Electron correlation effects in hyperfine interactions in $^{45}$Sc and $^{89}$Y

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Abstract

Relativistic coupled-cluster theory has been employed to calculate the magnetic dipole and electric quadrupole hyperfine structure constants for the stable isotopes $^{45}$Sc and $^{89}$Y. The results are in good agreement with available experimental data. The role of electron correlation is found to be important. The trend exhibited by these effects in the systems under consideration with d-valence electrons is rather different from previously studied s and p single valence atomic systems. The contributions of certain higher order correlation effects are about 10–20%. Electric quadrupole hyperfine structure constants for $4d^2D_3/2$ and $4d^2D_5/2$ states are presented for the first time.

1. Introduction

Electron correlation effects play a crucial role in the accurate determination of hyperfine structure constants [1]. We have previously calculated these constants for several atomic systems with single s valence electrons [2, 3] using the relativistic coupled-cluster (RCC) theory which takes into account the interplay of relativistic and correlation effects. Our recent work on Pb$^+$ [4] reveals the dominant role of core-polarization effects in the calculation of the hyperfine constant of the $6p^2P_{3/2}$ state. Recently, systematic studies have been carried out on the influence of core-polarization effects on magnetic dipole hyperfine structure in d valence electrons [5, 6]. In the present work, we apply the RCC theory to investigate how electron correlation effects influence the hyperfine structure in the d valence electron systems.

We have carried out an ab initio calculation of the magnetic dipole ($A$) and electric quadrupole ($B$) hyperfine structure constants for the stable Scandium ($^{45}$Sc) and Yttrium ($^{89}$Y) isotopes which have 3d and 4d valence electrons, respectively. Hyperfine structure constants for the ground and the first excited states for these two atoms have been measured using atomic
beam magnetic resonance, optogalvanic and fluorescence spectroscopy [7–13]. Earlier these constants were calculated by Desclaux and Bessis [14] using the restricted and unrestricted relativistic Hartree–Fock–Slater (Dirac–Fock–Slater (DFS)) methods for $^{45}$Sc. Bieroń and Grant [15] had used the multi-configuration Dirac–Fock (MCDF) method to extract the nuclear quadrupole moment ($Q$) of $^{45}$Sc and obtained a slightly larger value than those obtained by Fricke et al [7] and Childs et al [8]. In this work, we employ the $Q$ value given by Harris [16] to calculate $B$. In the RCC theory, the Dirac–Fock (DF) wavefunction is considered as the reference wavefunction and the electron correlation effects are included to all orders in the residual Coulomb interaction corresponding to a given level of excitation [17]. These effects are highlighted by giving the explicit contributions from different RCC terms.

2. Theory

The hyperfine structure interaction constants are given by [18–20]

$$A_K = \langle JJ | T^K_0 | JJ \rangle M^K_0 = \left( \begin{array}{cc} J & K \\ -J & 0 \end{array} \right) \langle JJ | T^K | JJ \rangle M^K_0,$$  

(2.1)

where $T^K_0$ and $M^K_0$ are zero components of the spherical tensors with rank $K$ representing electronic and nuclear parts. For the magnetic dipole ($A$) and electric quadrupole ($B$) hyperfine constants $K = 1$ and $K = 2$, respectively. Explicitly, $A$ and $B$ are given by

$$A = \frac{A_1}{IJ} = \mu_N g_I \frac{\langle JJ | T^{(1)} | JJ \rangle}{\sqrt{J(J+1)(2J+1)}},$$

(2.2)

and

$$B = 4A_2 = 2eQ \left( \frac{2J(2J-1)}{(2J+1)(2J+2)(2J+3)} \right)^{1/2} \langle JJ | T^{(2)} | JJ \rangle,$$

(2.3)

where $g_I = \left[ \frac{\mu_I}{\mu_N} \right]$ is the nuclear Landé $g$-factor with $\mu_I$ being the nuclear dipole moment and $\mu_N = e\hbar/2m_pc$. $Q$ is the nuclear quadrupole moment. The reduced matrix elements of the electronic spherical operators in terms of single orbitals are given by

$$\langle \kappa_f | t^{(i)} | \kappa_i \rangle = -\langle \kappa_f | C^{(i)} | \kappa_i \rangle \int_0^{\infty} \frac{1}{r^2} d^2r \left( P_f Q_i + Q_f P_i \right),$$

