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

Effects of exchange-covalent bonds on the orbital moment of paramagnetic centers with unfilled $3d$ -shells[†]

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An effective operator of the interaction of the orbital moment of d -electrons with the magnetic field is derived by combining the method of secondary quantization with the technique of irreducible tensor operators. It is found that in addition to renormalization of the matrix elements of the total orbital momentum L there are new terms in the Hamiltonian of the interaction with the magnetic field. The effects are numerically calculated by the example of the ground term of Fe^{2+} ions in $\text{Fe}_2\text{Mo}_2\text{O}_8$. Additional magnetic dipole transitions with $\Delta M = \pm 3$ and $\Delta M = \pm 2$ are allowed when the magnetic field is directed along the c -axis of the crystal and in the perpendicular orientation, respectively.

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1. Introduction

A number of works have been devoted to the study of the effect of exchange-covalent bonds on the orbital moment of d electrons. In magnetic resonance, the effect is detected by the change in the magnetic moment. The method of molecular orbitals [1] is usually used in the interpretation of experimental data. The effect of these bonds is reduced to the reduction of matrix elements from the interaction operator of the orbital momentum with the external magnetic field, or, in other words, to the change in the components of the g -tensor for the ground state of the paramagnetic ion. Ions with orbitally nondegenerate states are usually chosen as objects of study.

In this work, the expressions for renormalization of the orbital momentum operator are derived. These expressions are applicable for arbitrary states of magnetic ions and require no preliminary determination of molecular orbitals. The problem is solved by the method of superposition of configurations. The fragment of a structure consisting of a magnetic ion and nearest diamagnetic ions (ligands) $3d^n L(2p^5 2s^2)$ is considered as the ground configuration. Excited states, in which electrons from the outer shells of ligands are transferred to the unfilled d shell, form configurations with charge transfer $3d^{n+1} L(2p^5)$, $3d^{n+1} L(2p^6 2s^1)$. The effect of overlapping electronic orbitals of the magnetic ion and ligands within the ground configuration taken into account is the same as in the generalized Heitler-London method [2] and is qualified as exchange. The effect of the admixture of states with charge transfer to the states of the ground configuration, the same as in the method of molecular orbitals, is called the covalency effect. Keeping in mind both exchange and the covalency effects, one may talk about the effect of exchange-covalent bonds of the orbital moment of paramagnetic centers.

[†]This paper is dedicated to Professor Boris I. Kochelaev on the occasion of his 90th birthday.

2. Derivation of the effective operator

In the secondary quantization approach developed in [2–4], an arbitrary one-particle operator for a metal-ligand pair taking into account virtual electron transfer processes is written as

$$F_{\text{eff}} = \frac{1}{2} \sum a_{\eta}^{\dagger} a_{\eta'} \{ \langle \eta | f | \eta' \rangle - 2 \langle \eta | f | \rho \rangle \lambda_{\rho \eta'} + \lambda_{\eta \kappa} \langle \kappa | f | \rho \rangle \lambda_{\rho \eta'} + \langle \eta | f | \xi \rangle [S_{\xi \rho} S_{\rho \eta'} - \gamma_{\xi \rho} \gamma_{\rho \eta'}] \} \quad (1)$$

+h.c.

where the sets of quantum numbers η , ξ refer to the $3d$ electron, and the sets of the quantum number ρ refer to the $2p$ and $2s$ electrons of oxygen, $S_{\eta \kappa}$ are overlap integrals, $\gamma_{\eta \rho}$ are covalency parameters that take into account virtual transfer processes of $2p$ and $2s$ electrons from oxygen to the $3d$ shell of the magnetic ion.

