HAMILTONIAN FOR EXCHANGE INTERACTION IN RARE EARTH METALS

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The spin Hamiltonian proposed in [1] for exchange interaction between f-electrons and conduction electrons is considered. Application of the irreducible tensor operator method and of the Yutsis-Levinson graphic methods yields simple analytical formulas for the calculation of the tensors connected with various interactions of the non-Heisenberg type. The sums involving products of the fractional parentage coefficients are expressed in terms of standard reduced matrix elements of the type $\langle f^n\gamma SL \| V^{(kr)} \| f^n\gamma' S'L' \rangle$, most of which have been tabulated. Some of the features of the properties of a number of rare earth metals, due to the dependence of the Hamiltonian coefficients on atomic number, are discussed qualitatively, and it is indicated in particular that the change in the direction of easy magnetization on going from Ho to Er may be attributed to the change in sign of some anisotropic exchange coefficients.

1. An earlier paper by one of the authors [1] dealt with exchange interaction of several magnetic f-electrons in an atom with the conduction electrons. It was shown that such an exchange interaction is connected with the spin Hamiltonian which contains the operators **s** and **J**. The operator **s** acts on the spin variables of the conduction electrons, and **J** acts on the total angular momentum variables of the atom. To calculate the spin-Hamiltonian coefficients, formulas were derived involving the sums of products of the fractional-parentage coefficients, j-symbols, and Wigner coefficients. Only for one of them was a simple analytic formula given:

$$C_{SLJ} = -\frac{4\pi e^2 N}{V} G_{11}^2(kk') \frac{9}{140}(g-2). \qquad (1)$$

Here g is the Lande factor, V the volume of the fundamental region, and $G^p_{ll'}(kk')$ the standard radial part of the exchange integral of the conduction electrons with the f-electrons:

$$G^p_{ll'}(kk') = \int\int R_{n_0 l_1}(r_1) j_l(kr_2) \frac{r_<^p}{r_>^{p+1}} R_{n_0 l_1}(r_2) \times j_{l'}(k'r_1) r_1^2 r_2^2 \, dr_1 \, dr_2, \qquad (2)$$

where j_l are spherical Bessel functions in which the wave functions of the conduction electrons are expanded.

2. In this paper we obtain formulas similar to (1) for other coefficients which enter in the invariants of the spin Hamiltonian. In addition, we present a general analytic expression for the spin Hamiltonian in the form of a series in l, l', and p; the terms of this series involve products of the type **sJ . . . J** and **JJ . . . J**. Simplification of the complex sums for the coefficients of the spin Hamiltonian was made possible by using graphic methods of jm-coefficient summation, developed by Yutsis, Levinson, and Vanagas [2]. We note that the diagram procedure used in [2] has been somewhat modified in a recent monograph [3]. We shall, however, adhere to the terminology and to the methods proposed in [2].

Since it is of the greatest interest, we shall consider the exchange part of the operator of electrostatic interaction, described by formula (17) in [1]

$$H_{ex} = \frac{1}{N} \sum_{\nu\Gamma_1\Gamma_2 k k' \sigma\sigma'} e^{i(\mathbf{k}-\mathbf{k}')\mathbf{v}} F(\Gamma_1 \mathbf{k}\sigma, \Gamma_2 \mathbf{k}'\sigma') A^+_{\nu\Gamma_1} a^+_{k\sigma} a_{k'\sigma'} A_{\nu\Gamma_2}. \qquad (3)$$

The quantity

$$F(\Gamma_1 \mathbf{k}\sigma, \Gamma_2 \mathbf{k}'\sigma') = -\left\langle \Gamma_1 \mathbf{k}\sigma \left| \sum_{i=1}^{n} \frac{e^2}{|r_i - r_c|} p_{ic} \right| \Gamma_2 \mathbf{k}'\sigma' \right\rangle, \qquad (4)$$

can, in analogy with [1], be represented (under the same assumptions as in [1]) in the form

$$F = \frac{4\pi e^2 N}{V} n \sum_{ll'p} (-1)^{l+1} i^{l+l'} (l_1 \| C^p \| l') (l \| C^p \| l_1) \times G^p_{ll'}(kk')[J][S][L] \sum_{\gamma_1 S_1 L_1} |G^{\gamma SL}_{\gamma_1 S_1 L_1}|^2 [l]^{1/2} [l']^{1/2} \times \sum_{mm'} (-1)^{l+m+m'} C^l_m(k) C^{l'}_{-m'}(k') (-1)^{p+J-M+1/2-\sigma}$$

