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The secondary quantization method with the nonorthogonal basis and its application to theory of localized magnetic fields on the nucleus of diamagnetic ions with a nonfilled 3d- and 4f- shells.

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A general characterization of the work

The work is the actual. When finding the spectrum of many-particle systems almost always use single-particle approximation, i.e., it is assumed that the state of each electron can be described by a wave function. In this case, the range and system status can be found in both extremes of the functional medium of the Hamiltonian of such a system. The wave function of the system is naturally represented as a superposition of Slater determinants of some composed of the desired particle functions. As a rule, these single-particle function orthonormality conditions are imposed. At the same time it is clear that a functional condition orthonormality particle functions and the lack of orthogonality conditions particle functions are different functionals and in general must have different extremes. In the V.A. Fock [1] noted that taking into account the excited configurations should require only a partial orthogonal orbitals. A number of studies, for example, [2, 3] the issue was studied by numerical solution of the Hartree - Fock approximation for the simplest configurations under different conditions with respect to orthogonal radial orbitals. It was concluded that the more the orthogonality conditions, the results are worse. Further development of the theory and practical application of the method of self-consistent field Hartree - Fock orbitals using orthogonal delayed because of mathematical difficulties. This applies to the calculation of the matrix elements of the operators in the Slater determinants constructed using a partially orthogonal orbitals and to computing in solving the equations themselves Hartree - Fock on such determinants in the coordinate representation.

Since the studied systems are almost always identical particles systems, it was natural to try to develop a method of second quantization as in the case of an orthonormal one-particle basis. In [4, 5] was an attempt of the second quantization method with a partially non-orthogonal single-particle basis for fermions. In these works, "bra" dual-vector basis are not Hermitian conjugate to the "cat" the vector and as a result of one- and two-particle operators are not Hermitian. Anticommutator creation and annihilation operators orbitals unlike ordinary

Kronecker symbol, receive equal to the corresponding overlap integral. Because of this, there are difficulties with the normalization of many states, etc. and any application of the proposed method of second quantization to the real system was no question of the so-called "non-orthogonality catastrophe" remains open. Thus, the problem of finding the exact form of Hermitian operators in second quantization representation with a partially non-orthogonal single-particle basis remained unsolved.

All of the above points to the relevance of the topic of the dissertation.

The work is the purpose.

The aim of this work is the construction of the second quantization method with linearly independent, non-orthogonal single-particle basis. At this stage, we considered the application of this method to a system in which is possible to use perturbation theory. These systems can be classified as ionic crystals. The main objects of study are impurity centers, with unfilled 3d- and 4f-shells, namely ligand hyperfine interactions (LSTV) in them.

Problems in the interpretation of experimental data LSTV arise even for ions of the iron group. Application of the standard variant of the method of molecular orbitals in some cases is difficult. Among the impurity centers with unfilled 3d-shell these include: paramagnetic centers with missing-bond complexes with orbital degeneracy, and a large class of systems with lower symmetry. In the case of rare-earths difficulty increases as the wave function of the ground state, as a rule, it is the sum of Slater determinants, so the calculation in the ordinary (phenomenological) scheme of molecular orbitals become is extremely time-consuming.

Furthermore, made for Gd^{3+} ions calculation parameters of the spin density transferred to the core ligands, with the replacement of the wave functions of electrons in the 4f-related molecular orbitals, even the sign do not agree with the experimental data. This raises the problem of the account of the spatial distribution and even the outer electron shells. However, the overlap integrals 6s-, 6p- and 5d-shells with ligands are big enough. This raises the problem of convergence of series with non-orthogonal integrals. This problem first arose in the theory of the chemical bond and is called "non-orthogonality catastrophe." It is known more for the work of Slater, but has remained unsolved to this day.

The defense is the provisions.

1. The expressions for the single-particle and two-particle operators in the second quantization method with linearly independent, partially non-orthogonal single-particle basis have been obtained. Operators have the form of a series of n - th powers of the commutator the operator Q c operator H^- with coefficients $c_n = E_{2n} / [2^{2n} (2n)!]$, Where E_{2n} are Euler numbers. The matrix elements of the operator H^- are a linear combination of matrix elements of the Hamiltonian H system. The coefficients of this linear combination are expressed in terms of matrix elements of the matrix $(I+S)^{-1}$, where I - the identity matrix, and S - the matrix of the overlap integrals of the selected single-particle basis. The matrix elements of Q is also expressed in terms of matrix elements of $(I+S)^{-1}$. For the convergence of the resulting series requires only the limitations of the matrix elements of n - th degrees commutator.

2. Solved the problem of "non-orthogonality catastrophe." These general expressions do not operate with a series of powers of the overlap integrals as a sufficiently large set of basic functions needed for the interpretation of the experiment, these series are divergent. At the same time, in the case of convergence of the overlap integrals sufficiently limited basis (taking, for example, as a probe) results obtained using the new formulations and old method coincidence.

3. A generalization of expressions for the amplitudes of the electron transition metal-ligand (analog covalency parameter in the method of molecular orbitals) allowing to calculate their values without assuming smallness of the corresponding overlap integrals. The proposed expressions for the transition amplitudes explain the closeness of the experimental values of the ligand hyperfine structure of impurity centers Yb^{3+}: CsCaF3 and Yb^{3+}: Cs2NaYF6, despite the fact

that the Yb^{3+} ions are introduced in different crystals, and in one case replacement isovalence and the other nonisovalent.

4. The operators of the effective interaction spin and the orbital moments of paramagnetic ions with neighboring nuclei of diamagnetic ions are obtained. It demonstrated the importance of integrating the virtual processes of charge transfer from the diamagnetic ions into the empty 5d-state rare-earth ions. The role of external polarization filled 5s- and 5p-shells. A mechanism for the creation of an extra field in the nuclei of the ligands associated with the action of the virtual excitation of the electric field from the hole on the ligand.

5. It has been demonstrated that the development of theory and proposed mechanisms transferred magnetic fields on the nuclei of diamagnetic ions are explains the main features of the formation of the local fields in the fluorine nuclei in a number of fluorides: Yb^{3+}: $CsCaF_3$ and Yb^{3+}: Cs_2NaYF_6.

6. The values of the local magnetic fields in LaMnO3, enriched isotopes 17O, in different types of cooperative orbital ordering of the ions Mn^{3+}. The best agreement with experiment is obtained under the assumption that the cooperative ordering e_g subshell electrons are in states with the wave function of the form $c_1|3z^2-r^2\rangle + c_2|x^2-y^2\rangle$ (in the local axes defined octahedral fragments MnO_6). So, at T = 298K coefficients are: c_1 = 0.995, c_2 = - 0.10. The importance of quantum interference effects is proportional to the product of c_1c_2. Thus, based on the experimental NMR data in collaboration with experimentalists work uniquely identified ground state wave function of ions Mn^{3+}, and thereby established the cooperative structure of orbital ordering in this compound in the paramagnetic phase.

The safe and innovate.

All the results of the thesis were obtained for the first time, its conclusions proved the reliability of the analytical methods, the agreement with the theoretical results obtained up to the squares of the overlap integrals in the early works, the agreement with the experimental data.

The values are scientific and practical.

The resulting expression for the effective operators transferred hyperfine fields on the nuclei of magnetic ions nearest diamagnetic anions useful in any crystal symmetry and the presence of orbital degeneracy of the ground states of magnetic ions. On concrete examples demonstrated that the developed method of secondary quantization partially non-orthogonal single-particle basis to successfully explain the main features of the existing experimental data obtained by electron-nuclear double (in the case of impurity centers) and nuclear magnetic resonance (for the crystals with high magnetic concentration).

Compact expressions are derived for the calculation of the Coulomb interaction of the electrons with the basis of their spatial distribution within the crystal lattice. The formula for the Fourier transform of this interaction has the translational symmetry of the crystal lattice.