In this work we consider the following operator f

$$f = \mu_B \mathbf{LH} = \mu_B \sum_k (-1)^q l_q^{(1)} H_{-q}^{(1)}, \quad (2)$$

where $l_q^{(1)}$ and $H_{-q}^{(1)}$ denote spherical components of the orbital momentum operator and the external magnetic field, respectively. Since the operator f is independent of spin variables, we replace pairs of secondary quantization operators in Eq.(1) by combinations of components of irreducible tensor operators [5]:

$$a_{lm}^{\dagger} a_{lm'} = \sum_{k,q} (2k+1) (-1)^{l-m} \begin{pmatrix} l & k & l \\ -m & q & m' \end{pmatrix} U_q^{(k)}. \quad (3)$$

The reduced matrix elements of one-electron operators $u_q^{(k)}$ are assumed to be unity, i.e.,

$$\langle lm | u_q^{(k)} | lm' \rangle = (-1)^{l-m} \begin{pmatrix} l & k & l \\ -m & q & m' \end{pmatrix}. \quad (4)$$

Substituting Eq.(3) into Eq.(1), we obtain

$$F_{\text{eff}} = \mu_B \sum_{k,q} (-1)^q (2k+1) \langle m | [l_q^{(1)}]_{\text{eff}} | m' \rangle (-1)^{l-m} \begin{pmatrix} l & k & l \\ -m & q & m' \end{pmatrix} U_q^{(k)} H_{-q}^{(1)}. \quad (5)$$

Here we introduce the notation

$$\begin{aligned} \langle m | [l_q^{(1)}]_{\text{eff}} | m' \rangle &= \langle m | l_q^{(1)} | m' \rangle - \langle m | l_q^{(1)} | \rho \rangle \lambda_{\rho m'} - \lambda_{m \rho} \langle \rho | l_q^{(1)} | m' \rangle + \lambda_{m \kappa} \langle \kappa | l_q^{(1)} | \rho \rangle \lambda_{\rho m'} \\ &+ \frac{1}{2} \langle m | l_q^{(1)} | \xi \rangle [S_{\xi \rho} S_{\rho m'} - \gamma_{\xi \rho} \gamma_{\rho m'}] + \frac{1}{2} [S_{m \rho} S_{\rho \xi} - \gamma_{\eta \rho} \gamma_{\rho \xi}] \langle \xi | l_q^{(1)} | m' \rangle. \end{aligned} \quad (6)$$

The matrix elements in Eq.(6) are most easily calculated when the local coordinate axes on the metal ion and on the ligand are chosen to be parallel. The z -axes are directed along the metal-ligand pair from the metal ion to the ligand. The nonzero matrix elements in the basis of d -electron states are given in Table 1.

Contributions to matrix elements due to overlap and covalency effects from operators $l_1^{(1)} = -\frac{1}{\sqrt{2}}(l_x + il_y)$, $l_0^{(1)} = l_z$, $l_{-1}^{(1)} = \frac{1}{\sqrt{2}}(l_x - il_y)$ are denoted by letters k_{12} , k_{01} , and k_{12} using row and column subscripts:

$$k_{01} = -\frac{1}{2}(\lambda_{\sigma}^2 + \lambda_{\pi}^2 + \lambda_s^2) + \frac{1}{\sqrt{3}}(\lambda_{\sigma} \lambda_{\pi} + \lambda_{\pi} R_{ps} \lambda_s), \quad k_{12} = -\frac{\lambda_{\pi}^2}{2}, \quad k_{11} = -\lambda_{\pi}^2. \quad (7)$$

Table 1. Matrix elements $\langle m|[l_q^{(1)}]_{\text{eff}}|m'\rangle$ in the basis of d -electron states

m/m'	2	1	0	-1	-2
2	2	$-\sqrt{2}(1+k_{12})$			
1	$\sqrt{2}(1+k_{12})$	$1+k_{11}$	$-\sqrt{3}(1+k_{01})$		
0		$\sqrt{3}(1+k_{01})$	0	$-\sqrt{3}(1+k_{01})$	
-1			$\sqrt{3}(1+k_{01})$	$-1-k_{11}$	$-\sqrt{2}(1+k_{12})$
-2				$\sqrt{2}(1+k_{12})$	-2

In Eqs.(7), standard notations are used for the overlap integrals [1]:

$$S_\sigma = \langle 3d0|2p0\rangle, \quad S_\pi = \langle 3d1|2p1\rangle = \langle 3d-1|2p-1\rangle, \quad S_s = \langle 3d0|2ps\rangle. \quad (8)$$