$$\times \sum_{\substack{M_L M_S M_L' M_S' \\ M_{L_1} M_{S_1} m_1 m_1' q}} (-1)^t \begin{pmatrix} L & S & J \\ M_L & M_S & -M \end{pmatrix} \begin{pmatrix} L & S & J \\ -M_L' & -M_S' & M' \end{pmatrix}$$

$$\times \begin{pmatrix} L_1 & l_1 & L \\ M_{L_1} & m_1 & -M_L \end{pmatrix} \begin{pmatrix} S_1 & 1/2 & S \\ -M_{S_1} & -\sigma & M_S' \end{pmatrix} \begin{pmatrix} S_1 & 1/2 & S \\ M_{S_1} & \sigma' & -M_S' \end{pmatrix}$$

$$\times \begin{pmatrix} L_1 & l_1 & L \\ -M_{L_1} & -m_1' & M_L' \end{pmatrix} \begin{pmatrix} l_1 & p & l' \\ -m_1 & q & m' \end{pmatrix} \begin{pmatrix} l & p & l_1 \\ -m & -q & m_1 \end{pmatrix},$$

$$[a] = 2a + 1. \tag{5}$$

In (5), n is the number of f-electrons ($l_1 = 3$), $C^l_m(k)$ is a spherical tensor of rank l:

$$C_m^l(k) = \left(\frac{4\pi}{2l+1}\right)^{1/2} Y_{lm}(\theta_k \varphi_k),$$

$(l_1 \| C^p \| l)$ is a reduced matrix element of the spherical functions,

$$t = L - M_L + S - M_S + L - M_L' + S - M_S' + l_1 - m_1' + p - q + l_1 - m_1 + L_1 - M_{L_1} + S_1 - M_{S_1},$$

$G^{\gamma SL}_{\gamma_1 S_1 L_1}$ is a fractional parentage coefficient,

$\begin{pmatrix} abc \\ \alpha\beta\gamma \end{pmatrix}$ is a Wigner coefficient, the index p fixes the terms of the series expansion of the electrostatic interaction $e^2/|r_i - r_c|$, and l the series expansion of the conduction-electron function

$$|k\sigma\rangle = \frac{4\pi}{V^{1/2}} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} i^l j_l(kr) (-1)^m Y_{l,-m}(\theta_k, \varphi_k) \times Y_{l,m}(\theta_r, \varphi_r) \chi_{1/2\sigma}. \tag{6}$$

The subsequent transformation, consisting of summing the Wigner coefficients, will be carried out, unlike in [1], by a graphic method. This makes it possible to transform (5) in the simplest manner to a form which, albeit identical to the equivalent equation given in [1], contains standard combinations of reduced matrix elements, thus greatly facilitating the calculations compared with [1].

The last sum over the nine angular momentum projections in (5) is a jm coefficient. It is shown graphically in the left part of the equation in the figure. In the figure, each node corresponds to a Wigner coefficient, the plus or minus sign is connected with the circuiting rule, the arrow indicates the sign of the projection of the angular momentum which enters in the Wigner coefficient, and a line joining two nodes corresponds to summation [2]. Expanding the obtained jm coefficient in terms of generalized Wigner coefficients (the first factor in the right side of the equal sign in the figure), we obtain an expansion with 18j-symbols as coefficients. Cutting the 18j-symbols along several lines, we can obtain a product of three 6j-symbols and a 12j-symbol.

Substituting the resultant expression in (5), we get

$$F = \sum_{b_1 b_2 \alpha_1 \alpha_2} (-1)^{\alpha_1 + \alpha_2} T^{b_1 b_2}_{\alpha_1 \alpha_2} (-1)^{J-M} \begin{pmatrix} J & b_2 & J \\ -M & -\alpha_2 & M' \end{pmatrix} \times (-1)^{1/2 - \sigma} \begin{pmatrix} 1/2 & b_1 & 1/2 \\ -\sigma & -\alpha_1 & \sigma' \end{pmatrix}, \tag{7}$$

and for the double tensor $T^{b_1 b_2}_{\alpha_1 \alpha_2}$ we get the following formula:

$$T^{b_1 b_2}_{\alpha_1 \alpha_2} = \frac{4\pi e^2 N}{V} [J] \sum_{ll'p} (-1)^{p+1} i^{l+l'} G^p_{ll'} \times (l_1 \| C^p \| l') (l \| C^p \| l_1) [l]^{1/2} [l']^{1/2} \sqrt{2/3} [b_1] [b_2] \times \sum_a (-1)^{a+b_1} \begin{Bmatrix} L & J & S \\ L & J & S \\ a & b_2 & b_1 \end{Bmatrix} \begin{Bmatrix} l_1 & l_1 & a \\ l & l' & p \end{Bmatrix} \langle l_1^n \gamma SL \| V^{(b_1 a)} \| l_1^n \gamma SL \rangle \times \sum_\beta \begin{bmatrix} b_1 & b_2 & a \\ \alpha_1 & \alpha_2 & \beta \end{bmatrix} v^{ll'a}_\beta, \tag{8}$$

where $[\begin{smallmatrix} j_1 j_2 j_3 \\ m_1 m_2 m_3 \end{smallmatrix}]$ is a Clebsch-Gordan coefficient and

