned} \tag{13}$$

where $\alpha_{ik}=\alpha_i+\beta_k$, $\left[n_s/2\right]$ is the integer part of the number in brackets $n_s/2$.

Using the transformation

$$v^2=\frac{\alpha_{ik}u^2}{1-u^2},\qquad \frac{dv}{\left(\alpha_{ik}+v^2\right)^{3/2}}=\frac{du}{\alpha_{ik}} \tag{14}$$

we obtain

$$F^{l}_{p,j}\left(n_1n_2n_3\right)=-q_p\sum_{i,k}\frac{a_ib_k}{\alpha_{ik}}\int_0^1 du\prod_{s=1}^{3}\left\{n_s!\sum_{m_s=0}^{[n_s/2]}\frac{\left(1-u^2\right)^{m_s}\left(A_su^2\right)^{n_s-2m_s}}{\left(4\alpha_{ik}\right)^{m_s}m_s!\left(n_s-2m_s\right)!}\right\}\exp\left[-\alpha_{ik}u^2\left(\sum_{w=1}^{3}A_w^2\right)\right]. \tag{15}$$

Let us $k_s=n_s-2m_s$. After multiplying the three braces in (15), we select the products

$$A_1^{k_1}A_2^{k_2}A_3^{k_3}\exp\left[-\alpha_{ik}u^2\left(A_1^2+A_2^2+A_3^2\right)\right], \tag{16}$$

which are present in each term of the resulting sum. We introduce the $\tilde{\mathbf{r}}=\left(x,y,z\right)$ vector setting $\left(x_p-x_j\right)a=x, \left(y_p-y_j\right)b=y, \left(z_p-z_j\right)c=z.$ Then A_i are written as

$$A_1=\left(l_1a+x\right)+\left(l_2b+y\right)\cos\alpha+\left(l_3c+z\right)\sin\theta\cos\varphi, \tag{17}$$

$$A_2=\left(l_2b+y\right)\sin\alpha+\left(l_3c+z\right)\sin\theta\sin\varphi,\quad A_3=\left(l_3c+z\right)\cos\theta. \tag{18}$$

Since the positions of the ions in the unit cell are arbitrary, we assume that the $\tilde{\mathbf{r}}=\left(x,y,z\right)$ vector is defined at all points of the unit cell. We introduce the function $D\left(\tilde{\mathbf{r}},k_1,k_2,k_3\right)$ defined in the unit cell

$$D\left(\tilde{\mathbf{r}},k_1,k_2,k_3\right)=\sum_{l_1,l_2,l_3}A_1^{k_1}A_2^{k_2}A_3^{k_3}\exp\left[-\alpha_{ik}u^2\left(A_1^2+A_2^2+A_3^2\right)\right]. \tag{19}$$

The function $D\left(\tilde{\mathbf{r}},k_1,k_2,k_3\right)$ is a periodic function of $\tilde{\mathbf{r}}$, in the space with elementary translations a, b, c of the orthorhombic system. The same as in [5], integration over the unit cell can be transformed into integration over the whole space when finding the Fourier transform of the function $D\left(\tilde{\mathbf{r}},k_1,k_2,k_3\right)$. Then we have

$$D\left(\tilde{\mathbf{r}},k_1,k_2,k_3\right)=\sum_{\mathbf{g}}D\left(\mathbf{g},k_1,k_2,k_3\right)\exp\left[i\left(\mathbf{g}\tilde{\mathbf{r}}\right)\right], \tag{20}$$

$$D\left(\mathbf{g},k_1,k_2,k_3\right)=\frac{1}{\overline{v}_c}\int_V x_1^{k_1}x_2^{k_2}x_3^{k_3}\exp\left\{-\alpha_{ik}\left[x_1^2+x_2^2+x_3^2\right]u^2-i\left(g_xx+g_yy+g_zz\right)\right\}dxdydz, \tag{21}$$

$$x_1=x+y\cos\alpha+z\sin\theta\cos\varphi,\quad x_2=y\sin\alpha+z\sin\theta\sin\varphi,\quad x_3=z\cos\theta, \tag{22}$$

$$g_x=\frac{2\pi n_x}{a},\quad g_y=\frac{2\pi n_y}{b},\quad g_z=\frac{2\pi n_z}{c}, \tag{23}$$

