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THEORY OF EXCHANGE INTERACTION FOR THE CASE OF SEVERAL MAGNETIC ELECTRONS PER ATOM

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A technique based on the j-coefficient theory is proposed for analyzing the second-quantized Hamiltonian for interelectron interaction in the presence of a group of equivalent electrons in the system. The formulas for transitions between electron operators and spin-momentum operators, which are known for the case $S = 1/2$, are extended to the case of $S > 1/2$ by simultaneously taking into account the orbital angular momenta, and in particular the total momenta $\mathbf{J}$. The technique permits one to clarify the conditions of applicability of the Heisenberg model and to obtain new terms in the electrostatic interaction Hamiltonian. The concrete case of the Hamiltonian for interaction between j-electrons and conduction electrons in rare-earth metals is considered, and a new anisotropic contribution to the indirect exchange interaction between the f-shells is computed on this basis. The magnitude of the contribution is proportional to $(g - 2)^2 J(J + 1)$ and is related to a new type of exchange of the f-shell J-momenta via the orbital angular momenta of the conduction electrons.

MODERN theory of ferro- and antiferromagnetism is based on the Heisenberg Hamiltonian, the equivalence of which to the exchange part of the exact Coulomb Hamiltonian is known only for the case of one electron per atom, that is, for spin $S = 1/2$, and also under the assumption that the orbital momenta of the exchanging electrons are equal to zero, (that is, for s-states). Such a model corresponds to the situation prevailing in 3d elements, where the orbital momenta are quenched and the coupling between the d-electrons is broken by the strong crystalline field, so that the exchange is actually effected between individual electrons and naturally, $S = 1/2$. The latter circumstance is confirmed experimentally, particularly by the fact that the temperature dependence of the spontaneous magnetization for 3d metals agrees best with the theoretical curve calculated for $S = 1/2$. The situation is entirely different, however, in the case of rare-earth elements, where the crystalline field is small compared with the Coulomb field, and even with the relativistic spin-orbit interaction inside the f-shell. In this case, it is necessary to consider first of all the electromagnetic and spin-orbit interactions of the f-electrons with one another, and only then can one consider the interaction of an entire group of equivalent f-electrons with the conduction electrons or with some other particles or quasiparticles.

During the decade elapsed since the work of Racah,[1] new methods were developed in the field of atomic and nuclear spectroscopy, and have made it possible to simplify greatly the analysis of many-electron systems (see, for example, [2]). These methods, however, have so far not been applied to the theory of ferromagnetism, in spite of the obvious need for going beyond the framework of the Heisenberg model when considering real magnets. The latter circumstance is apparently connected with the fact that in the theory of ferromagnetism it is most convenient to represent the Hamiltonian in terms of the operators of the momenta, whereas in spectroscopy use is made of the energy matrix representation.

Up to now only a few specific results have been obtained for ferromagnets with several electrons per atom. Liu,[3] using the method of Young patterns and several additional assumptions, confirmed the form of the exchange Hamiltonian previously used by deGennes in the theory of magnetism of rare-earth metals.[4] A paper by Kondo,[5] devoted to galvanomagnetic effects in ferromagnets, contains several interesting formulas, but the methods whereby they are derived are not indicated. Finally, Kaplan and Lyons[6] recently calculated the indirect exchange interaction in rare-earth metals in a second-order perturbation-theory approximation and obtained new terms in the Hamiltonian which led, in particular, to the appearance of exchange anisotropy. The latter paper is the only one employing the formalism of the theory of addition of momenta, but in the same form as in the theory of spectra.

We propose in this paper a method which makes it convenient to use the Hamiltonian of a system of electrons containing a group of equivalent electrons in ferromagnetism theory. This method is based on the generalization of the known formulas for converting from single-electron Fermi second-quantization operators to the operators of the spin momenta, to allow for the orbital states and for formation of a bound group with arbitrary resultant spin, orbital, or total momenta. The corresponding coefficients can be obtained in simple fashion on the basis of the theory of j-coefficients. The method permits ready calculation of the conditions of applicability of the Heisenberg approximation. We also consider concretely the Coulomb and exchange Hamiltonians between the conduction electrons and the f-shell in rare-earths, new terms in which are of interest to the theory of electric and magnetic properties of rare-earth metals.[1)]

1. TRANSITION TO THE REPRESENTATION OF THE MOMENTUM HAMILTONIAN

The case $S > 1/2$ is realized in practice if the system includes a group of electrons whose interaction with one another is much stronger than all the remaining interactions (crystalline field, external field, etc.). Such a group behaves like a unit and can be characterized with good accuracy by the quantum numbers of the entire group, S, L, J, etc. As is well known, the Coulomb and spin-orbit interactions are diagonalized in the $\{SLJ\}$ interaction, and the remaining interactions can then be regarded as perturbations.

The wave function of the system of n electrons can be constructed from the single-wave functions in the usual manner in the form of a determinant, and will depend on n sets of single-electron quantum numbers. The transition from this representation to the representation of general quantum numbers is realized with the aid of the coefficients for vector addition and the so-called fractional parentage coefficients of Racah.[2] For example, for two equivalent electrons (n = 2) we have in the case of a Russel-Saunders coupling

$$\Psi_{SL\mu M}(l^2) = \sum_{m_1 m_2 \sigma_1 \sigma_2} C^{LM}_{lm_1,\, lm_2} C^{S\mu}_{1/2\sigma_1,\, 1/2\sigma_2} \psi_{lm_1\sigma_1,\, lm_2\sigma_2}(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2). \quad (1)$$

Here $\mathbf{r}_i s_i$ are the spatial and spin coordinates of electrons, l, m, and σ are the single-electron orbital, magnetic and spin quantum numbers, $SL\mu M$ are the corresponding quantum numbers of the configuration l^2, and ψ is the determinantal two-electron function. In place of the Clebsch-Gordan coefficients $C^{J\mu}_{J_1\mu_1 J_2\mu_2}$, it is more convenient in concrete cases to use the Wigner 3j-symbols

$$\begin{pmatrix} J_1 & J_2 & J \\ \mu_1 & \mu_2 & -\mu \end{pmatrix} = (-1)^{J_1 - J_2 + \mu} [J]^{-1/2} C^{J\mu}_{J_1\mu_1,\, J_2\mu_2}, \quad [J] = 2J + 1. \quad (2)$$

The wave function of the configuration l^n $(n > 2)$ can be obtained by successive construction from (1) by means of the formula

$$\Psi_{SL\mu M}(l^n) = \sum_{i=1}^{n} \frac{(-1)^{n-i}}{\sqrt{n}} \sum_{S'L'\mu'M'm\sigma} G^{SL}_{S'L'} C^{LM}_{L'M',\, lm} C^{S\mu}_{S'\mu',\, 1/2\sigma} \times \Psi_{S'L'\mu'M'}(l^{n-1}) \psi_{lm\sigma}(\mathbf{r}_i s_i), \quad (3)$$

where $G^{SL}_{S'L'}$ are fractional parentage coefficients which relate the terms $S'L'$ of the initial configuration l^{n-1} with the term SL of configuration l^n. The wave functions (3) can be set in correspondence with the second-quantization operators A^+_Γ and A_Γ ($\Gamma = \{\gamma SL\mu M\}$, γ—the remaining quantum numbers contained in the complete set Γ). The operators A^+_Γ and A_Γ are connected with the single-electron Fermi operators a^+_λ and a_λ ($\lambda = \{lm\sigma\}$) in the same fashion as the function Ψ_Γ is connected with the functions ψ_λ, and the products $A^+_\Gamma A_\Gamma$ are "occupation numbers" pertaining to the entire system of n electrons. The symmetry properties of A_Γ can be obtained from the indicated considerations (see Appendix 1). Simpler and more convenient for our purposes is a different method of defining the operators A_Γ introduced by us, consisting in expressing them in terms of the momentum operator $\hat{\mathbf{J}}$. Such a definition is possible, naturally, for a group of states with specified order of J, differing only in the value of M_J, that is, for example for states belonging to the given term SL in the $\{SL\mu M\}$ representation, or to the given multiplet SLJ in the $\{SLJM_J\}$ representation (for more details, see Appendix 2).[2)]

The momentum operator $\hat{\mathbf{J}}$ (like any other ad-

[1)] Such Hamiltonians were not obtained by Kaplan and Lyons[6], who considered directly the second-order perturbation theory approximation and took into account only part of the terms of like order.

