Exchange interactions in crystals with orbit-degenerate atomic configurations

V. Yu. Irkhin and Yu. P. Irkhin

Institute of Physics of Metals Ural Branch of the Russian Academy of Sciences, 620219 Ekaterinburg, Russia

(Submitted 6 July 1993)
Zh. Eksp. Teor. Fiz. **104**, 3868–3885 (November 1993)

We use the method of irreducible tensor operators in the second-quantization representation to derive the equivalent Hamiltonian of intersite Coulomb and exchange interactions for orbit-degenerate atomic states. The fact that the atomic wave functions at different sites are not orthogonal is consistently taken into account. We obtain a multipole expansion for the Heisenberg Hamiltonian in powers of the orbital angular momentum operators and the vectors connecting the sites of the crystal lattice. The cases of weak and strong spin-orbit coupling are considered. Within the degenerate Hubbard model, with allowance for orbital dependence of transport integrals, we obtain the Hamiltonian of superexchange interaction for a magnetic insulator; we also study the dependence of the sign of spin and orbital exchange on the quantum numbers of the virtual states of ions. For the case of a narrow-band conductor (double exchange interaction) we find a representation of this model in terms of the spin and orbital angular momenta.

1. INTRODUCTION

Dirac's derivation[1] of the Heisenberg Hamiltonian for *s*-states (spin $\frac{1}{2}$) laid the foundation for the theory of exchange interaction in solids. Atomic-spectroscopy methods developed by Racah (see Ref. 2) made it possible to examine the case of real degenerate atomic configurations and obtain the Hamiltonian in the Heisenberg model for higher spins.[3] Subsequent theoretical papers focused on studying, within the *s-f* model, the indirect exchange interaction, via conduction electrons, between multielectron 4*f*-shells of rare-earth ions.[4–9] The exchange interaction in systems of *d*-electrons[10–12] was basically treated in the single-electron representation, which corresponds to the approximation of a strong crystalline field completely destroying atomic states. This assumption, however, is not justified in some cases since the Coulomb interaction is fairly strong.

In this paper we examine systematically the real mechanisms of the exchange interaction between magnetic ions with degenerate atomic configurations and unfrozen orbital magnetic moments. Use of the technique of irreducible tensor operators in the second-quantization representation[13] enabled us to derive the Hamiltonian of the Heisenberg model for the direct exchange interaction by reasoning along lines more simple than those used in Ref. 3, and to represent the result in a more compact form. Although the case of direct exchange is of interest mainly from the methodological point of view, examining this simple example reveals the structure of the Hamiltonian, which remains intact in more complex situations. Contrary to the usual approach, we use in addition to spin operators S operators of total orbital momentum L, which makes it possible to study the orbit-dependent anisotropic contributions to the Coulomb and exchange interactions.

We consider the limits of weak spin-orbit coupling (Sec. 3) and strong spin-orbit coupling (Sec. 4) in the Russell–Saunders coupling scheme, that is, the approximations of moderate and weak crystalline fields; in the latter case the Hamiltonian is expressed in terms of operators of total angular momentum J.

In Sec. 5 we employ the method of multielectron X-operators to study the exchange interaction through the valence band in a magnetic insulator; in describing this we use the Hubbard model with degenerate atomic configurations. A canonical transformation reduces this model to a Hamiltonian of the Heisenberg type. Finally, remaining within the same model, we study in Sec. 6 a magnetic semiconductor or a metal with strong intratomic interaction and a narrow conduction band. Indirect interaction between magnetic moments in such systems is essentially non-Heisenberg. We also transform the kinetic-energy Hamiltonian to the spin and orbital angular momenta representation.

2. THE MULTIELECTRON HAMILTONIAN OF THE CRYSTAL

Let us examine the Hamiltonian of the system of interacting electrons in a solid:

$$H=\sum_i\left(-\frac{1}{2m}\Delta_{\mathbf{r}_i}+V(\mathbf{r}_i)\right)+\frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\mathbf{r}_i-\mathbf{r}_j|},\qquad(1)$$

with $V(\mathbf{r})$ the periodic crystalline potential. With a view to considering orbit-degenerate configurations weakly perturbed by the crystalline field, we use the tight-binding approximation with the atomic wave functions

$$\phi_{lm\sigma}(\mathbf{r},s)=\phi_{lm}(\mathbf{r})\chi_\sigma(s)=R_l(r)Y_{lm}(\hat{\mathbf{r}})\chi_\sigma(s),\qquad(2)$$

where l is the magnetic quantum number (for the sake of brevity we drop the principal quantum number), and s is the spin coordinate.

When going over to the second-quantization representation, we must use orthogonal wave functions. Generally, this condition is not valid for functions (2) at different sites ν. Nonorthogonality constitutes a fairly difficult problem

1063-7761/93/110858-10$10.00

in the theory of magnetism.[1] Here we use Bogolyubov's orthogonalization procedure,[14] which in the lowest order in the overlap of wave functions at different sites yields

$$\psi_{\nu lm}(\mathbf{r})=\phi_{\nu lm}(\mathbf{r})-\frac{1}{2}\sum_{\nu'\neq\nu}\sum_{l'm'}\phi_{\nu' l'm'}(\mathbf{r})\int d^3\mathbf{r}' \times\phi^*_{\nu' l'm'}(\mathbf{r}')\phi_{\nu lm}(\mathbf{r}'). \quad (3)$$

Then, after second quantization, the Hamiltonian (1) assumes the form

$$H=\sum_{\nu lm\sigma}\varepsilon_l a^+_{\nu lm\sigma}a_{\nu lm\sigma} +\sum_{\nu_1\neq\nu_2}\sum_{l_im_i\sigma}\beta_{\nu_1\nu_2}(l_1m_1,l_2m_2)a^+_{\nu_1l_1m_1\sigma}a_{\nu_2l_2m_2\sigma} +\frac{1}{2}\sum_{\nu_il_im_i\sigma_1\sigma_2}I_{\nu_1\nu_2\nu_3\nu_4}(l_1m_1,l_2m_2,l_3m_3,l_4m_4) \times a^+_{\nu_1l_1m_1\sigma_1}a^+_{\nu_2l_2m_2\sigma_2}a_{\nu_4l_4m_4\sigma_2}a_{\nu_3l_3m_3\sigma_1}, \quad (4)$$

where we used the fact that the spin functions $\chi_\sigma(s)$ are orthogonal,

$$\varepsilon_l=\int_0^\infty dr r^2R_l(r)\left[-\frac{1}{2mr^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)+\frac{l(l+1)}{2mr^2}+v(r)\right]R_l(r) \quad (5)$$

is the energy of single-electron levels in the potential $v(r)$ of a given site (we ignore the effect of potentials of neighboring sites, i.e., crystalline-field effects),

$$\beta_{\nu_1\nu_2}(l_1m_1,l_2m_2)=\int d^3r\psi^*_{\nu_1l_1m_1}(\mathbf{r})V(\mathbf{r})\psi_{\nu_2l_2m_2}(\mathbf{r}) \quad (6)$$

are the transport integrals between sites ν_1 and ν_2, and

$$I_{\nu_1\nu_2\nu_3\nu_4}(l_1m_1,l_2m_2,l_3m_3,l_4m_4) =\int d^3\mathbf{r}d^3\mathbf{r}'\psi^*_{\nu_1l_1m_1}(\mathbf{r})\psi^*_{\nu_2l_2m_2}(\mathbf{r}')\frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \times\psi_{\nu_3l_3m_3}(\mathbf{r})\psi_{\nu_4l_4m_4}(\mathbf{r}') \quad (7)$$

are the matrix elements of interelectron electrostatic interaction.