Similar notations are adopted for the covalence parameters γ_σ , γ_π , and γ_s . The integral on the ligand wave functions:

$$R_{ps} = -\frac{R}{\sqrt{2}} \left(2p1 \left| \frac{\partial}{\partial x} + i \frac{\partial}{\partial y} \right| 2s \right). \quad (9)$$

is similar to that in the method of molecular orbitals, R is the metal-ligand distance. The value R_{ps} we calculated at $R = 2 \text{ \AA}$ on the wave functions of O^{2-} from Tables [6] is -1.425 , which is somewhat less than the value -1.6 obtained in [7] for the Ni^{2+} - F^- pair, which is explained by a more diffuse distribution of the electron density of the $2p$ and $2s$ electrons near the O^{2-} nucleus.

To derive the energy operator for the interaction of the d -ion surrounded by several ligands with a magnetic field, we first use the formula:

$$H_{-q}^{(1)} U_q^{(k)} = \sum_{k,q} (-1)^{1-k} \sqrt{(2p+1)} \begin{pmatrix} 1 & k & p \\ -q & q & 0 \end{pmatrix} \left\{ H^{(1)} U^{(k)} \right\}_0^{(p)}. \quad (10)$$

Substituting Eq. (10) into Eq. (5), we obtain the energy operator

$$F_{\text{eff}} = \mu_B \sum_{p,q} \tilde{l}^{(k)} (-1)^{1-k} \sqrt{(2p+1)} \begin{pmatrix} 1 & k & p \\ -q & q & 0 \end{pmatrix} \left\{ H^{(1)} U^{(k)} \right\}_0^{(p)}, \quad (11)$$

where

$$\tilde{l}^{(k)}(R_b) = \sum_{m,m'} (2k+1) (-1)^q \langle m|[l_q^{(1)}]_{\text{eff}}|m'\rangle (-1)^{l-m} \begin{pmatrix} l & k & l \\ -m & q & m' \end{pmatrix}. \quad (12)$$

The subscript b is introduced to denote the position of the ligand, which is separated from the metal ion by a distance R_b . If we consider $l = 2$, k can be 1 and 3.

Using Eq. (12), one gets the following expressions for internal parameters for a selected metal-ligand pair

$$\begin{aligned} \tilde{l}_1^{(1)}(R_b) = \tilde{l}_{-1}^{(1)}(R_b) &= -\sqrt{\frac{6}{5}}(5 + 3k_{01} + 2k_{12}), & \tilde{l}_0^{(1)}(R_b) &= \sqrt{\frac{6}{5}}(5 + k_{11}), \\ \tilde{l}_1^{(3)}(R_b) = \tilde{l}_{-1}^{(3)}(R_b) &= 2\sqrt{\frac{21}{5}}(k_{01} - k_{12}), & \tilde{l}_0^{(3)}(R_b) &= -4\sqrt{\frac{7}{10}}k_{11}. \end{aligned} \quad (13)$$

In the right-hand side of Eq. (11), we note invariant combinations of k_{12} , k_{01} , and k_{11} with respect to rotations around the axis of the metal-ligand pair

$$l^{(1k)p}(R_b) = \sum_q \tilde{l}_q^{(k)} (-1)^{1-k} \sqrt{(2p+1)} \begin{pmatrix} 1 & k & p \\ -q & q & 0 \end{pmatrix}. \quad (14)$$

In our case, these combinations are written as

$$\begin{aligned} l^{(11)0} &= -\sqrt{90} - \sqrt{\frac{2}{5}}(k_{11} + 4k_{12} + 6k_{01}), & l^{(11)2} &= \frac{2}{\sqrt{5}}(k_{11} - 2k_{12} - 3k_{01}), \\ l^{(13)2} &= \frac{2\sqrt{6}}{\sqrt{5}}(k_{11} - 2k_{12} + 2k_{01}), & l^{(13)4} &= \frac{4}{\sqrt{10}}(-2k_{11} - 3k_{12} + 3k_{01}). \end{aligned} \quad (15)$$

The equation (11) at $p = 0$ describes the interaction of the isotropic (spherically symmetric) part of the orbital momentum with the magnetic field. It can be seen from Eqs. (13) and (15) that the exchange-covalent bonding with the ligand is determined by the terms containing k_{11} , k_{12} , and k_{01} .

