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Electron Spin-Spin Contact Interaction in Many-Electron Atoms*

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A general formulation has been developed for the evaluation of the total electron spin-spin contact interaction in many-electron atoms, including both the intra- and inter-shell contributions. Calculations have been carried out, using existing analytical Hartree-Fock functions, for the positive ions, neutral systems, and negative ions for all the atoms from He to Kr.

Es wird ein allgemeiner Formalismus zur Berechnung der gesamten Elektronen-Spin-Spin-Kontakt-Wechselwirkung in Vielelektronen-Atomen angegeben, der sowohl die Anteile der Wechselwirkung innerhalb einer Schale als auch zwischen einzelnen Schalen berücksichtigt. Berechnungen wurden unter Benutzung vorhandener analytischer Hartree-Fock-Funktionen für die positiven Ionen, die neutralen Systeme und die negativen Ionen aller Atome von He bis Kr durchgeführt.

Introduction

The electron spin-spin contact interaction has received little attention in the past by comparison with the better known fine and hyperfine interactions.

The formulation for the intrashell contribution to this interaction has been developed by Sessler and Foley [22] (s^n configurations), Fraga and Thorhallsson [13] (p^n configurations), and Armstrong [1, 2] (d^n and f^n configurations). Numerical values have been determined for the highest occupied shell of the positive ions, neutral systems, and negative ions from He to Kr by Fraga, Thorhallsson, and Fisk [14] and for a large number of lanthanide ions by Saxena, Lo, and Fraga [21].

It is now intended to present the complete theoretical formulation and use it for the evaluation of the total electron spin-spin contact interaction in the positive ions, neutral systems, and negative ions for all the atoms from He to Kr.

Theoretical Formulation

The electron spin-spin contact hamiltonian operator is (Armstrong [1] and Fontana and Meath [12])

$$\begin{aligned} \boldsymbol{H}_{\text{ssc}} &= -(32\pi/3)\,\mu_B^2 \sum_{i<j} (\boldsymbol{s}_i \cdot \boldsymbol{s}_j)\,\delta(\boldsymbol{r}_i - \boldsymbol{r}_j) \\ &= -(8\pi/3)\,\alpha^2 \sum_{i<j} (\boldsymbol{s}_i \cdot \boldsymbol{s}_j)\,\delta(\boldsymbol{r}_i - \boldsymbol{r}_j)\,, \end{aligned}$$

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the last expression being given in a.u. The position and spin angular momentum vector operators are denoted by $\boldsymbol{r}$ and $\boldsymbol{s}$, $\delta(\boldsymbol{r}_i - \boldsymbol{r}_j)$ represents the three-dimensional delta function, and the summation extends over all the pairs of electrons in the system; μ_B denotes the Bohr magneton and α is the fine structure constant.

The total electron spin-spin contact interaction may be written as

$$E_{\text{ssc}} = \langle \Psi | \boldsymbol{H}_{\text{ssc}} | \Psi \rangle = \sum_{a} E_{\text{ssc,aa}} + \sum_{a<b} E_{\text{ssc,ab}},$$

where distinction is made between the intra- and inter-shell contributions; the summations extend over all the occupied shells. The total, antisymmetric function, Ψ, may be written in a given coupling scheme, using the notation of Innes and Ufford [15], as

$$\Psi = | l_1^{n_1} \gamma_1 \Gamma_1, l_2^{n_2} \gamma_2 \Gamma_2, l_3^{n_3} \gamma_3 \Gamma_3, \ldots, l_g^{n_g} \gamma_g \Gamma_t \rangle,$$

where γ_i denotes the total quantum numbers for the shell l_i, occupied by n_i electrons. Γ_i is obtained by coupling of γ_i with Γ_{i-1}, and so on; Γ_1 is identical to γ_1 and Γ_t represents the quantum numbers for the state under consideration, standing in the present work for τLS, where τ denotes whatever additional quantum numbers are required to completely determine the state.

Using the general coefficients of fractional parentage (CFP) (Chisholm *et al.* [5]), the two types of contributions mentioned above may be expressed as linear combinations of matrix elements over antisymmetrized two-electron states. (In this connection see the work of Armstrong [3, 4], de-Shalit and Talmi [7], Donlan [8], Doyle [10], Fano [11], Innes and Ufford [15] and Shore [23].) One obtains