where $\overline{v}_c=abc$ is the volume of the unit cell of the orthorhombic system, **g** is the reciprocal lattice vector, n_x, n_y, n_z are integer numbers, *i* is the imaginary unit. We introduce new integration variables x_1, x_2, x_3. Then (21) will be written as

$$D\left(\mathbf{g},k_1,k_2,k_3\right)=\frac{1}{v_c}\int_V x_1^{k_1}x_2^{k_2}x_3^{k_3}\exp\left\{-\alpha_{ik}\left[x_1^2+x_2^2+x_3^2\right]u^2-i\left(\tilde{g}_1x_1+\tilde{g}_2x_2+\tilde{g}_3x_3\right)\right\}dx_1dx_2dx_3, \tag{24}$$

where $v_c=abc\sin\alpha\cos\theta$ is the volume of the unit cell of the triclinic symmetry crystal under consideration, and

$$\tilde{g}_1=g_x,\quad \tilde{g}_2=\frac{-\cos\alpha g_x+g_y}{\sin\alpha},\quad \tilde{g}_3=\frac{\sin\theta\sin\left(\varphi-\alpha\right)g_x-\sin\theta\sin\varphi g_y+\sin\alpha g_z}{\sin\alpha\cos\theta}. \tag{25}$$

Performing the integration in (24), we obtain

$$D\left(\mathbf{g},k_1,k_2,k_3\right)=\frac{\pi^{3/2}}{v_c u^3\alpha_{ik}^{3/2}}\exp\left(-\frac{\tilde{g}^2}{4\alpha_{ik}u^2}\right)\prod_{s=1}^{3}\left\{\frac{k_s!}{2^{k_s}}\sum_{h_s=0}^{[k_s/2]}\frac{\left(-i\tilde{g}_s\right)^{k_s-2h_s}}{h_s!\left(k_s-2h_s\right)!\left(\alpha_{ik}u^2\right)^{k_s-h_s}}\right\}. \tag{26}$$

We introduce the function $F\left(n_1n_2n_3\,|\,\tilde{\mathbf{r}}\right)$, using the expressions (15), (20), (26).

$$\begin{aligned}F\left(n_1n_2n_3\,|\,\tilde{\mathbf{r}}\right)=&-\frac{q_p\pi^{3/2}}{v_c}\sum_{i,k}\frac{a_ib_k}{\alpha_{ik}^{5/2}}\int_0^1\frac{du}{u^3}\prod_{s=1}^{3}\left\{n_s!\sum_{m_s=0}^{[n_s/2]}\frac{\left(1-u^2\right)^{m_s}}{\left(4\alpha_{ik}\right)^{m_s}m_s!}\right.\\&\left.\times\sum_{h_s=0}^{\left[\frac{n_s-2m_s}{2}\right]}\frac{Z_s^{\,n_s-2m_s-2h_s}}{h_s!\left(n_s-2m_s-2h_s\right)!}\left(\frac{u^2}{4\alpha_{ik}}\right)^{h_s}\right\}\exp\left(-\frac{\tilde{g}^2}{4\alpha_{ik}u^2}+i\mathbf{g}\tilde{\mathbf{r}}\right),\end{aligned} \tag{27}$$

where $Z_s=-\,i\tilde{g}_s/2\alpha_{ik}$.

We substitute $x=\left(x_p-x_j\right)a,\ y=\left(y_p-y_j\right)b,\ z=\left(z_p-z_j\right)c$ into the expression obtained (27) and perform the summation over the $\tilde{\mathbf{r}}_p=\left(x_pa,\ y_pb,\ z_pc\right)$ vectors of the unit cell. These transformations are cumbersome, but fairly simple and analogous to the transformations in [5, 6] for the orthorhombic lattice. As a result, we obtain

$$\begin{aligned}F_j\left(n_1n_2n_3\right)=&\sum_p F\left(n_1n_2n_3\left|\tilde{\mathbf{r}}_p-\tilde{\mathbf{r}}_j\right.\right)=-\frac{\pi^{3/2}}{v_c}n_1!n_2!n_3!\sum_{i,k}\frac{a_ib_k}{\alpha_{ik}^{5/2}}\int_0^1\frac{du}{u^3}\\&\times\sum_{\mathbf{g}}f\left(n_1,\tilde{g}_1\right)f\left(n_2,\tilde{g}_2\right)f\left(n_3,\tilde{g}_3\right)\exp\left(-\frac{\tilde{g}^2}{4\alpha_{ik}u^2}\right)\left(\sum_p q_p\exp\left[i\mathbf{g}\left(\tilde{\mathbf{r}}_p-\tilde{\mathbf{r}}_j\right)\right]\right),\end{aligned} \tag{28}$$