To analyze the m-dependence of two-site matrix elements, it is convenient to expand the wave functions $\psi_{\nu_2}(r)$ in terms of functions centered at site ν_1. Following Ref. 15, we perform the Fourier transformation

$$\phi_{lm}(\mathbf{r})=\int d^3\mathbf{k}\exp(i\mathbf{kr})\widetilde{R}_l(k)Y_{lm}(\hat{\mathbf{k}}), \quad (8)$$

with $\widetilde{R}_l(k)$ the Fourier transforms of the radial functions, and expand the plane waves in spherical harmonics:

$$\exp(i\mathbf{kr})=4\pi\sum_{\lambda\mu}i^\lambda j_\lambda(kr)Y^*_{\lambda\mu}(\hat{\mathbf{k}})Y_{\lambda\mu}(\hat{\mathbf{r}}), \quad (9)$$

where $j_l(x)$ are the spherical Bessel functions. Integration yields

$$\phi_{\nu_2lm}(\mathbf{r})=\phi_{\nu_1lm}(\mathbf{r}+\rho) =\sum_{l'm'\lambda\mu}\widetilde{C}^{l'm'}_{lm,\lambda\mu}R_{ll'\lambda}(r,\rho)Y^*_{\lambda\mu}(\hat{\rho})Y_{l'm'}(\hat{\mathbf{r}}), \quad (10)$$

where the quantities

$$\widetilde{C}^{l_1m_1}_{l_2m_2,l_3m_3}=\int_0^\pi\sin\theta d\theta\int_0^{2\pi}d\phi Y^*_{l_1m_1}(\hat{\mathbf{r}})Y_{l_2m_2}(\hat{\mathbf{r}})Y_{l_3m_3}(\hat{\mathbf{r}}) =\left(\frac{[l_1][l_2]}{4\pi[l_1]}\right)^{1/2}C^{l_10}_{l_20,l_30}C^{l_1m_1}_{l_2m_2,l_3m_3}\quad([A]\equiv 2A+1) \quad (11)$$

are the matrix elements of spherical functions and are nonzero for even-valued $l_1+l_2+l_3$ (see Refs. 2 and 16), the quantities C are the Clebsch–Gordan coefficients, and

$$R_{ll'\lambda}(r,\rho)=\int_0^\infty k^2dkR_l(k)i^{\lambda+l'}j_{l'}(kr)j_\lambda(k\rho). \quad (12)$$

Substituting (10) into (6), we obtain

$$\beta_{\nu_1\nu_2}(l_1m_1,l_2m_2) =4\pi\sum_{\lambda\mu}\widetilde{C}^{l_2m_2}_{l_1m_1,\lambda\mu}\bar{\beta}_{\nu_1\nu_2}(l_1l_2,\lambda)Y_{\lambda\mu}(\hat{\rho}_{\nu_1\nu_2}), \quad (13)$$

where we have again retained only the potential of site ν_1, a procedure justified in the case of a rapidly decreasing $v(r)$ (in this approximation there are no nonorthogonality corrections to the transport integral[14]), with

$$\hat{\beta}_{\nu_1\nu_2}(l_1l_2,\lambda)=\int_0^\infty r^2drR_{l_1}(r)v(r)R_{l_2l_1\lambda}(r,\rho_{\nu_1\nu_2}). \quad (14)$$

Clearly, for even-valued l_1-l_2 (in particular, at $l_1=l_2$) λ is even, while for odd-valued l_1-l_2 (e.g., for the matrix elements of *s-p*, *p-d*, and *d-f* hybridization) an angular dependence with $\lambda=1$ may emerge.

In what follows we use Eq. (13) with $l_1=l_2$ when we examine superexchange and double exchange. Now we proceed with the analysis of electrostatic interaction.

3. INTERATOMIC COULOMB AND EXCHANGE INTERACTIONS AND DERIVATION OF THE HEISENBERG HAMILTONIAN

By employing Eqs. (3) and (10) we can examine the electrostatic interaction between two shells of different atoms by analogy with the intra-atomic interaction (see Ref. 2). The contribution to (7) with $\nu_1l_1=\nu_3l_3$ and $\nu_2l_2=\nu_4l_4$ describes direct Coulomb interaction. Since this contribution is not small in the wave-function overlap, nonorthogonality can be ignored. Using the expansion

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|}=\sum_{p=0}^{\infty}\frac{4\pi}{[p]}\frac{r^p_<}{r^{p+1}_>}\sum_{q=-p}^{p}Y_{pq}(\hat{\mathbf{r}})Y^*_{pq}(\hat{\mathbf{r}}'), \quad (15)$$

Eq. (11), and the formula for multiplying spherical harmonics

$$Y_{\lambda_1\mu_1}(\hat{\rho})Y_{\lambda_2\mu_2}(\hat{\rho})=\sum_{\lambda\mu}\widetilde{C}^{\lambda\mu}_{\lambda_1\mu_1,\lambda_2\mu_2}Y_{\lambda\mu}(\hat{\rho}) \quad (16)$$

and transforming the product of Clebsch–Gordan coefficients via the $9j$-symbol, we find that

$$H_{\text{Coul}}=(4\pi)^{1/2}\sum_{pb\lambda}\sum_{\lambda_1\lambda_2\eta_1\eta_2}F^{(p)}(l_1l_2\eta_1\eta_2\lambda_1\lambda_2)[b][\lambda_1][\lambda_2]$$
$$\times[l_2]^{1/2}(-1)^{\lambda_1}C$$
$$\times(l_1pl_1,l_2\lambda_1\eta_1,\eta_2p\eta_1,l_2\lambda_2\eta_2,\lambda_1\lambda_2\lambda)$$
$$\times\begin{Bmatrix} l_2 & \lambda_1 & \eta_1\\ l_2 & \lambda_2 & \eta_2\\ b & \lambda & p\end{Bmatrix}[W_1^{(0p)}\times W_2^{(0b)}]^{(\lambda)}\cdot Y^{(\lambda)}(\hat{\boldsymbol{\rho}}), \tag{17}$$

where

$$F^{(p)}(l_1l_2\eta_1\eta_2\lambda_1\lambda_2)$$
$$=e^2\int_0^\infty r_1^2dr_1r_2^2dr_2R_{l_1}^2(r_1)R^*_{l_2\eta_2\lambda_2}(r_2,\rho)\frac{r_<^p}{r_>^{p+1}}$$
$$\times R_{l_2\eta_1\lambda_1}(r_2,\rho) \tag{18}$$

are the Slater integrals for two-site interaction,

$$C(a_1b_1c_1,a_2b_2c_2,\ldots)=\prod_i C^{c_i0}_{a_i0,b_i0},$$

$Y^{(\lambda)}$ is the irreducible tensor operator with components $Y_{\lambda\mu}$, the double irreducible tensor operator $W^{(\kappa k)}$ is examined in the Appendix, and the irreducible tensor product of rank c and the scalar product are defined as in Ref. 16:

$$[A^{(a)}\times B^{(b)}]^{(c)}_\gamma=\sum_{\alpha\beta}C^{c\gamma}_{a\alpha,b\beta}A^{(a)}_\alpha B^{(b)}_\beta, \tag{19}$$

$$(A^{(a)}\times B^{(a)})=(-1)^a[a]^{1/2}[A^{(a)}\times B^{(a)}]^{(0)}$$
$$=\sum_\alpha(-1)^\alpha A^{(a)}_\alpha B^{(a)}_{-\alpha}. \tag{20}$$

Equation (17) clearly shows that p, λ, and $\lambda_1+\lambda_2$ assume only even values (b is also even in view of invariance under time reversal), $p\leqslant 2l_1$, $b\leqslant 2l_2$, and $\lambda\leqslant 2(l_1+l_2)$.