(2.4)

and

$$\langle \kappa_f | t^{(2)} | \kappa_i \rangle = -\langle \kappa_f | C^{(2)} | \kappa_i \rangle \int_0^{\infty} \frac{1}{r^2} d^2r \left( P_f P_i + Q_f Q_i \right),$$

(2.5)

where $i$ and $f$ represent initial and final orbitals, respectively. The reduced matrix elements of the spherical tensors ($C^K$) are given by

$$\langle \kappa_f | C^K | \kappa_i \rangle = (-1)^{i+j+1/2} \sqrt{\langle 2j_f + 1 \rangle \langle 2j_i + 1 \rangle} \left( \begin{array}{c} j_f \\ 1/2 \end{array} \right) \left( \begin{array}{c} j_i \\ 0 \end{array} \right) \pi(l_f, K, l_i),$$

(2.6)

where $t^K$ is the single particle representation of $T^K$ and $\pi(l_f, K, l_i) = 1$ if $l_f + K + l_i = \text{even}$, otherwise zero for the orbital and total angular momentum quantum numbers $l$ and $j$, respectively. $\kappa$ is the relativistic quantum number which is defined as $\kappa = l(l+1) - j(j+1) - \frac{1}{4}$.

3. Method of calculation : relativistic coupled-cluster theory

We have performed our calculations in the Dirac–Coulomb (DC) approximation which embodies the dominant relativistic and correlation effects. The Breit interaction which is of order $\alpha^2$ compared to the Coulomb interaction has been omitted.
The Dirac–Coulomb atomic Hamiltonian is given by

\[
H = \sum_j \Lambda^+_j [c \alpha \cdot \mathbf{p}_j + (\beta - 1)c^2 + V_{\text{nuc}}(r_j)] \Lambda_j^+ + \sum_{j<l} \Lambda_j^+ \Lambda_l^+ \frac{1}{r_{jl}} \Lambda_j^+ \Lambda_l^+, \tag{3.1}
\]

where \(\Lambda^+\) are energy projection operators representing only the positive energy states, \(\alpha\) and \(\beta\) are the usual Dirac matrices and \(V_{\text{nuc}}(r_j)\) is the potential at the site of the \(j\)th electron due to the atomic nucleus. In our derivation, we have employed atomic units \((m_e = 1, |e| = 1\) and \(\hbar = 1\)). The rest-mass energy of the electron is subtracted from the energy eigenvalues.

We first solve the relativistic Hartree–Fock (Dirac–Fock (DF)) equations to obtain the single particle orbitals and their energies. The corresponding DF Hamiltonian is given by

\[
H_{\text{DF}} = \sum_j \Lambda^+_j [c \alpha \cdot \mathbf{p}_j + (\beta - 1)c^2 + V_{\text{nuc}}(r_j) + U_j] \Lambda_j^+. \tag{3.2}
\]

The residual Coulomb interaction is given by

\[
V_{rs} = \sum_{j<l} \Lambda_j^+ \Lambda_l^+ \frac{1}{r_{jl}} \Lambda_j^+ \Lambda_l^+. \tag{3.3}
\]

The single particle orbitals are obtained by solving the following equation self-consistently:

\[
(t_j + U_j) |\phi_j\rangle = \epsilon_j |\phi_j\rangle, \tag{3.4}
\]

where

\[
t_j = c \alpha \cdot \mathbf{p}_j + (\beta - 1)c^2 + V_{\text{nuc}}(r_j)
\]

and

\[
U_j |\phi_j(\vec{r}_1)\rangle = \sum_{a=1}^{\text{occ}} \langle \phi_a(\vec{r}_2) | \frac{1}{r_{12}} | \phi_a(\vec{r}_2) \rangle |\phi_j(\vec{r}_1)\rangle - \langle \phi_a(\vec{r}_2) | \frac{1}{r_{12}} | \phi_j(\vec{r}_2) \rangle |\phi_a(\vec{r}_1)\rangle. \tag{3.5}
\]

occ represents the total number of occupied orbitals.

The single particle relativistic orbitals can be expressed as

\[
|\phi_j(r)\rangle = \frac{1}{r} \left( \frac{P_j(r) |\chi_{s,m_j}\rangle}{i Q_j(r) |\chi_{-s,m_j}\rangle} \right),
\]

where \(P_j(r)\) and \(Q_j(r)\) are the radial part of the large and small components, respectively, and \(|\chi_{s,m_j}\rangle\) and \(|\chi_{-s,m_j}\rangle\) are their respective spin angular momentum components and \(\epsilon_j\)'s are the single particle energies.

