Eur. Phys. J. D **14**, 271–277 (2001)

THE EUROPEAN PHYSICAL JOURNAL D
EDP Sciences

The multi-configuration Dirac-Fock calculation of the low-lying levels of Sm

A. Dilip[1,a], I. Endo[1], A. Fukumi[2], M. Iinuma[1], T. Kondo[2], and T. Takahashi[1]

[1] Graduate School of Advanced Sciences of Matter, Hiroshima University, Higashi-Hiroshima 739-8526, Japan
[2] Department of Physics, Hiroshima University, Higashi-Hiroshima 739-8526, Japan

Received 10 October 2000 and Received in final form 23 January 2001

Abstract. The excitation energies and hyper-fine structure constants of the low-lying levels of Sm atom are calculated using the multi-configuration Dirac-Fock (MCDF) method. The results show that the excitation energies of the ground state multiplets can be calculated accurately using a small orbital set but the higher levels need larger orbital sets. Similar inference can also be drawn from the discrepancy between the calculated values of the hyper-fine constants and the experimental data. A sequence of MCDF calculation demonstrates the effect of the MCDF potential on the orbitals. Among the rare earth atoms Sm is a promising candidate for discrete symmetry violation experiments in atoms. This makes accurate theoretical calculations necessary since parameters in particle physics can be derived by combining the experimental results with the theoretical results. And these could be a probe for the physics beyond the standard model.

PACS. 31.15.Ar Ab initio calculations – 31.25.Jf Electron correlation calculations for atom and ions: excited states – 32.10.Fn Fine and hyperfine structure

1 Introduction

The most accurate experimental results of atomic parity non-conservation (PNC) were obtained using cesium (Cs) [1]. A recent theoretical analysis has shown that the deviation of the ^{133}Cs weak charge from the standard model is 1.0σ [2] after the inclusion of the Breit and neutron nuclear distribution corrections. But another recent work [3] concludes that the correction from the Breit interaction is half of the previous work [2]. The theoretical uncertainty is placed at 0.4% after the recent experimental results [4]. However, the theoretical calculations claim an accuracy of 1% [5,6]. To understand the PNC effects in atoms, it is important to confirm the Cs results using atoms of other elements and if possible improve the accuracy. A good choice is one which has an advantage over Cs.

A preliminary selection criterion is the Z^3 effect [7] in the atomic PNC induced $E1$ amplitude $E1$PNC, where Z is the nuclear charge. This makes an atom with Z higher than Cs preferable. Among the high Z atoms, the rare earth atoms are good candidates as they have closely spaced opposite parity states. This further enhances the $E1$PNC due to the inverse dependence on the energy spacing between the PNC mixed opposite parity states. An approach to improving the accuracy is reducing the uncertainty from atomic many-body theory, which is a major source of error. There are two possible ways to achieve this: first, choose an atom with simple atomic structure and second, eliminate the uncertainty from the atomic theory using the experimental results from isotope chains [8]. The rare earth atoms satisfies the second condition as many of them have several stable isotopes. Among the rare earth atoms Sm is a promising candidate for studying PNC as well as time-reversal violations. It has been studied before [9] and is also the choice of ongoing experimental studies. The levels of interest in Sm are 15 639.80 cm^{-1} and 15 650.55 cm^{-1}, these are under experimental investigations for PNC experiments in our group [10,11]. The same levels have been proposed for EDM measurement at Berkeley [12].

An experiment with the isotope chain of Sm can remove the need of the atomic theory calculations, however it is desirable to have an estimate of the expected $E1$PNC. In addition, the two levels do not mix directly through the PNC interaction Hamiltonian and there is the possibility of cancellations due to opposite mixing signs. A theoretical estimate can provide an understanding to these. An accurate calculation of the $E1$PNC requires atomic wave-functions which are accurate at all radial ranges. It is therefore important to check the accuracy of the wave-function by comparing the theoretically calculated atomic properties with the experimental data. The structure calculation of the rare earth atoms is very difficult due to the strong configuration mixing arising from the electrons in the $4f$ shell. Among the lanthanide atoms, the structure calculation of Sm is one of the most complicated as it lies within the mid range of the series. The structure

---

[a] e-mail: `angom@photon.hepl.hiroshima-u.ac.jp`

calculation for the levels of interest is even more complicated as these are high-lying levels. As a preliminary step we have calculated the properties of the low-lying levels and we are in the process of improving the properties of the high-lying levels. In this paper we report the results of our recent calculations. The properties of the low-lying levels were also studied in earlier works of Cheng and Childs [13] and Porsev [14]. All our calculations are done with a parallel C-version of GRASP92 [15] and all quantities are in a.u. unless specifically mentioned.