For a state with fixed S and L we can now use the representation (A8) of orbital angular momentum operators:

$$W_i^{(0k)}=([S_i][L_i])^{-1/2}\langle S_iL_i\|W_i^{(0k)}\|S_iL_i\rangle\, L_i^{(k)}, \tag{21}$$

with the reduced matrix elements defined in (A9). Applying the recurrence formula

$$[L^{(k-p)}\times L^{(p)}]^{(k)}=(-1)^k([k-p][p][L])^{1/2}$$
$$\times\begin{Bmatrix} k-p & p & k\\ L & L & L\end{Bmatrix}l^{(k)} \tag{22}$$

and factorizing the spherical harmonics via Eq. (16), we can proceed from irreducible tensors to the ordinary vectors L_1 and L_2. For one thing, we have

$$(L_1^{(2)}\cdot L_2^{(2)})=\frac{20}{3}6\sqrt{15}\prod_{i=1,2}[L_i]^{1/2}(2L_i-1)^{-1}$$
$$\times(2L_i+3)^{-1}\{\tfrac{1}{3}L_1(L_1+1)L_2(L_2+1)$$
$$-(L_1L_2)^2-\tfrac{1}{2}(\mathbf{L}_1\mathbf{L}_2)\}, \tag{23}$$

$$[L_i^{(2)}Y^{(2)}(\hat{\boldsymbol{\rho}})]=5(2\pi)^{-1/2}[L_i]^{1/2}(2L_i-1)^{-1}$$
$$\times(2L_i+3)^{-1}\{\tfrac{1}{3}L_i(L_i+1)$$
$$-(\mathbf{L}_i\rho)^2/\rho^2\}. \tag{24}$$

As a result we arrive at a multipole expansion of the form

$$H_{\text{Coul}}(\nu_1\nu_2)=\sum_{\alpha\beta\gamma}Q_{\alpha\beta\gamma}(\mathbf{L}_1\rho)^\alpha(\mathbf{L}_2\rho)^\beta(\mathbf{L}_1\mathbf{L}_2)^\gamma/\rho^{-(\alpha+\beta)}, \tag{25}$$

where the coefficients $Q_{\alpha\beta\gamma}$ are linear combinations of Slater integrals. The total powers of each operator L_1 and L_2 and of the direction vector $\hat{\boldsymbol{\rho}}$ in each term are even, with $\alpha+\gamma\leqslant 2l_1$ and $\beta+\gamma\leqslant 2l_2$. Interestingly, the Hamiltonian has terms of the type (24) that depend on the orientation in the lattice of only one vector, L_1 or L_2, owing to the absence of conservation of orbital angular momentum in the crystal. Note that the expansion contains no terms with vector products since[16]

$$([\mathbf{L}_1\times\mathbf{L}_2]\rho)^2=\det\begin{pmatrix} L_1(L_1+1) & (\mathbf{L}_1\mathbf{L}_2) & (\mathbf{L}_1\rho)\\ (\mathbf{L}_1\mathbf{L}_2) & L_2(L_1+1) & (\mathbf{L}_2\rho)\\ (\mathbf{L}_1\rho) & (\mathbf{L}_2\rho) & \rho^2\end{pmatrix}. \tag{26}$$

The exchange contribution in (7) ($\nu_1l_1=\nu_4l_4$ and $\nu_2l_2=\nu_3l_3$) is of the second order in the overlap of the wave functions at different sites, with the result that we must allow for corrections of the same order caused by nonorthogonality. (The direct-exchange problem without allowance for nonorthogonality was studied in Ref. 11.) Employing (3) and successively applying (10), (16), and (11) we get

$$H_{\text{exch}}(\nu_1\nu_2)=-\frac{1}{2}\sum_{k_1k_2\kappa\lambda}(4\pi)^{1/2}[\kappa]^{3/2}$$
$$\times(-1)^\kappa I(l_1l_2k_1k_2\lambda)$$
$$\times[W_1^{(\kappa k_1)}\times W_2^{(\kappa k_2)}]^{(0\lambda)}\cdot Y^{(\lambda)}(\hat{\boldsymbol{\rho}}_{12}), \tag{27}$$

where the effective exchange parameters are

$$I(l_1l_2k_1k_2\lambda)=\frac{1}{2}\left(\sum_{p\eta_1\eta_2\lambda_1\lambda_2}\left\{G^{(p)}(l_1l_2\eta_1\eta_2\lambda_1\lambda_2)-\mathrm{Re}[G^{(p)}(l_1l_2\eta_1\eta_2\lambda_1)Z(l_2\eta_2\lambda_2)]+\frac{1}{4}G^{(p)}(l_1\eta_1\eta_2)Z(l_2\eta_1\lambda_1)Z^*(l_2\eta_2\lambda_2)\right\}\right.$$

$$\times(-1)^{l_1-l_2}[k_1][k_2][\lambda_1][\lambda_2]\left(\frac{[l_2][\eta_1]}{[\lambda]}\right)^{1/2}C(\eta_1pl_1,l_1p\eta_2,l_2\lambda_2\eta_2,l_2\lambda_1\eta_1,\lambda_1\lambda_2\lambda)\begin{Bmatrix}\eta_1&\eta_2&k\\l_1&l_1&p\end{Bmatrix}$$

$$\times\begin{Bmatrix}l_2&\lambda_1&\eta_1\\l_2&\lambda_2&\eta_2\\k_2&\lambda&k_1\end{Bmatrix}+\frac{1}{4}\sum_{p\lambda_i\eta_i\Lambda_ia}F^{(p)}(l_1l_2\eta_1\eta_2\eta_3\eta_4\lambda_2\lambda_3\lambda_4)Z(l_1\eta_1\lambda_1)Z(l_2\eta_3\lambda_3)(-1)^{\eta_3}\prod_{i=1}^{4}[\lambda_i][k_1][k_2][a]$$

$$\times C(l_1\lambda_1\eta_1,\eta_3pl_1,\eta_1\lambda_4\eta_4,l_2\lambda_3\eta_3,\eta_2p\eta_4,l_2\lambda_2\eta_2,\lambda_1\lambda_4\Lambda_1,\Lambda_1\lambda_3\Lambda_2,\Lambda_2\lambda_2\lambda)([\Lambda_1][\Lambda_2][\eta_1][\eta_3]/[\lambda])^{1/2}$$

$$\left.\times\begin{Bmatrix}l_1&\eta_4&\Lambda_1\\\lambda_4&\lambda_1&\eta_1\end{Bmatrix}\begin{Bmatrix}l_2&a&\Lambda_2\\\Lambda_1&\lambda_3&\eta_3\end{Bmatrix}\begin{Bmatrix}l_1&\eta_3&p\\l_1&\Lambda_1&\eta_4\\k_1&a&\eta_2\end{Bmatrix}\begin{Bmatrix}l_2&\lambda_2&\eta_2\\l_2&\Lambda_2&a\\k_2&\lambda&k_1\end{Bmatrix}+\frac{1}{2}[(\nu_1l_1k_1)\leftrightarrow(\nu_2l_2k_2)]^*.\qquad(28)\right.$$

Here we have introduced the generalized Slater integrals

$$G^{(p)}(l_1l_2\eta_1\eta_2\lambda_1\lambda_2)$$
$$=e^2\int r_1^2dr_1r_2^2dr_2R_{l_1}(r_1)R^*_{l_2\eta_2\lambda_2}(r_2,\rho)\ (r_<^p/r_>^{p+1})$$
$$\times R_{l_2\eta_1\lambda_1}(r_1,\rho)R_{l_1}(r_2),\qquad(29)$$

$$G^{(p)}(l_1l_2\eta_1\eta_2\lambda_1)$$
$$=e^2\int r_1^2dr_1r_2^2dr_2R_{l_1}(r_1)R_{\eta_2}(r_2)\ (r_<^p/r_>^{p+1})$$
$$\times R_{l_2\eta_1\lambda_1}(r_1,\rho)R_{l_1}(r_2),\qquad(30)$$

$$G^{(p)}(l\eta_1\eta_2)$$
$$=e^2\int r_1^2dr_1r_2^2dr_2R_l(r_1)R_{\eta_2}(r_2)\ (r_<^p/r_>^{p+1})$$
$$\times R_{\eta_1}(r_1)R_l(r_2),\qquad(31)$$

$$F^{(p)}(l_1l_2\eta_1\eta_2\eta_3\eta_4\lambda_2\lambda_3\lambda_4)$$
$$=e^2\int r_1^2dr_1r_2^2dr_2R_{l_1}(r_1)R^*_{l_2\eta_2\lambda_2}(r_2,\rho)\ (r_<^p/r_>^{p+1})$$
$$\times R_{l_2\eta_3\lambda_3}(r_1,\rho)R_{\eta_1\eta_4\lambda_4}(r_2,\rho)\qquad(32)$$

and the nonorthogonality integrals

$$Z(l\eta\lambda)=\int_0^\infty r^2drR_l(r)R_{l\eta\lambda}(r,\rho).\qquad(33)$$

The last contribution in (28) (the one in square brackets) is the most complicated and is caused by the term that contains, after (3) has been substituted into (7), the product of pairs of wave functions at different sites but with the same argument, that is, possessing the structure of a Coulomb integral, which is transformed into (32). Being of the same order in the wave-function overlap, this contribution contains, in comparison to other corrections, an additional smallness caused by the fact that the Coulomb interaction decreases with distance.