The isotropic part of the change in the spherical components of the orbital moment is equal to the sum over the surrounding ligands and is proportional to $L_q^{(1)}$ of the proportionality coefficient given by

$$\delta = \frac{1}{15} \sum_b (k_{11} + 4k_{12} + 6k_{01}). \quad (16)$$

Here, the summation index b refers to the surrounding ligands. The total energy operator of the complex containing the magnetic ion and surrounding ligands is

$$F_{\text{eff}} = \mu_B \mathbf{LH}(1 + \delta) + \mu_B \sum_{b,p \neq 0,t} l^{(1k)p}(R_b) \left\{ H^{(1)} U_q^{(k)} \right\}_t^{(p)} (-1)^t C_{-t}^{(p)}(\vartheta_b \varphi_b), \quad (17)$$

where $C_{-t}^{(p)}(\vartheta_b \varphi_b)$ are components of the spherical tensor fixing the direction of metal-ligand pairs with respect to the crystallographic coordinate system. Equation (17) is directly used in the basis of many-electron wave functions $|d^n S L M_S M_L\rangle$. The construction of molecular orbitals is not required. In Eq. (17), a simple summation over the positions of the surrounding ligands is carried out, the same as in the crystal field theory. The symmetry of the position of the magnetic ion can be arbitrary.

We note that during calculations of matrix elements of the interaction operator of the orbital momentum with the magnetic field, it is convenient to rewrite it in the form

$$F_{\text{eff}} = \mu_B \mathbf{LH}(1 + \delta) + \mu_B \sum_{b,p \neq 0,t} L_t^{(1k)p} \left\{ H^{(1)} U_q^{(k)} \right\}_t^{(p)}, \quad (18)$$

where the quantities

$$L_t^{(1k)p} = \sum_b l^{(1k)p}(R_b) (-1)^t C_{-t}^{(p)}(\vartheta_b \varphi_b) \quad (19)$$

are characteristics of the complex (a paramagnetic ion+ligands). The sum $1 + k + p$ can only be even, as it should be for the Hermite conjugate operator. In the case of d electrons, k takes the values of 1 and 3. The quantities $L_t^{(1k)p}$ at $p = 2$ and 4 correspond to the anisotropic terms of the effective orbital momentum. They have not been discussed earlier in the literature.

3. Numerical estimates for $\text{Fe}_2\text{Mo}_3\text{O}_8$ and discussion of results

The compound $\text{Fe}_2\text{Mo}_3\text{O}_8$ is a magnetoelectric with a record high electric polarization [8,9]. Iron Fe^{2+} ions occupy tetrahedral and octahedral positions in equal proportions, which are usually denoted by the letters A and B, respectively [10]. Both positions have trigonal distortions. The point group symmetry is C_3 . The subscript t in Eq. (19) takes the values 0 and ± 3 . For the

choice of coordinate systems as explained in Tables 2 and 3, the imaginary parts of the $L_3^{(13)4}$ and $L_{-3}^{(13)4}$ values are zero. Thus, we have the following set of quantities for both positions:

$$\begin{aligned}
L_0^{(11)2} &= \sum_b l^{(11)0}(R_b)C_0^{(2)}(\vartheta_b\varphi_b), & L_0^{(13)2} &= \sum_b l^{(13)2}(R_b)C_0^{(2)}(\vartheta_b\varphi_b), \\
L_0^{(13)4} &= \sum_b l^{(13)4}(R_b)C_0^{(4)}(\vartheta_b\varphi_b), & L_3^{(13)4} &= -\sum_b l^{(13)4}(R_b)C_{-3}^{(4)}(\vartheta_b\varphi_b).
\end{aligned}
\tag{20}$$

Table 2. Coordinates of nearest oxygens (in Å) near Fe(A) positions in the Cartesian coordinate system [11, 12].

