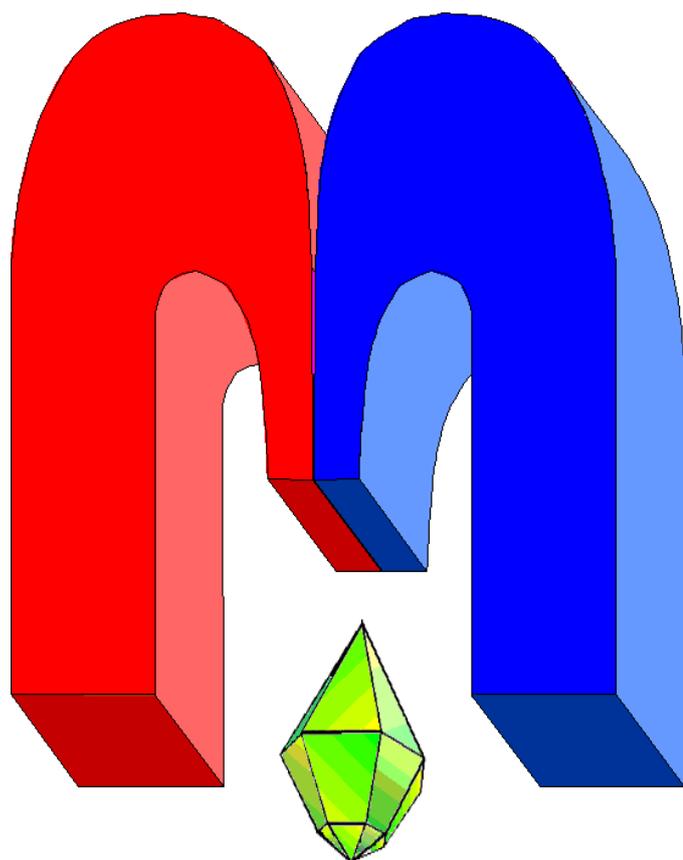


ISSN 2072-5981



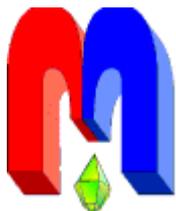
***Magnetic  
Resonance  
in Solids***

Electronic Journal

*Volume 17,  
Issue 1  
Paper No 15102,  
1-5 pages  
2015*

<http://mrsej.kpfu.ru>

<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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# The method of secondary quantization in the strong bond approximation

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(Received December 5, 2015; revised December 16, 2015; accepted December 17, 2015)

Expressions for the calculation of the Fourier transform of the direct Coulomb interaction of electrons have been derived in the method of strong bond. It was shown that in the elaborated method it is not necessary to spread out nuclear charges over the crystal as it is done in the case of delocalized electrons.

**PACS:** 76.60.-k, 74.72.Dn, 74.25.Jb

**Keywords:** strong bond approximation, secondary quantization, NQR, NMR

## 1. Introduction

Experimental data on the hyperfine (HF) and supertransferred hyperfine (STHF) structure in the case of impurity centers, and also nuclear magnetic resonance (NMR) data give direct information about the electron structure of studied crystals, i.e., wave functions of electrons. For example, in [1-4] experimental STHF and NMR data for diamagnetic ions were considered theoretically in a series of crystals. Hartree-Fock functions of free ions are used in calculations, since they are a good zero approximation in the case of ion crystals. At the same time, under doping conductivity, superconductivity, strong magnetoresistive dependence, i.e., properties of high practical importance, appear in a series of similar crystals. Systems appearing at such doping are systems with strong electron correlations, for which the method of strong bond is good zero approximation. It should be expected that processes of virtual transitions of electrons found in the works cited above should be manifested also in NQR and NMR experiments [5-7] in these systems. However, unlike [1-4], where the calculations were performed on localized orbitals, the method of strong bond leads to necessity of calculations of matrix elements depending on wave vectors of the Brillouin zone. The main difficulty arises during the calculation of matrix elements of two-particle operators, i.e., the Coulomb interaction of electrons. In this work it was shown by the example of the direct Coulomb interaction of electrons (or holes), the states of which are described by Bloch wave functions, that this problem can be solved in the general form. It should be noted that to date the Fourier transform of the Coulomb interaction of electrons in a crystal is written from phenomenological considerations (see, e.g., [8]). Expressions derived in this work make it possible to derive exact expressions for Fourier transform of the Coulomb interaction of electrons in the crystal, if ion orbitals are written in the Gauss basis. It is also noted that the method under development makes it possible to consider systems having, e.g., infinite sizes over  $x$ ,  $y$  axes, and the finite number of unit cells over the  $z$  axis.