The values of the indices in (27) are limited by the conditions that $k_1\leqslant 2l_1$, $k_2\leqslant 2l_2$, $\lambda\leqslant 2(l_1+l_2)$, and $\kappa\leqslant 1$, with $\lambda_1+\lambda_2$, λ, and k_1+k_2 even-valued. In contrast to the Coulomb contribution, k_1 and k_2 separately can be odd-valued. Thus, the exchange Hamiltonian acquires terms linear in the scalar products (L_1L_2) and dipole-type terms proportional to

$$([\mathbf{L}_1\times\mathbf{L}_2]^{(2)}Y^{(2)}(\hat{\rho}))$$
$$=(8\pi)^{-1/2}\{\tfrac{1}{3}(\mathbf{L}_1\mathbf{L}_2)-(\mathbf{L}_1\rho)(\mathbf{L}_2\rho)/\rho^2\}\qquad(34)$$

etc. At the same time, for the "even" terms of the types (23) and (24) the Coulomb term must be predominant. The presence of orbital contributions to the exchange and Coulomb Hamiltonians can play a significant role in determining the properties of the crystal, for instance, their anisotropy.[7]

Employing double irreducible tensor operators makes it possible to express the bilinear spin- and orbital-exchange Hamiltonians in terms of the single-electron exchange integrals (28) without resorting to the multielectron representation. Assuming that $k_1=k_2=0$ and $\lambda=0$ and employing (A2) and (A3), we arrive at the ordinary Heisenberg terms of the Hamiltonian, which does not contain orbital angular momentum operators:

$$\sum_\kappa H^{\kappa 0}_{\mathrm{exch}}(\nu_1\nu_2)=-\tfrac{1}{2}I(l_1l_2000)[n_1n_2+4(S_1S_2)].\qquad(35)$$

The sign of the exchange interaction is determined by the relations between the integrals (29)–(33). For instance, for the hydrogen molecule the resulting interaction is antiferromagnetic, since the contributions caused by nonorthogonality dominate over common ferromagnetic exchange.[1]

Similarly, putting $\kappa=0$ and $k_1=k_2=1$, we find the orbital-exchange Hamiltonian:

$$H^{(01)}_{\text{exch}}(\nu_1\nu_2)=-\tfrac{1}{2}\{l_1(l_1+1)l_2(l_2+1)\}^{-1/2}\{I(l_1l_2110)\times(\mathbf{L}_1\mathbf{L}_2)+(8\pi)^{-1/2}I(l_1l_2112)\times[\tfrac{1}{3}(\mathbf{L}_1\mathbf{L}_2)-(\mathbf{L}_1\rho)(L_2\rho)/\rho^2]\}. \tag{36}$$

The contributions to the exchange Hamiltonian with $k+\kappa>1$ can be considered for a specific state with given S and L values after going over to the irreducible tensor operators (A7) and (A8). Proceeding further, as for the Coulomb term, to ordinary vectors, we arrive at the following multipole expansion:

$$H_{\text{exch}}(\nu_1\nu_2)=-\sum_{\alpha\beta\gamma\kappa}I_{\alpha\beta\gamma\kappa}(\mathbf{L}_1\rho)^\alpha(\mathbf{L}_2\rho)^\beta(\mathbf{L}_1\mathbf{L}_2)^\gamma(\mathbf{S}_1\mathbf{S}_2)^\kappa/\rho^{\alpha+\beta}. \tag{37}$$

Here $\alpha+\beta$ is even-valued, $\alpha+\gamma\leqslant 2l_1$, $\beta+\gamma\leqslant 2l_2$, and $\kappa=0$, 1. Note that the powers to which orbital operators can be raised are bounded from above not only by the "kinematic" value of $2L$ but also by the value of $2l$. For spin operators the maximum power is $\kappa=2s=1$. Higher powers can emerge only if we allow for higher-order overlap corrections; they are of the appropriate smallness. This fact must be taken into account when using phenomenological Hamiltonians containing invariants with $\kappa>1$ (Ref. 17).

The above discussion of the two-center problem is generally insufficient for obtaining the exchange Hamiltonian of the crystal (see Refs. 1 and 17). Indeed, in Eq. (3) we must allow for terms with $\nu'\neq\nu_1,\nu_2$ (cf. Ref. 14). However, neglect of multisite contributions is justified in the neatest-neighbors approximation. Corrections to the two-center approximation are especially important if some nearest neighbors form equilateral triangles in the lattice (say, in close-packed face-centered and hexagonal structures). In this case the contributions of three-center integrals and the last term in the square brackets in (28) have a smallness caused solely by the fairly weak decrease in the strength of the Coulomb interaction with distance, rather than by the exponential decrease in the wave-function overlap.

4. STRONG SPIN-ORBIT COUPLING

Let us now examine the case of strong (in comparison with the crystalline field) spin-orbit coupling, when the spin and orbital angular momenta are coupled via the Russell–Saunders scheme. The respective wave functions are

$$|SLJM_J\rangle=\sum_{\mu M}C^{JM_J}_{S\mu,LM}|SL\mu M\rangle. \tag{38}$$

Doing the summation

$$\sum_{\mu\mu'MM'}C^{JM_J}_{S\mu,LM}C^{JM'_J}_{S\mu',LM'}C^{S\mu}_{S\mu',\kappa\pi}C^{LM}_{LM',kq}=\sum_{p\xi}([S][L][J][p])^{1/2}C^{JM_J}_{JM'_J,p\xi}C^{p\xi}_{\kappa\pi,kq}\begin{Bmatrix}J&S&L\\J&S&L\\p&\kappa&k\end{Bmatrix}, \tag{39}$$

we find the relationship between the irreducible tensors,

$$[S^{(\kappa)}\times L^{(k)}]^{(p)}=([S][L][J][p])^{1/2}\begin{Bmatrix}J&S&L\\J&S&L\\p&\kappa&q\end{Bmatrix}J^{(p)}, \tag{40}$$

where

$$J^{(p)}_\xi=\sum_{M_JM'_J}|SLJM\rangle\langle SLJM'_J|C^{JM_J}_{JM'_J,p\xi}, \tag{41}$$

and $S^{(\kappa)}$ and $K^{(k)}$ are defined in (A7) and (A8). In Eq. (40), $k+\kappa+p$ is even-valued (otherwise the $9j$-symbol vanishes owing to symmetry properties[16]), and $|k-\kappa|\leqslant p\leqslant k+\kappa$. At $k=0$ or $\kappa=0$ the $9j$-symbol simplifies:

$$S^{(\kappa)}=(-1)^{J+S+L+\kappa}([S][J])^{1/2}\begin{Bmatrix}J&S&L\\S&J&\kappa\end{Bmatrix}J^{(\kappa)}, \tag{42}$$

$$L^{(k)}=(-1)^{J+S+L+k}([L][J])^{1/2}\begin{Bmatrix}J&L&S\\L&J&k\end{Bmatrix}J^{(k)}. \tag{43}$$

For one thing, at $\kappa=1$ and $k=1$ we have

$$\mathbf{S}=(g-1)\mathbf{J},\quad \mathbf{L}=(2-g)\mathbf{J}, \tag{44}$$

where

$$g=1+\frac{(\mathbf{JS})}{J(J+1)}$$

is the Landé factor.