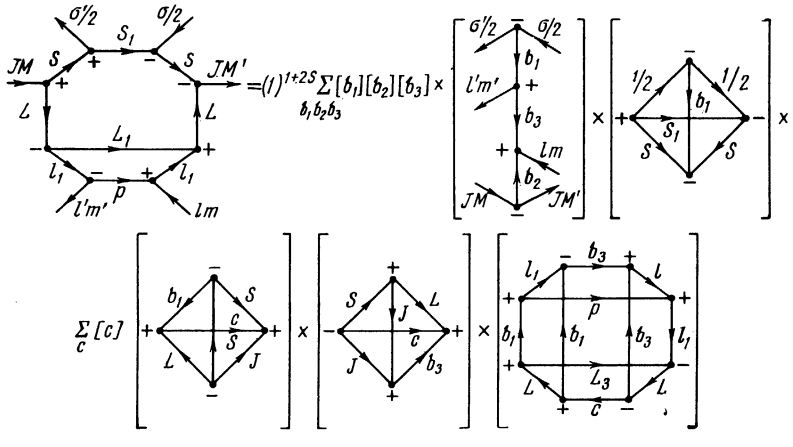

Diagram showing simplification of the jm-symbol.

$$v^{ll_a}_{\beta} = \sum_{mm'} C_{-m^l}(k) C_{m'^{l'}}(k') \begin{bmatrix} l & l' & a \\ -m & m & \beta \end{bmatrix}, \qquad (9)$$

$$\langle l_1^n \gamma SL \| V^{(b_1 a)} \| l_1^n \gamma SL \rangle = \sqrt{3/2}\,[L][S]\, n$$

$$\times \sum_{\gamma_1 S_1 L_1} (-1)^{l_1+L+L_1+a+1/2+S+S_1+b_1} |G^{\gamma SL}_{\gamma_1 S_1 L_1}|^2 \begin{Bmatrix} 1/2 & 1/2 & b_1 \\ S & S & S_1 \end{Bmatrix}$$

$$\times \begin{Bmatrix} l_1 & l_1 & a \\ L & L & L_1 \end{Bmatrix}. \qquad (10)$$

We shall hence forth use the symbol $V^{(b, a)}$ to denote (10). The sub-matrix elements of $V^{(b, a)}$ were tabulated for the principal terms of the rare-earth ions in [4,5].

3. The Wigner coefficients in (7) are connected with the irreducible unit tensors $u^{b_2}_{\alpha_2}$ and $v^{b_1}_{\alpha_1}$, making it possible to write H_{ex} in the form

$$H_{ex} = N^{-1} \sum_{\nu\Gamma_1\Gamma_2 k k' \sigma\sigma'} e^{i(\mathbf{k}-\mathbf{k}')\mathbf{v}} \sum_{b_1 b_2 \alpha_1 \alpha_2} T^{b_1 b_2}_{\alpha_1\alpha_2} u^{b_2}_{-\alpha_2} v^{b_1}_{\alpha_1} A^{+}_{\nu\Gamma_1} a^{+}_{k\sigma} a_{k'\sigma'} A_{\nu\Gamma_2}, \qquad (11)$$

where $\Gamma_1 = \{\gamma SLJM\}$, and $\Gamma_2 = \{\gamma SLJM'\}$. Expression (11) is the general Hamiltonian of the exchange of f-electrons with the conduction electrons in terms of irreducible tensor operators, thus solving in principle the problem of the present paper. The operator u^{b_2} acts on the variables of the total magnetic moment of the atom, and v^{b_1} acts on the variables of the intrinsic magnetic moment of the conduction electron. The transition to reducible tensors is by using the relation

$$\sum_{i_1 \ldots i_n,} T^{+}_{i_1 \ldots i_n} p_{i_1 \ldots i_{n'}} = \sum_{k, q} (-1)^q T_q{}^k p_{-q}{}^k, \qquad (12)$$

wherein new terms can appear in the expansion; these terms are connected with the operator $\underbrace{\mathbf{J} \ldots \mathbf{J}}_{n'}$ and $\underbrace{\mathbf{sJ} \ldots \mathbf{J}}_{n'}$, where n' is limited by the same conditions as in [1].