2 Method of atomic structure calculation

2.1 Calculating orbitals with multi-configuration Dirac-Fock potential

The starting point of an atomic structure calculation is obtaining a set of orbitals. Using these orbitals a hierarchy of wave-functions can be computed to represent the atomic state. An orbital $\psi(\mathbf{r})$ is represented in the relativistic notations as

$$\psi_{n\kappa}(\mathbf{r}) = \frac{1}{r}\begin{pmatrix} P_{n\kappa}(r)\chi_{\kappa m}(\theta,\phi) \\ \mathrm{i}Q_{n\kappa}(r)\chi_{-\kappa m}(\theta,\phi)\end{pmatrix} \tag{1}$$

where n is the principal quantum number, κ is an angular quantum number, m is the magnetic quantum number, $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ are large and small component radial functions respectively, and $\chi_{\kappa m}(\theta,\phi)$ and $\chi_{-\kappa m}(\theta,\phi)$ are the spinor spherical harmonics in the lsj coupling scheme. A set of Slater determinants can be constructed from the orbitals and linear combinations of these determinants can build up a set of orthonormal configuration state functions (CSFs). The calculations are carried out in terms of CSFs and Slater determinants are not used explicitly. A CSF is represented by $|\gamma PJM\rangle$, where P, J and M are the parity, total angular momentum and magnetic quantum numbers respectively, and γ is an additional quantum number to define each CSF uniquely. The CSFs satisfies the condition of orthonormality. Then, an atomic state function (ASF) which represents a stationary state of an atom is a linear combination of these CSFs

$$|\Gamma PJM\rangle = \sum_{r}^{n_\mathrm{c}} c_\Gamma^r|\gamma_r PJM\rangle \tag{2}$$

where Γ is a quantum number to define each ASFs uniquely, c_Γ^r are the mixing coefficients of the CSFs and n_c is the number of CSFs. Similar to the CSFs, the ASFs should also satisfy the condition of orthonormality

$$(\mathbf{c})^\dagger_{\Gamma_i}\mathbf{c}_{\Gamma_j} = \delta_{ij}. \tag{3}$$

The orbitals can be generated using an appropriate Hamiltonian. The Dirac-Coulomb Hamiltonian H^DC is the one chosen for our calculations. For an N electron atom

$$H^\mathrm{DC} = \sum_{i=1}^{N}\left[c\boldsymbol{\alpha}_i\cdot\mathbf{p}_i + c^2(\beta_i - 1) - \frac{Z(\mathbf{r}_i)}{r_i} + \sum_{j=i+1}^{N}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\right] \tag{4}$$

where $\boldsymbol{\alpha}_i$ and β_i are the Dirac matrices, $\mathbf{p}_i$ is the momentum of the electron, $Z(\mathbf{r}_i)$ is the effective nuclear-charge at $\mathbf{r}$ and the last term is the electron-electron coulomb interaction. It is important to choose an approximate form of the electron-electron coulomb interaction potential to reduce the problem to the independent particle level. The Dirac-Fock (DF) potential is a good choice for atoms with a few valence electrons but not for an atom like Sm, which has open $4f$ shell. It is more accurate to use a multi-configuration potential, so that the orbitals are generated with the potential that has important valence-valence correlation effects. This is important since perturbation techniques can break down when there are strong correlation effects. The energy of the ASF Γ is

$$E_\Gamma^\mathrm{DC} = \langle\Gamma PJM|H^\mathrm{DC}|\Gamma PJM\rangle = (\mathbf{c}_\Gamma^\mathrm{DC})^\dagger\mathsf{H}\mathbf{c}_\Gamma^\mathrm{DC}. \tag{5}$$

Requiring that E_Γ^DC be stationary with respect to variations in the mixing co-efficient subject to the condition (3) yields the eigen-value equation

$$(\mathsf{H}^\mathrm{DC} - E_\Gamma^\mathrm{DC}\mathbf{1})\mathbf{c}_\Gamma^\mathrm{DC} = 0 \tag{6}$$

where $\mathbf{1}$ is the $n_\mathrm{c}\times n_\mathrm{c}$ unit matrix. The mixing coefficients are the solutions of this equation.

The orbitals can be calculated self-consistently using the principle of variation [16] on the energy functional defined with respect to a set of ASFs

$$W^\mathrm{DC} = \sum_{r,s}^{n_\mathrm{c}} d_{rs}H_{rs}^\mathrm{DC} + \sum_{a=1}^{n_\mathrm{w}}\sum_{r=1}^{n_\mathrm{c}} d_{rr}q(a)\epsilon_a + \sum_{a=1}^{n_w-1}\sum_{b=a+1}^{n_w}\delta_{ab}\epsilon_{ab}N(ab) \tag{7}$$