where $\mathbf{g}\left(\tilde{\mathbf{r}}_p-\tilde{\mathbf{r}}_j\right)=g_x\left(x_p-x_j\right)a+g_y\left(y_p-y_j\right)b+g_z\left(z_p-z_j\right)c$,

$$f\left(n_s,\tilde{g}_s\right)=\sum_{m_s=0}^{[n_s/2]}\frac{\left(1-u^2\right)^{m_s}}{\left(4\alpha_{ik}\right)^{m_s}m_s!}\sum_{h_s=0}^{\left[\frac{n_s-2m_s}{2}\right]}\frac{Z_s^{\,n_s-2m_s-2h_s}}{h_s!\left(n_s-2m_s-2h_s\right)!}\left(\frac{u^2}{4\alpha_{ik}}\right)^{h_s}=\sum_{t=0}^{[n/2]}\frac{Z_s^{n-2t}}{t!\left(n-2t\right)!}\left(\frac{1}{4\alpha_{ik}}\right)^t. \tag{29}$$

For example $f\left(0,\tilde{g}_s\right)=1$, $f\left(1,\tilde{g}_s\right)=Z_s$, $f\left(2,\tilde{g}_s\right)=\frac{1}{2!}Z_s^2+\frac{1}{4\alpha_{ik}}$, $f\left(3,\tilde{g}_s\right)=\frac{1}{3!}Z_s^3+\frac{1}{4\alpha_{ik}}Z_s$, $f\left(4,\tilde{g}_s\right)=\frac{1}{4!}Z_s^4+\frac{1}{8\alpha_{ik}}Z_s^2+\frac{1}{32\alpha_{ik}^2}$.

It can be seen that the functions $f\left(n_s,\tilde{g}_s\right)$ do not depend on the integration variable *u*. We call the sum over *p* in parentheses in (28) as the structure factor $G_j\left(\mathbf{g}\right)$ and present it in the form

$$G_j\left(\mathbf{g}\right)=G_j^{(1)}\left(\mathbf{g}\right)+iG_j^{(2)}\left(\mathbf{g}\right)=\sum_p q_p\exp\left[i\mathbf{g}\left(\tilde{\mathbf{r}}_p-\tilde{\mathbf{r}}_j\right)\right],\quad G_j^{(1)}\left(\mathbf{g}\right)=\cos\left(\mathbf{g}\tilde{\mathbf{r}}_j\right)F_1\left(\mathbf{g}\right)+\sin\left(\mathbf{g}\tilde{\mathbf{r}}_j\right)F_2\left(\mathbf{g}\right), \tag{30}$$

$$G_j^{(2)}\left(\mathbf{g}\right)=\cos\left(\mathbf{g}\tilde{\mathbf{r}}_j\right)F_2\left(\mathbf{g}\right)-\sin\left(\mathbf{g}\tilde{\mathbf{r}}_j\right)F_1\left(\mathbf{g}\right),\quad F_1\left(\mathbf{g}\right)=\sum_p q_p\cos\left(\mathbf{g}\tilde{\mathbf{r}}_p\right),\ F_2\left(\mathbf{g}\right)=\sum_p q_p\sin\left(\mathbf{g}\tilde{\mathbf{r}}_p\right). \tag{31}$$

Substituting (30), (31) into (28), and integrating over *u*, we obtain the final expression for the function $F_j\left(n_1n_2n_3\right)$:

$$F_j\left(n_1n_2n_3\right)=-\frac{2\pi^{3/2}}{v_c}n_1!n_2!n_3!\sum_{i,k}\frac{a_ib_k}{\alpha_{ik}^{3/2}}\sum_{\mathbf{g}}f\left(n_1,\tilde{g}_1\right)f\left(n_2,\tilde{g}_2\right)f\left(n_3,\tilde{g}_3\right)\exp\left(-\frac{\tilde{g}^2}{4\alpha_{ik}}\right)\frac{G_j\left(\mathbf{g}\right)}{\tilde{g}^2}. \tag{32}$$

It can be seen that the structural factor $G_j(\mathbf{g})$ is the invariant of deformations, under which the difference of the relative coordinates is constant.

