Symmetry Properties of the Spin-Spin Contact Hamiltonian

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The spin-spin contact Hamiltonian has been separated into operators having well-defined symmetry properties. Analysis of the form of the spin-spin contact Hamiltonian shows that fewer symmetry operators are actually required in this separation than would be indicated by simple group-theoretical arguments. Matrix elements of most of those operators are evaluated by considering the Casimir operator Sp_{4l+2}; the remaining operators are evaluated by exploiting a proportionality to matrix elements of the Coulomb operator.

I. INTRODUCTION

IN 1949, Racah[1] separated the Coulomb interaction for f electrons into operators having well-defined symmetry properties with respect to the groups R_7 and G_2. Recently this procedure has been extended to several other fine-structure interactions for several types of configurations.[2–4] This separation has simplified calculations considerably by allowing the powerful selection rules of group theory to be more fully utilized. The results of these calculations have, in fact, often been even more simple than would have been expected on the basis of the obvious group-theoretical arguments, and more recent work has been concerned with trying to explain these simplifications.

In many ways the simplest of all fine-structure interactions is the spin-spin contact term. Because of its elementary character a study of its group-theoretical properties is less likely to be obscured by mathematical complications than are studies of more complicated interactions. Analysis of the symmetry properties of the spin-spin contact term is therefore a natural step in the effort to treat all the fine-structure interactions.

II. EVALUATION OF THE OPERATORS

The spin-spin contact Hamiltonian is given by[5,6]

$$H_{\rm ssc}=-(8\mu_0^2/3r^2)\delta(r_1-r_2)\sum_{k,i<j}(\mathbf{sC}^k)_i\cdot(\mathbf{sC}^k)_j[k]$$
$$=-(4\mu_0^2/3r^2)\delta(r_1-r_2)\sum_{k,i<j}(l\|C^k\|l)^2\mathbf{w}_i^{1k}\cdot\mathbf{w}_j^{1k}. \quad (1)$$

The operators w^{1k} (k even) transform like $W=(20)$ for d electrons and $WU=(200)(20)$ for f electrons,[7] where W is the representation in R_{2l+1} and U is the representation in G_2. Taking Kronecker products,[2,4] we find that

$$(20)\times(20)=(00)+(11)+(20)+(22)+(31)+(40) \quad (2)$$

for R_5;

$$(200)\times(200)=(000)+(200)+(220)+(400)+(110)+(310) \quad (3)$$

for R_7; and

$$(20)\times(20)=(00)+(20)^2+(21)^2+(22)+(40)+(10)+(11)+(30)+(31) \quad (4)$$

for G_2. The spin and orbital parts of $H_{\rm ssc}$ obviously transform like ^1S; the spin-spin contact term must therefore transform like those representations on the right-hand sides of Eqs. (2)–(4) which contain in their decompositions the state ^1S. These decompositions can be obtained from tables by Judd[7] and Jahn.[8] In this manner the spin-spin contact term for d electrons is found to be equal to $a_1w_1+a_2w_2$, where the a's are constants and w_1 transforms like $(00)^1S$ and w_2 transforms like $(22)^1S$; for f electrons $H_{\rm ssc}$ is equal to $b_1y_1+b_2y_2+b_3y_3$, where the b's are constants and y_1 transforms like $(000)(00)^1S$, y_2 like $(400)(40)^1S$, and y_3 like $(220)(22)^1S$. These are, of course, just the separations that can be made for the Coulomb operator.[1,7] Because $c(WW'(22))$, $c(UU'(22))$, and $c(UU'(40))$ are equal to either 0 or 1 for all states of d^2 and f^2, matrix elements of the components of the spin-spin contact term must therefore be proportional to matrix elements of the corresponding components of the Coulomb interaction.

The matrix elements of the w's and the y's can easily be obtained using either of two general approaches. First, one can explicitly construct the operators w and y, as was done by Racah[1] for the case of the Coulomb interaction, and evaluate matrix elements in the usual manner; second, one can exploit the proportionality to matrix elements of the Coulomb interaction in a manner analogous to that used by Judd.[2] The latter approach is undoubtedly the simpler. However, because of the particular characteristics of the spin-spin contact interaction, we find that an approach which is an admixture of both of these methods is the most interesting.