where d_{rs} and d_{rr} are the weight factors, H_{rs}^DC are the matrix element of H^DC between the CSFs $|\gamma_r PJM\rangle$ and $|\gamma_s PJM\rangle$, $q(a)$ is the occupation number of the ath subshell and n_w is the number of the orbitals. The quantity $N(ab)$ is the overlap integral between the ath and bth orbitals and ϵ_a and ϵ_{ab} are the Lagrange multipliers to enforce the orthonormality between the orbitals of the same symmetry. The condition of the variational procedure is that W^DC be stationary with respect to the variations of the radial components of the orbitals. The weight factors can be chosen in a number of ways, in our case these are chosen as

$$d_{rs} = \frac{1}{n_\mathrm{L}}\sum_{i}^{n_\mathrm{L}} c_{\Gamma_i}^r c_{\Gamma_i}^s \tag{8}$$

where n_{L} is the number of ASFs chosen for the MCDF calculation. This choice of weight factors is a version of the extended optimized level (EOL) calculation. The positronic states are also the solutions of the single particle equation obtained but only the bound orbital solutions can be selected by putting the boundary condition $\psi(\mathbf{r}) \to 0$ at $r \to \infty$ [17]. This is an important condition as the variational procedure can break down in presence of the positronic solutions. The positronic solutions contribute significantly to the properties of ions where the nuclear potential is strong but are less important for properties of atomic bound states. The MCDF calculations are done with the CSFs that contribute strongly to the required ASFs. The effective nuclear charge $Z(r)$ is calculated using the Fermi-nucleus model

$$\rho(r) = \frac{\rho_0}{1 + \exp[(r-c)/a]}, \quad a = t4\ln 3, \qquad (9)$$

where $\rho(r)$ is the radial charge density, ρ_0 is a constant, c is the half density radius and t is the skin thickness parameter. It is important to use a finite nuclear model as nuclear charge of Sm is high. The parameters c and a in our calculations are $1.1189 \times 10^{-4} a_0$ and $9.8906 \times 10^{-6} a_0$ respectively.

2.2 The correlation effects

The leading configuration of the ground state multiplet and eleven other even parity excited multiplets till 12 176 cm^{-1} are $4f^6 6s^2$ and $4f^6 5d6s$ respectively. And $4f^6 6s6p$ is the leading configuration of the odd parity levels below 18 000 cm^{-1}. Due to the $4f$ open-shell, each of these configurations produces many CSFs with the same J but with different intermediate angular momentum. And these can have strong correlation mixing. A significant portion of the valence-valence correlation, which has the largest contribution among the different types of correlation effects can be captured by including all the CSFs of the leading configurations in the MCDF calculation.

To choose the configurations in the MCDF calculations, it is important to make correct identification of the core and valence orbitals. For the rare earth lanthanide atoms, the orbitals upto $4f$ can be treated as the core. This is evident from the studies of Cheng and Childs on the lanthanide atoms [13], which demonstrated the stability of the $4f$ shell. The orbitals $5d$, $6s$ and $6p$ can be chosen as the minimal set of valence orbitals. The CSFs generated with these valence orbitals should be included in the MCDF calculation since $4f^6 6p^2$ and $4f^6 5d6p$ mix significantly with $4f^6 6s^2$ and $4f^6 6s6p$ respectively. The configuration $4f^6 5d^2$ does not mix with $4f^6 6s^2$ and $4f^6 5d6s$ as strongly as $4f^6 6p^2$ does with $4f^6 6s^2$. But it can mix with both $4f^6 6s^2$ and $4f^6 5d6s$ and the large number of CSFs generated by it can make the overall contribution from this configuration large. Thus the orbitals (1–5)s, (2–5)p, (3–4)d and $4f$ are core, and $5d$, $6s$ and $6p$ are valence. The others are virtual orbitals. The virtual orbitals are required to capture the correlation effects left out with only the core and valence orbitals as the orbital basis.

Apart from the valence-valence correlation effects, there are other types of correlation effects involving the core, valence and virtual shells. The important ones are the core-valence and valence-virtual. Contribution from all the types of correlation effects can be included in the calculation using the method of configuration interaction (CI). It is a straight forward diagonalization of the H^{DC} matrix with the CSFs generated from the core, valence and virtual orbitals. The matrix diagonalization need efficient algorithms since each of the configurations generates a large number of CSFs. A preferred choice is the Davidson algorithm [18].

2.3 Generation of the virtual orbitals

The initial MCDF calculation with the important configurations generates the core and valence orbitals. However, to include important correlation effects in CI calculations, the virtual orbitals are also required. Ideally, all the correlation effects can be captured with an active CSF space generated from a complete set of orbitals. But for a complex atom like Sm, computationally, this is beyond the existing expertise. The virtual orbitals satisfies the conditions of orthonormality and completeness, the method of generation is less important compared to these conditions.