[2)] In this paper we confine ourselves to the case of J. A similar generalization is possible also without this condition; by J in (4) and (5) we can mean either the spin, the orbital, or the total momentum.

ditive operator) can be written in the second-quantization representation in the form

$$\hat{\mathbf{J}} = \sum_{M_J M_J'} (JM_J | \hat{J} | JM_J') A^{+}_{JM_J} A_{JM_J'}, \tag{4}$$

the matrix elements in (4) being expressed in terms of the 3j Wigner symbols

$$(JM_J | \hat{J}^z | JM_J') = \delta_{M_J, M_J'} M_J$$

$$= (-1)^{-J+M_J} \sqrt{J(J+1)[J]} \begin{pmatrix} J & J & 1 \\ M_J & -M_J' & 0 \end{pmatrix},$$

$$(JM_J | \hat{J}^{\pm} | JM_J') = \varphi_J^{\mp}(M_J)\, \delta_{M_J, M_J' \pm 1}$$

$$= (-1)^{-J \pm M_J} \sqrt{2J(J+1)[J]} \begin{pmatrix} J & J & 1 \\ \mp M_J & \pm M_J' - 2 & 1 \end{pmatrix},$$

$$\varphi_J^{\pm}(M_J) = [(J \pm M_J)(J \mp M_J + 1)]^{1/2}. \tag{5}$$

Relations (4) and (5) are generalizations, to arbitrary J, of known relations (for $J = 1/2$) between the electron operators and the momentum operators. Indeed, when $J = 1/2$ we obtain (by adding the normalization condition)

$$\hat{\mathbf{J}}^z = {}^1\!/_2 (a_{1/2}{}^{+} a_{1/2} - a_{-1/2}{}^{+} a_{-1/2}),$$

$$\hat{J}^{\pm} = a_{\pm 1/2}{}^{+} a_{\mp 1/2}, \quad a_{1/2}{}^{+} a_{1/2} + a_{-1/2}{}^{+} a_{-1/2} = 1. \tag{6}$$

For $J > 1/2$ the system (4) does not suffice to determine all the possible combinations of the operators $A^{+}_{M}\, A'_{M_J}$. Therefore, in the general case, it is necessary to write down expressions for $\hat{\mathbf{J}}^0, \hat{\mathbf{J}}, \ldots, \hat{\mathbf{J}}^{2J}$ in analogy with (4) and solve the obtained system relative to the bilinear combinations of the operators A_{M_J}. It follows, therefore, that in the general case the second-quantization Hamiltonian in the operators $A^{+}_{JM_J}\, A'_{JM_J}$ can be reduced to a representation in terms of the momentum operator $\hat{\mathbf{J}}$, the components of the latter having a degree not higher than 2J. In many concrete cases, however, this degree can be lower, as will be shown later.

Let us apply the described method to an analysis of electrostatic interaction of a system consisting of two groups of electrons $l_1^{n_1}$ and $l_2^{n_2}$. In the second-quantization representation we have (without account of the change in the configuration)

$$\hat{\mathscr{H}}(l_1^{n_1}, l_2^{n_2}) = \sum_{\{\Gamma_k\} = \Gamma_1\Gamma_2\Gamma_3\Gamma_4} \Phi(\Gamma_1\Gamma_2\Gamma_3\Gamma_4) A_{\Gamma_1}{}^{+} A_{\Gamma_2}{}^{+} A_{\Gamma_4} A_{\Gamma_3}, \tag{7}$$

where

$$\Phi(\Gamma_1\Gamma_2\Gamma_3\Gamma_4) = \int \Psi_{\Gamma_1}{}^{*}(l_1^{n_1}) \Psi_{\Gamma_2}{}^{*}(l_2^{n_2})$$

$$\times \left[\sum_{i,\, j=1}^{n_1,\, n_2} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} (1 - p_{ij}) \right]$$

$$\times \Psi_{\Gamma_3}(l_1^{n_1}) \Psi_{\Gamma_4}(l_2^{n_2})\, do_1\, do_2. \tag{8}$$

Here p_{ij} is the permutation operator and the integral signs denote integration over the spatial coordinates and summation over the spin coordinates. In (8) we have retained terms corresponding to the interaction of electrons from different groups, since the electrostatic interaction within each of the groups is diagonal and is included in the energy of the corresponding terms $\{\gamma SL\}$.

Expression (8) can be readily represented in terms of single-electron matrix elements, it being sufficient to separate one arbitrary electron (by virtue of the equivalence) from each group. Thus, in the case of a Russel-Saunders coupling, substituting (3) in (8), we have

$$\Phi(\Gamma_1\Gamma_2\Gamma_3\Gamma_4) = n_1 n_2 \sum_{\{\Gamma_k'\}\{m_k\}\{\sigma_k\}} \prod_{k=1}^{4} \Big(G^{S_k L_k}_{S_k' L_k'},\, C^{L_k M_k}_{L_k' M_k',\, l_k m_k}$$

$$\times C^{S_k \mu_k}_{S_k' \mu_k',\, 1/2\sigma_k} \Big) \int |\Psi_{\Gamma_1'}{}^{*}(l_1^{n_1-1}) \psi_{\lambda_1}{}^{*}(\mathbf{r}_1 s_1) \Psi_{\Gamma_2'}{}^{*}(l_2^{n_2-1})$$

$$\times \psi_{\lambda_2}{}^{*}(\mathbf{r}_2 s_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} (1 - p_{12}) \Psi_{\Gamma_3'}(l_1^{n_1-1}) \psi_{\lambda_3}(\mathbf{r}_1 s_1)$$

$$\times \Psi_{\Gamma_4'}(l_2^{n_2-1}) \psi_{\lambda_4}(\mathbf{r}_s s_2)\, do_1\, do_2 = n_1 n_2$$

$$\times \sum_{\{\Gamma_k'\}\{m_k\}\{\sigma_k\}} \prod_{k=1}^{4} \Big(G^{S_k L_k}_{S_k' L_k'},\, C^{L_k M_k}_{L_k' M_k',\, l_k m_k}\; C^{S_k \mu_k}_{S_k' \mu_k',\, 1/2\sigma_k} \Big)$$

$$\times \delta_{\Gamma_1' \Gamma_3'} \delta_{\Gamma_2' \Gamma_4'} [Q(l_1 m_1, l_2 m_2, l_1 m_3, l_2 m_4)\, \delta_{\sigma_1 \sigma_3} \delta_{\sigma_2 \sigma_4}$$

$$- I(l_1 m_1, l_2 m_2, l_2 m_4, l_1 m_3)\, \delta_{\sigma_1 \sigma_4} \delta_{\sigma_2 \sigma_3}], \tag{9}$$

where Q and I are the ordinary Coulomb and exchange single-electron matrix elements, and the δ-symbols have appeared in (9) as a result of the orthogonality of the corresponding states.

In the Coulomb part of (9) we can immediately sum over the spin projections, using the equality

$$\sum_{\mu_1' \sigma_1} C^{S_1 \mu_1}_{S_1' \mu_1',\, 1/2\sigma_1}\, C^{S_3 \mu_3}_{S_1' \mu_1',\, 1/2\sigma_1} = \delta_{\mu_1 \mu_3} \delta_{S_1 S_3}, \tag{10}$$

that is, the Coulomb terms have nonvanishing matrix elements only between states of equal multiplicity. If we confine ourselves to a single state also in the exchange part, then it is likewise easy to carry out in it the summation over the spin projection. In fact, when $S_1 = S_3$ and $S_2 = S_4$, using the formula for summing 3j coefficients,[7] we have

$$\sum_{\mu_1' \mu_2' \sigma_1' \sigma_2'} C^{S_1 \mu_1}_{S_1' \mu_1',\, 1/2\sigma_1'}\, C^{S_2 \mu_2}_{S_2' \mu_2',\, 1/2\sigma_2'}\, C^{S_1 \mu_3}_{S_1' \mu_1',\, 1/2\sigma_2'}\, C^{S_2 \mu_4}_{S_2' \mu_2',\, 1/2\sigma_1'}$$

$$= [S_1][S_2](-1)^{2(S_1+S_2)+1-S_1'-S_2'-\mu_3-\mu_4}$$

$$\times \sum_{a\mu} (-1)^{-\mu+2a} [a] \begin{Bmatrix} 1/2 & 1/2 & a \\ S_2 & S_2 & S_2' \end{Bmatrix}$$

$$\times \begin{Bmatrix} 1/2 & 1/2 & a \\ S_1 & S_1 & S_1' \end{Bmatrix} \begin{pmatrix} S_1 & S_1 & a \\ -\mu_1 & \mu_3 & \mu \end{pmatrix} \begin{pmatrix} a & S_2 & S_2 \\ -\mu & -\mu_2 & \mu_4 \end{pmatrix}. \tag{11}$$

Alternately, substituting explicit expressions for the 6j-symbol[6] and using (5), we find that expression (11) is equal to

$$
\begin{gathered}
{}^{1}/_{2}\delta_{\mu_1\mu_3}\delta_{\mu_2\mu_4}+2\Delta(S_1S_2S_1{}'S_2{}')\,(\mu_1\,|\hat{\mathbf{S}}_1|\,\mu_3)\,(\mu_2\,|\hat{\mathbf{S}}_2|\,\mu_4),\\
\Delta(S_1S_2S_1{}'S_2{}')=[S_1{}']^{-1}\,[S_2{}']^{-1}\delta_{S_1,S_1{}'\pm{}^1\!/_2}\,(\delta_{S_2,S_2{}'\pm{}^1\!/_2}-\delta_{S_2,S_2{}'\mp{}^1\!/_2}).
\end{gathered}
\tag{12}
$$

Considering further only matrix elements which are diagonal in L, we have for the allowed terms SL of the l^n configuration the following relation ($i = z, \pm$):

$$
\sum_{\mu_1\mu_3}(\mu_1\,|\hat{S}^i|\,\mu_3)\overset{+}{A}_{SL\mu_1M_1}A_{SL\mu_3M_3}=\Theta_{LM_1M_3}(\hat{\mathbf{L}})\hat{S^i}. \tag{13}
$$

A formula of the type (13) was already used by Kondo[5] to separate the spin and orbital operators in the case of a single electron. The functions $\Theta_{LM_1M_2}$ can be calculated in each concrete case, but at present we are interested only in the form of the spin part.