Test of the works. The main results were reported «XIX International Seminar on Modern Magnetic Resonances, RAMIS» (Poznan-Bedlewo, Poland, 2001), «XI-th Feofilov symposium on spectroscopy of crystals activated by rare earth and transition metal ions» (Kazan, Russia, 2001), «European Conference Physics of Magnetism» (Poznan, Poland, 2002), «XII All-Russian Conference. Optics and Spectroscopy of Condensed Matter» (Krasnodar, Russia, 2006), «International conference. Modern development of magnetic resonance» (Kazan, Russia, 2007), «International conference. Modern development of magnetic resonanc» (Kazan, Russia, 2007), «XV All-Russian Conference. Optics and Spectroscopy of Condensed Matter» (Krasnodar, Russia, 2009), «XIV International Feofilov Symposium. Spectroscopy of crystals doped with rare earth and transition metal ions» (St.-Petersburg, Russia, 2010), «VII International Conference. Fundamental problems of optics "(St. Petersburg, Russia, 2012), «Actual problems of magnetic resonance and its application. XV International Youth Scientific School» (Kazan, Russia, 2012). «XV International Feofilov

Symposium. Spectroscopy of crystals doped with rare earth and transition metal ions» (Kazan, Russia, 2013).

The works are the publications.

The main results of the thesis were published in 17 articles in Russian and international journals included in the database SCOPUS (15 journals included in the list of VAC), as well as in the materials and theses of the above conferences.

The contribution is the personal. All the theoretical results presented in the dissertation were obtained by the author.

The dissertation is the structure and volume. The dissertation consists of an introduction, six chapters and a conclusion, stated on 191 typewritten pages, contains 3 figures, 2 charts, 18 tables and 3 appendices. Bibliography contains 100 references**.**

The dissertation is the content.

In the introduction the actuality of the topic, a brief overview of the current state of the problem, the study aim, set the tasks of work. The statutes is the defense.

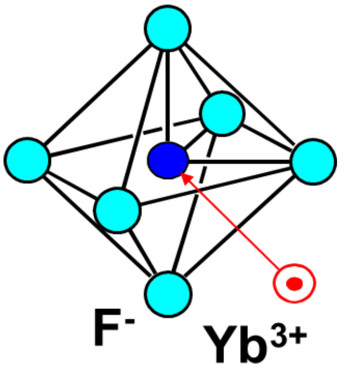
The first chapter discusses the results of [A1-A7], [6-11], which were obtained by the "approximate second quantization", in which the operators in the second quantization obtained up to the squares of the overlap integrals. It is emphasized that, even considering the covalence as adjustable parameters, without the involvement of new mechanisms for the formation of local magnetic fields at the nuclei of diamagnetic ions, it is impossible to explain the available experimental data on LSTV impurity centers. This is particularly clearly seen in the case of rare-earth compounds.

However, the implementation of this the program, is arise a number of fundamental problems. This is actually articulate statement of the work. As an illustration, we present some qualitative assessment. We write the Hamiltonian of the ligand hyperfine interaction H_{LSTV}, i.e., operator of the interaction of the impurity ion effective spin with the nuclear spin of the ligand selected through isotropic A_s and A_p anisotropic constants, respectively.

$$H_{ЛСТВ} = A_s\left(\mathbf{SI}\right) + A_p\left(2S_zI_z - S_xI_x - S_yI_y\right),\ \text{где}$$

$$A_s = \sum_i c_s^{(i)} f_{nls}^{(i)} a_s, \qquad a_s = \frac{16\pi}{3}\beta\beta_n g_n \left|\varphi_{2s}(0)\right|^2,$$

$$A_p = A'_p + A_d, \qquad A_d = \frac{2\beta\beta_n g_n}{R^3}$$



$f_{nls}^{(i)}$ – density of the spin; nl, s – orbital quantum numbers of ions.

The sign $c_s^{(i)}$ can be both larger and smaller Zero is depending on the mechanismthe emergence of spin density.

Fig.1. the impurity center is the model. CsCaF$_3$: Yb^{3+}.

The above operator of the interaction is one of the selected pairs of Yb^{3+} - F- and recorded in the local coordinate system with the z axis along the axis of the pair. The observed value A_p is markedly different from the magnetic dipole-dipole interaction of the impurity ions with the core of the ligand, which clearly points to the manifestation of the effects of covalency.

$$A'_p = \sum_i \left(c_\sigma^{(i)} f_{nl\sigma}^{(i)} + c_\pi^{(i)} f_{nl\pi}^{(i)} + c_{\sigma\pi}^{(i)} f_{nl\sigma\pi}^{(i)}\right) a_p, \quad a_p = \frac{4}{5}\beta\beta_n g_n \left\langle r^{-3}\right\rangle_{2p}.$$

The process of forming a covalent bond corresponding 4f-electron to 2p (2s) - electrons fluoride ($c_s^{(i)}$> 0) is fig. 1.1.

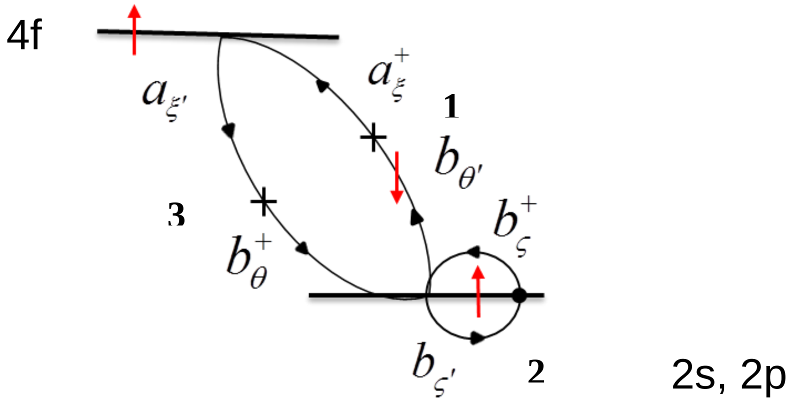


Fig. 1.1 The transferred hyperfine field on the nucleus of the fluorine is resulting in formation of a covalent bond.

In the case of the impurity center KMgF3: Tm^{2+}, Yb^{3+} and S = 1/2, it is decisive. [8] These numbers refer to the sequence of statements in the amendment of the second-order perturbation theory.

It is seen that the magnetic field produced by the electron remaining on the nucleus of the ligand has the same sign as the field produced by the electron of the central ion, i.e., isotropic constant $A_s > 0$, as is observed experimentally.

Diagram 1.2 Process involving the overlying unfilled shells ($c_s^{(i)} < 0$).

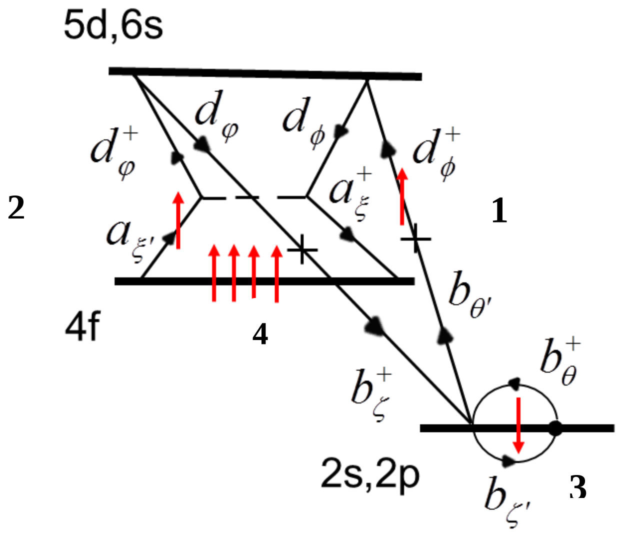


Fig. 1.2 Contribution to transferred hyperfine field of the transport processes in the empty shell 5d- or 6s-shell configuration $4f^7$.

The diagram 1.2 shows that the magnetic field generated by the remaining electron on the nucleus is the opposite sign of the ligand field produced by covalent contribution. The energy transition in 5d-, 6s-shell more energy transfer to the valence shell. Note, however, that the overlaps 5d-, 6s-shells with ligand orbital is considerably greater the overlap with the valence 4f-shell. Furthermore, unlike covalent contribution, wherein the selection rules is only possible transition 2s - 4f0, in processes involving the empty shells seven orbital configuration $4f^7$. Thus, the process diagram 1.2 can explain the negative value, which is observed experimentally in the case of impurity centers CaF2: Eu^{2+}, Gd^{3+} and S = 7/2 [12]. It is easy to see that the process beginning with the transition of an electron spin direction opposite to that shown in Figure 1.2, is forbidden by the selection rules.