A possible method to generate a set of virtual orbitals is to increase the CSF space in the MCDF calculation by adding selected CSFs that has virtual orbitals [19], while the orbitals generated in the previous calculations are kept frozen. The virtual orbitals can then be generated in layers. One layer is a set of s, p, d, f and g orbitals with the same principle quantum number. In our Sm structure calculation the first layer is $7s$, $7p$, $7d$, $7f$ and $7g$. The CSFs added to generate each layer of virtual orbitals are the single excitation from the valence orbitals. All the levels of Sm below 25 000 cm^{-1} has $6s$ orbital and many have the same configurations. As observed in earlier studies [19], the valence orbitals are term dependent. To get good results the correlation within the valence space is saturated with the $7s$, $7p$, $7d$ and $7f$, hence the layer with the principal quantum number 8 is the first layer of virtual orbitals generated by freezing the core orbitals.

2.4 Configuration interaction combined with perturbation theory

The large number of intermediate angular momentum after coupling the $4f$ shell makes the CSF space exceedingly large with a few virtual orbitals. It is very difficult to do a CI calculation when the core excitations from $4f$ are also included, where the CSF space could reach a million even with a single layer of virtual orbitals. It is preferable to treat the less important CSFs perturbatively [20]. To implement this, separate the CSF space into two groups: a zeroth order group, which accounts for a large portion of the correlation effects, and a first order group, which accounts for the remaining correlation effects. Consider the Hamiltonian matrix that has submatrices: H_{00} consisting of elements between the zeroth order CSFs, H_{01} consisting of the elements between the zeroth and first order CSFs and its transpose H_{10}, and $\mathrm{diag}(\mathsf{H}_{11})$ consisting of all the diagonal elements within the first order CSFs. The rest of the elements are set to zero. The Hamiltonian matrix appear as

$$\begin{pmatrix} \mathsf{H}_{00} & \mathsf{H}_{01} \\ \mathsf{H}_{10} & \mathrm{diag}(\mathsf{H}_{11}) \end{pmatrix}. \tag{10}$$

A CI calculation with such a Hamiltonian matrix includes all the important correlations effects from the zeroth order group but selectively from the first order group. The method is a part of the CI module in GRASP92 [15]. For some of the configurations, the individual contributions from each CSF is negligible but the net contribution from all the CSFs generated by the configuration can be significant. And since the level spacings are not very large, these contributions are important to get proper level sequence. The method described is useful in including such configurations in the CI calculation. At this stage the method used is a combination of MCDF, CI and many-body perturbation theory.

3 The calculation of the hyperfine constants

The magnetic dipole and electric quadrupole hyperfine constants A and B of an atomic state arises due to the interaction between the electromagnetic multipole moments of the nucleus and the electrons. These quantities indicate the strength of the interaction. An atomic state with the total angular momentum J has

$$A_J = \frac{\mu_I}{I} \frac{1}{[J(J+1)]^{1/2}} \langle \Gamma_J PJ || \mathsf{T}^{(1)} || \Gamma_J PJ \rangle \tag{11}$$

and

$$B_J = 2Q_I \left[\frac{J(2J-1)}{(J+1)(2J+3)} \right]^{1/2} \langle \Gamma_J PJ || \mathsf{T}^{(2)} || \Gamma_J PJ \rangle \tag{12}$$

where μ_I is the nuclear magnetic dipole moment, I is the nuclear spin, Q_I is the nuclear quadrupole moment, and $\mathsf{T}^{(1)}$ and $\mathsf{T}^{(2)}$ are electronic tensor operators of rank 1 and 2 respectively. For an atom with N electrons

$$\mathsf{T}^{(1)} = \sum_{i=1}^{N} -i\alpha \left[\boldsymbol{\alpha}_i \cdot \mathbf{1}\mathsf{C}_i^{(1)} \right] r^{-2} \tag{13}$$

and

$$\mathsf{T}^{(2)} = \sum_{i=1}^{N} -\mathsf{C}^{(2)} r^{-3}, \tag{14}$$

where α is the fine-structure constant, and $\mathsf{C}^{(1)}$ and $\mathsf{C}^{(2)}$ are spherical tensor operators in the electronic space. The reduced matrix elements in equations (11, 12) are calculated by expressing in terms of CSFs

$$\langle \Gamma_J PJ || T^{(K)} || \Gamma_J PJ \rangle = \sum_{r,s} c^r_{\Gamma_J} c^s_{\Gamma_J} \langle \gamma_r PJ || T^{(K)} || \gamma_s PJ \rangle. \tag{15}$$

Table 1. The lowest multiplet of Sm in units of cm^{-1}.