Using (13) and taking (9)–(12) into account, we obtain in lieu of (7)

$$
\begin{aligned}
\hat{\mathscr{H}}(l_1{}^{n_1},\,l_2{}^{n_2})=n_1n_2&\sum[G^{S_1L_1}_{S_1{}'L_1{}'}]^2\,[G^{S_2L_2}_{S_2{}'L_2{}'}]^2\\
&\times C^{L_1M_1}_{L_1{}'M_1{}',l_1m_1}C^{L_2M_2}_{L_2{}'M_2{}',l_2m_2}C^{L_1M_3}_{L_1{}'M_1{}',l_1m_3}C^{L_2M_4}_{L_2{}'M_2{}',l_2m_4}\\
&\times\Theta_{L_1M_1M_3}\Theta_{L_2M_2M_4}\,[Q(l_1m_1,\,l_2m_2,\,l_1m_3,\,l_2m_4)\\
&-\{{}^1/_2+2\Delta(S_1S_2S_1{}'S_2{}')\}\,(\hat{\mathbf{S}}_1\hat{\mathbf{S}}_2)\,I(l_1m_1,\,l_2m_2,\,l_2m_4,\,l_1m_3)].
\end{aligned}
\tag{14}
$$

Inasmuch as (14) is valid, in particular, for the case of localization of groups on different sites of the crystal lattice, we have proved by the same token, assuming orthogonality of their wave functions, the validity of the Heisenberg approximation for a system of two groups of equivalent electrons, in contradiction to the deductions of Izyumov[8] (which are erroneous from our point of view), who attempted to consider in the representation of single-electron functions exchange interaction in the presence of several electrons per atom.

From the foregoing deduction we can clearly determine the conditions for the applicability of the Heisenberg model: 1) the interaction of electrons within the group is much larger than the interaction between the groups and other interactions of the crystalline-field type; 2) the spin-orbit interaction is much smaller than the electrostatic interaction between groups (possibility of representation (13)); 3) the matrix elements of the electrostatic interaction between electrons from different groups and terms of different multiplicity are small and can be discarded, which is essentially valid when condition 1) is satisfied.

Conditions 1) and 3) are equivalent to the Russel-Saunders conditions, while condition 2) is equivalent to the case of a strong crystalline field. We emphasize that in the case under consideration there can appear no higher powers of the scalar product $(\hat{\mathbf{S}}_1\hat{\mathbf{S}}_2)^n$ ($n > 1$), so long as we stay within the framework of the pair interactions between electrons. This is clearly seen from formula (11), where $|\mu_1 - \mu_3|$ and $|\mu_2 - \mu_4|$ cannot be larger than unity. It is interesting to note that the orbital part of formula (14) can be transformed in similar fashion to the Hamiltonian of the orbital momenta, the latter having the form of scalar products $(\hat{\mathbf{L}}_1\hat{\mathbf{L}}_2)^n$ if the single-electron Coulomb and exchange integrals do not depend on the magnetic quantum numbers.

The application of the Heisenberg Hamiltonian (14) to the case $S > {}^1/_2$ is hardly meaningful when it comes to 3d-metals, since the Russel-Saunders coupling in such metals is broken by the strong crystalline field. On the other hand, in the case of rare-earth metals, it is necessary to take into account beforehand the spin-orbit interaction inside the f-shell and this, as will be shown further, leads to essentially new Heisenberg terms.

2. INDIRECT EXCHANGE WITH CONDUCTION ELECTRONS IN RARE-EARTH METALS

As shown by numerous experimental data, a good approximation for rare-earth metals, with the exception of Eu and Sm, is the Russel-Saunders coupling with the formation of total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$. The corresponding wave functions characterized by a set of quantum numbers $\{SLJM_J\}$ and the transition from the representation $\{SL\mu M\}$ (see (3)) is by means of the transformation

$$
\Psi_{SLJM_J}(l^n)=\sum_{\mu M}C^{JM_J}_{S\mu,\,LM}\Psi_{SL\mu M}(l^n). \tag{15}
$$

An analogous relation exists for the operators

$$
A_{SLJM_J}=\sum_{\mu M}C^{JM_J}_{S\mu,\,LM}\,A_{SL\mu M}. \tag{16}
$$

For the electrostatic interaction we shall have again the Hamiltonian (7), where now $\Gamma_i = S_iL_iJ_iM^i_J$. Since, apparently, the direct exchange between the j-electrons and the rare-earth metals is quite insignificant, the greatest interest is attached to consideration of exchange with conduction electrons. The latter will be characterized by quantum numbers $\mathbf{k}$ and σ, where $\mathbf{k}$ is the quasimomentum and σ the z-projection of the spin.[3] The Hamiltonian (7) between the conduction electrons and the f-electrons localized at points ν in the configuration f^n is of the form (c is the index of the conduction electron)

$$\hat{\mathscr{H}}(f^n, c) = \sum_{\nu\Gamma_1\Gamma_2\mathbf{k}\sigma\mathbf{k}'\sigma'} e^{i(\mathbf{k}-\mathbf{k}')\nu}\Bigl(\Gamma_1\,\mathbf{k}\sigma\Bigl|\sum_{i=1}^{n}\frac{e^2}{|\mathbf{r}_i-\mathbf{r}_c|}$$

$$\times(1-p_{ic})\Bigr|\Gamma_2\mathbf{k}'\sigma'\Bigr)A_{\nu\Gamma_1}{}^{+}a_{\mathbf{k}\sigma}{}^{+}a_{\mathbf{k}'\sigma'}A_{\nu\Gamma_2}. \tag{17}$$

Inasmuch as the matrix elements in (17) are much smaller than the distances between the SL terms and also between the levels of the multiplet with different J, we can retain in the sums over Γ_1 and Γ_2 only the terms with $\{S_1L_1J_1\} = \{S_2L_2J_2\}$. Then, taking (10), (12) and (15) into account we can again transform (17) to one-electron matrix elements Q and I:

$$\hat{\mathscr{H}}(f^n\,[SLJ], c) = n\sum_{\left(\substack{\nu M_J M_J'\mathbf{k}\sigma\mathbf{k}'\sigma'\\ \mu\mu' M M'}\right)} C^{JM_J}_{S\mu,\,LM}\,C^{JM_J'}_{S\mu',\,LM'}$$

$$\times\sum_{S'L'\{m_k\}}(G^{SL}_{S'L'})^2\,C^{LM}_{L'm_2,\,m_1}\,C^{LM'}_{L'm_4,\,m_3}\,\delta_{M',\;M-m_1+m_3}$$

$$\times\{\delta_{\mu\mu'}\delta_{\sigma\sigma'}\,Q\,(m_1\mathbf{k}m_3\mathbf{k}') - ({}^1/_2\,\delta_{\mu\mu'}\,\delta_{\sigma\sigma'}$$

$$+[S']^{-1}(\delta_{S,\,S'+1/2}-\delta_{S,\,S'-1/2})\,[2\delta_{\sigma\sigma'}(\mu\,|\,\hat{S}^z\,|\,\mu')$$

$$+\delta_{\sigma,\,1/2}\,\delta_{\sigma',\,-1/2}(\mu\,|\,\hat{S}^-\,|\,\mu')+\delta_{\sigma,\,-1/2}\,\delta_{\sigma',\,1/2}(\mu\,|\,\hat{S}^+\,|\,\mu')])$$

$$\times I\,(m_1\mathbf{k}\mathbf{k}'m_3)\}\,e^{i(\mathbf{k}-\mathbf{k}')\nu}A^{+}_{\nu M_J}A_{\nu M_J'}a_{\mathbf{k}\sigma}{}^{+}a_{\mathbf{k}'\sigma'}. \tag{18}$$