$$\begin{aligned} E_{\text{ssc,aa}} = {} & \frac{1}{2} n_a(n_a - 1) \\ & \cdot \Sigma \, [l_a^2 \Gamma; l_1^{n_1} \gamma_1 \Gamma_1 \ldots l_a^{n_a-2} \gamma_a'' \Gamma_a'' \ldots l_g^{n_g} \gamma_g \Gamma_t'' \,|\,\} \, l_1^{n_1} \gamma_1 \Gamma_1 \ldots l_a^{n_a} \gamma_a \Gamma_a \ldots l_g^{n_g} \gamma_g \Gamma_t] \\ & \cdot [l_a^2 \bar{\Gamma}; l_1^{n_1} \gamma_1 \Gamma_1 \ldots l_a^{n_a-2} \gamma_a'' \Gamma_a'' \ldots l_g^{n_g} \gamma_g \Gamma_t'' \,|\,\} \, l_1^{n_1} \gamma_1 \Gamma_1 \ldots l_a^{n_a} \gamma_a \Gamma_a \ldots l_g^{n_g} \gamma_g \Gamma_t] \\ & \cdot \langle l_a^2 \Gamma | \boldsymbol{A}^\dagger \boldsymbol{h}_{\text{ssc}} \boldsymbol{A} | l_a^2 \bar{\Gamma} \rangle, \end{aligned}$$

$$\begin{aligned} E_{\text{ssc,ab}} = {} & n_a n_b \Sigma \, [l_a l_b \Gamma; l_1^{n_1} \gamma_1 \Gamma_1 \ldots l_a^{n_a-1} \gamma_a' \Gamma_a' \ldots l_b^{n_b-1} \gamma_b' \Gamma_b'' \ldots l_g^{n_g} \gamma_g \Gamma_t'' \\ & \cdot |\,\} \, l_1^{n_1} \gamma_1 \Gamma_1 \ldots l_a^{n_a} \gamma_a \Gamma_a \ldots l_b^{n_b} \gamma_b \Gamma_b \ldots l_g^{n_g} \gamma_g \Gamma_t] \\ & \cdot [l_a l_b \bar{\Gamma}; l_1^{n_1} \gamma_1 \Gamma_1 \ldots l_a^{n_a-1} \gamma_a' \Gamma_a' \ldots l_b^{n_b-1} \gamma_b' \Gamma_b'' \ldots l_g^{n_g} \gamma_g \Gamma_t'' \\ & \cdot |\,\} \, l_1^{n_1} \gamma_1 \Gamma_1 \ldots l_a^{n_a} \gamma_a \Gamma_a \ldots l_b^{n_b} \gamma_b \Gamma_b \ldots l_g^{n_g} \gamma_g \Gamma_t] \\ & \cdot \langle l_a l_b \Gamma | \boldsymbol{A}^\dagger \boldsymbol{h}_{\text{ssc}} \boldsymbol{A} | l_a l_b \bar{\Gamma} \rangle, \end{aligned}$$

where the summations extend over all the coparent (Γ and $\bar{\Gamma}$) and preparent (Γ_t'') states; the primes and double primes indicate the loss of one and two electrons, respectively, and the expressions in brackets denote the corresponding CFP. $\boldsymbol{h}_{\text{ssc}}$ represents the spin-spin contact interaction operator for two electrons.

The two-electron matrix elements may be written as

$$
\begin{aligned}
\langle l_a^2 \Gamma | A^\dagger \boldsymbol{h}_{\mathrm{ssc}} A | l_a^2 \bar{\Gamma} \rangle &= \langle l_a^2 S M_S L M_L | \boldsymbol{h}_{\mathrm{ssc}} | l_a^2 \bar{S} \bar{M}_{\bar{S}} \bar{L} \bar{M}_{\bar{L}} \rangle \\
&= \frac{\alpha^2}{3} \left[\frac{3}{2} - S(S+1) \right] R_2(a,a) \left\{ \sum_k (2k+1) f_k(l_a l_a L) \right\} \\
&\quad \cdot \delta(S,\bar{S})\, \delta(M_S,\bar{M}_{\bar{S}})\, \delta(L,\bar{L})\, \delta(M_L,\bar{M}_{\bar{L}}) ,
\end{aligned}
$$

$$
\begin{aligned}
\langle l_a l_b \Gamma | A^\dagger \boldsymbol{h}_{\mathrm{ssc}} A | l_a l_b \bar{\Gamma} \rangle &= \langle l_a l_b S M_S L M_L | \boldsymbol{h}_{\mathrm{ssc}} | l_a l_b \bar{S} \bar{M}_{\bar{S}} \bar{L} \bar{M}_{\bar{L}} \rangle \\
&\quad + (-1)^{l_a + l_b + S - L} \langle l_b l_a S M_S L M_L | \boldsymbol{h}_{\mathrm{ssc}} | l_a l_b \bar{S} \bar{M}_{\bar{S}} \bar{L} \bar{M}_{\bar{L}} \rangle \\
&= \frac{\alpha^2}{3} \left[\frac{3}{2} - S(S+1) \right] R_2(a,b) \\
&\quad \cdot \left\{ \sum_k (2k+1) \left[f_k(l_a l_b L) + (-1)^S g_k(l_a l_b L) \right] \right\} \\
&\quad \cdot \delta(S,\bar{S})\, \delta(M_S,\bar{M}_{\bar{S}})\, \delta(L,\bar{L})\, \delta(M_L,\bar{M}_{\bar{L}}) ,
\end{aligned}
$$