Level	Expt	Cheng and Childs	Porsev	Present work
$^7\mathrm{F}_1$	292.58	237	285	278
$^7\mathrm{F}_2$	811.92	694	811	793
$^7\mathrm{F}_3$	1489.55	1328	1524	1491
$^7\mathrm{F}_4$	2273.09	2100	2377	2325
$^7\mathrm{F}_5$	3125.46	2970	3332	3257
$^7\mathrm{F}_6$	4020.66	3885	4361	4260

Further it can be converted to the reduced matrix elements between the orbitals using

$$\langle \gamma_r PJ || T^{(K)} || \gamma_s PJ \rangle = \sum_{a,b} d^K_{rs}(ab) \langle \psi_a || t^K || \psi_b \rangle, \tag{16}$$

where $d^K_{rs}(ab)$ are the angular factors to convert the reduced matrix element between jj-coupled CSFs to orbitals. Then, A_J and B_J depend on the angular factors $d^K_{rs}(ab)$, the CSF co-efficients $c^r_{\Gamma_J}$ and $c^s_{\Gamma_J}$ and the reduced matrix elements between the orbitals. However, the largest contribution is from the orbital reduced matrix elements. The radial dependence of A and B are r^{-2} and r^{-3} respectively. Due to the negative exponents, A and B has main contributions from the small **r** region where it is a large multiplying factor but a suppression factor in the large **r** region. The accuracy of the hyperfine constants can be considered as the measure of the accuracy of the wave-function in the small **r** region.

4 Results of the calculation

4.1 The MCDF and CI calculations

The ground state configuration $4f^6 6s^2$ generates 295 relativistic CSFs with the total angular momentum J in the range 0 to 12. The ten lowest levels are calculated using the MCDF method. The excitation energies of the ground state multiplet are given in Table 1. The results of earlier calculations [13,14] and the experimental data [21] are also given for comparison. Cheng and Childs calculated the ground state multiplet excitation energies and hyper-fine structures with the MCDF method using Desclaux's code [22]. However, the energy functional is different from the present case. In Desclaux's code the energy of the ASF is the sum of the average CSF energy and the off-diagonal double excitation coulomb matrix elements. This is further corrected with the Breit interaction as perturbation. Porsev calculated the excitation energies and transition properties of the levels in the low-lying multiplets $^7\mathrm{F}_J$,

Table 2. Excitation energy of the low-lying levels of Sm in cm^{-1}.

Level	Expt	Porsev	Present work		
			MCDF	CI1	CI2
$^7\mathrm{F}_1$	292.58	285	276	296	297
$^7\mathrm{F}_2$	811.92	810	790	—	—
$^9\mathrm{G}_0$	13796.36	11339	11147	11444	11533
$^9\mathrm{G}_1$	13999.50	11533	11337	11637	11726
$^9\mathrm{G}_2$	14380.50	11906	11704	—	—
$^9\mathrm{H}_1$	10801.10	12739	13227	12153	11842
$^9\mathrm{H}_2$	11044.90	12693	13444	—	—

$^9\mathrm{H}_J$, $^9\mathrm{D}_J$, $^9\mathrm{G}_J$ and $^9\mathrm{F}_J$. He used CI method with an orbital set in which the core and valence are generated by a Hartree-Fock-Dirac Code and the virtuals are generated as a function of these [23]. The following observations can be made after comparing the theoretical results of the ground state multiplet energies.

1. Cheng and Child's results are below the experimental values. The deviations range from 55.58 cm^{-1} in $^7\mathrm{F}_1$ to 173.09 cm^{-1} in $^7\mathrm{F}_4$.
2. The $^7\mathrm{F}_1$ and $^7\mathrm{F}_2$ excitation energies in Porsev's results are in very good agreement with the experimental values. The remaining levels are slightly higher than the experimental values.
3. Our results also exhibit the same pattern as Porsev's results. However, the higher levels are closer to the experimental data compared to his results.

The size of the CSF space in the MCDF calculation is increased in steps by increasing the number of orbitals and by including odd parity CSFs. None of the orbitals are frozen till the orbital set reaches (1–7)s, (2–7)p, (3–7)d and $4f$. The orbitals (1–6)s, (2–6)p, (3–6)d and $4f$ are spectroscopic type, and $7s$, $7p$ and $7d$ are correlation type. The spectroscopic orbitals have $(n-l-1)$ nodes, where n and l are the principle and orbital quantum numbers respectively. But the correlation orbitals can have any number of nodes. Generating the orbitals in steps without freezing prevents large modifications to the orbitals and avoid convergence failure, which can occur if there are large modifications to the orbitals. At each step the orbitals generated in the previous step are considered as the initial guess. To generate new orbitals Thomas-Fermi and Coulomb orbitals are chosen as the initial guess for spectroscopic and correlation orbitals respectively. The CSF space has all the possible excitations among the valence shells and to the saturation orbitals $7s$, $7p$ and $7d$ but no excitations from the core. The results of the MCDF calculation are given in the Table 2. To reduce the size of the CSF space, only those with $J=0,1,2$ are selected and the total number of CSFs is 39 313. This is a relatively large CSF space for an MCDF calculation, yet the excitation energies have not improved compared to Porsevs's results. It is to be noted that in both the theoretical results, the sequence of excitation energies is different from the experimental data.