We denote the LRCI Hamiltonian as H_{LR}. Then the matrix element H_{LR} on orbitals $\psi_\xi(\mathbf{r}-\mathbf{r}_j), \psi_{\xi'}(\mathbf{r}-\mathbf{r}_j)$ is written as

$$\int \psi_\xi^*(\mathbf{r}-\mathbf{r}_j) H_{LR} \psi_{\xi'}(\mathbf{r}-\mathbf{r}_j)\,dV = \int \psi_\xi^*(\mathbf{r}-\mathbf{r}_j)\left(-\sum_{l,p}{}' q_p \left|\mathbf{r}-\left(\mathbf{R}_l+\mathbf{r}_p\right)\right|^{-1}\right)\psi_{\xi'}(\mathbf{r}-\mathbf{r}_j)\,dV. \tag{33}$$

The stroke denotes that in the case $\xi = \xi'$ the term corresponding to the interaction of the charge q_j with the electron on the orbital $\psi_\xi(\mathbf{r}-\mathbf{r}_j)$ is absent in the sum.

As an example, we give the expression for the diagonal matrix element of the Hamiltonian H_{LR} in the case of the $\psi_{px}(\mathbf{r}) = (3/4\pi)^{1/2}\sum a_i x \exp(-\alpha_i r^2)$ orbital [6]:

$$\begin{aligned}\int \psi_{px}^*(\mathbf{r}-\mathbf{r}_j) H_{LR}\, \psi_{px}(\mathbf{r}-\mathbf{r}_j)\,dV &= \frac{3\pi^{1/2}}{2}\sum_{i,k}\frac{a_i a_k}{\alpha_{ik}^{5/2}} \\ &\times\left[\frac{\pi}{v_c}\sum_{\mathbf{g}}\left(\frac{\tilde{g}_1^2}{2\alpha_{ik}}-1\right)\frac{G_j(\mathbf{g})}{\tilde{g}^2}\exp\left(-\frac{\tilde{g}^2}{4\alpha_{ik}}\right)+\frac{1}{3}q_j\left(\frac{\alpha_{ik}}{\pi}\right)^{1/2}\right].\end{aligned} \tag{34}$$

The diagonal matrix elements on the $\psi_{py}(\mathbf{r})$, $\psi_{pz}(\mathbf{r})$ orbitals can be obtained from (34) by replacing $\tilde{g}_1$ by $\tilde{g}_2, \tilde{g}_3$, respectively.

3. Double-oblique crystal

As the first step, we perform test calculations on *s*-orbitals. According to [5], the energy of the *s*-orbital $E_j(s)$ determined by (32) can be written as

$$E_j(s) = \frac{\pi^{1/2}}{4}\sum_{i,k}\frac{a_i a_k}{\alpha_{ik}^{3/2}}\left[-\frac{4\pi}{v_c}\sum_{\mathbf{g}}\frac{G_j(\mathbf{g})}{\tilde{g}^2}\exp\left(-\frac{\tilde{g}^2}{4\alpha_{ik}}\right)+2q_j\left(\frac{\alpha_{ik}}{\pi}\right)^{1/2}\right]. \tag{35}$$

We denote the expression in square brackets in formula (35) as $E_j^{(1)}(s)$ and put $\alpha_{ik} = 2\varepsilon$.

$$E_j^{(1)}(s) = -\frac{4\pi}{v_c}\sum_{\mathbf{g}}\frac{G_j(\mathbf{g})}{\tilde{g}^2}\exp\left(-\frac{\tilde{g}^2}{8\varepsilon}\right)+2q_j\left(\frac{2\varepsilon}{\pi}\right)^{1/2}. \tag{36}$$

The expression (36) is the energy of the one-exponential *s*-orbital with exponent ε, $\psi_{1s} = (1/4\pi)^{1/2} a \exp\left(-\varepsilon r^2\right)$, $a = 2\left(8\varepsilon^3/\pi\right)^{1/4}$.