## 2. General part

Using results [9], it is possible to transfer mathematically strictly from the representation of secondary quantization on localized functions with partly non-orthogonal one-particle basis to the representation of secondary quantization with the one-particle basis of Bloch functions. Then the operator of the Coulomb interaction of electrons is written in the form

$$V = \frac{1}{4N} \sum a_{\mathbf{k}_1+\mathbf{q},\xi}^+ a_{\mathbf{k}_2-\mathbf{q},\eta}^+ a_{\mathbf{k}_2,\eta'} a_{\mathbf{k}_1,\xi'} \langle \xi | \mathbf{k}_1 + \mathbf{q} | \theta \rangle \langle \eta | \mathbf{k}_2 - \mathbf{q} | \zeta \rangle \langle \theta, \zeta | \mathbf{k}_2 - \mathbf{q}, \mathbf{k}_1, \mathbf{k}_2 | \xi', \eta' \rangle + h.c. \quad (1)$$

$$\langle \xi | \mathbf{k} | \theta \rangle = \sum_{\mathbf{n}} e^{i\mathbf{k}\mathbf{n}} \langle \mathbf{n}, \xi | (I + S)^{-1} | \mathbf{0}, \theta \rangle, \quad (2)$$

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$$\langle \theta, \zeta | \mathbf{k}_2 - \mathbf{q}, \mathbf{k}_1, \mathbf{k}_2 | \zeta', \eta' \rangle = \sum_{\mathbf{n}, \mathbf{p}, \mathbf{m}} e^{i(\mathbf{k}_2 - \mathbf{q}) \cdot \mathbf{n}} \langle \mathbf{0}, \theta; \mathbf{n}, \zeta | g | \mathbf{p}, \zeta'; \mathbf{m}, \eta' \rangle e^{-i \mathbf{k}_1 \cdot \mathbf{p}} e^{-i \mathbf{k}_2 \cdot \mathbf{m}}. \quad (3)$$

Here  $\xi, \eta, \theta, \dots$  are quantum numbers of orbitals of ions of the unit cell ordered in a selected way,  $\mathbf{k}, \mathbf{q}$  are wave vectors of the Brillouin zone,  $\mathbf{n}, \mathbf{m}, \dots$  are radius-vectors of unit cells,  $\mathbf{0}$  is the radius-vector of the unit cell in the origin of coordinates,  $g$  is the Coulomb interaction of electrons.  $N$  is the number of unit cells in the volume with cyclic boundary conditions.

The matrix element  $\langle \mathbf{n}, \xi | (I + S)^{-1} | \mathbf{0}, \eta \rangle$  is the matrix element of the matrix inverse to the matrix of overlapping integrals of orbitals of ions of the crystal. Such matrices are called cyclic owing to the periodic structure of the crystal. Methods of calculations of matrices inverse to the cyclic matrices are given, e.g., in [10, 11]. Thus, there arises the problem of the calculation of matrix elements of the form (3).