Table 3. The groundstate energy E_0 and excitation energy of the $4f^6 5d6s(^9\mathrm{H}_1)$ level $E(^9\mathrm{H}_1)$ in cm^{-1} and n_c is the number of CSFs; and $\Delta E(^9\mathrm{H}_1) = \Delta E_\mathrm{Expt}(^9\mathrm{H}_1) - \Delta E_\mathrm{Theor}(^9\mathrm{H}_1)$.

CSFs	n_c	E_0	$E(^9\mathrm{H}_1)$	$\Delta E(^9\mathrm{H}_1)$
$6s^2+5d6s+5d^2$	5540	-1009	8087	2714.1
$+6p^2$	6974	-4988	12155	-1353.9
$+6s6d+6d^2$	12407	-4778	11908	-1106.9
$6s^2+5d6s+5d^2$ $+6p^2+6s6p+5d6p$	13275	-4816	12846	-2044.9
$+6p6d+6s6d+6d^2$ $+5d6d$	31717	-4880	12593	-1791.9

The effects of electron-correlation at each step of the calculation can be studied by comparing selected properties. The ground state energy E_0 and $4f^6 5d6s(^9\mathrm{H}_1)$ level from each intermediate steps of the calculation are given in the Table 3. In this table the value of the E_0 is shifted by an amount of $-2\,289\,007\,890$ cm^{-1}, which is the value of E_0 in the MCDF calculation with the single configuration $4f^6 6s^2$. The quantity $\Delta E(^9\mathrm{H}_1)$ is the deviation of the calculated energy from the experimental value, that is $\Delta E(^9\mathrm{H}_1) = \Delta E_\mathrm{Expt}(^9\mathrm{H}_1) - \Delta E_\mathrm{Theor}(^9\mathrm{H}_1)$. From the Table 3 we can make the following observations.

1. Comparing the first and second rows in the table shows that the configuration $4f^6 6p^2$ decreases the E_0 by 3 979 cm^{-1} while $E(^9\mathrm{H}_1)$ is increased by 89 cm^{-1}. The shift in E_0 is the result of strong mixing between $4f^6 6s^2$ and $4f^6 6p^2$. And the increased value of $E(^9\mathrm{H}_1)$ indicates that the configuration $4f^6 6p^2$ modifies the $5d$ and $6s$ orbitals differently. The changes in the orbital energies confirms this, while the $6s$ energy changes by -0.0105 a.u. the $5d$ energy change is -0.0041 a.u. The change in $5d$ energy is taken as the mean of the values corresponding to $5d_{3/2}$ and $5d_{5/2}$ orbitals. A possible cause could be that the configuration $4f^6 6p^2$ produces larger modifications to the MCDF potential of $6s$ compared to that of $5d$.
2. The effect of the MCDF potential to the orbitals can be made obvious if the previous trend could be reversed by selective addition of configurations. This is demonstrated by the results in the third row. The configuration added are $4f^6 6s6d$ and $4f^6 6d^2$, the first configuration mixes strongly with the leading configuration in $^9\mathrm{H}_1$, $4f^6 5d6s$. The $6d$ orbital is a correlation orbital. The MCDF calculation result shows that E_0 is elevated by 210 cm^{-1} while $E(^9\mathrm{H}_1)$ is lowered by 48 cm^{-1}. In this calculation, the changes in the energies of $6s$ and $5d$ orbitals are 0.0061 a.u. and 0.0065 a.u. respectively. Since the $6d$ orbital is of a different kind it is not entirely accurate to compare the orbital energy change with the previous calculation.
3. From the third row onwards the calculations include odd parity configurations. The results shows that E_0 and $E(^9\mathrm{H}_1)$ exhibit similar trend observed in the previous calculations while adding $6p$ and $6d$. But both the level energies are larger compared to the calculations

Table 4. The energy and the hyperfine constants A and B for $^7\mathrm{F}_1$ state of $^{147}\mathrm{Sm}$ in units of cm^{-1} and MHz respectively.

CSFs	n_c	A (MHz)	B (MHz)
$6s^2+5d6s+5d^2$	5540	−16.88	−36.34
$+6p^2$	6974	−16.81	−35.91
$+6s6d+6d^2$	12407	−16.84	−35.84
$6s^2+5d6s+5d^2$			
$+6p^2+6s6p+5d6p$	13275	−16.87	−35.99
$+6p6d$ $+6s6d+6d^2$			
$+5d6d$	31717	−16.89	−35.98
Prev [13]		−33.77	−58.88
Expt		−33.493 [24]	−58.688 [24]

without the odd parity configurations. This could be due to the modification of the core orbitals.