One of the most unusual aspects of $H_{\rm ssc}$ is that the summation over k does not contain a radial depen-

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dence. The evaluation of matrix elements of H_{ssc} then becomes, aside from the straightforward evaluation of a single integral, the evaluation of the operator

$$\sum_{k,i<j}[l]^2\begin{pmatrix} l & k & l \\ 0 & 0 & 0\end{pmatrix}^2 \mathbf{w}_i^{1k}\cdot\mathbf{w}_j^{1k}. \tag{5}$$

Because of the unusual form of this operator, we can make a further simplification before beginning the calculation of the matrix elements. The operator $w_j^{1k}{}_{\pi q}w_j^{1k}{}_{-\pi-q}$ can be expanded as a sum of operators having specific symmetry properties by the relationship

$$w_j^{1k}{}_{\pi q}w_j^{1k}{}_{-\pi-q} = \sum((\gamma)1\pi kq;\,(\gamma)1-\pi k-q\,|\,(\beta)SM_SLM_L) \times[(\beta)SM_SLM_L], \tag{6}$$

where $\gamma=(20)$ or $(200)(20)$ and β stands for the group designations W or WU, for d or f electrons, respectively. The symbol $[(\beta)SM_SLM_L]$ indicates an operator having the corresponding symmetry properties, and the sum is over all states of the symmetry operator. Because of the separability of the spin and orbital spaces the coupling coefficient in Eq. (6) is a product of a spin-space and orbital-space coupling coefficient. Racah[1] and Judd[7] have discussed the orbital coupling coefficient for f electrons and found that for $S=L=0$, the dependence of

$$((200)(20)kq;\,(200)(20)k-q\,|\,WU00)$$

on k and q is given by

$$(-1)^q[k]^{-1/2}((20)k+f\,|\,U'F),$$

where $U'=(10)$, (30), or (21) as $WU=(000)(00)$, $(400)(40)$, or $(220)(20)$, respectively; a similar analysis for d electrons shows that the dependence of

$$((20)kq;\,(20)k-q\,|\,W00)$$

on k and q is given by

$$(-1)^q[k]^{-1/2}((20)k+d\,|\,W'D),$$

where $W'=(10)$ or (21) as $W=(00)$ or (22), respectively. Using the tables for $((20)k+f\,|\,U'F)$ in Judd,[6] we find that for $k\neq0$

$$\begin{pmatrix} 3 & 3 & k \\ 0 & 0 & 0\end{pmatrix}^2 = \alpha[k]^{-1/2}((20)k+f\,|\,(10)F) + \beta[k]^{-1/2}((20)k+f\,|\,(30)F). \tag{7}$$

One can also easily show that for $k\neq0$

$$\begin{pmatrix} 2 & 2 & k \\ 0 & 0 & 0\end{pmatrix}^2 = \gamma[k]^{-1/2}((20)k+d\,|\,(10)D). \tag{8}$$

In Eqs. (7) and (8) α, β, and γ do not depend on either k or q. We can therefore write for $k\neq0$

$$\begin{pmatrix} 3 & 3 & k \\ 0 & 0 & 0\end{pmatrix}^2 = (-1)^q[\delta((200)(20)kq;\,(200)(20)k-q\,|\,(000)(00)00) + \gamma((200)(20)kq;\,(200)(20)k-q\,|\,(400)(40)00)]$$

and

$$\begin{pmatrix} 2 & 2 & k \\ 0 & 0 & 0\end{pmatrix}^2 = (-1)^q\epsilon((20)kq;\,(20)k-q\,|\,(00)00), \tag{9}$$

where δ, γ, and ϵ do not depend on k or q. For $k=0$, the 3-j coefficients above are proportional to $((200)(20)00;\,(200)(20)00\,|\,(000)(00)00)$ and $((20)00;\,(20)00\,|\,(00)00)$, respectively. Using this fact, together with Eqs. (6) and (9) and the orthogonality conditions on the coupling coefficients, we immediately find that Eq. (5) becomes

$$\sum_{k,i<j}\mathbf{w}_i^{1k}\cdot\mathbf{w}_j^{1k}[l]^2\begin{pmatrix} l & k & l \\ 0 & 0 & 0\end{pmatrix}^2 = a[(00)^1S], \quad (d \text{ electrons})$$
$$= b[(000)(00)^1S]+c[(400)(40)^1S], \quad (f \text{ electrons}). \tag{10}$$

Equation (10) shows that we need consider even fewer operators than the original group-theoretical arguments would indicate.