As the first step, it is natural to consider matrix elements of the direct Coulomb interaction of electrons, i.e., satisfying conditions  $\theta = \zeta', \zeta = \eta', \mathbf{p} = \mathbf{0}, \mathbf{n} = \mathbf{m}$ . Then (3) has the form

$$\langle \theta, \zeta | \mathbf{q} | \theta, \zeta \rangle = \sum_{\mathbf{n}} e^{-i \mathbf{q} \cdot \mathbf{n}} \langle \mathbf{0}, \theta; \mathbf{n}, \zeta | g | \mathbf{0}, \theta; \mathbf{n}, \zeta \rangle. \quad (4)$$

Let the quantum numbers  $\theta$  determine the wave function of the ion with the radius-vector  $\mathbf{r}_j$  in the unit cell, and the quantum numbers  $\zeta$  determine the function of the ion with the radius-vector  $\mathbf{r}_p$  in the unit cell. Then the matrix element (4) can be written as

$$\langle \theta, \zeta | \mathbf{q} | \theta, \zeta \rangle = \sum_{\mathbf{n}} \exp(-i \mathbf{q} \cdot \mathbf{n}) \int \varphi_{\theta}^*(\mathbf{r}_1) \varphi_{\zeta}^*(\mathbf{r}_2) \left| \mathbf{r}_1 - \mathbf{r}_2 - (\mathbf{n} + \mathbf{r}_p - \mathbf{r}_j) \right|^{-1} \varphi_{\theta}(\mathbf{r}_1) \varphi_{\zeta}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \quad (5)$$

Hartree-Fock functions of electrons of free ions  $\varphi_{nlm}(\mathbf{r})$  can be expanded over the finite Gauss basis and present in the form

$$\varphi_{\theta}(\mathbf{r}) = \left[ (2l+1) / 4\pi \right]^{\frac{1}{2}} \sum_i a_i x^{s_1} y^{s_2} z^{s_3} \exp(-\alpha_i r^2), \quad (6a)$$

$$\varphi_{\zeta}(\mathbf{r}) = \left[ (2l+1) / 4\pi \right]^{\frac{1}{2}} \sum_j b_j x^{s_4} y^{s_5} z^{s_6} \exp(-\beta_j r^2). \quad (6b)$$

We introduce functions

$$F_{s_4, s_5, s_6}^{s_1, s_2, s_3}(\mathbf{q}) = \sum_{\mathbf{n}} e^{-i \mathbf{q} \cdot \mathbf{n}} \sum a_i b_j a_k b_l \int x_1^{s_1} x_2^{s_4} y_1^{s_2} y_2^{s_5} z_1^{s_3} z_2^{s_6} \exp[-(\alpha_i + \alpha_k) \mathbf{r}_1^2] \times \exp[-(\beta_j + \beta_l) \mathbf{r}_2^2] \times \left| \mathbf{r}_1 - \mathbf{r}_2 - (\mathbf{n} + \mathbf{r}_p - \mathbf{r}_j) \right|^{-1} d\mathbf{r}_1 d\mathbf{r}_2. \quad (7)$$

All quantities in (7) were determined above. Double indices, if the index is not indicated, mean summation as usual.

It is easy to see that each matrix element of the form (5) can be presented by the finite sum of functions (7) with coefficients determined by the wave functions.

The further course of the calculations, i.e., integrations and transformation to the pulse representation is performed analogous to that published in [12].

The Coulomb interaction, the same as in [12], is written in the form

$$\frac{1}{|\mathbf{r} - \mathbf{R}|} = \frac{2}{\sqrt{\pi}} \int_0^{\infty} dv \exp[-(\mathbf{r} - \mathbf{R})^2 v^2]. \quad (8)$$

The second transformation analogous to formulas (6) from [12] has the form

$$v^2 = \alpha_{ik} \beta_{jl} (\alpha_{ik} + \beta_{jl})^{-1} (1 - u^2)^{-1} u^2, \quad (9a)$$

$$\left[ \alpha_{ik} \beta_{jl} + (\alpha_{ik} + \beta_{jl}) v^2 \right]^{-\frac{3}{2}} dv = (\alpha_{ik} \beta_{jl})^{-1} (\alpha_{ik} + \beta_{jl})^{-\frac{1}{2}} du. \quad (9b)$$

where  $\alpha_{ik} = \alpha_i + \alpha_k$ ,  $\beta_{jl} = \beta_j + \beta_l$ . Then for functions (7) we obtain expression