with

$$
f_k(l_a l_b L) = (-1)^{L + l_a + l_b} \begin{Bmatrix} L & l_b & l_a \\ k & l_a & l_b \end{Bmatrix} \langle l_a \| \boldsymbol{C}^{(k)} \| l_a \rangle \langle l_b \| \boldsymbol{C}^{(k)} \| l_b \rangle ,
$$

$$
g_k(l_a l_b L) = (-1)^{l_a + l_b + k} \begin{Bmatrix} L & l_a & l_b \\ k & l_a & l_b \end{Bmatrix} \langle l_a \| \boldsymbol{C}^{(k)} \| l_b \rangle^2 ,
$$

in terms of $6-j$ symbols and double-barred matrix elements[1] of the spherical harmonics tensor operators; f_k and g_k represent the direct and exchange contributions, respectively. The radial integrals, $R_2(a,b)$, are defined by

$$
R_2(a,b) = \int_0^\infty P_a^2(r)\, P_b^2(r)\, r^{-2}\, dr ,
$$

with the radial function, $P_a(r)$, being normalized according to

$$
\int_0^\infty P_a^2(r)\, dr = 1 .
$$

The values of the CFP have been determined by Chisholm et al. [5] for configurations containing up to three shells of non-equivalent electrons. For more complex configurations the generalized CFP may be calculated from the single- and/or two-particle CFP, tabulated by Nielson and Koster [18], Karaziya *et al.* [16], and Donlan [9].

The above expressions[2] may be simplified in the case of electronic configurations with only one open shell. The formulas for the intra-shell contribution reduce

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[1] For the definition of the double-barred matrix elements, see the work (pp. 288–294) of Shore and Menzel [24].

[2] It should be mentioned that a different formulation has been given by Rudzikas and co-workers [19, 20].

then to those given by Sessler and Foley [22], Fraga and Thorhallsson [13], and Armstrong [2]. The inter-shell contribution, when at least one of the two shells is fully occupied, becomes (see de-Shalit and Talmi [7])

$$E_{\mathrm{ssc,ab}} = \frac{1}{4} n_a n_b \Sigma \, [(2S+1)(2\bar{S}+1)(2L+1)(2\bar{L}+1)]^{\frac{1}{2}}$$

$$\cdot [(2l_a+1)(2l_b+1)]^{-1} \langle l_a l_b S L | A^{\dagger} \boldsymbol{h}_{\mathrm{ssc}} A | l_a l_b \bar{S} \bar{L} \rangle$$

where the summation extends over L, $\bar{L}$, S, and $\bar{S}$, and $\bar{S}$. This expression can be rewritten as

$$E_{\mathrm{ssc,ab}} = \frac{\alpha^2}{3} n_a n_b R_2(a, b) \sum_k (2k+1) [f_k(l_a l_b) + g_k(l_a l_b)]$$

with

$$f_k(l_a l_b) = [4(2l_a+1)(2l_b+1)]^{-1} \langle l_a \| \boldsymbol{C}^{(k)} \| l_a \rangle \langle l_b \| \boldsymbol{C}^{(k)} \| l_b \rangle$$

$$\cdot \sum_L (-1)^{l_a+l_b+L} (2L+1) \begin{Bmatrix} L & l_b & l_a \\ k & l_a & l_b \end{Bmatrix}$$

$$\cdot \sum_S (2S+1) \left[\frac{3}{2} - S(S+1) \right],$$

$$g_k(l_a l_b) = (-1)^{l_a+l_b+k} [4(2l_a+1)(2l_b+1)]^{-1} \langle l_a \| \boldsymbol{C}^{(k)} \| l_b \rangle^2$$

$$\cdot \sum_L (-1)^{2L} (2L+1) \begin{Bmatrix} L & l_a & l_b \\ k & l_a & l_b \end{Bmatrix} \sum_S (-1)^S (2S+1) \left[\frac{3}{2} - S(S+1) \right].$$

Taking into account that these expressions reduce to

$$f_k(l_a l_b) = 0,$$

$$g_k(l_a l_b) = \frac{3}{4} (-1)^{l_a+l_b+k} [(2l_a+1)(2l_b+1)]^{-1} \langle l_a \| \boldsymbol{C}^{(k)} \| l_b \rangle^2,$$

one finally obtains, after carrying out the k-summation (see, e.g., Shore and Menzel [24]),

$$E_{\mathrm{ssc,ab}} = \frac{\alpha^2}{4} n_a n_b R_2(a, b).$$

Results and Discussion

The radial integrals, R_2, have been evaluated from the analytical Hartree-Fock functions of Clementi [6] and Malli [17]. Table 1 collects the values of the total electron spin-spin contact interaction for the positive ions, neutral systems, and negative ions for all the atoms from He to Kr; the relative weights of the intra- and inter-shell contributions are exemplified in Table 2 for Br.