The indices $\{SLJ\}$ have been left out of the operator A, being constant. The expression for Q and I can be obtained in the form of a function of the angular variables of the vectors $\mathbf{k}$ and $\mathbf{k}'$, using the following choice of wave functions:

$$\psi_{n_0l_1m}(\mathbf{r}) = N_{n_0l_1}R_{n_0l_1}(r)\,Y_{l_1m}(\vartheta,\varphi)\qquad(l_1=3),$$

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} = V^{-1/2}\sum_{l=0}^{\infty}[l]\,i^l j_l(kr)\,P_l(\cos\vartheta_{\mathbf{k}\mathbf{r}}), \tag{19}$$

where Y_{lm} are spherical functions, P_l Legendre polynomials, j_l spherical Bessel functions, N_{n_0l} the normalizing factor of the atomic n_0l functions, and V the volume of the crystal. The described method makes it possible in principle to consider the expansion of (19) in terms of arbitrary l. We confine ourselves here to terms $l = 0$ and $l = 1$ (see Sec. 3 concerning terms with $l = 2$), for even in this case we obtain new results and in the general case this expansion converges quite rapidly. We know, however, that when we confine ourselves only to the term $l = 0$ we can consider neither problems connected with magnetic anisotropy[6] nor many kinetic effects in ferromagnets.[5, 9] Using the well known expansion

$$\frac{1}{r_{12}} = \sum_{p=0}^{\infty}\frac{r_<{}^{p}}{r_>{}^{p+1}}P_p(\cos\widehat{\mathbf{r}_1\mathbf{r}_2}), \tag{20}$$

we obtain ($\mathbf{k}$ and $\mathbf{k}'$ are unit vectors)

$$Q(l_1m_1,\mathbf{k},l_1m_1',\mathbf{k}') = \frac{4\pi Ne^2}{V}[\delta_{m_1m_1'}\{F_{00}{}^{(0)}+3F_{11}{}^{(0)}(\mathbf{k}\mathbf{k}')\}$$

$$+B_1(l_1)F_{11}{}^{(2)}T_{m_1m_1'}(\mathbf{k},\mathbf{k}')],$$

$$I(l_1m_1,\mathbf{k},\mathbf{k}',l_1m_1') = \frac{4\pi Ne^2}{V}\Bigl[\delta_{m_1m_1'}G_{00}{}^{(l_1)}[l_1]^{-1}$$

$$+\sum_{p,m=-p}^{p}\Delta(l_1,p)\,G_{11}{}^{(p)}T^{m}_{m_1m_1'}(l_1,p,\mathbf{k},\mathbf{k}')\Bigr], \tag{21}$$

where

$$B_1(l_1) = (-1)^{l_1+1}\frac{l_1(l_1+1)}{5}[l_1]\left[\frac{(2l_1-2)!}{(2l_1+3)!}\right]^{1/2}$$

$$T_{m_1m_1'}(\mathbf{k},\mathbf{k}') = \sum_{m}(-1)^{m_1+m}\begin{pmatrix} l_1 & l_1 & 2\\ -m_1 & m_1' & m\end{pmatrix}T_{2m}(\mathbf{k},\mathbf{k}'), \tag{22}$$

$$T_{2m}(\mathbf{k},\mathbf{k}') = \sum_{m_2m_2'}(-1)^{m_2}\begin{pmatrix}1 & 1 & 2\\ m_2 & -m_2' & m\end{pmatrix}t_{m_2m_2'}$$

$$= \begin{cases}6\,(3k_zk_z'-\mathbf{k}\mathbf{k}') & m=0\\ \pm3\sqrt{6}\,(k_zk'^{\mp}+k^{\mp}k_z'), & m=\pm1;\\ 3\sqrt{6}\,k^{\mp}k'^{\mp}, & m=\pm2\end{cases}$$

$$t_{m_2m_2'} = Y_{1m_2}(\vartheta_{\mathbf{k}}\varphi_{\mathbf{k}})\,Y^{*}_{1m_2'}(\vartheta_{\mathbf{k}'}\varphi_{\mathbf{k}'}),$$

$$T^{m}_{m_1m_1'}(l_1,p,\mathbf{k},\mathbf{k}') = \sum_{m_2m_2'}(-1)^{m_1+m_2+m}\begin{pmatrix}l_1 & p & 1\\ -m_1 & m & m_2'\end{pmatrix}$$

$$\times\begin{pmatrix}l_1 & p & 1\\ m_1' & -m & -m_2\end{pmatrix}t_{m_2m_2'}, \tag{23}$$

$$\Delta(l_1,p) = 3\left(\delta_{p,l_1-1}\frac{l_1}{2l_1-1}+\delta_{p,l_1+1}\frac{l_1+1}{2l_1+3}\right);$$

$$F_{ll'}{}^{(p)} = N^2_{n_0l_1}\int r_1{}^2r_2{}^2\,dr_1\,dr_2\,[R_{n_0l_1}(r_1)]^2\frac{r_<{}^{p}}{r_>{}^{p+1}}\,j_l(kr_2)\,j_{l'}(k'r_2),$$

$$G_{ll'}{}^{(p)} = N^2_{n_0l_1}\int r_1{}^2r_2{}^2\,dr_1\,dr_2R_{n_0l_1}(r_1)\,j_l(kr_2)\,\frac{r_<{}^{p}}{r_>{}^{p+1}}$$

$$\times R_{n_0l_1}(r_2)\,j_{l'}(k'r_1). \tag{24}$$

Substituting (21)–(24) in (18) and expressing all the Clebsch-Gordan coefficients that remain there in terms of 3j symbols, we obtain sums of products of 3j-symbols, for the summation of which we can use a convolution formula which has already been used in (11), and also the following formula:[7]

$$\sum_{n_1n_2n_3n_4n_5}(-1)^{\Sigma_{i=1}^{5}(l_i-n_i)}\begin{pmatrix}l_1 & j_1 & l_2\\ n_1 & m_1 & -n_2\end{pmatrix}\begin{pmatrix}l_2 & j_2 & l_3\\ n_2 & m_2 & -n_3\end{pmatrix}$$

$$\times\begin{pmatrix}l_3 & j_3 & l_4\\ n_3 & m_3 & -n_4\end{pmatrix}$$

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[3] No difficulty is entailed in generalization to the case of the Bloch electron with the set $\{l\mathbf{k}\sigma\}$.

$$\times\begin{pmatrix} l_4 & j_4 & l_5 \\ n_4 & m_4 & -n_5\end{pmatrix}\begin{pmatrix} l_5 & j_5 & l_1 \\ n_5 & m_5 & -n_1\end{pmatrix}$$

$$= \sum_{a_1 a_2 \mu_1 \mu_2}[a_1][a_2](-1)^{2a_1-\mu_1-\mu_2+j_1-j_2+j_3+j_4+j_5+l_5+l_4}$$

$$\times\begin{Bmatrix} j_2 & j_3 & a_1 \\ l_4 & l_2 & l_3\end{Bmatrix}\begin{Bmatrix} a_1 & j_4 & a_2 \\ l_5 & l_2 & l_4\end{Bmatrix}\begin{Bmatrix} a_2 & j_5 & j_1 \\ l_1 & l_2 & l_5\end{Bmatrix}\begin{pmatrix} j_2 & j_3 & a_1 \\ m_2 & m_3 & -\mu_1\end{pmatrix}$$

$$\times\begin{pmatrix} a_1 & j_4 & a_2 \\ \mu_1 & m_4 & \mu_2\end{pmatrix}\begin{pmatrix} a_2 & j_5 & j_1 \\ -\mu_2 & m_5 & m_1\end{pmatrix} \qquad (25)$$