At the same the following problems are raises for multi-configuration approach:

- overlap integrals $\langle 6p|\theta\rangle, \langle 6s|\theta\rangle, \langle 5d|\theta\rangle$, etc., where $|\theta\rangle$ - orbitals of the ligands are not small, and the series of non-orthogonality are divergent,
- "non-orthogonality catastrophe" - the large number of particles and the orbitals. So even with a relatively small non-orthogonality integrals series do not converge.

For the first time it was mentioned in the works of Slater.

Accordingly, the purpose of the work can be summarized as follows:

a) develop a method to carry out calculations for arbitrary non-orthogonality integrals;

b) avoid disaster "non-orthogonality catastrophe", i.e. determine the criterion the possibility of using of a single-particle basis;

c) to construct a theory ligand hyperfine interactions with exact allowance for the effects of non-orthogonality, taken in the framework of the basis, in each order of perturbation theory.

The second chapter is the main. It discusses the difficulties encountered when trying to calculate the matrix elements in the Slater determinants composed of the non-orthogonal basis orbitals in the coordinate representation. Shows how can be eliminated "non-orthogonality catastrophe."

Section 2.2 the operator of the creation and annihilation of electron orbitals in the non-orthogonal basis satisfying the usual fermion relations are introduced, i.e.

$$a_{\mu'}a_{\mu}^{+} + a_{\mu}^{+}a_{\mu'} = \delta_{\mu\mu'}, \; a_{\mu'}a_{\mu} + a_{\mu}a_{\mu'} = a_{\mu'}^{+}a_{\mu}^{+} + a_{\mu}^{+}a_{\mu'}^{+} = 0, \; a_{\mu}|0\rangle = 0 \tag{5}$$

and input function

$$\langle\{\xi\}| = \langle 0| a_{\xi_1} a_{\xi_2} \ldots a_{\xi_{N-1}} a_{\xi_N}, \quad |\{\eta\}\rangle = a_{\eta_N}^{+} a_{\eta_{N-1}}^{+} \ldots a_{\eta_2}^{+} a_{\eta_1}^{+} |0\rangle. \tag{6}$$

It is shown. Let us $\left|\Phi_{\{\xi\}}\right\rangle$, $\left|\Phi_{\{\eta\}}\right\rangle$ are the Slater determinants with non-orthogonal basis of the orbitals and with the quantum numbers $\{\xi\},\{\eta\}$. Then the matrix element is

$$\left\langle\Phi_{\{\xi\}}\middle|h\middle|\Phi_{\{\eta\}}\right\rangle=\langle 0|a_{\xi_1}a_{\xi_2}...a_{\xi_{N-1}}a_{\xi_N}\times\hat{h}\times a^+_{\eta_N}a^+_{\eta_{N-1}}...a^+_{\eta_2}a^+_{\eta_1}|0\rangle, \tag{7}$$

where $h-$ single-particle operator, and the operator $\hat{h}$ has the form:

$$\hat{h}=N\left[\exp\left(\sum_{\xi\neq\xi'}a^+_\xi a_{\xi'}\langle\xi|\xi'\rangle\right)\sum a^+_\eta a_{\eta'}\langle\eta|h|\eta'\rangle\right] \tag{8}$$

and similarly $g-$ two-particle operator, and the operator

$$\hat{g}=N\left[\exp\left(\sum_{\xi\neq\xi'}a^+_\xi a_{\xi'}\langle\xi|\xi'\rangle\right)\frac{1}{2}\sum a^+_\xi a^+_\eta a_{\eta'}a_{\xi'}\langle\xi\eta|g|\xi'\eta'\rangle\right], \tag{9}$$

where N is a normal product.

In ***section 2.3***, using the results of the preceding paragraph shall be considered an integral overlap between Slater determinants $\left|\Phi_{\{\xi\}}\right\rangle$ and $\left|\Phi_{\{\eta\}}\right\rangle$ which can be calculated by the formula:

$$\left\langle\Phi_{\{\xi\}}\middle|\Phi_{\{\eta\}}\right\rangle=\langle 0|\left(\prod_{i=1}^{N}a_{\xi_i}\right)N\left[\exp\left(\sum_{\theta\neq\theta'}a^+_\theta a_{\theta'}\langle\theta|\theta'\rangle\right)\right]\left(\prod_{i=1}^{N}a^+_{\eta_i}\right)|0\rangle. \tag{10}$$

It is shown that the operator belongs in (10) can be represented as:

$$I_\Phi=N\left[\exp\left(\sum_{\theta\neq\theta'}a^+_\theta a_{\theta'}\langle\theta|\theta'\rangle\right)\right]=\exp(Q), \tag{11}$$

where an operator Q is defined by the following expression:

$$Q=\sum a^+_\xi a_{\xi'}\langle\xi|\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n}S^n|\xi'\rangle\equiv\sum a^+_\xi a_{\xi'}\langle\xi|\ln(I+S)|\xi'\rangle, \tag{12}$$

The matrix elements $\langle\xi|S|\xi'\rangle\equiv\langle\xi|\xi'\rangle$ are the matrix elements of S the overlap matrix, composed in the basis of one-electron orbitals. The definition is not based on a matrix usually involves some type of operator of the Taylor series [A11]. We present $\ln(I+S)$ in the form of an integral, which is then recorded by the sum of:

$$\ln(I+S) = S\int_0^1 (I+\alpha S)^{-1} d\alpha \approx S\sum_{i=1}^{N}(I+\alpha_i S)^{-1}\Delta\alpha, \tag{13}$$

where $(I+\alpha_i S)^{-1}$ the matrix is inverse to the matrix $(I+\alpha_i S)$, $\alpha_i = i/N$. The expression on the right side of (13) is an integral sum of this operator. It exists always, when $(I+S)^{-1}$ is an inverse matrix. At the same time, the determinant of the $(I+S)$ matrix, in the case of the choice of basis of linearly independent functions, positive and not zero, as is the Gram determinant [13]. It is easy to show by direct calculation that if the series (12) converges, it is already at a value equal to 10^6 and $\Delta\alpha = 10^{-6}$ the matrix elements of both notions coincide up to 8-10 decimal places. Thus, always $\ln(I+S)$ is defined and does not depend on the magnitude of overlap integrals, if the selected basis is linearly independent system functions.

A simple example illustrating the above method for eliminating non-orthogonality catastrophe is given in Annex I.

In ***section*** 2.4 is found in the form of an arbitrary operator in the many-particles of orthonormal basis functions. The many-electron system of orthonormal functions as follows. In the matrix form it can be written as:

$$\mathbf{\Psi} = \mathbf{\Phi} \times \exp\left(-\frac{1}{2}Q\right), \tag{14}$$

where $\mathbf{\Psi}$ and $\mathbf{\Phi}$ row matrix. The method of constructing the system of functions (14) is called symmetric orthogonalization [14], but is now held in the operator form. It is shown that the matrix element of the single-particle and two-particle operators on the wave function (14) can be calculated by the formulas:

$$\left\langle \Psi_{\{\eta'\}} \middle| H \middle| \Psi_{\{\eta\}} \right\rangle = \left\langle \{\eta'\} \middle| H_{\Psi} \middle| \{\eta\} \right\rangle, \tag{15}$$

$$H_{\Psi} = \exp\left(\frac{1}{2}Q\right) \times \tilde{H} \times \exp\left(-\frac{1}{2}Q\right). \qquad (16)$$

Here

$$\tilde{H} = \sum a_{\xi}^{+} a_{\xi'} \left\langle \xi \middle| \tilde{h} \middle| \xi' \right\rangle + \frac{1}{2} \sum a_{\xi}^{+} a_{\eta}^{+} a_{\eta'} a_{\xi'} \left\langle \xi\eta \middle| \tilde{g} \middle| \xi'\eta' \right\rangle,$$

$$\left\langle \xi \middle| \tilde{h} \middle| \xi' \right\rangle = \sum \left\langle \xi \middle| (I+S)^{-1} \middle| \theta \right\rangle \left\langle \theta \middle| h \middle| \xi' \right\rangle,$$

$$\left\langle \xi\eta \middle| \tilde{g} \middle| \xi'\eta' \right\rangle = \sum \left\langle \xi \middle| (I+S)^{-1} \middle| \theta \right\rangle \left\langle \eta \middle| (I+S)^{-1} \middle| \varsigma \right\rangle \left\langle \theta\varsigma \middle| g \middle| \xi'\eta' \right\rangle,$$

$\left\langle \xi \middle| (I+S)^{-1} \middle| \theta \right\rangle$ is the matrix element of the matrix inverse to the matrix $(I+S)$.