In the RCC theory, the exact atomic wavefunction for a closed-shell system can be expressed as [1]

\[
|\Psi_{\text{CC}}\rangle = e^T |\Phi\rangle, \tag{3.6}
\]

where \(T\) is the core-electron excitation operator. \(|\Phi\rangle\) is the above closed-shell determinantal state built out of the Dirac–Fock single particle orbitals. We have truncated the exponential expansion at the level of single and double excitations. This is known as the coupled-cluster singles and doubles (CCSD) approximation. In this approximation the \(T\) operator is expressed as

\[
T = T_1 + T_2 = \sum_{a,p} a^+_a a_t^p + \frac{1}{4} \sum_{ab,pq} a^+_a a^+_b a_t^p a_t^q
\]

with \(t_a^p\) and \(t_a^{pq}\) being the cluster amplitudes corresponding to single and double excitations in the closed-shell.
Therefore, the wavefunction given by equation (3.6) can be written in the CCSD approximation as
\[ |\Psi_{CC}\rangle = \left[ 1 + T_1 + T_2 + T_1 T_2 + \frac{1}{2!} T_1^2 + \frac{1}{2!} T_2^2 + \frac{1}{3!} T_1^2 T_2 + \frac{1}{4!} T_1^3 + \frac{1}{4!} T_2^3 \right] |\Phi\rangle, \] (3.7)
where other nonlinear terms do not contribute since the atomic Hamiltonian has only one-body and two-body terms.

In the closed-shell coupled-cluster theory, one starts with the equation
\[ H e^T |\Phi\rangle = E e^T |\Phi\rangle, \] (3.8)
The energy and amplitude determining equations are
\[ \langle \Phi^K | \tilde{H} | \Phi \rangle = E \delta_{0,K}, \] (3.9)
where \( \tilde{H} = e^{-T} H e^T \) and \( |\Phi^K\rangle \) is an excited determinantal state with \( K = 0, 1, 2, \ldots \), representing the index for the reference state, single, double excited states, etc. We have considered all possible nonlinear terms of the \( T \) operator in (3.8).

Goldstone \([1, 21, 22]\) and angular momentum \([1, 23]\) diagrammatic techniques are used for evaluating different radial integrals and angular factors. The normal ordered Hamiltonian is defined as
\[ H_N = H - \langle \Phi | H | \Phi \rangle = H - E_{DF}, \] (3.10)
where \( E_{DF} = \langle \Phi | H | \Phi \rangle \).

We first obtain the closed-shell cluster amplitudes by solving the closed-shell CC equations and then the open-shell cluster amplitudes using the open-shell CC (OSCC) method \([1, 24]\).

The new reference state of the open-shell system with one valence electron \( v \) can be expressed as \([24]\)
\[ |\Phi_v\rangle \equiv a^\dagger_v |\Phi\rangle, \] (3.11)
where \( a^\dagger_v \) is the particle creation operator. The exact atomic states are defined now, using the Fock-space OSCC method, as
\[ |\Psi_v\rangle = e^T \{ e^S \} |\Phi_v\rangle, \] (3.12)
where \( S_v \) is the valence excitation operator. Since we are considering systems with a single valence electron, the exponential series for the \( S_v \) operator naturally truncates at the linear term, i.e. the open-shell wavefunction has the form
\[ |\Psi_v\rangle = e^T \{ 1 + S_v \} |\Phi_v\rangle, \] (3.13)
where
\[ S_v = S_{1v} + S_{2v} = \sum_{p \neq v} a^\dagger_p a_v s^p_v + \frac{1}{2} \sum_{h, pq} a^\dagger_h a^\dagger_p a_v a_v s_{hp}^{pq} \]
with \( s^p_v \) and \( s_{hp}^{pq} \) being the cluster amplitudes corresponding to single and double excitations involving the valence electron.