As seen from (8), $T^{b_1 b_2}_{\alpha_1\alpha_2}$ is a decreasing series in powers of the parameter $k_F r_0$ (k_F is the wave vector of the Fermi surface and r_0 is the average radius of the 4f orbit for the rare earths [6]). We can assume with good approximation that $k_F r_0 \sim 0.5$, so that in the series in powers of $(k_F r_0)^{l+l'}$ the terms with $l + l' \neq 0$, which are connected with anisotropic effects, should be retained at least for $l + l' \leq 2$. Kasuya and Lyons [7], in particular, calculated the radial integrals $G^p_{ll'}$, which are the small parameters, for a certain concrete choice of radial wave functions of the 4f shell. They found that the quantities G^2_{11}, G^4_{11} and G^3_{02} are of the same order of magnitude ($\sim k_F^2 r_0^2$), so that such terms should be considered as equivalent in the expansion (7).

4. The numbers b_1 and b_2 determine the powers of the invariants of the spin Hamiltonian in terms of the operators $\mathbf{s}$ and $\mathbf{J}$, respectively. Confining ourselves to the condition $l + l' \leq 2$, we find that b_2 can take on values 0, 1, 2, 3 and b_1 values 0 and 1, in accordance with the conduction-electron spin $s = 1/2$.

Using now the connection between the operators A_Γ and the angular momenta $\mathbf{J}$ (see formula (4) of [1]), and calculating the matrix element $F(\Gamma_1 \mathbf{k}\sigma, \Gamma_2 \mathbf{k}'\sigma')$ by means of formulas (7)—(10), we arrive at the following expression for H_{ex} with the indicated values of b_1 and b_2:

$$\begin{aligned} H_{ex} = A_0 - \frac{4\pi e^2}{V} \sum_{\nu k\sigma k'\sigma'} e^{i(\mathbf{k}-\mathbf{k}')\mathbf{v}} a^{+}_{k\sigma} a_{k'\sigma'} \{ & A_1 (\mathbf{sJ}_\nu) \\ & + iA_2 ([\mathbf{kk}'] \hat{\mathbf{J}}_\nu) + A_3 \langle (\mathbf{kJ}_\nu)(\mathbf{k}'\mathbf{J}_\nu) \rangle + A_4 \langle (\mathbf{ks})(\mathbf{k}'\mathbf{J}_\nu) \rangle \\ & + A_5 [(\mathbf{k}'\mathbf{s})(\mathbf{k}'\mathbf{J}_\nu) + (\mathbf{ks})(\mathbf{kJ}_\nu)] + A_6 [(\mathbf{kJ}_\nu)^2 + (\mathbf{k}'\mathbf{J}_\nu)^2] \\ & + iA_7 \{(\mathbf{sJ}_\nu)([\mathbf{kk}'] \mathbf{J}_\nu)\} + A_8 ([\mathbf{s}[\mathbf{kk}']] \mathbf{J}_\nu) \\ & + A_9 \{(\mathbf{sJ}_\nu) \langle (\mathbf{kJ}_\nu)(\mathbf{k}'\mathbf{J}_\nu) \rangle\} \}. \end{aligned} \qquad (13)^*$$

The angle brackets $\langle\,\rangle$ denote here symmetrization with respect to k and k', and $\{A, B\} = AB + BA$.

Expression (13) coincides with formula (39) of [1]. Now, however, we have for the coefficients A the following simple formulas:

$$\begin{aligned} A_0 &= -\frac{4\pi N e^2}{V} \left\{ \frac{n}{14} [G^{l_1}_{00} + \eta_1] - J(J+1) \frac{2\sqrt{3}}{\sqrt{35}} D^2 \left[\eta^2 - \frac{10}{3} G^{l_1}_{02} \right] \right\}, \\ A_1 &= \frac{2(g-1)}{7} [G^{l_1}_{00} + \eta_1 (\mathbf{kk}')] - D_1 \left[\frac{6\sqrt{3}}{5\sqrt{7}} (\mathbf{kk}') \eta_2 + \frac{4\sqrt{2}}{\sqrt{7}} G^{l_1}_{02} \right], \\ A_2 &= \frac{(g-2)}{28} \eta_3 - \frac{3\sqrt{3}}{\sqrt{35}} \eta_2 D_2, \qquad A_3 = -\frac{6\sqrt{3}}{\sqrt{35}} D_2 \eta_2, \\ A_4 &= \frac{9\sqrt{3}}{5\sqrt{7}} \eta_2 D_1, \qquad A_5 = \frac{6\sqrt{2}}{\sqrt{7}} G^{l_1}_{02} D_1, \qquad A_6 = -\frac{2\sqrt{15}}{\sqrt{7}} G^{l_1}_{02} D_2, \\ A_7 &= A_8 = \frac{9\sqrt{5}}{\sqrt{7}} \eta_3 \frac{(2J+1)}{[(2J+3)^{(5)}]^{1/2}} \begin{Bmatrix} L & J & S \\ L & J & S \\ 1 & 2 & 1 \end{Bmatrix} V^{(11)}, \end{aligned} \qquad (14)$$