In ***section 2.5*** is found the form of the operator H_{Ψ} in the form of a series. The expression (16) includes a non-Hermitian operator and, in addition, the operator is in the exponent. Work directly with an expression difficult. Therefore, it is desirable to write it in the form of a convergent series, all members of which would represent Hermitian operators. It is shown that the operator H_{Ψ} can be represented as:

$$H_{\Psi} = \sum_{n=0}^{\infty} c_n \left[Q, \bar{H}\right]^{2n}, \qquad c_n = \frac{E_{2n}}{2^{2n}(2n)!}, \qquad (17)$$

$E_2 = -1$, $E_4 = 5$, $E_6 = -61$, $E_8 = 1385$, $E_{10} = -50521$, $E_{12} = 2702765$, $E_{14} = -199360981$. The numbers E_{2n} are **numbers Euler**.

$$\bar{H} = \sum a_{\xi}^{+} a_{\xi'} \left\langle \xi \middle| \bar{h} \middle| \xi' \right\rangle + \frac{1}{2} \sum a_{\xi}^{+} a_{\eta}^{+} a_{\eta'} a_{\xi'} \left\langle \xi\eta \middle| \bar{g} \middle| \xi'\eta' \right\rangle,$$

$$\left\langle \xi \middle| \bar{h} \middle| \xi' \right\rangle = \frac{1}{2} \sum \left\langle \xi \middle| (I+S)^{-1} \middle| \theta \right\rangle \left\langle \theta \middle| h \middle| \xi' \right\rangle + h.c.,$$

$$\left\langle \xi\eta \middle| \bar{g} \middle| \xi'\eta' \right\rangle = \frac{1}{2} \sum \left\langle \xi \middle| (I+S)^{-1} \middle| \theta \right\rangle \left\langle \eta \middle| (I+S)^{-1} \middle| \zeta \right\rangle \left\langle \theta\zeta \middle| g \middle| \xi'\eta' \right\rangle + h.c.$$

For the convergence of the series (17) is sufficient to set of matrix elements of the operators $\left[Q,\bar{H}\right]^{2n}$ has been limited. The expression show fast convergence for the coefficients c_n. For the example, $c_7 \approx 1.39576\times10^{-7}$.

In ***section 2.6*** is found form of the operator the number of particles in the developing formalism. It is shown that the particle number operator has its usual form:

$$N_\Psi = \sum_\xi a_\xi^+ a_\xi . \tag{18}$$

It is also noted that the analysis and transformation, similar transformation given above, show that the expression (17) retain their shape and bosons. This requires that the creation and annihilation operators satisfy the boson commutation relations:

$$a_\xi a_{\xi'}^+ - a_{\xi'}^+ a_\xi = \delta_{\xi\xi'},\ a_\xi a_{\xi'} - a_{\xi'} a_\xi = a_\xi^+ a_{\xi'}^+ - a_{\xi'}^+ a_\xi^+ = 0,$$

and the all calculations were carried out on the so-called permanents, i.e. symmetrized with respect to the pair of permutations of products of single-particle orbitals. Then, in the notation of this work the functions $\left|\{\eta\}\right\rangle$ should be:

$$\left|\{\eta\}\right\rangle = \prod_\xi \frac{\left(a_\xi^+\right)^{n_\xi}}{\sqrt{n_\xi !}}\left|0\right\rangle,$$

here n_ξ is the number of filling orbitals.

The **third chapter** deals with the mechanisms that lead to the spin density on the ligand. Conclusion of second-quantization, taking into account virtual transitions of electrons in the impurity center, carried out following [15].

In ***section 3.1*** the perturbation theory for the case where the main level of the zero approximation is degenerate or quasi-degenerate is considered [16] and annexed to the problem solved in the dissertation. If the zero-particle basis using orbital Hartree-Fock approximation, the perturbation operator is written as:

$$H_1 = \frac{1}{2}\sum_{i\neq j}^{N}\frac{1}{r_{ij}} - \sum_{i=1}^{N} U\left(r_i\right). \tag{19}$$

The operator $U(r_i)$ has chosen from the condition exclusion the parameters Raka $F^{(0)}$ for a one-center interaction and the matrix elements of the direct Coulomb interaction for the two-center interaction. The expression $U(r_i)$ commonly used (see an example. [15]) solves this problem only partially. This section provides the operator in the second quantization, which satisfies the required conditions.

In ***section 3.2*** discusses the processes of transition of an electron from the shell of the ligand to the shell of the central ion, which define a covalent bond to the impurity center. The operator describing these processes will be:

$$V_1 = \sum a_\xi^+ a_{\xi'} \left[\frac{1}{4}\langle \xi | q | \zeta\rangle \langle \theta | q | \xi'\rangle - \frac{1}{2}\bar{\gamma}_{\xi\zeta}\langle\theta||\xi'\rangle \right.$$

$$\left. - \frac{1}{2}\langle\xi||\zeta\rangle\bar{\gamma}_{\theta\xi'} + \bar{\gamma}_{\xi\zeta}\bar{\gamma}_{\theta\xi'}\right]\langle\zeta|v|\theta\rangle, \qquad (20)$$

$q \equiv \ln(I+S)$, $\langle\xi||\theta\rangle \equiv \langle\xi|(I+S)^{-1}|\theta\rangle$, $\bar{\gamma}_{\xi\zeta} = -\langle \xi|G|\zeta\rangle / \left|\Delta_{\{\xi\},\{\zeta\}}\right|$,

$G_{\xi\zeta} = \langle\xi|G|\zeta\rangle$ is the amplitude of the transition of an electron from the ligand to the central ion, $\left|\Delta_{\{\xi\},\{\zeta\}}\right|$ is energy transfer system from the ground state to an excited state.

In ***section 3.3*** discusses the following third-order process. An electron from a ligand transfer to the valence shell of the central ion, then the electrostatic field occurring holes on the ligand, i.e., electron-hole interaction is transfer into one of the overlying orbital $|\varphi\rangle$ and returns. Effective operator describing these processes is

$$V_2 = \sum a_\xi^+ a_{\xi'} \frac{\langle\xi|h_{eh}|\varphi\rangle}{|\Delta_{\xi\varsigma}|}\left[\frac{1}{4}\langle\varphi||\varsigma\rangle\langle\theta||\xi'\rangle - \frac{1}{2}\langle\varphi||\varsigma\rangle\bar{\gamma}_{\theta\xi'}\right.$$

$$\left. + \frac{1}{2}\bar{\gamma}_{\phi\varsigma}\langle\theta||\xi'\rangle - \left(1 + \frac{|\Delta_{\xi\varsigma}|}{|\Delta_{\phi\theta}|}\right)\bar{\gamma}_{\phi\varsigma}\bar{\gamma}_{\theta\xi'}\right]\langle\varsigma|v|\theta\rangle + h.c., \qquad (21)$$

ξ, ξ' are the quantum numbers of orbital valence shell, φ are the orbital quantum numbers of empty shells, θ, ζ is the quantum numbers of the ligand orbitals, h_{eh} is the operator of electron-hole interaction. In the dissertation also noted is the possibility of building operators and the diagram method.