$$\begin{aligned} F_{s_4, s_5, s_6}^{s_1, s_2, s_3}(\mathbf{q}) &= \frac{4\pi^4}{v_c} \sum a_i b_j a_k b_l \left( \frac{1}{\alpha_{ik} + \beta_{jl}} \right)^{\frac{3}{2}} \sum_{\mathbf{g}} \prod_{\mu=1}^3 \left\{ \left( -\frac{1}{2} \right)^{n_\mu} \sum_{m_\mu=0}^{n_\mu} c(m_\mu) m_\mu! \right. \\ &\times \sum_{\bar{m}_\lambda=0}^{\left[ \frac{m_\mu}{2} \right]} \left( \frac{1}{\alpha_{ik} + \beta_{jl}} \right)^{m_\mu - \bar{m}_\lambda} \frac{(\alpha_{ik} - \beta_{jl})^{m_\mu - 2\bar{m}_\lambda}}{\bar{m}_\lambda! (m_\mu - 2\bar{m}_\lambda)!} (n_\mu - 2\bar{m}_\lambda)! \times f(d, n_\mu - 2\bar{m}_\lambda, G_\mu) \left. \right\} \\ &\times \frac{\exp \left[ -\frac{(\mathbf{g} + \mathbf{q})^2}{4d} \right]}{(\mathbf{g} + \mathbf{q})^2} \exp \left[ i(\mathbf{g} + \mathbf{q})(\mathbf{r}_p - \mathbf{r}_j) \right], \end{aligned} \quad (10)$$

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

$$n_1 = s_1 + s_4, \quad n_2 = s_2 + s_5, \quad n_3 = s_3 + s_6,$$

$$d = \frac{\alpha_{ik} \beta_{jl}}{\alpha_{ik} + \beta_{jl}}, \quad G_1 = g_x + q_x, \quad G_2 = g_y + q_y, \quad G_3 = g_z + q_z,$$

$$c(m_1) = \sum_{\substack{w, h \\ w+h=m_1}} \frac{(-1)^{s_1-w} s_1! s_4!}{w!(s_1-w)! h!(s_4-h)!}, \quad c(m_2) = \sum_{\substack{w, h \\ w+h=m_2}} \frac{(-1)^{s_2-w} s_2! s_5!}{w!(s_2-w)! h!(s_5-h)!},$$

$$c(m_3) = \sum_{\substack{w, h \\ w+h=m_3}} \frac{(-1)^{s_3-w} s_3! s_6!}{w!(s_3-w)! h!(s_6-h)!}.$$

Functions  $f(d, n, G)$  are determined in [12, 13]

$$f(d, n, G) = \left( \frac{1}{2d} \right)^n \sum_{h=0}^{\left[ \frac{n}{2} \right]} \frac{d^h}{h!(n-2h)!} (-iG)^{n-2h}. \quad (11)$$

### 3. Coulomb interaction of p-electrons

Let one Bloch function be formed by the  $p_z$  wave function of the electron of the ion with the radius-vector  $\mathbf{r}_j$  in the unit cell, and the second Bloch function be  $p_z$  wave function of the electron of the ion with the radius-vector  $\mathbf{r}_p$  in the unit cell. The Fourier transform of the Coulomb interaction of these Bloch functions determined by functions (10) has the form

$$\begin{aligned} \langle p_z(\mathbf{r}_j), p_z(\mathbf{r}_p) | \mathbf{q} | p_z(\mathbf{r}_j), p_z(\mathbf{r}_p) \rangle &= \frac{9}{16\pi^2} F_{002}^{002} \\ &= \frac{9\pi^2}{64v_c} \sum a_i b_j a_k b_l (\alpha_{ik} \beta_{jl})^{-\frac{7}{2}} \sum_{\mathbf{g}} \left[ (g_z + q_z)^4 - 2(\alpha_{ik} + \beta_{jl})(g_z + q_z)^2 + 4\alpha_{ik} \beta_{jl} \right] \\ &\times \frac{1}{(\mathbf{g} + \mathbf{q})^2} \exp \left[ -\frac{\alpha_{ik} + \beta_{jl}}{4\alpha_{ik} \beta_{jl}} (\mathbf{g} + \mathbf{q})^2 + i(\mathbf{g} + \mathbf{q})(\mathbf{r}_p - \mathbf{r}_j) \right]. \end{aligned} \quad (12)$$

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Expression (12) determines the interaction between two electrons in the crystal. At the same time, owing to the electroneutrality of the crystal there has to be the interaction between the electron and nuclei of the crystal, which makes the energy of the crystal finite.

