Spin-Spin Interaction in Paramagnetic Ions

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Expressions for the intra-atomic spin-spin interaction parameter ρ for the Hund's-rule ground state are given in terms of the radial integrals M^k. These integrals occur also in the spin-other-orbit and orbit-orbit interactions. Using previously obtained values of the M^k, the expressions for ρ are evaluated for a number of p-, d-, and f-shell ions. Comparison with results of Pryce for $3d$ ions shows that his estimates were too large by as much as an order of magnitude.

THE effects of the magnetic spin-spin interaction on atomic and paramagnetic-resonance spectra have been considered by a number of authors in the past.[1–4] These effects have been found to be quite small, and the interaction is neglected except in special circumstances. This is because the effects of the spin-spin interaction are similar to those of the much larger spin-orbit interaction. However, the selection rules for the spin-spin interaction are such that, on occasion, it will enter in a perturbation description in lower order than the spin-orbit interaction. It then becomes necessary to have reliable estimates of the magnitude of the spin-spin interaction. Such estimates were obtained by Pryce[4] from experimental free-atom spectra by assuming that, in the multiplet splittings of ionic ground states, any deviations from the Landé interval rule were due to spin-spin interactions. These values have been widely used. It was later pointed out by Trees[2] that it is necessary to take into account the off-diagonal contributions of spin-orbit coupling in any analysis of deviations from the interval rule. Such an analysis is a difficult task and has not been carried out systematically.[5]

In this note we present estimates of the spin-spin interaction, within the ground-state manifold, based on free-atom Hartree-Fock wave functions. These involve radial M^k integrals which are common to spin-orbit, spin-other-orbit and orbit-orbit interactions, and we will rely on previous estimates of the spin-orbit coupling[6–8] in judging the accuracy of the present results. It has been found that Pryce's values appreciably overestimate the role of the spin-spin interaction for iron-series ions. Values of the constants are given for p-, d-, and f-shell ions.

The magnetic spin-spin interaction

$$V_{SS} = \frac{\alpha^2}{2} \sum_{i \neq j} \frac{1}{r_{ij}^3} \left(\mathbf{s}_i \cdot \mathbf{s}_j - 3 \frac{(\mathbf{s}_i \cdot \mathbf{r}_{ij})(\mathbf{s}_j \cdot \mathbf{r}_{ij})}{r_{ij}^2} \right), \quad (1)$$

where α is the fine-structure constant. A useful form for this interaction can be obtained by using the techniques discussed in Ref. 6. Using

$$V_{12} = \frac{1}{r_{12}^3} \left(\mathbf{s}_1 \cdot \mathbf{s}_2 - 3 \frac{(\mathbf{s}_1 \cdot \mathbf{r}_{12})(\mathbf{s}_2 \cdot \mathbf{r}_{12})}{r_{12}^2} \right)$$

$$= (\mathbf{s}_1 \cdot \nabla_1)(\mathbf{s}_2 \cdot \nabla_2) \frac{1}{r_{12}}$$

and then expressing the gradient in terms of spherical tensor operators [as in Eq. (A2) of Ref. 6] one obtains, after straightforward manipulation, the expression

$$V_{12} = 4\pi \sum_{\substack{qq'q'' \\ k,\mu\nu}} (-)^{\mu+\nu+q+q'+q''} s_1^\mu s_2^{-\nu} (2k+1)[k(k+1)]^{1/2} \left[\begin{pmatrix} k & 1 & k+1 \\ q & \nu & -q' \end{pmatrix} \begin{pmatrix} k & 1 & k-1 \\ -q & -\mu & -q'' \end{pmatrix} Y_{k-1,q''}(\hat{r}_1) \right.$$

$$\left. \times Y_{k+1,q'}(\hat{r}_2) \frac{r_1^{k-1}}{r_2^{k+2}} \epsilon(r_2 - r_1) + \begin{pmatrix} k & 1 & k-1 \\ q & \nu & -q' \end{pmatrix} \begin{pmatrix} k & 1 & k+1 \\ -q & -\mu & -q'' \end{pmatrix} Y_{k+1,q''}(\hat{r}_1) Y_{k-1,q'}(\hat{r}_2) \frac{r_2^{k-1}}{r_1^{k+2}} \epsilon(r_1 - r_2) \right]. \quad (2)$$