In ***section 3.4*** the next process of the emergence of spin density on the ligand is considered. An electron from a ligand enters the overlying empty shells $|\varphi\rangle$, $|\varphi'\rangle$ of the central ion. Because of the exchange interaction with electrons of the valence shell, the electron transition amplitude of the spin-up and spin-down will be different. This gives rise to a non-zero magnetic field at the nucleus of the ligand. The operator of these processes has the form:

$$V_3 = \sum a_{\xi}^{+} a_{\xi'} \frac{\langle \xi\varphi | g\left(1-P\right) | \xi'\varphi' \rangle}{\left|\Delta_{\varphi\zeta}\right|}$$

$$\times \left[\overline{\gamma}_{\varphi'\zeta} \overline{\gamma}_{\theta\varphi} - \frac{1}{4} \langle \varphi' \| \zeta \rangle \langle \theta \| \varphi \rangle \right] \langle \zeta | v | \theta \rangle + h.c. \tag{22}$$

In ***section 3.5*** the following process is considered the third-order perturbation theory. The corresponding operator is denoted by V_4. An electron from a ligand goes to the valence shell of the central ion. Then the electron-hole interaction is transfer into a different orbital and the electron returns. This process can be compared with the polarization of the ligand:

$$V_4 = \sum a_{\xi}^{+} a_{\xi'} \left[\frac{1}{4} \langle \xi \| \varsigma \rangle \langle \theta \| \xi' \rangle - \frac{1}{2} \langle \xi \| \varsigma \rangle \, \overline{\gamma}_{\theta\xi'} - \frac{1}{2} \overline{\gamma}_{\xi\varsigma} \langle \theta \| \xi' \rangle + \right.$$

$$\left. + \overline{\gamma}_{\xi\varsigma} \overline{\gamma}_{\theta\xi'} \right] \frac{\langle \varsigma | h_{eh} | \lambda \rangle}{\left|\Delta_{\xi\lambda}\right|} \langle \lambda | v | \theta \rangle + h.c., \tag{23}$$

The orbital quantum number ξ, ξ' is the valence shell. θ, ζ, λ is orbital quantum number of the ligand, h_{eh} is the operator of electron-hole interaction. It is evident that the operator V_4 is an amendment of the next order to the operator V_1. Shape operator also can be determined by the diagram.

In ***section 3.6*** considered LSTV contribution to due process core polarization on the central ion. Effect of the core polarization on the hyperfine structure of the impurity ions has been discussed for a long time [17, 18]. The role of the central ion core polarization in the formation of the ligand hyperfine structure by "approximate second quantization" was investigated in [19]. In [A11] the effect of polarization in the core of the central ion ligand hyperfine structure we evaluated following [19]. Then, in the framework of the method developed in this dissertation, we received the following statement, taking into account the processes of core polarization [A12]:

$$V_5^{(2)} = -\sum a_\xi^+ a_{\xi'} \frac{\left(\langle\varphi\|\varphi\rangle + \langle\alpha\|\alpha\rangle\right)}{2\left|\Delta_{\varphi\alpha}\right|}\langle\varphi\xi|g(1-P)|\alpha\xi'\rangle\left[\frac{1}{4}\langle\alpha|q|\zeta\rangle\langle\theta|q|\varphi\rangle\right.$$

$$\left.+\frac{1}{2}\frac{G_{\alpha\zeta}^{\varphi}}{\left|\Delta_{\varphi\varsigma}\right|}\langle\theta\|\varphi\rangle - \frac{1}{2}\langle\alpha\|\zeta\rangle\bar{\gamma}_{\theta\varphi} - \frac{G_{\alpha\zeta}^{\varphi}}{\left|\Delta_{\varphi\zeta}\right|}\bar{\gamma}_{\theta\varphi}\right]\langle\zeta|v|\theta\rangle + h.c., \tag{24}$$

$G_{\alpha\zeta}^{\varphi}$ is the amplitude of the transition of the electron orbitals with ligand $|\zeta\rangle$ on the vacant orbital $|\alpha\rangle$, belongs to the basic configuration, provided that the former empty orbitals $|\varphi\rangle$ it is an electron.

It is evident that the expressions obtained are substantially different from those obtained previously in calculations to within squares overlap integrals. The main difference is the renormalization of the product of various two-center integrals and covalence parameters. It is especially important to consider when determining the parameters of a covalent bond with the ligands on experimental data LSTV.

In **the fourth chapter** the amplitude of the transition of electrons between the ions and given expression for the spin densities are considered.

In ***section 4.1*** the expressions for calculating the amplitude of the transition of an electron from the ligand to the valence shell of the cation are suggested. The impact of the effects of non-orthogonality to the transition amplitude is determined by the nearest environment. The crystal lattice outside the first coordination sphere will be taken into account in the ion approximation. Then the one-particle Hamiltonian can be written as:

$$h = h_k - \frac{Z_a}{\left|\mathbf{r}-\mathbf{R}_a\right|} - \sum_b \frac{Z_b}{\left|\mathbf{r}-\mathbf{R}_b\right|} - \sum_{i\neq a,b} \frac{q_i}{\left|\mathbf{r}-\mathbf{R}_i\right|}, \tag{25}$$

h_k is the kinetic energy operator, Z_a, Z_b are the charges of the nuclei of the central ion and ligand, respectively, q_i are charges of ions in the host crystal.

The charge of the nucleus of the ion we write as: $Z_i = q_i + n_i + m_i$, where n_i the number of electrons of *i* - th ion to the present configuration, the number m_i - call charge defect and it is different from zero, if the charge is implanted ion is different from a charge q_i. Then $m_i > 0$ corresponds to a shortage, and $m_i < 0$ an excess of electrons. For the transition amplitude we obtained the following expression [A11]:

$$\begin{aligned}
2\langle\xi|G|\zeta\rangle = \langle\xi\|\zeta\rangle \Bigg[& \varepsilon_\xi^{q_e-1} + \sum_{\dot\eta_e} \langle\xi\dot\eta_e|g(1-P)|\xi\dot\eta_e\rangle\big(\langle\dot\eta_e\|\dot\eta_e\rangle - 1\big) \\
& + h_\xi - \langle\xi|\frac{n_b+m_b}{\left|\mathbf{r}-\mathbf{R}_b\right|}|\xi\rangle + \sum_{\dot\eta_b\neq\zeta} \langle\xi\dot\eta_b|g(1-P)|\xi\dot\eta_b\rangle\langle\dot\eta_b\|\dot\eta_b\rangle \\
& + \varepsilon_\zeta^{q_b} + \sum_{\eta_b} \langle\zeta\dot\eta_b|g(1-P)|\zeta\dot\eta_b\rangle\big(\langle\dot\eta_b\|\dot\eta_b\rangle - 1\big) \\
& + h_\zeta - \langle\zeta|\frac{n_e+m_e}{\left|\mathbf{r}-\mathbf{R}_e\right|}|\zeta\rangle + \sum_{\dot\eta_e\neq\xi} \langle\zeta\dot\eta_e|g(1-P)|\zeta\dot\eta_e\rangle\langle\dot\eta_e\|\dot\eta_e\rangle \Bigg]
\end{aligned}$$

$$\begin{aligned}
& + \big(\langle\xi\|\xi\rangle + \langle\zeta\|\zeta\rangle\big)\Big[\langle\xi|h_k|\zeta\rangle - \langle\xi|\frac{n_e+m_e}{\left|\mathbf{r}-\mathbf{R}_e\right|}|\zeta\rangle + \sum_{\dot\eta_e} \langle\xi\dot\eta_e|g(1-P)|\zeta\dot\eta_e\rangle\langle\dot\eta_e\|\dot\eta_e\rangle \\
& \qquad - \langle\xi|\frac{n_b+m_b}{\left|\mathbf{r}-\mathbf{R}_b\right|}|\zeta\rangle + \sum_{\dot\eta_b} \langle\xi\dot\eta_b|g(1-P)|\zeta\dot\eta_b\rangle\langle\dot\eta_b\|\dot\eta_b\rangle \Bigg],
\end{aligned} \tag{26}$$

where the sum of the orbitals of the central ion indicated by the letter *e*, and on the ligand orbitals index *b*, $\varepsilon_\xi^{q_e-1}$ and $\varepsilon_\zeta^{q_b}$ energy Hartree-Fock of the electron on the orbital $|\xi\rangle$ on the central ion and ligand orbital $|\zeta\rangle$, respectively. The value of:

$$h_{\xi} = -\langle \xi | \sum_{i \neq a} \frac{q_i}{|\mathbf{r} - \mathbf{R}_i|} | \xi \rangle, h_{\varsigma} = -\langle \varsigma | \sum_{i \neq b} \frac{q_i}{|\mathbf{r} - \mathbf{R}_i|} | \varsigma \rangle, h_{\xi\zeta} = -\langle \xi | \sum_{i} \frac{q_i}{|\mathbf{r} - \mathbf{R}_i|} | \zeta \rangle, \qquad (27)$$

h_{ξ} is coulomb interaction energy of the electron on the orbitals $|\xi\rangle$ of the central ion with an infinite lattice, taken ionic approximation, h_{ζ} is energy on the ligand, n_e + m_e, n_b + m_b is the number of electrons and charge defects in the basic configuration of the central ion and ligand, respectively.