Nearest neighbors	X(O-Fe)	Y(O-Fe)	Z(O-Fe)	R(Fe-O)
O1	-1.7872	0	-0.9068	2.0041
O2	0.8936	1.5478	-0.9068	2.0041
O3	0.8936	-1.5478	-0.9068	2.0041
O4	0	0	1.9456	1.9456

Table 3. Coordinates of nearest oxygens around Fe(B) (in Å)

Nearest neighbors	X(O-Fe)	Y(O-Fe)	Z(O-Fe)	R(Fe-O)
O1	1.3398	-0.7735	-1.5056	2.1588
O2	0	1.5471	-1.5056	2.1588
O3	-1.3398	-0.7735	-1.5056	2.1588
O4	-1.4452	0.8344	1.2238	2.0694
O5	0	-1.6688	1.2238	2.0694
O6	1.4452	0.8344	1.2238	2.0694

Table 4. Overlap integrals S and covalency parameters γ and k_{01}, k_{12}, k_{11} for $\text{Fe}_2\text{Mo}_3\text{O}_8$

R (in Å)	1.9456	2.0041	2.0694	2.1588
$\gamma_{3d0,2p0}$	-0.24	-0.23	-0.21	-0.19
$\gamma_{3d1,2p1}$	0.23	0.18	0.16	0.14
$\gamma_{3d0,2s}$	-0.03	-0.03	-0.02	-0.02
$S_{3d0,2p0}$	-0.0721	-0.0679	-0.0633	-0.0573
$S_{3d1,2p1}$	0.0576	0.0522	0.0470	0.0408
$S_{3d0,2s}$	-0.0770	-0.0697	-0.0622	-0.0534
k_{01}	-0.162	-0.140	-0.100	-0.080
k_{12}	-0.043	-0.036	-0.029	-0.022
k_{11}	-0.007	-0.006	-0.004	-0.003

The Hartree-Fock wave functions $\text{Fe}^{2+}(3d)$ and $\text{O}^{2-}(2p, 2s)$ were taken from [6]. To estimate γ at $R = 1.988 \text{ \AA}$, we used their values determined for Ni-O and Cr-O pairs in oxides by magnetic resonance methods [13, 14], and their variation as a function of R was calculated under the assumption that $\gamma(R) \approx S(R)$. To calculate the overlap integrals as functions of R , the Gaussian-type decompositions of radial wave functions on orbitals (GTO) were used. These decompositions are given in Ref. [15]. We note that Eq. (17) can be rewritten as follows:

Table 5. Calculated parameters $L_t^{(1k)p}$ for sites Fe(A) and Fe(B)

site	$L_0^{(11)2}$	$L_0^{(13)2}$	$L_0^{(13)4}$	$L_3^{(13)4}$
A	0.256	-0.265	-0.194	-0.544
B	0.196	-0.204	0.576	0.599

$$F_{\text{eff}} = \mu_B \mathbf{LH}(1 + \delta) + \mu_B \sum_{k,p \neq 0,q} (-1)^q T_q^{(kp)1} H_{-q}^{(1)}, \quad (21)$$

where

$$T_q^{(kp)1} = \sqrt{(2p+1)} \sum_{t,q'} (-1)^{1-k+q'} \begin{pmatrix} 1 & k & p \\ q & -q' & t \end{pmatrix} L_t^{(1k)p} U_{q'}^{(k)}. \quad (22)$$

In this form, Eq. (21) may be conveniently compared with Eq. (2). It is a generalization of Eq. (2) to take into account exchange-covalent effects in paramagnetic centers. For both types of fragments, tetrahedral (FeO_4) and octahedral (FeO_6) ones, the operator (21) of the effective magnetic field interaction is written as in μ_B :