Explicit forms for w_1, y_1, and y_2 are easily constructed since the coefficients needed for the construction are proportional to the coefficients needed to construct the equivalent Coulomb operators.[1,7] Thus we find that

$$w_1=\sum_{i<j}(7\mathbf{w}_i^{10}\cdot\mathbf{w}_j^{10}+2\mathbf{w}_i^{12}\cdot\mathbf{w}_j^{12}+2\mathbf{w}_i^{14}\cdot\mathbf{w}_j^{14}),$$

$$y_1=\sum_{i<j}(9\mathbf{w}_i^{10}\cdot\mathbf{w}_j^{10}+2\mathbf{w}_i^{12}\cdot\mathbf{w}_j^{12} +2\mathbf{w}_i^{14}\cdot\mathbf{w}_j^{14}+2\mathbf{w}_i^{16}\cdot\mathbf{w}_j^{16}),$$

and

$$y_2=\sum_{i<j}(286\mathbf{w}_i^{12}\cdot\mathbf{w}_j^{12}-260\mathbf{w}_i^{14}\cdot\mathbf{w}_j^{14}+70\mathbf{w}_i^{16}\cdot\mathbf{w}_j^{16}). \tag{11}$$

Comparison with Eq. (1) shows that

$$a_1=-(4\mu_0^2/3r^2)\delta(r_1-r_2)(5/7),$$
$$b_1=-(4\mu_0^2/3r^2)\delta(r_1-r_2)(7/9),$$

and

$$b_2=-(4\mu_0^2/3r^2)\delta(r_1-r_2)(6435)^{-1}. \tag{12}$$

Aid in evaluating w_1, y_1, and y_2 can be obtained by considering the Casimir operator[9] for Sp_{4l+2}. The infinitesimal operators for Sp_{4l+2} are the double tensors $W^{\kappa k}$, where $\kappa+k$ is odd. Using the technique outlined by

[9] H. Casimir, Proc. Koninkl. Akad. Wetenschap. Amsterdam **34**, 844 (1931).

Judd,[10] we find immediately that

$$G(\mathrm{Sp}_{4l+2})=(4l+4)^{-1}\sum \mathbf{W}^{\kappa k}\cdot\mathbf{W}^{\kappa k}, \tag{13}$$

where the sum is over $\kappa+k$ odd. In order to evaluate Eq. (13) we define the operator

$$X_{\rho\beta\nu\mu}=\sum(-1)^{l-\nu+\frac{1}{2}-\rho}([\kappa][k])^{1/2}\times\begin{pmatrix} l & k & l\\ -\nu & q & \mu\end{pmatrix}\begin{pmatrix} \frac{1}{2} & \kappa & \frac{1}{2}\\ -\rho & \pi & \beta\end{pmatrix}\times(1-(-1)^{\kappa+k})W^{\kappa k}{}_{\pi q}, \tag{14}$$

where the sum is over κ, k, π, and q. Equation (13) then becomes

$$G(\mathrm{Sp}_{4l+2})=\tfrac{1}{4}(4l+4)^{-1}\sum X_{\rho\beta\nu\mu}X_{\beta\rho\mu\nu}, \tag{15}$$

where the sum is over all the subscripted indices.

We now consider the effect of Eq. (15) on a wave function Ψ having the maximum allowed value of m_l and the corresponding highest allowed value of m_s. Using an argument similar to that used by Judd,[10] we can then write Eq. (15) as

$$G(\mathrm{Sp}_{4l+2})=\tfrac{1}{4}(4l+4)^{-1}[6\sum X_{\rho\rho\nu\nu}+\sum X_{\rho\beta\nu\mu}X_{\beta\rho\mu\nu}], \tag{16}$$

where the first sum is over $\nu\geq 0$ and all ρ, and the second sum is over all ρ and β for $\nu>\mu$, $\rho>\beta$ for $\nu=\mu$, and where both $\nu=-\mu$ and $\rho=-\beta$ are not simultaneously true. The second sum in Eq. (16) can, in a straightforward fashion, be shown to be

$$\sum X_{\rho\beta\nu\mu}X_{\beta\rho\mu\nu}=\sum[X_{\rho\beta\nu\mu},X_{\beta\rho\mu\nu}]=\sum(X_{\rho\rho\nu\nu}-X_{\beta\beta\mu\mu}). \tag{17}$$