In ***section 4.2***, the expressions for the amplitudes of the transition of an electron from a ligand to the unfilled and filled, in the basic configuration, of the shells of the central ion are obtained. The conclusions of these expressions are similar to the findings of the amplitude in the valence shell. Where $\langle \varphi | G | \zeta \rangle \equiv G_{\varphi\zeta}$ is the amplitude of the transition of the electron from the orbitals of the ligand $|\zeta\rangle$ to the orbital $|\varphi\rangle$, empty shell in the basic configuration, $\langle \alpha | G^{\varphi} | \zeta \rangle \equiv G^{\varphi}_{\alpha\zeta}$ is the amplitude of the transition of an electron to the vacant orbital of the filled shell.

In ***section 4.3***, the expressions for the contributions of the considered processes are recorded through spin density [A11], just as it is done, for example, in [20]. Let us the $\langle \xi | q | \zeta \rangle \equiv q_{\xi\zeta}$ and $\langle \xi || \theta \rangle \equiv p_{\xi\theta}$. Then, the spin density can be written as follows.

For example, for covalent contribution, i.e. operator V_1, we have:

$$f^{(1)}_{fi} = \frac{1}{4} q^2_{4fi} - p_{4fi} \bar{\gamma}_{4fi} + \bar{\gamma}^2_{4fi}, \quad i = s, \sigma, \pi, \qquad (28a)$$

$$f^{(1)}_{f\sigma\pi} = \frac{1}{4} q_{4f\sigma} q_{4f\pi} - \frac{1}{2} p_{4f\sigma} \bar{\gamma}_{4f\pi} - \frac{1}{2} \bar{\gamma}_{4f\sigma} p_{4f\pi} + \bar{\gamma}_{4f\sigma} \bar{\gamma}_{4f\pi}. \qquad (28б)$$

The designations s, σ, π correspond to those adopted in the theory of covalent bond [20]. Spin density corresponding to the processes of excitation of an electron from the central ion induced electron-hole interaction and describes the operator V_2, written as follows:

$$f_{di}^{(2)} = \frac{h_{ri}}{\left|\Delta_{4fi}\right|}\left(\frac{1}{4}p_{5di}p_{4fi} - \frac{1}{2}p_{5di}\overline{\gamma}_{4fi} + \frac{1}{2}\overline{\gamma}_{5di}p_{4fi} - \left(1+\frac{\left|\Delta_{4fi}\right|}{\left|\Delta_{5di}\right|}\right)\overline{\gamma}_{5di}\overline{\gamma}_{4fi}\right) \tag{29a}$$

$i = s, \sigma, \pi$.

$$\overline{f}_{d\sigma\pi}^{(2)} = \frac{h_\sigma}{\left|\Delta_{4f,2p}\right|}\left[\frac{1}{4}p_{5d\sigma}p_{4f\pi} - \frac{1}{2}p_{5d\sigma}\overline{\gamma}_{4f\pi} + \frac{1}{2}\overline{\gamma}_{5d\sigma}p_{4f\pi} - \overline{\gamma}_{5d\sigma}\overline{\gamma}_{4f\pi}\left(1+\frac{\left|\Delta_{4f,2p}\right|}{\left|\Delta_{5d,2p}\right|}\right)\right],$$

$$f_{d\sigma\pi}^{(2)} = \overline{f}_{d\sigma\pi}^{(2)} + \overline{f}_{d\pi\sigma}^{(2)}, \tag{29б}$$

$\overline{f}_{d\pi\sigma}^{(2)}$ is obtained from expressions $\overline{f}_{d\sigma\pi}^{(2)}$ permutation of the indices σ and π.

The contribution to the spin density due to the polarization of the ligand, i.e., corresponding to the operator V_4, is written as:

$$f_{f\sigma s}^{(4)} = \frac{h_{l\sigma s}}{\left|\Delta_{4fs}\right|}\left(\frac{1}{4}p_{4f\sigma}p_{4fs} - \frac{1}{2}p_{4f\sigma}\overline{\gamma}_{4fs} - \frac{1}{2}\overline{\gamma}_{4f\sigma}p_{4fs} + \overline{\gamma}_{4f\sigma}\overline{\gamma}_{4fs}\right). \tag{30}$$

Similar expressions are obtained for the deposits associated with other processes.

Thus, the contributions of the processes under consideration for the series rare-earth elements and transition metal will be expressed through the introduction of this section the spin density.

In the **fifth chapter** the expressions for calculating the matrix elements of the operators belonging to the amplitude of the transition of electrons between the ions are obtained.

In ***section 5.1***, we obtain expressions for the matrix elements of the Coulomb interaction between the electron and the charge, fixed at some point in space, and allows computing on the orbitals belonging to different ions.

Let us the radial part R_{nl} of ion orbital $\left|\psi_{nlm}(\mathbf{r})\right\rangle$ is an expansion of the Gaussian type orbitals (GTO):

$$R_{nl} = \sum a_i r^l \exp\left(-\alpha_i r^2\right). \tag{31}$$

This expansion, as we know, is extremely convenient for the calculation of two-center integrals [21]. However, in contrast to the method of calculation described in [21], we do not use the pre-conversion of the Coulomb interaction operator to its Fourier transform. In the proposed method of calculation the formula for the two-center matrix elements are more compact.

Let the first ion is in the site with the radius vector $\mathbf{R_0}$ + $\mathbf{r}_j$, $\mathbf{R}_0 = 0$**.** The second ion in the site with the radius vector $\mathbf{r}_b$. In the site with the radius vector $\mathbf{R}_n$ + r_p, where $\mathbf{R}_n$ is the radius vector n-th unit cell of the crystal, it is a charge q_p and $\mathbf{r}_p$ is the radius vector of ion in the unit cell. Then, as shown in [A9], the matrix element is the form:

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

and it can be expressed in terms of functions:

$$F\left(n_1n_2n_3\right) = -q_p\sum a_ib_k\left(\frac{1}{\alpha_{ik}}\right)\int_0^1 du\prod_{s=1}^{3}\left\{n_s!\sum_{m_s=0}^{\left[\frac{n_s}{2}\right]}\frac{\left(1-u^2\right)^{m_s}}{\left(4\alpha_{ik}\right)^{m_s}m_s!}\right.$$

$$\left.\times\sum_{w_s=0}^{n_s-2m_s}\frac{\left[\left(R_s-c_s\right)u^2\right]^{n_s-2m_s-w_s}}{w_s!\left(n_s-2m_s-w_s\right)!}c_s^{w_s}\right\}$$

$$\times\exp\left[-\alpha_{ik}\left(\mathbf{R}-\mathbf{c}\right)^2u^2\right]\exp\left(-\frac{\alpha_i\beta_k}{\alpha_{ik}}\mathbf{r}_0^2\right), \qquad (32)$$

where $[n_s/2]$ is the integer part of the number in parentheses; $x_{01}=x_0, x_{02}=y_0, x_{03}=z_0$ is coordinates of vector $\mathbf{r}_0=\mathbf{r}_b-\mathbf{r}_j$; $\alpha_{ik}=\alpha_i+\alpha_k$, $c_s=\beta_k x_{0s}/\alpha_{ik}$ is coordinates of vector $\mathbf{c}$; $R_1=R_x, R_2=R_y, R_3=R_z$ is coordinates of vector $\mathbf{R}=\mathbf{R}_n-\left(\mathbf{r}_j-\mathbf{r}_p\right)$. For example, the matrix element is calculated on the functions $\left|p_z\left(\mathbf{r}\right)\right\rangle$ will be:

$$\left\langle p_z\left(\mathbf{r}\right)\right| - \frac{q_p}{\left|\mathbf{r}-\mathbf{R}\right|}\left|p_z\left(\mathbf{r}-\mathbf{r}_0\right)\right\rangle = \frac{3}{2}\left[F\left(002\right)-z_0F\left(001\right)\right].$$

A calculation by the formulas (32) does not require special programming and can be easily calculated in user mode, such as the program "Mathematics".