We assume the angle $\theta = 0$ and α is an arbitrary angle. We determine the ion charge and the basis vectors of the unit cell of the crystal in relative units as $q_1 = 1$, $\mathbf{r}_1(0,0,0)$, $q_2 = -1$, $\mathbf{r}_2(a/2, b/2, c/2)$. The energy $E_j^{(1)}(s)$ for such lattice is written as

$$E_1^{(1)}(s) = -\frac{\sin\alpha}{abc\pi}\sum_{\mathbf{n}\neq 0}\frac{1-(-1)^{n_x+n_y+n_z}}{d_1}\exp\left[-\frac{\pi^2 d_1}{2\varepsilon\sin^2\alpha}\right]+2q_j\left(\frac{2\varepsilon}{\pi}\right)^{1/2}, \tag{37}$$

where $d_1 = \frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}-\frac{2n_x n_y}{ab}\cos\alpha+\frac{n_z^2}{c^2}\sin^2\alpha.$

For $a = b$ and $\alpha = 120^\circ$ we obtain the expression

$$E_1^{(1)}(s) = -\frac{\sqrt{3}}{2\pi c}\sum_{\mathbf{n}\neq 0}\frac{1-(-1)^{n_x+n_y+n_z}}{d_2}\exp\left[-\frac{2\pi^2 d_2}{3\varepsilon a^2}\right] + 2q_j\left(\frac{2\varepsilon}{\pi}\right)^{1/2}, \tag{38}$$

where $d_2 = n_x^2 + n_y^2 + n_x n_y + \dfrac{3a^2 n_z^2}{4c^2}$.

Let $a = b = c = 7.838587$ be constant lattices. Then according to (38) we obtain

$$\varepsilon = 2:\quad E_j^{(1)}(s) = 0.291432860377413,$$

$$\varepsilon = 8:\quad E_j^{(1)}(s) = 0.291432860377413.$$

It can be seen that the energy $E_j^{(1)}(s)$ for the exponent $\varepsilon \geq 2$ is the same (with the given accuracy). The explanation of this fact is obvious. According to Gauss's theorem, if the spherically symmetric charge distribution does not overlap with a point charge, then this charge distribution can be regarded as a point charge.

Let $a = b = c = 7.838587$ be lattice constants, and $\alpha = 120^\circ$, $\varphi = 60^\circ$ and $\theta = 60^\circ$ the angles of the unit cell. The expressions (25) for the $\tilde{\mathbf{g}}$ vector are

$$\tilde{g}_1 = g_x, \qquad \tilde{g}_2 = \frac{1}{\sqrt{3}}\left(g_x + 2g_y\right), \qquad \tilde{g}_3 = -\sqrt{3}g_x - \sqrt{3}g_y + 2g_z. \tag{39}$$

Substituting these lattice constants and the expressions (39) into (36), we obtain

$$E_1^{(1)}(s) = -\frac{4\sqrt{3}}{a\pi}\sum_{\mathbf{n}\neq 0}\frac{1-(-1)^{n_x+n_y+n_z}}{d_3}\exp\left\{-\frac{\pi^2 d_3}{6a\varepsilon}\right\} + 2q_j\left(\frac{2\varepsilon}{\pi}\right)^{1/2}, \tag{40}$$

where $d_3 = 13\left(n_x^2 + n_y^2\right) + 22n_x n_y + 12n_z\left(n_z - \sqrt{3}\,n_x - \sqrt{3}\,n_y\right)$.

$$\varepsilon = 4:\quad E_j^{(1)}(s) = 0.68670778474898,$$

$$\varepsilon = 20:\quad E_j^{(1)}(s) = 0.68670778474898.$$

It is seen that the energy $E_j^{(1)}(s)$ is the same (with the given accuracy) for the values $\varepsilon \geq 4$.

4. BaTiO$_3$ crystal

We consider the application of the obtained expression (36) to the hexagonal BaTiO$_3$ structure. According to [9], the lattice constants are $a = b = 5.7238$ Å, $c = 13.9649$ Å. The basis vectors of the unit cell ions in relative units have the form