In the next step, we include approximate triple excitations by contracting the two-body operator \( (V_{ex}) \) and the double excitation operators \( (T_2, S_{2v}) \) in the following way \([25]\):
\[ S_{ppq}^{vbc} = \frac{V_{ex} T_2 + V_{ex} S_{2v}}{\epsilon_v + \epsilon_b + \epsilon_c - \epsilon_p - \epsilon_q - \epsilon_r}, \] (3.14)
where we use the notations \( a, b, c, \ldots, p, q, r, \ldots \) and \( i, j, k, \ldots \) for the core (occupied), particle (unoccupied) and general orbitals, respectively. Goldstone diagrams representing typical triple excitations are shown in figure 1.
The equations for the open-shell cluster amplitudes are determined from
\[ \langle \Phi_v | H_N \{1 + S_v\} | \Phi_v \rangle = \Delta E(v) \]  
(3.15)
and
\[ \langle \Phi_v^* | H_N \{1 + S_v\} | \Phi_v \rangle = \Delta E(v) \langle \Phi_v^* \{S_v\} | \Phi_v \rangle, \]  
(3.16)
where \( \Delta E(v) \) is the electron attachment energy which is equal to the negative of the ionization potential for the valence electron \( v \) and \( | \Phi_v^* \rangle \) is the excited state with respect to \( | \Phi_v \rangle \).

The expectation value for a general one particle operator in a given valence electron \( (v) \) state can be expressed in the RCC theory as
\[ \langle O \rangle_v = \frac{\langle \Psi_v | O | \Psi_v \rangle}{\langle \Psi_v | \Psi_v \rangle} = \frac{\langle \Phi_v | [1 + S_v] e^{\dagger} O e^{T} [1 + S_v] | \Phi_v \rangle}{1 + N_v} \]
(3.17)
where the normalization term for the \( v \)th valence electron state is obtained from
\[ N_v = \langle \Phi_v | \pi_v^+ \pi_v \pi_v^+ S_v + \pi_v S_v \pi_v + \pi_v S_v^+ | \Phi_v \rangle \]
(3.18)
with
\[ \pi_v^+ = (e^{T} O e^{T})_{f.c.} + (e^{T} O e^{T})_{o.b.} + (e^{T} O e^{T})_{t.b.} + \cdots \]
(3.19)
and
\[ \pi_v + 1 = (e^{T} e^{T})_{f.c.} + (e^{T} e^{T})_{o.b.} + (e^{T} e^{T})_{t.b.} + \cdots \]
(3.20)
The f.c., o.b., t.b. . . . abbreviations are used for the fully contracted, effective one-body, effective two-body, . . . terms, respectively [2]. Since we have utmost one \( S_{2v} \) and one of its conjugate operators at both ends of the numerator and denominator, terms containing only up
to effective three-body diagrams will contribute. The fully contracted terms are excluded on
the basis of the linked-diagram theorem [1] in the evaluation of \( \mathcal{O} \) and \( \pi_\sigma \). All the one-body
terms have been taken into account as their contribution to the correlation effects is the largest.
The dominant parts of the two-body terms have also been computed [2]. Finally, these terms
are contracted with \( S_\sigma \) and \( S_\nu \) operators.

Contributions from the normalization factor have been determined in the following way:

\[
\text{Norm.} = \langle \Psi_\nu | O | \Psi_\nu \rangle \left\{ \frac{1}{1 + N_\nu} - 1 \right\}.
\]

(3.21)

4. Results and discussion

We have used Gaussian type orbitals (GTOs) [26] for the construction of single particle orbitals
of the Dirac–Fock wavefunction (\( | \Phi_1 \rangle \)) given by

\[
F_{i,k}(L/S)(r) = \sum_i c_{i,k}^{(L/S)} r^k e^{-\alpha_i r^2}
\]

(4.1)

with \( k = 0, 1, 2, \ldots \) for s, p, d, \ldots, respectively. The function \( F_{i,k}^{(L/S)}(r) \) stands for the large
(L) and small (S) components of the Dirac wavefunction and \( c_{i,k}^{(L/S)} \) is the expansion coefficient
of the corresponding large and small components, respectively. The kinetic balance condition
[27] has been imposed between the large and small components of the GTOs. For the
exponents, the even tempering condition [28]

\[
\alpha_i = \alpha_i - 1, \quad i = 1, \ldots, N
\]

(4.2)

has been applied. Here, \( N \) stands for the total number of basis functions for a specific symmetry.
All orbitals are generated on a grid using a two-parameter Fermi nuclear charge distribution
approximation given by

\[
\rho(r) = \rho_0 \left( 1 + e^{(r - c)/a} \right)
\]

(4.3)

where \( \rho_0 \) is the average nuclear density, the parameter \( c \) is the half-charge radius and \( a \) is
related to the skin thickness which is defined as the interval of the nuclear thickness in which
the nuclear charge density falls from close one to close zero. We use the values of \( c \) and \( a \) as
given by Parpia and Mohanty [29].