In ***section 5.2***, the expressions for calculating the single-center and two-center matrix elements of the form (27) are obtained. They included in the expression for the transition amplitude [A13]. The matrix elements of the operator's H_{LR} are determined:

$$\left\langle \psi_{\xi}\left(\mathbf{r}-\mathbf{r}_j\right)\right| H_{LR} \left|\psi_{\xi'}\left(\mathbf{r}-\mathbf{r}_b\right)\right\rangle = \left\langle \psi_{\xi}\left(\mathbf{r}-\mathbf{r}_j\right)\right| -\sum_{n,p} \frac{q_p}{\left|\mathbf{r}-\left(\mathbf{R}_n+\mathbf{r}_p\right)\right|} \left|\psi_{\xi'}\left(\mathbf{r}-\mathbf{r}_b\right)\right\rangle, \quad (33)$$

Sum n is the sum taken over the unit cells of the infinite crystal lattice, and the sum of p sum taken over the ions in the unit cell. Unlike Ewald method [22], in the final expressions the sum is just sum taken over the reciprocal lattice vectors.

Results: that the matrix elements of the form (33) can be expressed over functions:

$$F_{jb}\left(n_1 n_2 n_3\right) = -\frac{2\pi^{\frac{3}{2}}}{v_c} n_1! n_2! n_3! \sum a_i b_k \left(\frac{1}{\alpha_{ik}}\right)^{\frac{3}{2}} \exp\left(-\frac{\alpha_i b_k}{\alpha_{ik}} \mathbf{r}_0^2\right) \times$$

$$\times \sum_{\boldsymbol{g}} f_{jb}\left(n_1, g_x\right) f_{jb}\left(n_2, g_y\right) f_{jb}\left(n_3, g_z\right) \exp\left(-\frac{\mathbf{g}^2}{4\alpha_{ik}}\right) \frac{G_j(\mathbf{g})}{\mathbf{g}^2} \exp\left[-i(\mathbf{gc})\right], \quad (34)$$

$f_{jb}(n, g_s)$ is the polynomial of degree n and g_s is the component of the reciprocal lattice vector **g**. Example,

$$f_{jb}\left(3, g_s\right) = \frac{1}{3!} Z_s^3 + \frac{1}{4\alpha_{ik}} Z_s, \quad f_{jb}\left(4, g_s\right) = \frac{1}{4!} Z_s^4 + \frac{1}{8\alpha_{ik}} Z_s^2 + \frac{1}{32\alpha_{ik}^2},$$

$Z_s = \beta_k x_{0s} / \alpha_{ik} - i g_s / 2\alpha_{ik}$. The value $G_j(\mathbf{g})$ is the structural factor, which depends only on the radius vector $\mathbf{r}_j$, and the reciprocal lattice vector.

Thus, all the matrix elements of the H_{LR} can be calculated for the s-, p-, d- and f-orbitals of the ions.

In ***section 5.3***, the expressions for the one-center matrix elements of the operator H_{LR} for the s-, p-, d-electrons selected ion [A14] are obtained. The matrix elements of this type arise when calculating transition amplitudes in the 5s, 5p, and 5d shell of rare earth ions, as well as the transitions of electrons in anion-cation LaMnO3. In the case of the s-electron matrix element is the interaction energy of the s-electron and is determined by the formula:

$$E_j(s)=\frac{\pi^{\frac{1}{2}}}{4}\sum a_i a_k\left(\frac{1}{\alpha_{ik}}\right)^{\frac{3}{2}}\left[-\frac{4\pi}{v_c}\sum_{\mathbf{g}\neq 0}\frac{G_j(\mathbf{g})}{\mathbf{g}^2}\exp\left(-\frac{\mathbf{g}^2}{4\alpha_{ik}}\right)+2q_j\left(\frac{\alpha_{ik}}{\pi}\right)^{\frac{1}{2}}\right], \quad (35)$$

where v_c is the unit cell volume, a,b,c is the lattice constants, $G_j(\mathbf{g})$ is the structural factor, q_j is the charge of the substitutable ion. For example, in the case of p-electrons to the off-diagonal matrix element functions p_x, p_y is:

$$\langle x|H_{LR}|y\rangle=\frac{3\pi^{\frac{3}{2}}}{4v_c}\sum_{i,k}a_i a_k\left(\frac{1}{\alpha_{ik}}\right)^{\frac{7}{2}}\sum_{\mathbf{g}\neq 0}g_x g_y\frac{G_j(\mathbf{g})}{\mathbf{g}^2}\exp\left(-\frac{\mathbf{g}^2}{4\alpha_{ik}}\right). \quad (36)$$

In ***section 5.4***, the expression for the matrix elements of the operator's H_{LR} which are part of the transition amplitude of an electron from the anion to the 4f-shell of a rare-earth ion [A16] were obtained. For example, the matrix element:

$$\langle f,2|H_{LR}|f,2\rangle=\frac{105}{16}\left[F_j(402)+F_j(042)+2F_j(222)\right]+3q_j\sum a_i a_k\left(\frac{1}{\alpha_{ik}}\right)^4.$$

Annex II. The general expressions for the calculation of two-center matrix elements of the Coulomb interaction of the electrons, necessary for calculating transition amplitudes, are obtained.

Annex III. The formulas for calculating the overlap integrals, direct, hybrid, exchange of the Coulomb integrals, using the results of Annex II are obtained. All calculations are done in user mode, such as the program, "Mathematics".

In the **sixth chapter** of the calculated tensor LSTV impurity centers Yb^{3+}: $CsCaF_3$, Cs_2NaYF_6 and ^{17}O: $LaMnO_3$.

In ***section 6.1*** the general expression for the amplitude of the transition of an electron in the valence shell are specified for the impurity center Yb^{3+}: $CsCaF_3$. The numerical values of the matrix elements needed to calculate these amplitudes are obtained. For the amplitudes following values were obtained:

$$\langle 4f0|G|2s\rangle=0.01465, \langle 4f0|G|2p0\rangle=0.01738,$$

$$\langle 4f1|G|2p1\rangle=-0.007943$$

In ***section 6.2*** of the general expressions for the amplitudes of the transition of an electron to the 5d and 6s are specified for the shell of the impurity center Yb^{3+}: $CsCaF_3$. The numerical values of the matrix elements needed to calculate these amplitudes are obtained. For the amplitudes following values were obtained:

$$\langle 5d0|G|2s\rangle = -0.2293,\ \langle 5d0|G|2p0\rangle = -0.1133,$$

$$\langle 5d1|G|2p1\rangle = 0.06164,$$

$$\langle 6s|G|2s\rangle = -0.4642,\ \langle 6s|G|2p0\rangle = -0.1293.$$

In section 6.3 the general expressions for the amplitudes of the electron transition in the 5s and 5p shell are specified for the impurity center Yb^{3+}: $CsCaF_3$. The numerical values of the matrix elements needed to calculate these amplitudes are obtained. The amplitudes $G_{5ss}^{5d} \approx G_{5ss}^{6s} \approx 0.003$, is at least an order of magnitude smaller than the other transition amplitudes, and for the amplitudes of the following values are obtained:

$$G_{5ss}^{5d} = G_{5ss}^{6s} = 0,\ G_{5s\sigma}^{5d} = -0.0638,\ G_{5s\sigma}^{6s} = -0.0581.$$

The semi-empirical calculations almost always include 6p shell. However, for the inclusions of these orbitals in the scheme of perturbation theory, perhaps insufficiently approximations that are used to calculate the above transition amplitudes. 6p orbitals overlap with the orbitals of the ligand shell is sufficiently large, so it is necessary to evaluate the terms dropped in the derivation of the expressions for the amplitudes of the transition. To estimate the order of magnitude and sign of the contributions from 6p shell with the basis of this work and in the notation for the spin densities where accepted $q_{6pi} = -p_{6pi} = \gamma_{6pi} = s_i$, i.e. value equal to the overlap integrals, taken with the appropriate sign. Performing similar calculations were received:

$$G_{5ps}^{6p} \approx 0, \qquad G_{5p\sigma}^{6p} \approx 0.06623, \qquad G_{5p\pi}^{6p} \approx -0.026487.$$

In the ***section 6.4*** covalence parameters are calculated for the impurity centers Yb^{3+}: $CsCaF_3$, Cs_2NaYF_6. In the case of the non-isovalent substitution, i.e. for impurity centers Yb^{3+}: $CsCaF_3$, covalence parameters for the valence shell are

$$\bar{\gamma}_{4fs} = -0.0134, \qquad \bar{\gamma}_{4f\sigma} = -0.0653, \qquad \bar{\gamma}_{4f\pi} = 0.0298.$$