This interaction, as expected, is not negligible; a value of about 1 a.u. is predicted for Kr. It must be concluded that, when considering the absolute magnitude of the relativistic corrections, this interaction should be included.

The difference observed in the values for the various states arising from a given configuration is very small. On the other hand, however, the energies of other excited states relative to the groundstate may be affected considerably by consideration of this interaction, depending on what shell the electron(s) has (have) been excited from.

Table 1. Total electron spin-spin contact interaction (in cm^{-1}) for positive ions, neutral atoms and negative ions

Configuration[a]	State	Positive ions		Neutral atoms		Negative ions	
		System	E_{ssc}	System	E_{ssc}	System	E_{ssc}
$1s^2$	^1S	Li	57	He	14		
$2s^1$	^2S	Be	151	Li	58		
$2s^2$	^1S	B	325	Be	154	Li	58
$2p^1$	^2P	C	587	B	322		
$2p^2$	^3P	N	965	C	582	B	320
	^1D		970		584		321
	^1S		976		587		321
$2p^3$	^4S	O	1484	N	959	C	579
	^2D		1495		965		581
	^2P		1502		968		582
$2p^4$	^3P	F	2196	O	1491	N	961
	^1D		2206		1496		963
	^1S		2221		1504		966
$2p^5$	^2P	Ne	3120	F	2201	O	1491
$2p^6$	^1S	Na	4292	Ne	3124	F	2199
$3s^1$	^2S	Mg	5745	Na	4295		
$3s^2$	^1S	Al	7515	Mg	5750	Na	4296
$3p^1$	^2P	Si	9617	Al	7511		
$3p^2$	^3P	P	12094	Si	9612	Al	7509
	^1D		12096		9613		7509
	^1S		12096		9613		7510
$3p^3$	^4S	S	14981	P	12089	Si	9609
	^2D		14983		12090		9611
	^2P		14983		12091		9611
$3p^4$	^3P	Cl	18316	S	14977	P	12087
	^1D		18317		14978		12088
	^1S		18320		14979		12088
$3p^5$	^2P	A	22136	Cl	18313	S	14975
$3p^6$	^1S	K	26476	A	22133	Cl	18310
$4s^1$	^2S	Ca	31384	K	26482		
$4s^2$	^1S			Ca	31391	K	26481
$3d^1$	^2D			Sc	36831		
$3d^2$	^3F	Sc	36775	Ti	42873	Sc	36794
$3d^3$	^4F	Ti	42808	V	49548	Ti	42825
$3d^4$	^5D	V	49478	Cr	56896	V	49496
$3d^5$	^6S	Cr	56812	Mn	64947	Cr	56863
$3d^6$	^5D	Mn	64886	Fe	73792	Mn	64909
$3d^7$	^4F	Fe	73718	Co	83428	Fe	73743
$3d^8$	^3F	Co	83342	Ni	93881	Co	83375
$3d^9$	^2D	Ni	93782	Cu	105214		

Table 1 (continued)

Configuration[a]	State	Positive ions		Neutral atoms		Negative ions	
		System	E_{ssc}	System	E_{ssc}	System	E_{ssc}
$3d^{10}$	^1S	Cu	105105				
$4s^1$	^2S	Zn	117419	Cu	105134	Ni	93947
$4s^2$	^1S	Ga	130741	Zn	117451	Cu	105136
$4p^1$	^2P	Ge	145001	Ga	130739		
$4p^2$	^3P	As	160405	Ge	145040	Ga	130732
	^1D		160408		145042		130733
	^1S		160409				
$4p^3$	^4S	Se	176885	As	160404	Ge	145036
	^2D		176881		160402		145034
	^2P		176880		160405		145036
$4p^4$	^3P	Br	194503	Se	176882	As	160400
	^1D		194504		176879		160398
	^1S		194507		176884		160397
$4p^5$	^2P	Kr	213321	Br	194507	Se	176873
$4p^6$	^1S			Kr	213316	Br	194497

[a] The positive ions of the transition elements (from Sc through Cu) have configurations $4s^0\,3d^n$.

Table 2. Inter- and intra-shell contributions (in cm^{-1}) to the electron spin-spin contact interaction in Br

	1s	2s	3s	4s	2p	3p	4p	3d
1s	119993							
2s	18926	1634						
3s	2925	422	63					
4s	274	39	10	2				
2p	16813	6217	763	70	14260			
3p	2509	540	270	20	2958	461		
4p	138	29	11	5	158	41	5	
3d	68	700	337	26	1821	997	44	959

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