In the Coulomb term, the transition to the J-representation is done by substituting (43) into (21), so that the structure of expansion (25) is retained when J_i is substituted for L_i.

In the exchange term we must carry out additional summation of the Clebsch–Gordan coefficients. As a result we arrive at the following substitution in (27):

$$[W_1^{(\kappa k_1)}\times W_2^{(\kappa k_2)}]^{(0\lambda)}$$

$$\to[\kappa]^{-1/2}\sum_{p_1p_2}\begin{Bmatrix}p_1 & p_2 & \lambda\\ k_1 & k_2 & \kappa\end{Bmatrix}\prod_{i=1,2}[p_i]$$

$$\times([S_i][L_i][J_i])^{1/2}\begin{Bmatrix}J_i & S_i & L_i\\ J_i & S_i & L_i\\ p_i & \kappa & k_i\end{Bmatrix}$$

$$\times\langle S_iL_i\|W^{(\kappa k_i)}\|S_iL_i\rangle[J_1^{(p_1)}\times J_2^{(p_2)}]^{(\lambda)}. \qquad (45)$$

Reasoning in the same way as with (25) and (37), we find that

$$H_{\text{exch}}(\nu_1\nu_2)=-\sum_{\alpha\beta\gamma}I_{\alpha\beta\gamma}(\mathbf{J}_1\rho)^{\alpha}(\mathbf{J}_2\rho)^{\beta}(\mathbf{J}_1\mathbf{J}_2)^{\gamma}/\rho^{\alpha+\beta}, \qquad (46)$$

where $\alpha+\gamma\leqslant 2l_1$, $\beta+\gamma\leqslant 2l_2+1$, and $\alpha+\beta$ is even-valued.

In the limit of strong spin-orbit coupling considered here, terms with the Dzyaloshinskiĭ–Moriya structure,

$$H_{\text{DM}}(\nu_1\nu_2)=-(\mathbf{K}_{12}\cdot[\mathbf{J}_1\times\mathbf{J}_2]), \qquad (47)$$

can be obtained for certain lattices if one allows for the crystalline field;[11,12] here the components of the pseudovector $\mathbf{K}_{12}$ are determined by the matrix elements of electrostatic interaction in the local system of coordinates.

5. SUPEREXCHANGE INTERACTION

In reality the exchange interactions between magnetic ions are realized not through direct exchange but by other mechanisms. In magnetic insulators, superexchange through the valence band is usually the dominant interaction. As related to the simplest nondegenerate Hubbard model, this mechanism was examined by Anderson,[18] who arrived at the following expression for the Heisenberg Hamiltonian in second-order perturbation theory in transport:

$$\widetilde{H}=-\sum_{\nu_1\nu_2\sigma\sigma'}(2\beta^2_{\nu_1\nu_2}/U)\,Pa^{+}_{\nu_1\sigma}a_{\nu_2\sigma}a^{+}_{\nu_2\sigma'}a_{\nu_1\sigma'}P$$

$$=\sum_{\nu_1\nu_2}(\beta^2_{\nu_1\nu_2}/U)\,[-1+4(\mathbf{S}_1\mathbf{S}_2)-1], \qquad (48)$$

where U is the parameter of the intratomic Coulomb interaction, and P is the operator of projection on singly occupied states.

We examine the Hubbard model with a degenerate l-shell. This model contains an electron-transport term and a term representing the intratomic Coulomb interaction. When the latter is strong, it is convenient to go over to the representation that uses Hubbard X-operators

$$X(\Gamma,\Gamma')=|\Gamma\rangle\langle\Gamma'|, \qquad (49)$$

in which the interaction Hamiltonian is diagonal:

$$H=\sum_{\nu\Gamma}E_{\Gamma}X_{\nu}(\Gamma,\Gamma)$$

$$+\sum_{\nu_1\nu_2m_1m_2\sigma}\beta_{\nu_1\nu_2}(lm_1,lm_2)a^{+}_{\nu_1lm_1\sigma}a_{\nu_2lm_2\sigma}. \qquad (50)$$

Here the energies of the states $\Gamma=\{SL\mu M\}$ are independent of the projections of spin and orbital angular momenta and are given by the following expression:

$$E_{\Gamma}=\frac{1}{2}\sum_{p}(C^{l0}_{l0,p0})^2F^{(p)}(l)$$

$$\times\left\{\sum_{L'}(\langle SL\|W^{(0p)}\|SL'\rangle)^2[S]^{-1}[L]^{-1}-n\right\}, \qquad (51)$$

where

$$F^{(p)}(l)=\int r_1^2dr_1r_2^2dr_1R_l^2(r_1)R_l^2(r_2)\,(r^{p}_{<}/r^{p+1}_{>}) \qquad (52)$$

[calculations are done in the same manner that led to (17); cf. Ref. 2]. In the case of an insulator (integral-valued occupation), in the zeroth approximation all atoms are in states corresponding to the lowest state Γ_n, so that perturbation expansions in interelectron transport can be employed. Excluding the transport by applying a canonical transformation, we arrive at the following second-order effective Hamiltonian:

$$\widetilde{H}=2\sum_{\nu_im_i\sigma_i}\beta_{\nu_1\nu_2}(lm_1,lm_2)\beta_{\nu_2\nu_1}(lm_3,lm_4)\sum_{\Gamma_n^{(i)}\Gamma_{n+1}\Gamma_{n-1}}(2E_{\Gamma_n}-E_{\Gamma_{n+1}}-E_{\Gamma_{n+1}})^{-1}$$

$$\times\langle\Gamma_n|a^{+}_{\nu_1lm_1\sigma_1}|\Gamma_{n-1}\rangle\langle\Gamma_{n-1}|a_{\nu_1lm_4\sigma_2}|\Gamma'_n\rangle\langle\Gamma''_n|a_{\nu_2lm_2\sigma_1}|\Gamma_{n+1}\rangle\langle\Gamma_{n+1}|a^{+}_{\nu_2lm_3\sigma_2}|\Gamma'''_n\rangle X_{\nu_1}(\Gamma_n,\Gamma'_n)X_{\nu_2}(\Gamma''_n,\Gamma'''_n). \qquad (53)$$

Here summation over $\Gamma_n^{(i)}$ stands for summation over the projections of the angular momenta corresponding to state Γ_n.

The matrix elements of the Fermi operators have the form[19]

$$\langle\Gamma_n|a^{+}_{lm\sigma}|\Gamma_{n-1}\rangle=\sqrt{n}G^{S_nL_n}_{S_{n-1}L_{n-1}}C^{S_n\mu_n}_{S_{n-1}\mu_{n-1},\frac{1}{2}\sigma}C^{L_nM_n}_{L_{n-1}\mu_{n-1},lm}, \qquad (54)$$

where the G are Racah's fractional parentage coefficients.