[This equation is also useful in other calculations involving interactions similar to (1). An example is the transferred hyperfine interaction between a paramagnetic ion and a neighboring nuclear spin.] We are interested in matrix elements of this operator within the ground-state manifold. In this case it is well known that

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[1] M. H. L. Pryce, Phys. Rev. **80**, 1107 (1950).
[2] R. E. Trees, Phys. Rev. **82**, 683 (1951).
[3] H. Horie, Progr. Theoret. Phys. (Koyto) **10**, 296 (1953).
[4] F. R. Innes, Phys. Rev. **91**, 31 (1953).
[5] See, however, Ref. 3.

[6] M. Blume and R. E. Watson, Proc. Roy. Soc. (London) **A270**, 127 (1962).
[7] M. Blume and R. E. Watson, Proc. Roy. Soc. (London) **A271**, 565 (1963).
[8] M. Blume, A. J. Freeman, and R. E. Watson, Phys. Rev. **134**, A320 (1964).

the matrix elements of (1) are equal to those of the operator

$$V_{SS}' = -\rho[(L \cdot S)^2 + \tfrac{1}{2}(L \cdot S) - \tfrac{1}{3}L(L+1)S(S+1)], \quad (3)$$

where ρ is a constant depending on the particular ion and on L and S. An expression for ρ can be obtained by calculating a single matrix element of (3) and equating it to the same matrix element of (1). This can be done straightforwardly for the Hund's-rule ground state by using a determinantal wave function and the expression given in Eq. (2) for the spin-spin interaction. The results are in terms of the radial integrals

$$M^k(ll) \equiv \frac{\alpha^2}{4} \int_0^\infty \int_0^\infty dr_1 dr_2 r_1^2 r_2^2 R_l^2(r_1) R_l^2(r_2)$$

$$\times \frac{r_2^k}{r_1^{k+3}} \epsilon(r_1 - r_2), \quad (3)$$

where $R_l(r)$ is the radial wave function for the outer electrons and

$$\epsilon(r_1 - r_2) = 1, \quad r_1 > r_2$$
$$= 0, \quad r_1 < r_2.$$

These same integrals occur in calculations of spin-orbit, spin-other-orbit, and orbit-orbit interactions, and were obtained previously for p-, d-, and f-shell ions in connection with the calculation of spin-orbit coupling parameters. Expressions for ρ are given in terms of the M^k integrals in Table I. For the d shell these expressions are in agreement with those of Pryce.

Using the numerical values for the M^k's given in Refs. 7 and 8 we have calculated the values of ρ for a number of atoms and ions. These are presented in Table II, along with Pryce's estimates for comparison. Also given are values of the matrix elements of V_{SS} for $J = L + S$ and $J = |L - S|$ to give some feeling for the actual size of the interaction (which is not necessarily given by the size of ρ alone). Our calculated values for the $3d$-shell ions lie below Pryce's estimates, and for Ni^{2+} the difference is an order of magnitude. For $(3d)^4$ Abragam and Pryce[9] have extracted a value of $\rho \sim 0.1$ cm^{-1} from experimental data, in good agreement

TABLE II. Values of ρ and the spin-spin matrix elements for $J = L + S$ and $L - S$, for various ions.