$$\begin{aligned} F_{\text{eff}} = & \mathbf{LH}(1 + \delta) \\ & - \left\{ -\sqrt{\frac{2}{3}} L_0^{(11)2} U_0^{(1)} + \left[\sqrt{\frac{3}{7}} L_0^{(13)2} - \sqrt{\frac{4}{7}} L_0^{(13)4} \right] U_0^{(3)} + \frac{1}{2} \left[L_3^{(13)4} U_3^{(3)} + L_{-3}^{(13)4} U_{-3}^{(3)} \right] \right\} H_z \\ & + \sqrt{\frac{1}{6}} L_0^{(11)2} \left(U_{-1}^{(1)} H_1^{(1)} + U_1^{(1)} H_{-1}^{(1)} \right) + \left[\sqrt{\frac{2}{7}} L_0^{(13)2} + \sqrt{\frac{3}{14}} L_0^{(13)4} \right] \left(U_{-1}^{(3)} H_1^{(1)} + U_1^{(3)} H_{-1}^{(1)} \right) \\ & + \sqrt{\frac{3}{4}} \left(L_3^{(13)4} U_2^{(3)} H_1^{(1)} + L_{-3}^{(13)4} U_{-2}^{(3)} H_{-1}^{(1)} \right). \end{aligned} \quad (23)$$

It can be seen from Eq. (23) that when the external field is directed along the c -axis of the crystal, matrix elements with the selection rule $\Delta M = \pm 3$ appear, and in the case, when the magnetic field is perpendicular to the c -axis, additional transitions with $\Delta M = \pm 2$ are implemented. The matrix elements we calculated according to Eq. (23) are given in Tables 6 and 7. Tables 6 and

Table 6. Calculated matrix elements at $p \neq 0$ and $q > 0$ for Fe(A) (in μ_B), $\delta = -0.27$.

m/m'	2	1	0	-1	-2
2	$-0.080H_z$	$0.021H_{-1}^{(1)}$	$-0.126H_1^{(1)}$	$0.073H_z$	0
1		$-0.032H_z$	$-0.072H_{-1}^{(1)}$	0	$0.073H_z$
0			0	$-0.072H_{-1}^{(1)}$	$0.126H_1^{(1)}$
-1				$0.032H_z$	$0.021H_{-1}^{(1)}$
-2					$0.080H_z$

7 show that the order of magnitude of the change in the orbital moment is the same as that in the method of molecular orbitals. It can also be seen that the effect of exchange-covalent bonds is not reduced to simple renormalization of the matrix elements of the orbital moment. There are additional matrix elements with selection rules $\Delta M = \pm 2$ and $\Delta M = \pm 3$. Moreover, these new matrix elements are on the same order of magnitude as those that are usually taken into account by the orbital momentum reduction.

Table 7. Calculated matrix elements at $p \neq 0$ and $q > 0$ for Fe(B) (in μ_B), $\delta = -0.26$.

m/m'	2	1	0	-1	-2
2	$-0.126H_z$	$-0.053H_{-1}^{(1)}$	$0.139H_1^{(1)}$	$-0.080H_z$	0
1		$0.107H_z$	$0.001H_{-1}^{(1)}$	0	$-0.080H_z$
0			0	$0.001H_{-1}^{(1)}$	$-0.139H_1^{(1)}$
-1				$-0.107H_z$	$-0.053H_{-1}^{(1)}$
-2					$0.126H_z$

4. Concluding remarks

Operators (17) and (21) are applicable for arbitrary symmetries of paramagnetic complexes and allow the description of the effects of exchange-covalent coupling with ligands of many-electron ions without construction of Slater determinants from molecular orbitals. It is found that in addition to renormalization of the matrix elements of the total orbital momentum L , there are new terms in the Hamiltonian of the interaction with the magnetic field, which have not been discussed in the literature. These new terms have other selection rules of matrix elements. They make the magnetic-dipole transitions with selection rules $\Delta M = \pm 2$ and $\Delta M = \pm 3$ possible. In paramagnetic centers without inverse symmetry such transitions may be important in the study of the effects caused by interference of magnetic and induced electric dipole transitions. Such interference underlies the phenomena of irreversibility in the light passing through the plates and is of interest for applications, such as calculations of the efficiency of optical diodes. We note that the expressions we obtained are also applicable to compounds with unfilled $5d$ and $6d$ shells. Exchange-covalent bonds of $5d$ and $6d$ electrons with their surrounding ligands are expected to be especially strong.

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