where

$$\begin{aligned} \eta_1 &= (9/5\, G_{11}{}^2 + 4/3\, G_{11}{}^4), \quad \eta_2 = (9/5\, G_{11}{}^2 + 5/9\, G_{11}{}^4), \\ \eta_3 &= (9/5\, G_{11}{}^2 - G_{11}{}^4); \\ D_1 &= \sqrt{\frac{2J+1}{J(J+1)}} \begin{Bmatrix} L & J & S \\ L & J & S \\ 2 & 1 & 1 \end{Bmatrix} V^{(12)}, \end{aligned} \qquad (15)$$

*$[\mathbf{kk}'] \equiv \mathbf{k} \times \mathbf{k}'$.

$$D_2 = (-1)^{S+L+J} \begin{Bmatrix} L & J & S \\ J & L & 2 \end{Bmatrix} \frac{(2J+1)}{[(2J+3)^{(5)}]^{1/2}} v^{(2)},$$

$$(2J+3)^{(5)} = \frac{(2J+3)!}{(2J-2)!}, \quad v^{(2)} = \frac{2}{\sqrt{3}} (2S+1)^{-1/2} V^{(02)}. \quad (16)$$

We do not present an analytic formula for the coefficients A connected with $b_2 = 3$, since they have a cumbersome form in terms of the reducible tensor operator. Calculations with invariants of this type are simplest to carry out in a system of irreducible tensors.

The coefficients (14) determine the different terms of the Hamiltonian (13) as functions of the quantum numbers SLJ, i.e., as functions of the atomic number in the periodic table, since the ground state of all rare-earth metals (with the possible exception of Sm and Eu) is well determined by these quantum numbers. The values of the coefficients D_1 and D_2 are:

	Gd^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}
D_1:	0	−0.0075	−0.0060	−0.0022	0.0024	0.0075	0.0129
D_2:	0	0.0018	0.0011	0.0014	−0.0023	−0.0018	−0.0051

As is seen from (14)—(16), the largest is the coefficient A_1 for isotropic exchange of a de Gennes type, proportional to $g - 1$ and determining essentially, after calculating the indirect exchange, the Curie temperature $T_C \sim (g-1)^2 \times J(J+1)$. The coefficients A_2—A_8 of the terms making the contribution to the anisotropic exchange [1] are smaller by approximately one or two orders of magnitude than A_1 (owing both to the numerical coefficients and to the values of the integrals $G^p_{ll'}$).

Expressions (13) and (14) are the starting point for a quantitative calculation of the different properties and effects in rare-earth metals, primarily the contribution of the anisotropic exchange to the magnetic-anisotropy constants. We are presently at work on the latter calculation. However we can already make a few useful qualitative remarks.

First, the role of the anisotropic term is greatly enhanced by the rather rapid decrease of the quantity $g - 1$ when the number of the element decreases from Tb to Tu. It is possible that for Tu it becomes of the same order as the terms of isotropic exchange. In this respect, the more complete Hamiltonian of our paper leads to the same conclusions as in the paper by Kaplan and Lyons [6] (we note, however, that we did not succeed in obtaining agreement between Kaplan and Lyons principal anisotropic contribution of the P_1 type and our calculation, although a few other contributions do indeed coincide exactly).

Second, a very remarkable fact is that the sign of the coefficients D_1 and D_2 changes on going from the configuration $f^{11}(f^3)$ to $f^{10}(f^4)$. It is very possible that this fact is the very cause of the actual change in the direction of the easy magnetization on going from Ho to Er.

Finally, we wish to point out that appreciable interest attaches to an account of the anisotropic form of the Fermi surface [8] of the conduction electrons in calculating the anisotropic exchange. It is quite possible that the existing uniaxial symmetry of the magnetic structure of the rare-earth metals is connected with the uniaxial nature of the Fermi surface of the conduction electrons that effect the indirect exchange.

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