The results of a CI calculation using the orbitals generated so far are given in column CI1 in Table 2. The CSF space consists of all the possible single and double excitations from the configurations $4f^66s^2$ and $4f^6s6p$. In total there are 106 234 CSFs in this calculation. To reduce the size of the CSF space only the $J=0$, 1 have been considered in this calculation. The result indicates an improvement in the excited levels compared to the MCDF results: the $^9\mathrm{G}_0$ and $^9\mathrm{G}_1$ increases while $^9\mathrm{H}_1$ decreases. An important configuration which is missing from this calculation is the $4f^55d^26p$, it contributes to the correlation effects of the levels with the leading configuration $4f^65d6s$ like $^9\mathrm{H}_1$. The CI results after including the CSFs corresponding to the configurations $4f^55d^26p$ and $4f^5d^27p$ are given in the column CI2, the number of the CSFs is 114 572 and the excited levels are improved further.

The CI calculations are done using the full Hamiltonian matrix. A test calculation is done to check the CI method combined with the perturbation. The CSFs in the zeroth order group are selected using the mixing coefficients. We find that the same results can be reproduced by treating the CSFs with mixing coefficients less than or equal to 0.0001 perturbatively. Starting from the next virtual orbital layer, the CI calculations are done using this method and these are in progress.

4.2 The hyperfine constants calculations

The hyperfine structure (HFS) constants A and B are calculated at all stages of the computation. And the values for the $4f^66s^2(^7\mathrm{F}_1)$ level corresponding to the sequence of MCDF run in Table 3 are given in Table 4. The HFS constants for other levels are also calculated but the deviation from the experimental data are much larger than that of $4f^66s^2(^7\mathrm{F}_1)$. Comparing the results in Tables 3 and 4 indicates that the HFS constants of the $4f^66s^2(^7\mathrm{F}_1)$ level is very stable even though E_0 undergoes large changes. This is not surprising, since a large number of the CSFs arises due to the addition of configurations with high angular momentum orbitals $5d$ and $6d$. The direct contributions to the HFS constants from these orbitals is negligible. But these can contribute significantly through the orbital polarization, referred as the Sternheimer effect in case of B. However, the configurations in this sequence of calculation are chosen to gauge the nature of valence-valence correlations and its effects. Thus, it is clear that the valence-valence correlation effects has negligible effect on the HFS constants. For a comparison, the results from the previous theoretical calculation of Cheng and Childs [13] and the experimental results are also given.

Table 5. The energy and the hyperfine constants A and B for $^7\mathrm{F}_1$ state in units of cm^{-1} and MHz respectively.

CSFs	n_c	A (MHz)	B (MHz)
$6s^2\xrightarrow{2}6p,(5,6)d$			
$+5s^25p^64f^56s^26p$			
$+5s^25p^54f^66s^26p$			
$+5s5p^64f^66s^26d$	43927	−16.71	−31.34
$+4s^24p^65s^25p^64f^66s^26p$			
$+4s^14p^65s5p^64f^66s^26d$	56481	−16.74	−30.94

The core polarization effects can contribute to the HFS constants through the spin polarization and orbital polarization, the later produces the Sternheimer effect. The core polarization effects in a CI calculation can be introduced by including the configurations with single excitations from the core. The spin polarization contributions from the core s and $p_{1/2}$ excitations could be large for HFS constant A due to the contact interactions. To study these effects, the hyper-fine constants are calculated with the CI wave-functions with the configuration space that has single excitations from $4s$, $4p$, $5s$ and $5p$ to the valence shells. The results are given in Table 5. It is observed that the HFS constant A is not affected by the configurations added but the HFS constant B changes noticeably. This indicates that the configurations added contributes to the Sternheimer effect and not to the core polarization effects that contributes to the HFS constant A. The configurations added in these calculations capture the effect of the valence shell induced core polarization effects and the orbital polarization in particular. The other type of excitations that can contribute to the core polarization effects are the configurations with core electrons excited to the virtual shells. The extensive study of these effects are currently under study. These calculations require longer runtime as the number of CSFs are very large due to the larger number of open shells. In general, the contribution from the core polarization effects are larger than the correlation effects.

The next calculation of the HFS constants is using the MCDF wave-function generated with the saturated configuration space. The results from this calculation are given in Table 6. Both the HFS constant improves by almost equal amount. Since the saturation orbitals $7s$, $7p$, $7d$ and $7f$ contribute to the correlation effects, the change in the HFS constants arises from two contributions: first, the mixing coefficients and second, the presence of low angular momentum orbitals $7s$ and $7p$. It is to be noted

Table 6. The hyperfine constants A and B for $^7\mathrm{F}_1$ state in units of MHz.