After substituting (54) into (53) we sum over the projections of the spin Clebsch–Gordan coefficients:

$$\sum_{\mu_{n+1}\mu_{n-1}\sigma_1\sigma_2} C^{S\mu}_{S_{n-1}\mu_{n-1},\frac{1}{2}\sigma_1} C^{S_{n+1}\mu_{n+1}}_{S\mu'',\frac{1}{2}\sigma_1} C^{S_{n+1}\mu_{n+1}}_{S\mu''',\frac{1}{2}\sigma_2'} C^{S\mu'}_{S_{n-1}\mu_{n-1},\frac{1}{2}\sigma_2}$$

$$=\frac{[S_{n+1}][S]}{2}\left\{\delta_{\mu\mu'}\delta_{\mu''\mu'''}-\frac{(-1)^{S_{n+1}-S_{n-1}}4S(S+1)}{[S_{n+1}][S_{n-1}]}\right.$$

$$\left.\times\sum_{\xi}(-1)^{\xi}C^{S\mu}_{S\mu',1\xi}C^{S\mu''}_{S\mu''',1\xi}\right\}. \qquad (55)$$

Allowing for the m-dependence of the transport integrals (13) and summing over the product of six orbital coefficients,[16] we obtain

$$\hat{H}=\sqrt{4\pi}n(n+1)\sum_{\nu_i k_i \lambda_i \lambda}\sum_{\{S_{n\pm1},L_{n\pm1}\}}\frac{\bar{\beta}_{\nu_1\nu_2}(ll\lambda_1)\bar{\beta}_{\nu_1\nu_2}(ll\lambda_2)}{E_{\Gamma_{n+1}}+E_{\Gamma_{n-1}}-2E_{\Gamma_n}}$$

$$\times(G^{\Gamma_n}_{\Gamma_{n-1}}G^{\Gamma_{n+1}}_{\Gamma_n})^2C(l\lambda_1 l,l\lambda_2 l,\lambda_1\lambda_2\lambda)[\lambda_1][\lambda_2][k_1]$$

$$\times[k_2][L_{n+1}][\lambda]^{-1/2}(-1)^{L_{n+1}-L_{n-1}}$$

$$\times\begin{Bmatrix} L & L & k_1 \\ l & l & L_{n-1}\end{Bmatrix}\begin{Bmatrix} L & L & k_2 \\ l & l & L_{n+1}\end{Bmatrix}\begin{Bmatrix} k_1 & k_2 & \lambda \\ l & l & \lambda_1 \\ l & l & \lambda_2\end{Bmatrix}$$

$$\times([L_1^{(k_1)}\times L_2^{(k_2)}]^{(\lambda)}Y^{(\lambda)}(\hat{\rho}_{12})$$

$$\times\{-1+4(-1)^{S_{n+1}-S_{n-1}}$$

$$\times[S_{n+1}]^{-1}[S_{n-1}]^{-1}(\mathbf{S}_1\mathbf{S}_2)\}. \qquad (56)$$

Here λ_1, λ_2, λ, and k_1+k_2 are even-valued, $l_{1,2}\leqslant 2l$, and $k_{1,2},k\leqslant\min\{2l,2L\}$. The multipole expansion of Hamiltonian (56) has the same form as in (37).

The sign of the contribution of the pair of states Γ_{n-1} and Γ_{n+1} to the superexchange interaction is determined by the values of their spins. If $S_{n+1}=S_{n-1}=S\pm\frac{1}{2}$, the virtual electron transitions lead to a situation in which antiparallel orientation of local spins is advantageous. If $S_{n+1}-S_{n-1}=\pm1$, the interaction is ferromagnetic.

Similar rules for the interaction of orbital angular momentum can be obtained by substituting the appropriate expressions for the $6j$-symbols. Orbital exchange ($k_1=k_2=1$ and $\lambda_1=\lambda_2=\lambda=0$) is "antiferromagnetic" if the signs of the two differences,

$$L(L+1)+l(l+1)-L_{n\pm1}(L_{n\pm1}+1),$$

coincide, and "ferromagnetic" if they do not.

Note that generally the method of double irreducible tensor operators (A1) in the single-electron representation does not hold true for the degenerate Hubbard model, since the energy denominator in (53) depends on the multielectron quantum numbers S and L characterizing the virtual states Γ_{n-1} and Γ_{n+1}. The method, however, can be used if we leave in (51) only the term with $p=0$, so that the energy of a state, $E_\Gamma=n(n-1)F^{(0)}/2$, depends only on the number of electrons. Then at $k_i=0$ or at $k_i=1$ and $\kappa=0$ we can sum over the fractional parentage coefficients in (56) by employing Eqs. (A11) and (A12), and we arrive at the Hamiltonian of spin or orbital exchange in the form (35) or (36). For instance, putting $k_1=k_2=\lambda_1=\lambda_2=0$, we obtain

$$\widetilde{H}=\sum_{\nu_1\nu_2}\{\bar{\beta}_{\nu_1\nu_2}(ll0)/F^{(0)}(l)\}\{n_1n_2+4(\mathbf{S}_1\mathbf{S}_2)$$

$$-[l](n_1+n_2)\}. \qquad (57)$$

In this approximation the exchange is always antiferromagnetic.

As in the case of direct exchange, multisite corrections are especially important for lattices in which nearest neighbors form triangles, but in this case the corrections contain an additional smallness owing to the fact that the potential of a lattice site decreases with distance. If we use Eq. (13) for the transport integral, such corrections lead to excessive accuracy, since in deriving this equation we ignored the potentials of all sites except the central one.

Biquadratic exchange and the higher-order terms in spin operators can be obtained in the higher orders of perturbation theory,[17,18] which correspond, as they do in the case of direct exchange, to the higher orders in the overlap of different-site wave functions, since the transport integral is of the first order in the overlap.[14]

6. DOUBLE EXCHANGE INTERACTION

Let us now examine the case where the number of electrons per atom is a noninteger, $n<c<n+1$, so that the there are current carriers in the conduction bands. Owing to the degeneracy of the ground state (in the zeroth approximation the "excess" of electrons can be at any site), perturbation theory does not work in this situation. To describe such a system in the limit of a strong intratomic interaction, we can use the Hubbard model with allowance only for the lowest atomic states $\Gamma_N=\{sl\}$ and $\Gamma_{n+1}=\{S'L'\}$. Here the diagonal Hamiltonian of the interaction can be dropped, since allowing for it only shifts the point of reference of the electron energy. We then have

$$H=\sum_{\nu_1\nu_2 m_1 m_2\sigma}\beta_{\nu_1\nu_2}(lm_1,lm_2)d^+_{\nu_1 lm_1\sigma}d_{\nu_2 lm_2\sigma}, \qquad (58)$$

$$d^+_{\nu lm\sigma}=(n+1)^{1/2}G^{\Gamma_{n+1}}_{\Gamma_n}\sum_{\mu\mu' MM'}C^{S'\mu'}_{S\mu_1,\frac{1}{2}\sigma}C^{L'M'}_{LM,lm}$$

$$\times X_\nu(S'L'\mu'M',SL\mu M). \qquad (59)$$

The d-operators can again be expressed in terms of single-electron operators and the operators of spin and orbital angular momenta corresponding to the state Γ_n. To this end we use the following formula for isolating one electron:[3]

$$|S'L'\mu'M'\rangle=(n+1)^{-1/2}G^{\Gamma_{n+1}}_{\Gamma_n}\sum_{m\sigma\mu''M''}C^{S'\mu'}_{S\mu'',\frac{1}{2}\sigma}C^{L'M'}_{LM'',lm}$$

$$\times a^+_{lm\sigma}|SL\mu''M''\rangle. \qquad (60)$$

Substituting (59), (60), and (13) into (58) and rearranging the indices in the products of Clebsch–Gordan coefficients via $6j$- and $9j$-symbols, we obtain

$$H=(4\pi)^{1/2}(G_{\Gamma_n}^{\Gamma_{n+1}})^4 \sum_{\nu_i m_i=\sigma_i\sigma} \sum_{k_i k\lambda pq} \bar{\beta}_{\nu_1\nu_2}(ll\lambda)$$
$$\times[k_1][k_2][k]^{1/2}[p]^{1/2}[L']^2[L]^{-1}$$
$$\times\begin{Bmatrix} L & L & k_1 \\ l & l & L' \end{Bmatrix}\begin{Bmatrix} L & L & k_2 \\ l & l & L' \end{Bmatrix}\begin{Bmatrix} k_1 & l & l \\ k_2 & l & l \\ k & p & \lambda \end{Bmatrix}$$
$$\times(-1)^q C_{l0,\lambda 0}^{l0} C_{lm_2,pq}^{lm_1} a_{\nu_1 lm_1\sigma_1}^{+} P_{\nu_1\sigma_1\sigma}[Y^{(\lambda)}(\hat{\rho}_{12})$$
$$\times[L_1^{(k_1}\times L_2^{(k_2)}]^{(k)}]_{-q}^{(p)} P_{\nu_2\sigma\sigma_2} a_{\nu_2 lm_2\sigma_2}, \qquad (61)$$

where

$$P_{\nu\sigma\sigma'}=\frac{1}{2[S]}([S']\delta_{\sigma\sigma'}+(-1)^{S-S'+1/2}2(\mathbf{S}_\nu\cdot\sigma_{\sigma\sigma'})), \qquad (62)$$

the σ are the Pauli matrices, $\lambda\leqslant 2l$ are even-valued, and $k_1,k_2\leqslant\min\{2l,2L\}$. The Hamiltonian (61) describes the interaction of carriers with the spin and orbital angular momenta in a narrow conduction band. The respective "double" exchange interaction between localized spins cannot be described by a Heisenberg-type Hamiltonian.