Ion	l^n	State	ρ	ρ (Pryce)	$\langle J|V_{SS}|J\rangle$ $J = L + S$	$\langle J|V_{SS}|J\rangle$ $J = |L - S|$
Pr^{3+}	$4f^2$	^3H	0.21 cm^{-1}		-1.58 cm^{-1}	-0.53 cm^{-1}
Nd^{3+}	$4f^3$	^4I	0.11		-3.63	-2.64
Sm^{3+}	$4f^5$	^6H	0.05_7		-4.28	-3.56
Tb^{3+}	$4f^8$	^7F	0.03_7		-2.59	-2.15
Dy^{3+}	$4f^9$	^6H	0.07_9		-5.93	-4.94
Ho^{3+}	$4f^{10}$	^5I	0.12		-7.99	-6.53
Er^{3+}	$4f^{11}$	^4I	0.22		-7.23	-5.26
Tm^{3+}	$4f^{12}$	^3H	0.49		-3.71	-1.24
Ti^{2+}	$3d^2$	^3F	0.16	0.24 cm^{-1}	-0.40	$+0.08$
V^{2+}	$3d^3$	^4F	0.11	0.4	-0.83	-0.33
V^{3+}	$3d^2$	^3F	0.26	0.24	-0.65	$+0.13$
Cr^{2+}	$3d^4$	^5D	0.12	0.42	-0.72	-0.24
Cr^{3+}	$3d^3$	^4F	0.17	0.44	-1.28	-0.51
Mn^{3+}	$3d^4$	^5D	0.18	0.8	-1.08	-0.36
Fe^{2+}	$3d^6$	^5D	0.18	0.95	-1.08	-0.36
Fe^{4+}	$3d^4$	^5D	0.25		-1.50	-0.50
Co^{2+}	$3d^7$	^4F	0.24	1.50	-1.80	-0.72
Ni^{2+}	$3d^8$	^3F	0.53	5.31	-1.33	$+0.27$
Zr^{2+}	$4d^2$	^3F	0.05		-0.13	$+0.03$
Pd^{2+}	$4d^8$	^3F	0.17		-0.43	$+0.09$
C	$2p^2$	^3P	0.97		-0.97	0
O	$2p^4$	^3P	2.76		-2.76	0
Si	$3p^2$	^3P	0.20		-0.20	0
S	$3p^4$	^3P	0.52		-0.52	0
Ge	$4p^2$	^3P	0.17		-0.17	0
Se	$4p^4$	^3P	0.34		-0.34	0

with our calculated value. The $2p$-shell results, on the other hand, can be compared with the parameters extracted by Horie[3] from optical free-ion spectra. The agreement is quite good for carbon, but there is a 15% discrepancy for oxygen. We are inclined to believe that this discrepancy is due in part to the difficulty of extracting the experimental parameter from the optical data, rather than to inaccuracy in the theory, because these parameters represent small corrections to larger spin-orbit effects.[10]

The close agreement of previously calculated spin-orbit coupling constants with experiment[7] gives some confidence in the spin-spin parameters presented here, because similar integrals occur in the spin-orbit calculations, and it is much easier to get accurate spin-orbit constants from experiment. The spin-orbit results give a measure of the accuracy expected for those ions for which no experimental data are currently available. Results for spin-orbit parameters from Refs. 7 and 8 lead us to expect that our $3d$ and $4d$ spin-spin parameters are accurate to within 5%, while the theoretical parameters for the $4p$- and $4f$-shell ions would seem to be about 10% too low or too high, respectively. One expects these parameters to be modified somewhat in a solid by effects of bonding on the wave functions. The values given here should be usable as a good first estimate of the actual value.

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TABLE I. The spin-spin constant ρ in terms of $M^k(l,l)$ integrals for $(l)^n$ ion ground manifolds.

l	n	Ground state	ρ
1	2,4	^3P	$(12/5)M^0$
2	2,8	^3F	$-(4/35)M^0 + (152/245)M^2$
	3,7	^4F	$+(8/105)M^0 + (8/105)M^2$
	4,6	^5D	$+(2/7)M^0 - (16/49)M^2$
3	2,12	^3H	$-(4/45)M^0 + (136/495)M^2 + 0.97487M^4$
	3,11	^4I	$-(8/495)M^0 + (232/5445)M^2 + 0.09542M^4$
	4,10	^5I	$+(2/165)M^0 + (28/5445)M^2 - 0.02935M^4$
	5,9	^6H	$+(8/225)M^0 - (4/495)M^2 - 0.03292M^4$
	6,8	^7F	$+(1/21)M^0 - (8/210)M^2 - 0.04329M^4$

[9] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) A205, 135 (1951).

[10] R. H. Garstang [Monthly Notices Roy. Astron. Soc. 111, 115 (1951)] has obtained M^k values from optical data for Si and S. In these cases the spin-orbit effects are even larger, and this difficulty is more pronounced.