CSFs	n_c	A (MHz)	B (MHz)
$6s^2 \xrightarrow{2} 7s, (6\text{–}7)p, (5,7)d$	39313	−23.12	−35.70

that the singly excited CSFs important for the core polarization effects have small mixing coefficients. It is also observed that the HFS constants are stable with respect to changes in the Fermi-nuclear model parameters c and a.

5 Conclusions

From the results of our calculation the following conclusions can be drawn.

1. The sequence of the MCDF calculation shows that the valence-valence correlation effects can influence the properties of the orbitals generated. And the change is sensitive to the configurations chosen. This is due to the strong mixing between the CSFs arising from the open $4f$ shell.
2. Though the core excitation are expected to contribute to the HFS A and B, only the changes in B is significant if the excited orbitals are of high orbital angular momentum. This could due to the limited number of configurations used in the calculation and the added configurations are more important for the Sternheimer effect.
3. The present calculation is one of the largest MCDF calculation to date, yet the discrepancy of the HFS constants from the experimental values is very large. This could improve with more correlation effects included in the calculation. It is also possible that the combination of orbitals and configurations chosen for the MCDF calculations are not the best possible combination.

All the numerical calculations presented in our paper were done using the computing facilities of Institute of Numerical Simulations and Mathematics, Hiroshima University, specially the Paradragon Cluster. One of the authors, Angom Dilip would like to thank the Japan Society for Promotion of Science for the Post-Doctoral Fellowship.

References

1. C.S. Wood, S.C. Bennet, D. Cho, B.P. Masterson, J.L. Roberts, C.E. Tanner, C.E. Weiman, Science **275**, 1759 (1997).
2. A. Derevianko, Phys. Rev. Lett. **85**, 1618 (2000).
3. M.G. Kozlov, S.G. Porsev, I.I. Tupitsyn, `asXiv: physics/0101053`.
4. S.C. Bennet, C.E. Wieman, Phys. Rev. Lett. **82**, 2484 (1999).
5. V.A. Dzuba, V.V. Flambaum, O.P. Sushkov, Phys. Lett. A **141**, 147 (1989).
6. S.A. Blundell, W.R. Johnson, J. Sapirstein, Phys. Rev. Lett. **65**, 147 (1989); S.A. Blundell, W.R. Johnson, J. Sapirstein, Phys. Rev. D **45**, 1602 (1992).
7. M.-A. Bouchiat, C. Bouchiat, Phys. Lett. B **48**, 111 (1974).
8. V.A. Dzuba, V.V. Flambaum, I.B. Khriplovich, Z. Phys. D **1**, 243 (1986).
9. D.M. Lucas, R.B. Warrington, D.N. Stacy, C.D. Thompson, Phys. Rev. A **58**, 3457 (1998).
10. A. Fukumi, I. Endo, T. Horiguchi, Y. Ishida, T. Kondo, T. Kuwamoto, H. Matsuzaki, T. Nakamura, T. Takahashi, Z. Phys. D **42**, 243 (1997).
11. A. Fukumi, I. Endo, T. Horiguchi, M. Iinuma, T. Kondo, H. Matsuzaki, T. Takahashi, `http://photon.hepl.hiroshima-u.ac.jp/members/fukumi/ICAP16`
12. S. Rochester, C.J. Brown, D. Budker, D. DeMille, M. Zolotorev, Phys. Rev. A **59**, 3840 (1999).
13. K.T. Cheng, W.J. Childs, Phys. Rev. A **31**, 2775 (1985).
14. S. G. Porsev, Phys. Rev. A **56**, 3535 (1997).
15. F.A. Parpia, C. Froese Fischer, I.P. Grant, Comp. Phys. Comm. **94**, 249 (1996).
16. K.G. Dyall, I.P. Grant, C.T. Johnson, F.A. Parpia, E.P. Plummer, Comp. Phys. Commun. **55**, 425 (1989).
17. I.P. Grant, H.M. Quiney, Adv. At. Mol. Phys. (Academic Publishers), Vol. 23.
18. E.R. Davidson, J. Comput. Phys. **17**, 87 (1975); Comput. Phys. Commun. **53**, 49 (1989).
19. J. Bieron, F.A. Parpia, C. Froese Fischer, Phys. Rev. A **51**, 4603 (1995).
20. C. Froese Fischer, J. Phys. B **26**, 855 (1993).
21. C. Martin, R. Zalubas, L. Hagen, *Atomic Energy Levels–The Rare Earth Elements*, Natl. Bur. Stand. U.S. Ref. Data Ser. No. NSRDS-NBS 60 (U.S. GPO, Washington, DC, 1978).
22. J.P. Desclaux, Comp. Phys. Commun. **9**, 31 (1974).
23. M.G. Kozlov, S.G. Porsev, V.V. Flambaum, J. Phys. B **29**, 689 (1996).
24. W.J. Childs, L.S. Goodman, Phys. Rev. A **6**, 2011 (1972).