Ba$_1$: (0, 0, 0.25),	Ba$_2$: (1/3, 2/3, 0.09671),	Ba$_3$: (1/3, 2/3, 0.40329),
Ba$_4$: (2/3, 1/3, 0.59671),	Ba$_5$: (0, 0, 0.75),	Ba$_6$: (2/3, 1/3, 0.90329),
Ti$_1$: (0, 0, 0),	Ti$_2$: (2/3, 1/3, 0.15367),	Ti$_3$: (2/3, 1/3, 0.34633),
Ti$_4$: (0, 0, 0.5),	Ti$_5$: (1/3, 2/3, 0.65367),	Ti$_6$: (1/3, 2/3, 0.84633),
O$_1$: (0.3302, 0.1651, 0.0802),	O$_2$: (0.8349, 0.1651, 0.0802),	O$_3$: (0.8349, 0.6698, 0.0802),
O$_4$: (0.51849, 0.03699, 0.25),	O$_5$: (0.96301, 0.48151, 0.25),	O$_6$: (0.51849, 0.48151, 0.25),
O$_7$: (0.3302, 0.1651, 0.4198),	O$_8$: (0.84903, 0.1651, 0.4198),	O$_9$: (0.8349, 0.6698, 0.4198),
O$_{10}$: (0.1651, 0.3302, 0.5802),	O$_{11}$: (0.6698, 0.83490, 0.58020),	O$_{12}$: (0.1651, 0.8349, 0.5802),
O$_{13}$: (0.03699, 0.51849, 0.75),	O$_{14}$: (0.48151, 0.51849, 0.75),	O$_{15}$: (0.48151, 0.96301, 0.75),
O$_{16}$: (0.1651, 0.3302, 0.9198),	O$_{17}$: (0.6698, 0.8349, 0.9198),	O$_{18}$: (0.1651, 0.8349, 0.91980).

For BaTiO3 $F_2(\mathbf{g})=0$, and $F_1(\mathbf{g})$ has the form

$$
\begin{aligned}
F_1(\mathbf{g}) = {} & 4\Big\{ 1+(-1)^{n_z}+4(-1)^{n_x+n_y+n_z}\cos\big[\pi\big(n_x/3-n_y/3-n_z/2\big)\big]\cos\big[\pi\big(0.19266n_z\big)\big]\Big\}+ \\
& +4\Big\{ (-1)^{n_z}\cos\big(\pi\, n_z/2\big)+2(-1)^{n_x+n_y+n_z}\cos\big[\pi\big(n_x/3-n_y/3+n_z/2\big)\big]\cos\big[\pi\big(0.30658n_z\big)\big]\Big\} \\
& -4(-1)^{n_x+n_y+n_z}\Big\{ \cos\big[\pi\big(0.03698\big(n_x-n_y\big)-0.5n_z\big)\big]+2\cos\big[\pi\big(0.4815\big(n_x-n_y\big)-0.5n_z\big)\big] \\
& \times\cos\big[0.44452\pi\big(n_x+n_y\big)\big]+2\cos\big[\pi\big(0.3396n_z\big)\big]\Big\{ \cos\big[\pi\big(0.6698\big(n_x-n_y\big)-0.5n_z\big)\big] \\
& +2\cos\big[0.5047\pi\big(n_x+n_y\big)\big]\cos\big[\pi\big(0.1651\big(n_x-n_y\big)-0.5n_z\big)\big]\Big\}\Big\}.
\end{aligned}
\tag{41}
$$

According to (36) and (38), we have for BaTiO3

$$
E_j^{(1)}(s)=-\frac{\sqrt{3}}{2\pi c}\sum_{\mathbf{n}\neq 0}\frac{\cos\big(\mathbf{g}\mathbf{r}_j\big)F_1(\mathbf{g})}{d_2}\exp\left\{-\frac{2\pi^2 d_2}{3a^2\varepsilon}\right\}+2q_j\left(\frac{2\varepsilon}{\pi}\right)^{1/2}. \tag{42}
$$

The ions in BaTiO3 have two non-equivalent positions. We present further the values of energies $E_j^{(1)}(s)$ (in a.u.) for ions in BaTiO3 $(\varepsilon \geq 4)$:

Ti^{4+}(1): $\cos\big(\mathbf{g}\mathbf{r}_j\big)=1,$ $\quad E_j^{(1)}(s)=1.4582510001,$ (43)

Ti^{4+}(2): $\cos\big(\mathbf{g}\mathbf{r}_j\big)=\cos\left[2\pi\left(\frac{2n_x}{3}+\frac{n_y}{3}+0.15367n_z\right)\right],$ $\quad E_j^{(1)}(s)=1.6877963539,$ (44)

Ba^{2+}(1): $\cos\big(\mathbf{g}\mathbf{r}_j\big)=\cos\big[2\pi\big(0.25n_z\big)\big],$ $\quad E_j^{(1)}(s)=0.7947950353,$ (45)