Using also relations (4) and (5), we obtain the Hamiltonian of the momenta in the form of different invariants made up of the vectors $\mathbf{k}$, $\mathbf{k}'$, and $\mathbf{J}_\nu$. (The Hamiltonian has been written out for the general case of the configuration l_1^n, with $l_1 = 3$ in our case)

$$\hat{\mathcal{H}}(l_1{}^n[SLJ],\, c) = \hat{\mathcal{H}}_{coul} + \hat{\mathcal{H}}_{ex}, \qquad \hat{\mathcal{H}}_{ex} = \hat{\mathcal{H}}_{ex}(00)$$

$$+ \hat{\mathcal{H}}_{ex}{}^{(0)}(11) + \mathcal{H}_{ex}{}^{(1)}(11), \qquad (26)$$

$$\hat{\mathcal{H}}_{coul} = n\frac{4\pi Ne^2}{V}\sum_{\mathbf{k}\mathbf{k}'\nu\sigma}\{(F_{00}{}^{(0)} + 3F_{11}{}^{(0)})\,\delta_{\mathbf{k}\mathbf{k}'} + B_2(l_1SLJ)\,F_{11}{}^{(2)}$$

$$\times[3\langle\mathbf{k},\,\mathbf{k}'\hat{\mathbf{J}}_\nu\rangle - 2J(J+1)]\}e^{i(\mathbf{k}-\mathbf{k}')\boldsymbol{\nu}}a_{\mathbf{k}\sigma}{}^{+}a_{\mathbf{k}'\sigma}, \qquad (27)$$

where

$$\langle\mathbf{k},\,\mathbf{k}'\hat{\mathbf{J}}_\nu\rangle = (\mathbf{k}\hat{\mathbf{J}}_\nu)(\mathbf{k}'\hat{\mathbf{J}}_\nu) + (\mathbf{k}'\hat{\mathbf{J}}_\nu)(\mathbf{k}\hat{\mathbf{J}}_\nu), \qquad (28)$$

$$B_2(l_1SLJ) = \sum_{S'L'}(-1)^{-J-S-L'}12B_1(l_1)\,[J]\,[l]\left[\frac{(2J-2)!}{(2J+3)!}\right]^{1/2}$$

$$\times(G^{SL}_{S'L'})^2\begin{Bmatrix} 2 & J & J \\ S & L & L\end{Bmatrix}\begin{Bmatrix} 2 & L & L \\ L' & l_1 & l_1\end{Bmatrix}, \qquad (29)$$

$$\hat{\mathcal{H}}_{ex}(00) = -n\,\frac{4\pi Ne^2}{V}\sum_{\nu\mathbf{k}\mathbf{k}'\sigma\sigma'S'L'}(-1)^{J-S-L-1}$$

$$\times\left(\frac{[J]\,[S]}{[l_1]}\right)^{1/2}G_{00}{}^{(l_1)}\,(G^{SL}_{S'L'})^2\left[\frac{1}{2}\delta_{\sigma\sigma'}\begin{Bmatrix} 0 & J & J \\ L & S & S\end{Bmatrix}\right.$$

$$-\frac{2(\delta_{S,\,S'+1/2} - \delta_{S,\,S'-1/2})}{[S']}\left[\frac{S(S+1)}{J(J+1)}\right]^{1/2}$$

$$\left.\times\begin{Bmatrix} 1 & J & J \\ L & S & S\end{Bmatrix}(\hat{\mathbf{s}}\hat{\mathbf{J}}_\nu)\right]e^{i(\mathbf{k}-\mathbf{k}')\boldsymbol{\nu}}a_{\mathbf{k}\sigma}{}^{+}a_{\mathbf{k}'\sigma'}, \qquad (30)$$

$$\hat{\mathcal{H}}_{ex}{}^{(0)}(11) = -n\frac{4\pi Ne^2}{V}\sum_{\nu\mathbf{k}\mathbf{k}'p\sigma S'L'}\frac{9}{2}[J]\,[L]\,[l_1]\begin{pmatrix} l_1 & p & 1 \\ 0 & 0 & 0\end{pmatrix}^2$$

$$\times G_{11}{}^{(p)}(G^{SL}_{S'L'})^2\sum_{j_{11}a_1}[j_{11}]\,[a_1]\begin{Bmatrix} p & L' & j_{11} \\ L & 1 & l_1\end{Bmatrix}^2$$

$$\times\begin{Bmatrix} j_{11} & a_1 & S \\ J & L & 1\end{Bmatrix}^2\Phi_{a_1}(\mathbf{k},\,\mathbf{k}',\,\hat{\mathbf{J}}_\nu)\,e^{i(\mathbf{k}-\mathbf{k}')\boldsymbol{\nu}}a_{\mathbf{k}\sigma}{}^{+}a_{\mathbf{k}'\sigma}, \qquad (31)$$

$$\hat{\mathcal{H}}_{ex}{}^{(1)}(11) = -n\frac{4\pi Ne^2}{V}\sum_{\nu\mathbf{k}\mathbf{k}'\sigma\sigma'S'L'p}(-1)^{J-S+L}$$

$$\times\frac{18(\delta_{S',\,S-1/2} - \delta_{S',\,S+1/2})}{[S']}[J]\,[L]\,[l_1]\sqrt{S(S+1)[S]}$$

$$\times\begin{pmatrix} l_1 & p & 1 \\ 0 & 0 & 0\end{pmatrix}^2G_{11}{}^{(p)}(G^{SL}_{S'L'})^2\sum_{j_{11}a_1a_2}(-1)^{2a_1+1}$$

$$\times[j_{11}]\,[a_1]\,[a_2]\begin{Bmatrix} p & L' & j_{11} \\ L & 1 & l_1\end{Bmatrix}^2\begin{Bmatrix} J & 1 & a_1 \\ j_{11} & S & L\end{Bmatrix}\begin{Bmatrix} a_1 & 1 & a_2 \\ L & S & j_{11}\end{Bmatrix}$$

$$\times\begin{Bmatrix} a_2 & J & 1 \\ S & S & L\end{Bmatrix}\hat{\mathbf{s}}\boldsymbol{\Phi}_{a_1a_2}e^{i(\mathbf{k}-\mathbf{k}')\boldsymbol{\nu}}a_{\mathbf{k}\sigma}{}^{+}a_{\mathbf{k}'\sigma'}, \qquad (32)$$

where

$$\Phi_{a_1}(\mathbf{k},\,\mathbf{k}',\,\hat{\mathbf{J}}) = -\sqrt{J(J+1)[J]}\,(\hat{\mathbf{J}})^{-1}\boldsymbol{\Phi}_{a_1,J}(\mathbf{k},\,\mathbf{k}',\,\hat{\mathbf{J}}), \qquad (33)$$

and $\boldsymbol{\Phi}_{a_1a_2} \equiv \boldsymbol{\Phi}_{a_1a_2}(\mathbf{k},\,\mathbf{k}',\,\hat{\mathbf{J}})$ has in accordance with the possible values of a_1 and a_2 the form

$$\boldsymbol{\Phi}_{J-1,\,J} = N(J)\frac{1}{J(2J-1)}[\mathbf{x}_1 + i(2J-1)\mathbf{x}_2 - 4J^2\mathbf{x}_3$$

$$-(2J-1)\mathbf{x}_4 + i\mathbf{x}_7],$$

$$\boldsymbol{\Phi}_{J,\,J} = N(J)\frac{1}{J(J+1)}(-\mathbf{x}_1 + i\mathbf{x}_2 - \mathbf{x}_4 - i\mathbf{x}_7),$$

$$\boldsymbol{\Phi}_{J+1,\,J} = N(J)\frac{1}{(J+1)(2J+3)}[\mathbf{x}_1 - i(2J+3)\mathbf{x}_2$$

$$-4(J+1)^2\mathbf{x}_3 + (2J+3)\mathbf{x}_4 + i\mathbf{x}_7],$$

$$\boldsymbol{\Phi}_{J-1,\,J-1} = \frac{1}{\alpha(J-1)\alpha_1{}^2(J-1)}(\mathbf{X}_1 + \mathbf{X}_2),$$

$$\boldsymbol{\Phi}_{J,\,J-1} = \frac{1}{\alpha(J)\alpha_1{}^2(J-1)}(\mathbf{X}_1 - \mathbf{X}_2), \qquad (34)$$

$$\mathbf{X}_1 = J[i\mathbf{x}_2 + (2J-1)\mathbf{x}_4 - 2iJ^2\mathbf{x}_5],$$

$$\mathbf{X}_2 = \mathbf{x}_1 - i\mathbf{x}_2 - 2J\mathbf{x}_3 - (2J-1)\mathbf{x}_4 + 2iJ^2\mathbf{x}_5 - J(2J-1)\mathbf{x}_6$$

$$-i(\mathrm{J}-1)\mathbf{x}_7,$$

$$\boldsymbol{\Phi}_{J,\,J+1} = \frac{1}{\alpha(J)\alpha_1{}^2(J)}(\mathbf{X}_3 + \mathbf{X}_4),$$

$$\boldsymbol{\Phi}_{J+1,\,J+1} = \frac{1}{\alpha(J+1)\alpha_1{}^2(J)}(\mathbf{X}_3 - \mathbf{X}_4 - 2i\mathbf{x}_2 + 2(2J+3)\mathbf{x}_4$$

$$+4i(J+1)^2\mathbf{x}_5),$$

$$\mathbf{X}_3 = J[-i\mathbf{x}_2 + (2J+3)\mathbf{x}_4 + 2i(J+1)^2\mathbf{x}_5],$$

$$\mathbf{X}_4 = -\mathbf{x}_1 - 2(J+1)\mathbf{x}_3 + (2J+3)(J+1)\mathbf{x}_6 - i(J+2)\mathbf{x}_7,$$