In the present calculation, we have used \( \alpha = 0.00525 \) and \( \beta = 2.73 \) for all symmetries
in both systems. We have considered 35s_{1/2}, 30p_{1/2}, 30p_{3/2}, 30d_{3/2}, 30d_{5/2}, 20f_{5/2} and 20f_{7/2},
and 38s_{1/2}, 35p_{1/2}, 35p_{3/2}, 35d_{3/2}, 35d_{5/2}, 20f_{5/2} and 20f_{7/2} GTOs to obtain the Dirac–Fock
wavefunction in \(^{45}\text{Sc}\) and \(^{89}\text{Y}\), respectively. All the core electrons have been excited in the
present calculations.

We have calculated both the hyperfine constants \( A \) and \( B \) for 3d \(^2\)D_{3/2} and 3d \(^2\)D_{5/2} states
for \(^{45}\text{Sc}\) and 4d \(^2\)D_{3/2} and 4d \(^2\)D_{5/2} states for \(^{89}\text{Y}\). We have used \( g_I = 1.359 \) and \( Q = 0.22 \) barn
for \(^{45}\text{Sc}\) and \( g_I = 0.3268 \) and \( Q = 0.125 \) barn for \(^{89}\text{Y}\), respectively. All calculated results
with the corresponding experimental results are presented in tables 1 and 2. Results of \(^{45}\text{Sc}\) are
compared with other calculated results by Desclaux and Bessis [14]. To our knowledge there
are no experimental results available for \( B \) in \(^{89}\text{Y}\) and we have presented only our calculated
results.

In tables 3 and 4, we present contributions from different RCC terms for \( A \) and \( B \),
respectively. The diagrams corresponding to the terms whose contributions are significant
are given in figure 2. The first term \( O \) represents the DF value and is given in figure 2(i).
The second term \( \bar{O} - O \) is the contribution from the correlation between the core electrons.
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Table 1. Magnetic dipole ($A$) hyperfine structure constants in MHz of ground state and first excited state for $^{45}\text{Sc}$ and $^{89}\text{Y}$.

| States            | Theory (Desclaux and Bessis) [14] | Experiment (This work) | Theory (This work) | Experiment |
|-------------------|-----------------------------------|-------------------------|--------------------|------------|
| $^{45}\text{Sc}$ |                                    |                         |                    |            |
| $3d^2D_{3/2}$     | 294                               | 252                     | 268.7 (1.5)        | 269.556 (1)|            |
| $4d^2D_{3/2}$     | 125                               | 105                     | 110.8 (0.8)        | 109.032 (1)| 29.2 (1.3) |
| $^{89}\text{Y}$  |                                    |                         |                    |            |
| $3d^2D_{3/2}$     |                                    |                         | 269.556 (1)        | 57.3 (0.6) |
| $4d^2D_{3/2}$     |                                    |                         | 109.032 (1)        | 57.217 (15)|            |

Table 2. Electric quadrupole ($B$) hyperfine structure constants in MHz of ground state and first excited state for $^{45}\text{Sc}$ and $^{89}\text{Y}$.

| States            | Theory (Desclaux and Bessis) [14] | Experiment (This work) | Theory (This work) | Experiment |
|-------------------|-----------------------------------|-------------------------|--------------------|------------|
| $^{45}\text{Sc}$ |                                    |                         |                    |            |
| $3d^2D_{3/2}$     | 32                                |                         | 27.5 (0.6)         | 26.346 (4)|            |
| $3d^2D_{5/2}$     | 41                                |                         | 38.6 (0.4)         | 37.31 (10)| 31.8 (0.2) |
| $^{89}\text{Y}$  |                                    |                         |                    |            |
| $3d^2D_{3/2}$     |                                    |                         | 23.4 (0.2)         |            |
| $3d^2D_{5/2}$     |                                    |                         | 26.346 (4)         |            |

Table 3. Contributions from different coupled-cluster terms to the magnetic dipole hyperfine structure constant ($A$) in MHz, where cc stands for the complex conjugate part of the corresponding terms.