Ba^{2+}(2): $\cos\big(\mathbf{g}\mathbf{r}_j\big)=\cos\left[2\pi\left(\frac{n_x}{3}+\frac{2n_y}{3}+0.09671n_z\right)\right],$ $\quad E_j^{(1)}(s)=0.6515284065,$ (46)

O^{2-}(1): $\cos\big(\mathbf{g}\mathbf{r}_j\big)=\cos\big[2\pi\big(0.5149n_x+0.03699n_y+0.25n_z\big)\big],$ $\quad E_j^{(1)}(s)=-0.9016606636,$ (47)

O^{2-}(2): $\cos\big(\mathbf{g}\mathbf{r}_j\big)=\cos\big[2\pi\big(0.3302n_x+0.1651n_y+0.0802n_z\big)\big],$ $\quad E_j^{(1)}(s)=-0.6683044552.$ (48)

It can be seen that the energy $E_j^{(1)}(s)$ has the same value for $\varepsilon \geq 4$. The values are given with the accuracy indicating the absolute convergence of the series with respect to the reciprocal lattice vectors. Table 1 shows the energies $E_j^{(1)}(s)$ of the present work and the energies obtained in [3]. A small difference in the values of the energies $E_j^{(1)}(s)$ is due to the fact that the lattice constants in [3] were taken from [10], in which $a=5.735$ Å, $c=14.05$ Å.

Table 1. The values of the energies of electron in the lattice site, i.e., in a point is obtained in the work [3] and the energies $E_j^{(1)}(s)$ of the present work (in a.u.).

	The work [3]	The present work
Ba(1)	0.81144	0.7947950353
Ba(2)	0.70417	0.6515284065
Ti(1)	1.57409	1.4582510001
Ti(2)	1.68474	1.6877963539
O(1)	−0.88351	−0.9016606636
O(2)	−0.86721	−0.6683044552

In this paper, we also calculated the diagonal matrix elements (34) on the $\psi_{px}(\mathbf{r})=\sqrt{\frac{3}{4\pi}}\sum a_i x\exp\big(-\alpha_i r^2\big)$, $\psi_{py}(\mathbf{r})=\sqrt{\frac{3}{4\pi}}\sum a_i y\exp\big(-\alpha_i r^2\big)$, $\psi_{pz}(\mathbf{r})=\sqrt{\frac{3}{4\pi}}\sum a_i z\exp\big(-\alpha_i r^2\big)$

orbitals of oxygen $O^{2-}(1)$. The Hartree-Fock function of p-orbitals were taken from [11]. The following values were obtained.

$$\int \psi^{*}_{p\,x}\left(\mathbf{r}-\mathbf{r}_j\right) H_{LR}\, \psi_{p\,x}\left(\mathbf{r}-\mathbf{r}_j\right) dV = -\,0.77608\ \text{a.u.}, \tag{49}$$

$$\int \psi^{*}_{p\,y}\left(\mathbf{r}-\mathbf{r}_j\right) H_{LR}\, \psi_{p\,y}\left(\mathbf{r}-\mathbf{r}_j\right) dV = -1.10451\ \text{a.u.}, \tag{50}$$

$$\int \psi^{*}_{p\,z}\left(\mathbf{r}-\mathbf{r}_j\right) H_{LR}\, \psi_{p\,z}\left(\mathbf{r}-\mathbf{r}_j\right) dV = -\,0.857581\ \text{a.u.} \tag{51}$$

The values (49)-(51) have the splitting on the order of 2-8 eV and differ markedly from the value $E_j^{(1)}(s)$ in (47) obtained for a sufficiently localized s-orbital.

5. Summary

It is shown that there is the possibility of calculating LRCI matrix elements on orbitals of the arbitrary symmetry in the case of the low symmetry of the crystal. It can be seen from the expressions (32), (34) and (35) that the structure of the functions $F_j(n_1 n_2 n_3)$ of this paper is the same as the structure of the functions (20) for the orthorhombic system [5]. The difference lies in the redefinition of the structural factor and the reciprocal lattice vectors. Thus, all expressions for the matrix elements on s, p, d, and f-orbitals obtained in [5, 6, 8] for orthorhombic systems can be used for low-symmetric systems with allowance for the above redefinition.

This approach can also be used to derive two-centered LRCI matrix elements [5].

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