where

$$N(J) = {}^1/_4[J]^{-3/2}[J(J+1)]^{-1/2}, \quad \alpha(J)$$

$$= [2J(2J+1)(2J+2)]^{1/2},$$

$$\alpha_1(J) = [(2J+1)(2J+2)(2J+3)]^{1/2}, \qquad (35)$$

$$\mathbf{x}_1 = \{\hat{\mathbf{J}},\,\langle\mathbf{k},\,\mathbf{k}'\hat{\mathbf{J}}\rangle\}, \quad \mathbf{x}_2 = \{\hat{\mathbf{J}},\,[\mathbf{k},\,\mathbf{k}']\hat{\mathbf{J}}\}, \quad \mathbf{x}_3 = (\mathbf{k}\mathbf{k}')\hat{\mathbf{J}},$$

$$\mathbf{x}_4 = [[\mathbf{k},\,\mathbf{k}'],\,\hat{\mathbf{J}}], \quad \mathbf{x}_5 = [\mathbf{k},\,\mathbf{k}'], \; \mathbf{x}_6 = \mathbf{k}'(\mathbf{k}\hat{\mathbf{J}}) + \mathbf{k}(\mathbf{k}'\hat{\mathbf{J}}),$$

$$\mathbf{x}_7 = ([\mathbf{k},\,\hat{\mathbf{J}}](\mathbf{k}'\hat{\mathbf{J}}) + (\mathbf{k}'\hat{\mathbf{J}})[\mathbf{k},\,\hat{\mathbf{J}}] + (\mathbf{k}\leftrightarrow\mathbf{k}')),$$

$$\{\hat{\mathbf{A}},\,\hat{\mathbf{B}}\} = \hat{\mathbf{A}}\hat{\mathbf{B}} + \hat{\mathbf{B}}\hat{\mathbf{A}}. \qquad (36)$$

Formulas (27)–(36) solve the problem of obtaining the Hamiltonian and exchange interaction between conduction electrons and rare-earth lattice ions with account of the next term of the expansion in the parameter $(k_F r_0) \approx 0.5$ [3] for the entire series of rare-earth metals, since the numerical value of the coefficients can be readily calculated for each concrete set $\{SLJ\}$ with the aid of the existing tables of 6j symbols (for a bibliography see [2]). The fractional parentage coefficient can be taken from the tables given in the book of Sobel'man[2] for the configurations $f^1 - f^7$, and from Racah's paper[1] for $f^8 - f^{13}$.

Thus, for the case of the Hund terms, substituting the explicit expressions for the 6j symbols and using the equality established by us

$$\sum_{S'L'} (G^{SL}_{S'L'}) \frac{(\delta_{S,\, S'-1/2} - \delta_{S,\, S'+1/2})}{[S']} = \frac{1}{n}, \tag{37}$$

where n is the number of electrons in the configuration l^{n}, we obtain from (30)

$$\hat{\mathcal{H}}_{ex}(00) = -n \frac{4\pi N e^2}{V} \sum_{\boldsymbol{\nu}\mathbf{k}\mathbf{k}'\sigma\sigma'} \frac{G^{(l_1)}_{00}}{[l_1]} \left[\frac{1}{2} \delta_{\sigma\sigma'} + \frac{2}{n} (g-1)(\hat{\mathbf{s}}\hat{\mathbf{J}}_\nu) \right]$$

$$\times e^{i(\mathbf{k}-\mathbf{k}')\boldsymbol{\nu}} a_{\mathbf{k}\sigma}{}^{+} a_{\mathbf{k}'\sigma'}, \tag{38}$$

which coincides with the deGennes Hamiltonian[4] (g-g factor). The Hamiltonians (31) and (32) have been obtained in this general form for the first time and are of considerable interest for the analysis of magnetic, electric, and other properties of rare-earth metals. Terms containing products of the vectors **k** and **k′**, for example, were used recently in the calculation of the spontaneous Hall effect in ferromagnets.[5,9]

After transforming and reducing like terms in (31) and (32), the exchange Hamiltonian takes the form

$$\hat{\mathcal{H}}_{ex}(l^n[SLJ], c)$$

$$= \sum_{\boldsymbol{\nu}\mathbf{k}\sigma\mathbf{k}'\sigma'} e^{i(\mathbf{k}-\mathbf{k}')\boldsymbol{\nu}} a^{+}_{\mathbf{k}\sigma} a_{\mathbf{k}'\sigma'} \Big\{ A \left[\frac{n}{2} + 2(g-1)(\hat{\mathbf{s}}\hat{\mathbf{J}}_\nu) \right]$$

$$+ (B\langle\mathbf{k}, \mathbf{k}'\hat{\mathbf{J}}_\nu\rangle + \iota C[\mathbf{k}, \mathbf{k}']\hat{\mathbf{J}}_\nu + D(\mathbf{k}\mathbf{k}'))\delta_{\sigma\sigma'}$$

$$+ E\{(\hat{\mathbf{s}}\hat{\mathbf{J}}_\nu), \langle\mathbf{k}, \mathbf{k}'\hat{\mathbf{J}}_\nu\rangle\} + iF\{(\hat{\mathbf{s}}\hat{\mathbf{J}}_\nu), [\mathbf{k}, \mathbf{k}']\hat{\mathbf{J}}_\nu\}$$

$$+ G(\hat{\mathbf{s}}\hat{\mathbf{J}}_\nu)(\mathbf{k}\mathbf{k}') + iH[\mathbf{k}, \mathbf{k}']\hat{\mathbf{s}}$$

$$+ I[(\hat{\mathbf{s}}\mathbf{k}')(\mathbf{k}\hat{\mathbf{J}}_\nu) + (\hat{\mathbf{s}}\mathbf{k})(\mathbf{k}'\hat{\mathbf{J}}_\nu]\}, \tag{39}$$

with all the real coefficients of $B = B_{SLJ}(k, k')$ etc. calculated from expressions (30)–(35).

We see from (39) that the highest power q of the invariants $(\hat{\mathbf{J}}\mathbf{Y})$ is equal to three, which corresponds to its non-Heisenberg character, and is connected with the fact that we took only terms with $l \le 1$ in the expansion (19) for the conduction-electron wave. In the general case, $q = 2(l + 1/2) = 2j$ when $j < J$, and $q = 2J$ when $j > J$ in accordance with the general rule indicated above. The most important difference between (39) and the deGennes case is the direct connection between the vectors of the quasimomenta of the electrons and the momenta J_ν of the f-shells, which is manifest in the presence of the corresponding invariants in (39). Such a connection makes it possible to consider, from the microscopic point of view, the dependence of the magnetic properties of the rare-earth metals on the **k**-space characteristics of the system of conduction electrons, and in particular on the shape of the Fermi surface,[10] wherein the corresponding coefficients are known functions of {SLJ}, that is, they can be traced in the entire group of rare-earth metals. It is also of interest to consider the inverse problem: to ascertain the dependence of the properties of conduction electrons on the character of the ordering of the magnetic ions, as was done, for example, for Heisenberg exchange in earlier papers,[11] where a splitting of the energy bands in antiferromagnets was obtained as the result of appearance of new Brillouin zones.

Another important consequence of the Hamiltonian (39) is the occurrence of indirect exchange of an entirely new type. This exchange differs essentially from the deGennes exchange in that it takes place without perturbation of the conduction-electron spin. The physical picture consists in the fact that the total momenta $\mathbf{J}_\nu$, which include the orbital components, can exchange with one another via the orbital momenta **l** of the conduction electrons, something which is excluded in the deGennes model, which corresponds to $l = 0$. By way of example we consider in the next section one of the terms of the Hamiltonian (39), leading to an exchange of this type.