For the impurity center

For the impurity center Yb^{3+}:Cs_2NaYF_6, i.e. isovalent replacement charge defects m_e, m_b in the basic configuration are equal to zero, unlike the Yb^{3+}: $CsCaF_3$. At the same time in the excited configuration the interaction of the electron-hole [23] is aroused. It also noted that it is significantly dependent on the actual distribution of the electron density. The several matrix elements of these interactions is cite:

т.е. изовалентного замещения, зарядовые дефекты m_e, m_b в основной конфигурации равны нулю, в отличие от Yb^{3+}:$CsCaF_3$. В то же время в возбужденной конфигурации возникает взаимодействие электрон-дырка [23]. Там же отмечается, что оно заметно зависит от реального распределения электронной плотности. Приведем для сравнения несколько матричных элементов от этих взаимодействий:

$$\langle 2s|1/|\mathbf{r}-\mathbf{R}_e||2s\rangle = 0.24051, \quad \sum_k c_k^2 \langle \xi_k, 2s|g|\xi_k, 2s\rangle = 0.24053,$$

$$\langle 4f0|1/|\mathbf{r}-\mathbf{R}_e||2s\rangle = -0.00372, \quad \sum_k c_k^2 \langle \xi_k, 4f0|g|\xi_k, 2s\rangle = -0.00373,$$

where $|\Gamma_6\rangle = \sum c_k |\xi_k\rangle$ is the lower Kramers doublet. For the rest of the matrix elements are performed similar relations. It can be seen that the replacement of the left column on the right, by the transition from Yb^{3+}: $CsCaF_3$ to Yb^{3+}: Cs_2NaYF_6, almost does not change the value of the amplitude of the transition. The slight change is also because of the sums of matrix elements of the operator's H_{LR}. Thus, it is shown that the parameters of covalence within the approximations can be taken the same for Yb^{3+}: $CsCaF^3$ and Yb^{3+}: Cs_2NaYF_6. For other parameters covalence are obtained the following values:

$$\bar{\gamma}_{5ds} = 0.152, \ \bar{\gamma}_{5d\sigma} = 0.167, \ \bar{\gamma}_{5d\pi} = -0.0906, \ \bar{\gamma}_{6ss} = 0.290, \ \bar{\gamma}_{6s\sigma} = 0.165.$$

These estimates is allow us to explain the underlying cause of the proximity of the experimental values of the tensor components LSTV, though ions are introduced in different crystals, and in one case replacement non-isovalent and the other isovalence.

In ***section 6.5***, the spin Hamiltonian formalism is used and compared with experimental data for impurity centers Yb^{3+}: $CsCaF_3$, Cs_2NaYF_6. In the case of cubic impurity centers, in which an impurity ion is ion Yb^{3+}, the ligand hyperfine interaction Hamiltonian can be written as follows:

$$H_{LS} = T_{\|}\tilde{S}_z I_z + T_{\perp}\left(\tilde{S}_x I_x + \tilde{S}_y I_y\right). \tag{37}$$

The transition from the operators V_i to the spin Hamiltonian is conducted in the standard manner [8, 20].

The wave function of the doublet $\left|\Gamma_6\right\rangle$ is:

$$\left|\Gamma_6,\tilde{\mp}\right\rangle = \left(\frac{1}{3}\right)^{1/2}\left|4f\,0,+\right\rangle + \frac{1}{2}\left|4f\,1,-\right\rangle + \left(\frac{5}{12}\right)^{1/2}\left|4f\,-3,-\right\rangle. \tag{38}$$

Here are the expressions for contributions to the tensor components LSTV for the some processes. The contribution from the effects of non-orthogonality and covalent 4f-shell will be determined by the formulas [A11]

$$T_{\|}^{(1)} = \frac{1}{3} f_{4fs}^{(1)} a_s + \left(\frac{2}{3} f_{4f\sigma}^{(1)} + \frac{3}{2} f_{4f\pi}^{(1)} - \sqrt{\frac{3}{2}} f_{4f\sigma\pi}^{(1)}\right) a_p,$$

$$T_{\perp}^{(1)} = -\frac{1}{3} f_{4fs}^{(1)} a_s + \left(\frac{1}{3} f_{4f\sigma}^{(1)} + \frac{3}{4} f_{4f\pi}^{(1)} - \frac{13}{6}\sqrt{\frac{3}{2}} f_{4f\sigma\pi}^{(1)}\right) a_p.$$

The contribution from the operator V_2, taking into account virtual excitation of electrons from the 4f-shell overlying shell electron-hole interaction, will be determined by the formulas [A11]

$$T_{\|}^{(2)} = \frac{2}{3} f_{ds}^{(2)} a_s + \left(\frac{4}{3} f_{d\sigma}^{(2)} + 3 f_{d\pi}^{(2)}\right) a_p - \sqrt{\frac{3}{2}} f_{d\sigma\pi}^{(2)} a_p,$$

$$T_{\perp}^{(2)} = -\frac{2}{3} f_{ds}^{(2)} a_s + \left(\frac{2}{3} f_{d\sigma}^{(2)} + \frac{3}{2} f_{d\pi}^{(2)}\right) a_p - \frac{13}{6}\sqrt{\frac{3}{2}} f_{4f\sigma\pi}^{(2)} a_p.$$

In the experimental works the tensor of LSTV is usually lead to isotropic part $A_s = \left(T_\parallel + 2T_\perp\right)/3$ and anisotropic part $A_p = \left(T_\parallel - T_\perp\right)/3$. In Table 4 are given the contributions from all the above processes, as well as experimental data.

Table 4

The theoretical values of the parameters LSTV A_s and A_p (in MHz) of the first coordination sphere of F- for Yb^{3+} in $CsCaF_3$ and Cs_2NaYF_6. The experimental data are taken from [A11]

Crystal		A_d	V_1	V_2	V_3	V_4	V_5	Sum	Exper.
$CsCaF_3$	A_s	0	9.88	4.34	0.68	0	5.18	20.08	20.577
Cs_2NaYF_6						0.9		20.98	22.111
$CsCaF_3$	A_p	− 9.0	2.89	1.38	− 0.95	0	0.62	− 5.06	− 5.963
Cs_2NaYF_6						− 0.8		− 5.86	− 6.208

In ***section 6.6*** the isotropic component tensor LSTV ^{17}O ions at room temperature for the crystal $LaMnO_3$ is calculated. A comparison with the experimentally observed shift of the NMR line is conducted. We get enough good agreement with experiment [A15, A17]. Thus, according to NMR data it was determined cooperative picture in this compound.

In **conclusion**, the main results of the dissertation are short state.

1. The second quantization expressions for the single-particle and two-particle operators in the basis of the product of the wave functions of the interacting ions are obtained. The matrix elements can be calculated with any precision at the overlap integrals.

2. It is proved that in the developed formalism "non-orthogonality catastrophe" does not arise. The series of overlap integrals are finite.

3. The expression for the probability amplitudes of electron transition metal-ligand (analog covalency parameter in the method of molecular orbitals) is generalization. The calculations can be carried out without the assumption of smallness of the overlap integrals.

4. The theory of the interaction of spin and orbital moments of paramagnetic ions with neighboring nuclei of diamagnetic ions is developed. The most important virtual processes of charge transfer from the diamagnetic ions in the cladding of rare-earth ions are found. The important role of external polarization filled 5s- and 5p-shells is highlights. A mechanism for the creation of an extra field in the nuclei of the ligands associated with the electric field virtually excited hole-state on the ligand is offered.

5. A detailed comparison with experiments on the row of compounds is conducted. The development of theory and proposed mechanisms transferred magnetic fields on the nuclei of diamagnetic ions help to explain the main features of the formation of the local fields at the fluorine nuclei in impurity centers: Yb^{3+} in $CsCaF_3$ and Yb^{3+} in Cs_2NaYF_6.

6. The values of the local magnetic fields at the nuclei ^{17}O in $LaMnO_3$, with different ordering of the orbitals of the ions Mn^{3+}, are calculated. By comparison with experimental data set form of the wave functions of Mn^{3+} ions and thereby the picture of cooperative ordering in this compound is determined.

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