Noting that

$$X_{\rho\rho\nu\nu}|\tfrac{1}{2}m_s l m_l)=|\tfrac{1}{2}\rho l\nu)\delta(m_s,\rho)\delta(m_l,\nu)-|\tfrac{1}{2}-\rho l-\nu)\delta(m_s,-\rho)\delta(m_l,-\nu) \tag{18}$$

and using Eq. (17), we find that the effect of $G(\mathrm{Sp}_{4l+2})$ acting on Ψ is given by

$$\tfrac{1}{4}(4l+4)^{-1}[\sum_{\nu\geq 0}(8\nu+6)X_{\frac{1}{2}\frac{1}{2}\nu\nu}+\sum_{\nu>0}(8\nu+2)X_{-\frac{1}{2}-\frac{1}{2}\nu\nu}]. \tag{19}$$

The seniority (v) of Ψ is just $\sum X_{\rho\rho\nu\nu}$, where the sum is for $\nu>0$, all ρ, and $\nu=0$, $\rho=\frac{1}{2}$. Equation (19) can therefore be written as

$$G(\mathrm{Sp}_{4l+2})=(4l+4)^{-1}[(2l+2)v-\tfrac{1}{2}v^2]. \tag{20}$$

Equations (13) and (20) can now be used to evaluate matrix elements of w_1 and y_1. Equation (13) is first rewritten as

$$G(\mathrm{Sp}_{4l+2})=(4l+4)^{-1}\sum_{k\ \mathrm{even}}\mathbf{W}^{1k}\cdot\mathbf{W}^{1k}+(8l+8)^{-1}\sum_{k\ \mathrm{odd}}\mathbf{V}^{k}\cdot\mathbf{V}^{k}$$

or

$$\sum_{k\ \mathrm{even}}\mathbf{W}^{1k}\cdot\mathbf{W}^{1k}=(4l+4)G(\mathrm{Sp}_{4l+2})-\tfrac{1}{2}(2l-1)G(R_{2l+1})=-\tfrac{3}{8}v^2+\tfrac{3}{2}(l+1)v+\tfrac{1}{2}S(S+1). \tag{21}$$

In order to express w_1 and y_1 in terms of the operators $w^{1k}\cdot w^{1k}$, we use the relationship

$$\sum_{i<j}\mathbf{w}_j{}^{1k}\cdot\mathbf{w}_j{}^{1k}=\tfrac{1}{2}\mathbf{W}^{1k}\cdot\mathbf{W}^{1k}-3N[k](4[l])^{-1}. \tag{22}$$

We note that W^{1k} with k even has quasispin zero; because of the equivalence (22), H_{scc} [Eq. (1)] will be diagonal in quasispin and therefore diagonal in seniority.

Using Eqs. (11), (21), and (22), we obtain immediately

$$\langle w_1\rangle=-\frac{3}{2}\left[\frac{7(N-v)}{2}+\frac{v(v+2)}{4}-S(S+1)\right]$$

and

$$\langle y_1\rangle=-\frac{3}{2}\left[\frac{9(N-v)}{2}+\frac{v(v+2)}{2}-S(S+1)\right]. \tag{23}$$

As predicted above, the matrix elements of w_1 and y_1 are indeed proportional to matrix elements[1,7] of the corresponding Coulomb interactions e_1. The matrix elements of y_2 can be found by evaluating H_{ssc} for states of f^2, substracting off $\langle y_1\rangle$, and noting that matrix elements of y_2 should be proportional to matrix elements of e_2. In this manner one easily finds that

$$\langle y_2\rangle=-(21/2)\langle e_2\rangle; \tag{24}$$

matrix elements of e_2 have been tabulated by Racah.[1]

III. DISCUSSION

The spin-spin contact Hamiltonian has been expanded in a sum over operators having well-defined symmetry properties. Analysis of the symmetry properties of $\mathbf{w}^{1k}\cdot\mathbf{w}^{1k}$ indicates that the operators required in this expansion should have the same group-theoretical designations as the operators required in the expansion of the Coulomb interaction. By expressing the 3-j symbols appearing in H_{ssc} in terms of coupling coefficients, however, it was shown that not all of the operators allowed by the symmetry properties of $\mathbf{w}^{1k}\cdot\mathbf{w}^{1k}$ would actually be needed in the expansion of H_{ssc}. In fact, only one operator for d electrons and two for f electrons were required. Two of these operators were easily evaluated using the Casimir operator for Sp_{4l+2}, and the third was shown to be proportional to Racah's e_2.