3. CALCULATION OF THE INDIRECT EXCHANGE

After calculating the second approximation of perturbation theory with the Hamiltonian (39), we obtain the effective exchange Hamiltonian containing not only the usual Heisenberg invariant, but also terms of the type $(\mathbf{J}_{\nu_1}\hat{\mathbf{J}}_{\nu_2})^2$ and $(\hat{\mathbf{J}}_{\nu_1}\mathbf{J}_{\nu_2})^3$ which, as already noted, corresponds to a degree $q = 2(l + 1/2)$ $(l = 1)$ of the Hamiltonian (39).[4] In

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[4] Such terms were left out in the paper of Kaplan and Lyons[6] as a result of the approximation employed there. They considered terms only of the type $l = 0$, $l' = 2$ and $l = 2$, $l' = 0$ which have the same order of magnitude in the parameter $(k_F r_0)$ as those with $l = 1$ and $l' = 1$ considered by us. The terms taken into account in[6] can be readily obtained in our procedure, but they are not included in the Hamiltonian (39), since they are of no interest for kinetic problems (the absence of matrix elements with $k, k' \neq 0$) and their role in the indirect exchange was considered in[6].

this paper we consider by way of an example the contribution to the indirect exchange made by only one of the new terms, namely the term with coefficient C in (39) in which there is no spin operator of the conduction electron. This coefficient was calculated by us for all the main terms of the entire series of rare-earth elements, by summing the products of 6j symbols, and was found to be simply proportional to ~ (g – 2) for all the elements[5)]

$$C_{SLJ}(k, k') = \frac{4\pi N e^2}{V} G_{11}^{(2)}(k, k') \frac{9}{140}(g-2). \tag{40}$$

The second-approximation correction to the energy as T → 0 takes the form

$$E_{ex}^{(2)} = -\sum_{\substack{\nu_1\nu_2\sigma,\ \mathbf{k}<\mathbf{k}_\Phi \\ \mathbf{k}'>\mathbf{k}_\Phi}} \frac{|C_{SLJ}(k, k')|^2}{\varepsilon_{\mathbf{k}'\sigma} - \varepsilon_{\mathbf{k}\sigma}} \times ([\mathbf{k}, \mathbf{k}'] \hat{\mathbf{J}}_{\nu_1}) ([\mathbf{k}, \mathbf{k}'] \hat{\mathbf{J}}_{\nu_2}) e^{i(\mathbf{k}-\mathbf{k}')(\boldsymbol{\nu}_1-\boldsymbol{\nu}_2)}. \tag{41}$$

Anisotropic exchange in (41) can occur both because of the non-sphericity of the conduction-electron energy band, and the difference in the distances to the various nearest neighbors. The first of these causes gives the intrinsic anisotropy at $\nu_1 = \nu_2$, while the second leads to anisotropy only when $\nu_1 \neq \nu_2$. The anisotropy of **k**-space should be taken into account from the very beginning, and therefore to estimate the order of magnitude of the effect we shall consider only terms with $\nu_1 \neq \nu_2$. Integrating over the angles in (41) we obtain for $\nu_1 \neq \nu_2$

$$E_{ex}^{(2)} = -\sum_{\substack{\sigma,\ \nu_1\neq\nu_2,\ k<k_\Phi \\ k'>k_\Phi}} \frac{|C_{SLJ}(k, k')|^2}{\varepsilon_{k'\sigma} - \varepsilon_{k\sigma}} [\varphi_i(k, k', R_{\nu_1\nu_2}) (\hat{\mathbf{J}}_{\nu_1}\hat{\mathbf{J}}_{\nu_2}) + \varphi_a(k, k', R_{\nu_1\nu_2}) (\mathbf{r}_{\nu_1\nu_2}\hat{\mathbf{J}}_{\nu_1}) (\mathbf{r}_{\nu_1\nu_2}\hat{\mathbf{J}}_{\nu_2})], \tag{42}$$

where $\mathbf{r}_{\nu_1\nu_2} = \mathbf{R}_{\nu_1\nu_2}/R_{\nu_1\nu_2}$, and

$$\varphi_i(k, k', R_{\nu_1\nu_2}) = h(\alpha)\frac{\sin\alpha'}{\alpha'} + h(\alpha')\frac{\sin\alpha}{\alpha} - 4h(\alpha)h(\alpha'),$$

$$\varphi_a(k, k', R_{\nu_1\nu_2}) = 6h(\alpha)h(\alpha') - h(\alpha)\frac{\sin\alpha'}{\alpha'} - h(\alpha')\frac{\sin\alpha}{\alpha},$$

$$h(\alpha) = \alpha^{-3}(\sin\alpha - \alpha\cos\alpha), \quad \alpha = kR_{\nu_1\nu_2}, \quad \alpha' = k'R_{\nu_1\nu_2}. \tag{43}$$

Relations (43) have an oscillatory Ruderman-Kittel form, but differ somewhat from the usual form because of the specific features of the exchange mechanism.

Assuming as a rough estimate $\epsilon_{k'\sigma} - \epsilon_{k\sigma} \sim \epsilon_F \sim 5 \times 10^{-12}$ erg and $C_{SLJ}(k, k') = \text{const} = (g-2) \times 10^{-14}$ erg,[5] we obtain

$$E_{ex}^{(2)} \cong (g-2)^2 J(J+1) \cdot 5 \cdot 10^{-17} \text{ erg}. \tag{44}$$

The quantity $(g-2)^2 J(J+1)$ takes on values from 10 to 40, and consequently $E_{ex}^{(2)}$ reaches an order of several dozen degrees on the temperature scale, which qualitatively corresponds to the value of the anisotropy observed in Dy[12] and Ho.[13] For a more detailed investigation of the anisotropy energy it is necessary to calculate the contributions of the remaining terms, including those taken into account in [6], which calls for a special analysis. We wish only to note the existence of a new anisotropic contribution ~ $(g-2)^2 J(J+1)$, which has a direct physical meaning, namely, it is proportional to the orbital component of the total angular momentum of the rare-earth ions. We see from (42) that there is also an additional contribution to the isotropic exchange, of the same order of magnitude as (44), as a result of which the theoretical dependence of the Curie point on the element number, proposed by deGennes, is slightly altered.[4]

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APPENDIX 1

INTRODUCTION OF THE ELECTRON GROUP OPERATOR A_Γ

To illustrate the formulas of the type (7) and (17) of the text, let us consider the simple case of a system of three electrons, two of which are equivalent, that is, a configuration of the type $l^2 l^1$. The Coulomb Hamiltonian of such a system, in the representation of the single-electron quantum numbers in the single-configuration approximation, is of the form

$$\hat{\mathscr{H}} = \frac{1}{2}\sum_{i\neq j}\sum_{\left(\substack{\lambda_1\lambda_2\lambda_3 \\ \lambda_1'\lambda_2'\lambda_3'}\right)} \int \psi^*_{\lambda_1\lambda_2}(\rho_1\rho_2)\psi^*_{\lambda_3}(\rho_3) Q_{ij} \psi_{\lambda_1'\lambda_2'}(\rho_1\rho_2) \times \psi_{\lambda_3'}(\rho_3)\, do\, do' a^+_{\lambda_1} a^+_{\lambda_2} a^+_{\lambda_3} a_{\lambda_3'} a_{\lambda_2'} a_{\lambda_1'}. \tag{I}$$

Here $Q_{ij} = e^2(1 - p_{ij})/r_{ij}$; $\lambda = l, m, \sigma$; $\rho = r, s$, $\psi_{\lambda_1\lambda_2}(\rho_1, \rho_2)$ are the determinantal functions of two equivalent electrons. Expression (I) can, of course, be written also in terms of fully symmetrized functions of three electrons. The notation presented here implies further diagonalization of the Coulomb interaction between the equivalent electrons.

[5)] In (40) we have retained only the largest term with $G_{11}^{(2)}$ (p = 2), and the term with p = 4 has been omitted for simplicity.

In fact, let us denote

$$\frac{1}{\sqrt{2}} \overset{+}{a}_{\lambda_1} \overset{+}{a}_{\lambda_2} = \overset{+}{b}_{\lambda_1\lambda_2}, \qquad \frac{1}{\sqrt{2}} a_{\lambda_2'} a_{\lambda_1'} = b_{\lambda_1'\lambda_2'} \tag{II}$$

and let us introduce new operators $A_\Gamma \equiv A_{SL\mu M}$ by means of the formula

$$b_{\lambda_1\lambda_2} = \sum_{SL\mu M} C^{LM}_{lm_1,\, lm_2} C^{S\mu}_{½\sigma_1,\, ½\sigma_2} A_{SL\mu M}. \tag{III}$$

By virtue of the orthogonality relations of the Clebsch-Gordan coefficients, the inverse relation also holds true:

$$A_{SL\mu M} = \sum_{m_1 m_2 \sigma_1 \sigma_2} C^{LM}_{lm_1,\, lm_2} C^{S\mu}_{½\sigma_1,\, ½\sigma_2} b_{lm_1\sigma_1,\, lm_2\sigma_2}. \tag{III'}$$

From the symmetry properties of the operators $b_{\lambda_1\lambda_2}$ and of the Clebsch-Gordan coefficients with respect to permutation of λ_1 and λ_2 it follows immediately that $A_{SL\mu M} \neq 0$ only for even $S + L$ — the well known rule for the two-electron configuration.