Now we turn to the case where the carriers and the localized magnetic moments are formed from states belonging to different shells. Assuming for simplicity that $L=0$ and that the carriers are described by s-functions, we arrive at the s-d exchange model. Here the value $S'=S\pm\frac{1}{2}$ corresponds to a large positive (negative) s-d exchange parameter A. Then instead of Eqs. (58) and (59) we obtain

$$H=\sum_{\nu_1\nu_2\sigma}\beta_{\nu_1\nu_2}d_{\nu_1\sigma}^{+}d_{\nu_2\sigma}, \qquad (63)$$

$$d_{\nu\sigma}^{+}=\sum_{\sigma'}a_{\nu\sigma'}^{+}(1-n_{\nu,-\sigma'})P_{\nu\sigma\sigma'}. \qquad (64)$$

This formula for $d_{\nu\sigma}^{+}$ was obtained by Kubo and Ohata[20] via a canonical transformation. Substituting (64) into (63), we find the quantum Hamiltonian for a narrow-band conductor:

$$H=[S]^{-2}\sum_{\nu_1\nu_2\sigma\sigma'}\beta_{\nu_1\nu_2}\biggl\{\left(\frac{1}{4}[S']^2+(\mathbf{S}_1\mathbf{S}_2)\right)\delta_{\sigma\sigma'}$$
$$+\frac{1}{2}[S']\times\operatorname{sgn}A[\sigma_{\sigma\sigma'}\cdot(\mathbf{S}_1+\mathbf{S}_2)]$$
$$+2i(\sigma_{\sigma\sigma'}\cdot[\mathbf{S}_1\times\mathbf{S}_2])\biggr\}$$
$$\times a_{\nu_1\sigma}^{+}(1-n_{\nu_1,-\sigma})(1-n_{\nu_2,-\sigma'})a_{\nu_2\sigma'}. \qquad (65)$$

The terms with vector products of spin and orbital operators in (61) and (65) describe anisotropic scattering and are of interest when kinematic effects are considered, for instance, the anomalous Hall effect. These terms can also play an important role in describing states with unusual "chiral" order parameters in a two-dimensional situation. At present such states are under intensive investigation within the Heisenberg model and the t-J model in connection with the problem of high-T_c superconductivity.[21,22]

7. CONCLUSION

We have studied various exchange mechanisms for systems with multielectron atomic shells. A detailed study of the simplest mechanism, the direct exchange interaction, has revealed the structure of the multipole expansions for the Coulomb and exchange Hamiltonians. Note that the structure obtained in Sec. 4 for the case of strong spin-orbit coupling remains valid for the RKKY mechanism (indirect exchange between rare-earth ions via conduction electrons). Of particular interest is a detailed analysis of the respective anisotropic contributions to the magnetic properties of rare-earth metals and their compounds. The discussion can easily be extended to incorporate the jj-coupling (actinide compounds).

The problem of the existence of multielectron quantum numbers L in crystals with d-elements is complicated. Apparently, in pure metals the crystalline field dominates the intratomic Coulomb interaction and disrupts the multielectron states. However, in d-compounds, especially in those with narrow conduction bands, this situation may change. Moreover, the size of the Coulomb interaction may be essentially different for different atomic configurations of the d^n- and $s(p)d^{n-1}$-type, which are mixed by the crystalline field. From the experimenter's view, the simplest direct manifestations of the existence of orbital angular momenta are the magnetic anisotropy and the deviation of the g-factor from 2. In most d-metals this deviation amounts to roughly 10%, but it is large for vanadium and titanium.[23] A promising path of research is the analysis of x-ray and optical spectra, in which the selection rules in L for different transitions to the d-electron bands manifest themselves.

In deriving Hamiltonians that incorporate orbital degrees of freedom we have ignored the effect of the crystalline field. Of course, for d- and $5f$-systems this approximation cannot be justified, generally speaking. Even in the case of a moderate crystalline field, a nonspherical potential may "freeze" the orbital momenta or modify them drastically owing to the splitting of atomic states. In the latter case, however, our discussion can be generalized by employing irreducible point-group representations, which describe orbital angular quasimomenta, and the appropriate Clebsch–Gordan coefficients[24] (see also the study of the case of a strong crystalline field in Refs. 10–12). Note also that there is the possibility of partial "defrosting" of orbital angular momenta by the Coulomb interaction or by the crystalline field proper owing to the mixing of different atomic states.

Within the framework of the multielectron scheme under discussion various physical systems can be explored where orbital angular momenta play an important role, for instance, systems where orbital ordering sets in (the properties of such systems are usually discussed in the single-electron setting; see, e.g., Ref. 25). Also of interest is the analysis of superexchange interaction in more complicated situations than the models of Sec. 5 (e.g., in the presence of several types of orbitals[18,26]). This problem may be important for high-T_c superconductors, which exhibit a sizable anisotropy in magnetic susceptibility, caused by the orbital contribution.[27]

APPENDIX: THE FORMALISM OF IRREDUCIBLE TENSOR OPERATORS

Let us introduce the double irreducible tensor operators $W^{(\kappa k)}$ ($\kappa=0,1$ and $k=0,...,2l$) with the following components:

$$W^{(\kappa k)}_{\xi q}=\sum_{mm'\sigma\sigma'} C^{\frac{1}{2}\sigma}_{\frac{1}{2}\sigma',\kappa\xi} C^{lm}_{lm',kq} a^{+}_{lm\sigma} a_{lm'\sigma'} \tag{A1}$$

(we use a definition that differs somewhat from that given in Ref. 13). Any operator of the type

$$F=\sum_i f_i,$$

where f_i is an arbitrary operator acting on the ith electron can be expressed in terms of the operators defined in (A1). For example,

$$W^{(00)}=\sum_{m\sigma} a^{+}_{lm\sigma} a_{lm\sigma}=n \tag{A2}$$

coincides with the operator of the number of particles in the lth shell, and for the cyclic components of the operators of total spin and angular momenta of the shell we have

$$S_\xi=\frac{\sqrt{3}}{2} W^{(10)}_\xi, \quad L_q=\sqrt{l(l+1)}\, W^{(10)}_q, \tag{A3}$$

where

$$A_0=A^z, \quad A_\pm=\mp(A^x \pm iA^y). \tag{A4}$$

Using Eqs. (A3), we immediately obtain the Hamiltonians (35) and (36) without resorting to the multielectron representation.

In contrast to (A3), the operators (A1) with $k+\kappa>1$ have nonzero matrix elements between different states. Employing the Wigner–Eckart theorem, we get

$$\begin{aligned}\langle SL\mu M\alpha | W^{(\kappa k)}_{\xi q} | S'L'\mu' M'\alpha'\rangle &=([S][L])^{-1/2} C^{S\mu}_{S'\mu',\kappa\xi} C^{LM}_{L'M',kq}\\ &\quad\times\langle SL\alpha \| W^{(\kappa k)} \| S'L'\alpha'\rangle,\end{aligned} \tag{A5}$$

where α stand for the additional quantum numbers that distinguish states with the same S and L (in the main text of the paper these were omitted). For one thing, within a given SL-state we have

$$W^{(\kappa k)}_{\xi q}=([S][L])^{-1/2} \langle SL\alpha \| W^{(\kappa k)} \| SL\alpha\rangle S^{(\kappa)}_\xi L^{(k)}_q, \tag{A6}$$

where we have introduced irreducible tensor operators with components

$$S^{(\kappa)}_\xi=\sum_{\mu\mu' M} C^{S\mu}_{S\mu',\kappa\xi} |SL\mu M\alpha\rangle\langle SL\mu' M\alpha|, \tag{A7}$$

$$L^{(k)}_q=\sum_{\mu\mu M'} C^{LM}_{LM',kq} |SL\mu M\alpha\rangle\langle SL\mu M'\alpha|, \tag{A8}$$

with

$$S_\xi=\sqrt{S(S+1)}S^{(1)}_\xi, \quad L_q=\sqrt{L(L+1)}\,L^{(1)}_q. \tag{A9}$$

The operators (A8) are similar to the Stevens operators in crystalline-field theory.