The two sets of matrix elements evaluated using the Casimir operator were shown to be proportional to matrix elements of Racah's e_1. Because of this proportionality, and the proportionality of the third set of matrix elements to Racah's e_2, we find that one can express the sum of the Coulomb and spin-spin contact

[10] Reference 7, pp. 123–126.

Hamiltonians by the expression

$$e_0E^0+e_1\bar{E}^1+e_2E^2$$

for d electrons and by

$$e_0E^0+e_1\bar{E}^1+e_2\bar{E}^2+e_3E^3$$

for f electrons. The angular dependence of these operators, which is given by the e_i's, is exactly the same as in the pure Coulomb case.[1,7] The E^i's are the usual sums of Slater integrals used in the Coulomb Hamiltonian,[1,7] and the $\bar{E}^i$'s are defined for d electrons by

$$\bar{E}^1=E^1+(10/7)R_2;$$

and for f electrons by

$$\bar{E}^1=E^1+(14/9)R_2,$$
$$\bar{E}^2=E^2+(14/6435)R_2,$$

where

$$R_2=\mu_0{}^2\int\frac{[R_l(r)]^4}{r^2}dr.$$

The integral R_2 will always be positive; therefore the effect of the spin-spin contact term is always to enhance the value of certain of the E^i's over the purely Coulombic results. Thus, values of E^i obtained from the usual analysis of experimental data must always be corrected downwards in order to find the contribution from the Coulomb interaction alone.

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Effect of Strong Collisions on the H_α Profile*

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Strong collision effects are appreciable for the H_α spectral line. Including these effects in H_α profile calculations, we find agreement between experiment and theory within experimental error.

THE Stark-broadened profiles of several hydrogen lines in a plasma have been calculated by Griem, Kolb, and Shen.[1] They later modified these calculations[2] for the H_β line to include the effects of strong collisions, the Mozer-Baranger ion field-strength distribution functions, and electron-impact broadening of both the upper and the lower levels including the cross terms. With these modifications for H_β the agreement between the measured and the calculated line shapes is $\pm 2\%$,[3] which is within experimental error. The half-width of the H_β line is used where practical to determine electron densities in plasmas because of these refined theoretical calculations of the profiles and the good agreement between theory and experiment. Corresponding modifications were made by us in an attempt to develop a theoretical profile that corresponded more closely to experimental data. The profiles as originally proposed by GKS I had half-widths about 20% smaller than the best experimental data, as shown in Fig. 1. The inclusion of these modifications into the theory alters the calculated line profiles for H_α such that the agreement between the theoretical and experimental half-widths is now within experimental error over the plasma densities tested. The purpose of this paper is to report our results and to demonstrate the relative importance of the various modifications to the GKS I theory.

In the calculations of GKS I for the H_α line, the effects of close or strong collisions (called strong interactions here) were taken to be negligible as compared with distant or weak collisions (called weak interactions here). The electron-impact broadening was considered only for the upper level and the central component of the lower level. Also, the ion field-strength distribution functions of Ecker were used.[4]

To calculate the H_α profiles reported in this paper, the following general equation, due originally to GKS II, was used:

$$S(\alpha)=\frac{1}{\pi}\int df\,W(f)\,\mathrm{Re}\langle\alpha|\mu|\beta\rangle \times\langle\langle\alpha\beta|[i(\alpha+\mathbf{C}f)+\phi_{ab}]^{-1}|\alpha'\beta'\rangle\rangle\langle\beta'|\mu|\alpha'\rangle, \quad (1)$$

where $W(f)$ is the distribution of the ion-field strength f, and μ is the dipole-moment operator. For transitions

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