Substituting (III) in (I), we obtain

$$\hat{\mathscr{H}} = \sum_{i \neq j} \sum_{\left(\substack{\lambda_1\lambda_2\lambda_3\Gamma \\ \lambda_1'\lambda_2'\lambda_3'\Gamma'}\right)} C^{LM}_{lm_1,\, lm_2} C^{S\mu}_{½\sigma_1,\, ½\sigma_2}$$
$$\times C^{L'M'}_{lm_1',\, lm_2'} C^{S'\mu'}_{½\sigma_1',\, ½\sigma_2'} \int \psi_{\lambda_1\lambda_2}(\rho_1\rho_2)\, \psi_{\lambda_3}(\rho_3)$$
$$\times Q_{ij}\, \psi_{\lambda_1'\lambda_2'}(\rho_1\rho_2)\, \psi_{\lambda_3'}(\rho_3)\, do\, do'\, A_{\Gamma}{}^{+} \overset{+}{a}_{\lambda_3} a_{\lambda_3'} A_{\Gamma'}. \tag{IV}$$

But by definition (see formula (1) in the text) the product of the Clebsch-Gordan coefficients in (IV) allows us to go over in the wave functions to the SLμM, that is,

$$\hat{\mathscr{H}} = \sum_{i \neq j} \sum_{\Gamma\Gamma'\lambda_3\lambda_3'} \int \Psi_{\Gamma}{}^{*}(l^2)\, \psi_{\lambda_3}{}^{*}(\rho_3)\, Q_{ij} \Psi_{\Gamma'}(l^2)$$
$$\times \psi_{\lambda_3'}(\rho_3)\, do\, do' A_{\Gamma}{}^{+} a_{\lambda_3}{}^{+} a_{\lambda_3'} A_{\Gamma'}. \tag{V}$$

The transformation of the Hamiltonian from the form (I) into (V) is simply a transition from the representation of the single-electron quantum numbers to the {SLμM} representation. Since, however, the Coulomb interaction between the electrons l^2 is the angle in this representation, we are left after its separation and evaluation of the energy of the terms SL in (V) with only the interaction between the electrons in the state l' and SL. Since usually the latter are much smaller than the energy distance between the different terms, further solution of the problem is greatly simplified.

In analogy with the foregoing, we can obtain also the general formula (7) of the text. The corresponding operators A_Γ for $n > 2$ can be constructed successively from the single-electron operators a_λ with the aid of the relation

$$A_{\Gamma}{}^{+}(l^n) = \sum_{\Gamma'\lambda} G^{SL}_{S'L'} C^{LM}_{L'M',\, lm} C^{S\mu}_{S'\mu',\, ½\sigma} A_{\Gamma'}{}^{+}(l^{n-1})\, a_\lambda{}^{+}. \tag{VI}$$

Formulas (II), (III), (III'), (VI) give the explicit form of the connection between the group operators A_Γ and the ordinary Fermi operators.

APPENDIX 2

CONNECTION BETWEEN THE MOMENTUM OPERATORS AND THE OPERATORS A_Γ

The derivation of formula (V) as given in Appendix 1 makes the meaning of formula (4) of the text perfectly obvious. This formula represents the momentum operator in terms of the second-quantization operator of the group of electrons that produce this momentum, in a representation where $\hat{J}^2$ and $\hat{J}^z$ are diagonal. Such a representation is convenient when J is a good quantum number.[6] Obviously, the system of n electrons in a state with fixed values of J and with arbitrary possible values of M_J (all the remaining quantum numbers are likewise fixed) can in this case be described either with the aid of $2J + 1$ occupation numbers $\overset{+}{A}_{JM_J} A_{JM_J}$ or in terms of $2J + 1$ quantities $(\hat{J}^z)^0, \hat{J}^z \ldots (\hat{J}^z)^{2J}$. The nondiagonal combinations $\overset{+}{A}_{JM_J \pm m} A_{JM_J}$ are expressed in this case in terms of the operators of the type $(\hat{J}^{\pm})^m (1 \leq m \leq 2J)$.

The transition from one description to the other is given by formula (4) and by the corresponding formula for the higher powers of $\hat{J}^z, \hat{J}^{\pm}$. The coefficients of the formula (4) can be easily determined from the condition that the matrix elements of the right side of formula (4) in the representation of the occupation numbers give the matrix elements of the momentum $\hat{J}$.

Such a definition takes into account all the properties of the operator $\hat{J}$, and in particular it is easy to verify the satisfaction of the commutation relation.

Let us consider, for example, the case of a two-electron configuration with specified values of S and L. Then, according to (4)

$$L^z = (-1)^{-L} \sum_{MM'} (-1)^M \sqrt{L(L+1)[L]}$$
$$\times \begin{pmatrix} L & L & 1 \\ M & -M' & 0 \end{pmatrix} \overset{+}{A}_{SL\mu M} A_{SL\mu M'},$$

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[6] In the general case we can introduce in analogy with (4) operators that are not diagonal in J, but they will have a different meaning, since the momentum itself is no longer conserved in this case.

$$L^{+}=(-1)^{-L}\sum_{MM'}(-1)^{M}\sqrt{2L(L+1)[L]}$$
$$\times\begin{pmatrix} L & L & 1 \\ +M & -M'-2 & 1 \end{pmatrix} \overset{+}{A}_{SL\mu M}A_{SL\mu M'}. \tag{VII}$$

Omitting henceforth the fixed indices SLμ, we obtain for the commutator

$$[L^{+}, L^{z}]=L(L+1)[L]\sqrt{2}\sum_{MM'M_1M_1'}(-1)^{M+M_1}\begin{pmatrix} L & L & 1 \\ M & -M' & 0 \end{pmatrix}$$
$$\times\begin{pmatrix} L & L & 1 \\ +M_1 & -M_1'-2 & 1 \end{pmatrix}[\overset{+}{A}_{M_1}A_{M_1'}, A_{M}{}^{+}A_{M'}]$$
$$=L(L+1)[L]\sqrt{2}\sum_{MM'M_1M_1'}(-1)^{M+M_1}\begin{pmatrix} L & L & 1 \\ M & -M' & 0 \end{pmatrix}$$
$$\times\begin{pmatrix} L & L & 1 \\ +M_1 & -M_1'-2 & 1 \end{pmatrix}\{A_{M}{}^{+}[A_{M_1}{}^{+}, A_{M'}]A_{M_1'}$$
$$-A_{M_1}{}^{+}[A_{M}{}^{+}, A_{M_1'}]A_{M'}\}. \tag{VIII}$$

Since in accordance with (III′)

$$[A_{M}{}^{+}, A_{M'}]=\sum_{\lambda_1\lambda_2\lambda_1'\lambda_2'} C^{LM}_{m_1; m_2}C^{LM'}_{m_1', m_2'}C^{S\mu}_{\sigma_1, \sigma_2}C^{S\mu}_{\sigma_1', \sigma_2'}[\overset{+}{b}_{\lambda_1\lambda_2}, b_{\lambda_1'\lambda_2'}], \tag{IX}$$

and the commutator

$$[\overset{+}{b}_{\lambda_1\lambda_2}, b_{\lambda_1'\lambda_2'}]={}^{1}/{}_{2}[\delta_{\lambda_1\lambda_2'}\delta_{\lambda_1'\lambda_2}-\delta_{\lambda_1\lambda_1'}\delta_{\lambda_2\lambda_2'}+\hat{\Phi}_{\lambda_1\lambda_2\lambda_1'\lambda_2'}], \tag{X}$$

where $\hat{\Phi}_{\lambda_1\lambda_2\lambda_1'\lambda_2'}$ is the operator term containing the combinations of the operators of the type $\overset{+}{a}_{\lambda}a_{\lambda'}$, and consequently makes no contribution to expression (VIII), since the groups of six operators $\overset{+}{a}_{\lambda_1}\overset{+}{a}_{\lambda_2}\overset{+}{a}_{\lambda_3}a_{\lambda_3'}a_{\lambda_2'}a_{\lambda_1'}$ obtained there from it have only zero matrix elements for the two-electron functions.

Using the symmetry properties of the Clebsch-Gordan coefficients and the parity of the number S + L, and carrying out the summation, we find that the non-operator part of the commutator (IX) is simply equal to $-\delta_{M,M'}$ and is in fact independent of μ.

In this case (VIII) takes the form

$$[L^{+}, L^{z}]=-L(L+1)[L]\sqrt{2}\sum_{MM'M_1M_1'}(-1)^{M+M_1}\begin{pmatrix} L & L & 1 \\ M & -M' & 0 \end{pmatrix}$$
$$\times\begin{pmatrix} L & L & 1 \\ +M & -M_1'-2 & 1 \end{pmatrix}\{\delta_{M_1M'}A_{M}{}^{+}A_{M_1'}$$
$$-\delta_{MM_1'}A_{M_1}{}^{+}A_{M'}\}$$

or, substituting explicit expressions for 3j symbols, we obtain ultimately

$$[L^{+}, L^{z}]=-\sum_{MM_1}M[(L-M_1)(L-M_1+1)]^{1/2}\{\delta_{M_1M}A_{M}{}^{+}A_{M_1-1}$$
$$-\delta_{M;M_1-1}A_{M_1}{}^{+}A_{M}\}$$
$$=-\sum_{M}[(L-M)(L-M+1)]^{1/2}A_{M}{}^{+}A_{M-1}=-L^{+} \tag{XI}$$

in accordance with the usual rule.

Analogous proofs for n electron configurations can be obtained with the aid of formula (VI).

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