The reduced matrix elements in (A6) can be calculated by isolating one electron in the state vectors via (60):

$$\begin{aligned}&\langle SL\alpha \| W^{(\kappa k)} \| S'L'\alpha'\rangle\\ &\quad=n(2[L][L'][S][S'][l])^{1/2} \sum_{\{\bar S\bar L\bar\alpha\}} G^{SL\alpha}_{\bar S\bar L\bar\alpha} G^{S'L'\alpha'}_{\bar S\bar L\bar\alpha}\\ &\qquad\times(-1)^{\frac{1}{2}+l+S+L+\bar S+\bar L+\kappa+k}\begin{Bmatrix}\frac{1}{2} & \kappa & \frac{1}{2}\\ S & \bar S & S'\end{Bmatrix}\\ &\qquad\times\begin{Bmatrix} l & k & l\\ L & \bar L & L'\end{Bmatrix}.\end{aligned} \tag{A10}$$

Comparing (A6) and (A8) with (A3) and using the expressions for the matrix elements of angular momentum operators, we arrive at a relationship linking the fractional parentage coefficients:

$$\begin{aligned}&n\sum_{\{\bar S\bar L\bar\alpha\}} G^{SL\alpha}_{\bar S\bar L\bar\alpha} G^{S'L\alpha'}_{\bar S\bar L\bar\alpha}\begin{Bmatrix}\frac{1}{2} & 1 & \frac{1}{2}\\ S & \bar S & S'\end{Bmatrix}(-1)^{S+\bar S-1/2}\\ &\quad=\delta_{SS'}\delta_{\alpha\alpha'}\left(\frac{2}{3}\frac{S(S+1)}{[S]}\right)^{1/2},\end{aligned} \tag{A11}$$

$$\begin{aligned}&n\sum_{\{\bar S\bar L\bar\alpha\}} G^{SL\alpha}_{\bar S\bar L\bar\alpha} G^{S'L'\alpha'}_{\bar S\bar L\bar\alpha}\begin{Bmatrix} l & 1 & l\\ L & \bar L & L'\end{Bmatrix}(-1)^{l+L+\bar L+1}\\ &\quad=\delta_{LL'}\delta_{\alpha\alpha'}\left(\frac{L(L+1)}{l(l+1)[l][L]}\right)^{1/2}.\end{aligned} \tag{A12}$$

Substituting the explicit expressions for the $6j$-symbols at $SL\alpha=S'L'\alpha'$, we obtain

$$\sum_{\{\bar S\bar L\bar\alpha\}} (G^{SL\alpha}_{\bar S\bar L\bar\alpha})^2(-1)^{S-\bar S+\frac{1}{2}}[\bar S]^{-1}=\frac{1}{n}, \tag{A13}$$

$$\sum_{\{\bar S\bar L\bar\alpha\}} (G^{SL\alpha}_{\bar S\bar L\bar\alpha})^2\bar L(\bar L+1)=l(l+1)+\left(1-\frac{2}{n}\right)L(L+1). \tag{A14}$$

The identity (A13) was found empirically for Hund states in Ref. 3. Interestingly, Eqs. (A13) and (A14) may become invalid at $S=0$ and $L=0$, respectively.

Thus, using the double irreducible tensor operators (A1) makes it possible to carry out effective summation of the fractional parentage coefficients and obtain the Hamiltonians of spin and orbital exchange, Eqs. (35) and (36), in the simplest form.

[1] D. C. Mattis, *The Theory of Magnetism I: Ground State and Elementary Excitations*, Springer, Berlin (1988).

[2] I. I. Sobelman, *Atomic Spectra and Radiative Transitions*, Springer, Berlin (1979).

[3] Yu. P. Irkhin, Zh. Eksp. Teor. Fiz. **50**, 379 (1966) [Sov. Phys. JETP **23**, 253 (1966)].

[4] J. Kondo, Prog. Theor. Phys. **27**, 272 (1962); T. A. Kaplan and D. H. Lyons, Phys. Rev. **129**, 2072 (1963).

[5] V. V. Druzhinin and Yu. P. Irkhin, Zh. Eksp. Teor. Fiz. **51**, 1856 (1966) [Sov. Phys. JETP **24**, 1250 (1967)].

[6] V. V. Druzhinin, Yu. P. Irkhin, and A. A. Kazakov, Zh. Eksp. Teor. Fiz. **54**, 1183 (1968) [Sov. Phys. JETP **27**, 633 (1968)].

[7] Yu. P. Irkhin, Usp. Fiz. Nauk **154**, 321 (1988) [Sov. Phys. Usp. **31**, 163 (1988)].

[8] F. Specht, Phys. Rev. **162**, 389 (1967).

[9] H. H. Teitelbaum and P. M. Levy, Phys. Rev. B **14**, 3058 (1976).

[10] R. J. Elliott and M. J. Torpe, J. Appl. Phys. **39**, 802 (1968).

[11] P. M. Levy, Phys. Rev. Lett. **20**, 1366 (1968); Phys. Rev. **177**, 509 (1969).

[12] G. M. Copland and P. M. Levy, Phys. Rev. B **1**, 3043 (1970).

[13] B. Judd, *Second Quantization and Atomic Spectroscopy*, Baltimore, (1967).

[14] N. N. Bogolyubov, *Lectures on Quantum Statistics. Selected Works*, Vol. 2, Naukova Dumka, Kiev (1970) p. 287 [in Russian].

[15] A. B. Bolotin and V. K. Shugurov, Zh. Vychisl. Mat. Mat. Fiz. **3**, 560 (1963).

[16] D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskiĭ, *Quantum Theory of Angular Momentum*, Nauka, Leningrad (1975) [in Russian].

[17] É. L. Nagaev, *Magnets with Complex Exchange Interactions*, Nauka, Moscow (1988) [in Russian].

[18] P. W. Anderson, in *Solid State Physics: Advances in Research and Applications*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull, Vol. 14, Academic Press, New York (1963) p. 99.

[19] Yu. P. Irkhin, Zh. Eksp. Teor. Fiz. **66**, 1005 (1974) [Sov. Phys. JETP **39**, 490 (1974)].

[20] K. Kubo and N. Ohata, J. Phys. Soc. Jpn. **33**, 21 (1972).

[21] X. G. Wen, F. Wilczek, and A. Zee, Phys. Rev. B **39**, 11413 (1989).

[22] O. Narikiyo, K. Kuboki, and H. Fukuyama, J. Phys. Soc. Jpn. **59**, 2443 (1990).

[23] É. V. Galoshina, Usp. Fiz. Nauk **113**, 105 (1974) [Sov. Phys. Usp. **17**, 345 (1974)].

[24] D. T. Sviridov and Yu. F. Smirnov, *Theory of Optical Spectra of Transition-Metal Ions*, Nauka, Moscow (1977) [in Russian].

[25] K. I. Kugel' and D. I. Khomskiĭ, Usp. Fiz. Nauk **136**, 621 (1982) [Sov. Phys. Usp. **25**, 231 (1982)].

[26] J. B. Goodenough, *Magnetism and the Chemical Bond*, Wiley, London (1963).

[27] D. C. Johnston and J. H. Cho, Phys. Rev. B **42**, 810 (1990).

Translated by Eugene Yankovsky.

This article was translated in Russia and is reproduced here the way it was submitted by the translator, except for stylistic changes by the Translation Editor.