To this end, we consider the limiting value (12) when  $(\mathbf{g} + \mathbf{q})$  tends to zero. Then

$$\langle p_z(\mathbf{r}_j), p_z(\mathbf{r}_p) | \mathbf{q} | p_z(\mathbf{r}_j), p_z(\mathbf{r}_p) \rangle \approx \frac{3\pi^{\frac{3}{2}}}{2v_c} \sum a_i a_j \left( \frac{1}{\alpha_{ik}} \right)^{\frac{5}{2}} \frac{3\pi^{\frac{1}{2}}}{8} \sum b_j b_l \left( \frac{1}{\beta_{jl}} \right)^{\frac{5}{2}} \frac{1}{(\mathbf{g} + \mathbf{q})^2}. \quad (13)$$

We consider the interaction between the selected orbital  $p_z$  of the ion with the radius-vector  $\mathbf{r}_j$  in the unit cell and unit positive charges in the sites  $\mathbf{r}_p$  of the unit cell. Then according to [12] we have

$$\begin{aligned} & \langle p_z(\mathbf{r}_j) | - \sum \frac{1}{|\mathbf{r} - (\mathbf{n} + \mathbf{r}_p - \mathbf{r}_j)|} | p_z(\mathbf{r}_j) \rangle \\ &= \frac{3\pi^{\frac{3}{2}}}{2v_c} \sum a_i a_j \left( \frac{1}{\alpha_{ik}} \right)^{\frac{5}{2}} \sum_{\mathbf{g}} \left( \frac{g_z^2}{2\alpha_{ik}} - 1 \right) \frac{1}{\mathbf{g}^2} \exp \left[ -\frac{\mathbf{g}^2}{4\alpha_{ik}} + i \mathbf{g}(\mathbf{r}_p - \mathbf{r}_j) \right]. \end{aligned} \quad (14)$$

Expression (14) at  $\mathbf{g}$  tending to zero has the form

$$\langle p_z(\mathbf{r}_j) | - \sum_{\mathbf{n}} \frac{1}{|\mathbf{r} - (\mathbf{n} + \mathbf{r}_p - \mathbf{r}_j)|} | p_z(\mathbf{r}_j) \rangle \approx -\frac{3\pi^{\frac{3}{2}}}{2v_c} \sum_{i,k} a_i a_k \left( \frac{1}{\alpha_{ik}} \right)^{\frac{5}{2}} \frac{1}{\mathbf{g}^2}. \quad (15)$$

But in (13) the quantity

$$\langle p_z | p_z \rangle = \frac{3\pi^{\frac{1}{2}}}{8} \sum b_j b_l \left( \frac{1}{\beta_{jl}} \right)^{\frac{5}{2}} = 1. \quad (16)$$

Thus, expressions (13) and (15) are cancelled when  $(\mathbf{g} + \mathbf{q})$  and  $\mathbf{g}$ , respectively, tend to zero and the energy of the crystal remains finite, since the sum of expressions (12) and (14) is converging.

## 4. Conclusion

In this work, the method of secondary quantization for calculations in the strong bond approximation is developed. The Fourier transform of two electrons with Bloch wave functions was obtained in the strong bond approximation. This method of calculations shows that exact the matrix element can be calculated as well. It was shown that unlike current approaches, it is not necessary to spread out the charge of nuclei of ions of the crystal over the whole crystal, i.e., all calculations can be performed with real nuclei of ions of the crystal. The method of calculations can be transferred to crystals with infinite sizes in  $x, y$  planes and having the finite number of unit cells along the  $z$  axis. To this end, it is necessary to take two-dimensional translation vectors when building Bloch functions.

## Acknowledgments

The work is supported from the subsidy allocated to Kazan Federal University for performing the project part of the state assignment in the area of scientific activities.

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