| CCSD(T) terms | $^{45}\text{Sc}$ | $^{89}\text{Y}$ |
|---------------|-------------------|------------------|
| $O$ (DF)      | 235.93            | 56.06            |
| $\overline{O} - O$ | 4.82              | 2.37             |
| $\overline{O}S_{1v} + cc$ | 40.02             | 7.62             |
| $\overline{O}S_{2v} + cc$ | -20.09            | -8.27            |
| $S^1_{1v} \overline{O}S_{1v}$ | 1.85              | 0.26             |
| $S^1_{1v} \overline{O}S_{2v} + cc$ | 1.21              | 0.32             |
| $S^1_{2v} \overline{O}S_{2v} + cc$ | 25.79             | 3.62             |

Important effective two-body terms of $\overline{O}$

| $S^1_{1v} OT_1 + cc$ | -9.07            | -2.05            |
| $S^1_{2v} OT_2 + cc$ | 0.00             | -0.32            |
| Norm.               | -10.94           | -2.38            |
| Total               | 268.67           | 57.34            |

$O S_{1v}$ (figures 2(ii) and (iii)) and $O S_{2v}$ (figures 2(iv)–(viii)) which represent pair-correlation and core-polarization effects, respectively, make important contributions for both the atoms. It is interesting to note that the contributions of $S^1_{2v} O S_{2v}$ (figures 2(vii)–(xiii)) are far more significant for $^{45}\text{Sc}$ and $^{89}\text{Y}$ than for atomic systems with single s and p valence electrons [2–4]. One of the strengths of coupled-cluster theory is that it can account for such intricate correlation effects to all orders in the residual Coulomb interaction [1]. The two-body $\overline{O}$ and the normalization terms, (3.21), make non-negligible contributions. From tables 3 and 4, it is clear that these contributions are essential to achieve accurate results.
Table 4. Contributions from different coupled-cluster terms to the electric quadrupole hyperfine structure constant ($B$) in MHz, where cc stands for the complex conjugate part of the corresponding terms.

| CCSD(T) terms | $^{45}$Scandium $3d^2D_{3/2}$ | $3d^2D_{5/2}$ | $^{89}$Yttrium $4d^2D_{3/2}$ | $4d^2D_{5/2}$ |
|---------------|-------------------------------|---------------|-------------------------------|---------------|
| $O$ (DF)      | 23.34                        | 32.76         | 16.01                         | 21.78         |
| $\frac{\partial}{\partial}S_{1v} + cc$ | 0.78                         | 0.84          | 0.69                          | 0.76          |
| $\frac{\partial}{\partial}S_{2v} + cc$ | −0.97                        | −1.18         | 3.90                          | 5.78          |
| $S_{1v} \frac{\partial}{\partial}S_{1v}$ | 0.18                         | 0.24          | 0.07                          | 0.11          |
| $S_{1v} \frac{\partial}{\partial}S_{2v} + cc$ | −0.24                        | −0.33         | 0.06                          | 0.99          |
| $S_{2v} \frac{\partial}{\partial}S_{2v} + cc$ | 2.74                         | 3.99          | 2.03                          | 2.44          |

Important effective two-body terms of $\mathcal{D}$:

| $S_{1v} O T_1 + cc$ | −0.91 | −1.16 | −0.59 | −0.79 |
| $S_{1v} O T_2 + cc$ | 0.00  | 0.00  | −0.01 | −0.10 |
| Norm.               | −1.14 | −6.7  | −0.97 | −1.30 |
| Total               | 27.45 | 38.56 | 23.37 | 31.75 |

We have estimated the error margins due to the omission of the higher order residual Coulomb interaction terms by considering the difference of our calculations with single, double and leading triple excitations and just single and double excitations.

5. Conclusion

We have performed calculations of the hyperfine constants $A$ and $B$ for $^{45}$Sc and $^{89}$Y using the RCC theory. The importance of electron correlation effects have been highlighted. Our results are in good agreement with the available experiments. This indeed clearly demonstrates the power of RCC theory to handle the interplay of relativistic and correlation effects in the d valence electron atomic systems. The pair correlation and core-polarization effects make the
dominant correlation contributions, but their signs are opposite. Correlation contributions arising from $S_{1/2} \sigma S_{1/2}$ are relatively large. These effects are about 1–2% in Ba$^+$ [2], Ca$^+$ [3] and Pb$^+$ [4], where in the systems studied here these contributions are about 10–20% of the total results in hyperfine structure calculations.

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