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Correlation trends in the magnetic hyperfine structure of atoms: A relativistic coupled-cluster case study

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The role of electron correlation in the hyperfine structure of alkali metals and alkaline earth metal monopositive ions in their ground electronic configuration is investigated using the *Z*-vector method in a relativistic coupled-cluster regime within the singles and doubles approximation. The systematic effects of core-correlating functions, polarization of core electrons, and high-lying virtual functions on core electrons correlation are studied. The study reveals that the core-correlating function plays a significant role in core polarization and thus is very important for precise calculation of the wave function near the nuclear region. The inner-core electrons ($1s$-$2p$) require very high virtual energy functions for proper correlation. Therefore, the all-electron correlation treatment and the inclusion of higher-energy virtual functions are the key factors for precise calculation of the hyperfine structure constant of atoms. Our calculated values are in excellent agreement with the available experimental values, which also implies that the wave function produced by the *Z*-vector method is accurate enough for further calculation of the parity- and time-reversal symmetry-violating properties in atoms and molecules.

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I. INTRODUCTION

Correlation effects of electrons are very important for precise calculation of the chemical and spectroscopic properties of atomic and molecular systems. Similarly, the relativistic effect is another key factor for accurate description of the energy levels and various properties of atoms, ions, and molecules. Usually relativistic effects are more prominent in heavy systems. Accurate theoretical methods which properly incorporate both effects have always been in demand in the areas of quantum physics and chemistry. Although the Dirac-Hartree-Fock (DHF) method can extensively take care of the effect of relativistic motion of electrons, it misses the static and dynamic correlation of the opposite-spin electrons due to the single-determinant nature of the wave function. For proper treatment of the missing electron correlation, a number of correlation methods, *viz.*, the multiconfigurational self-consistent field theory [1,2], configuration interaction (CI) [1,3], many-body perturbation theory [1], and coupled-cluster (CC) method [4–6], are widely used. Of all these, the single-reference coupled-cluster (SRCC) methodology, which incorporates dynamic correlation effects to all orders and is size extensive at any level of truncation, is perhaps the most efficient and reliable tool for correlation calculation with the best possible accuracy in many-electron systems. Normally, CC equations are solved nonvariationally to obtain the energy, which is not necessarily upper bound to the exact energy of the system [7]. Also, it does not satisfy the generalized Hellmann-Feynman theorem. It is a well-known fact that the expectation value method and energy derivative method to calculate first-order properties are not identical in the nonvariational approach [8,9]. The energy derivative method to calculate first-order properties of atoms, molecules, or ions is found to be better than the expectation value method. The *Z*-vector approach [10] and the Lagrange multiplier method of Helgaker and coworkers [11] within the nonvariational CC framework are widely used to calculate the energy derivative. However, it is worth mentioning that the CC energy equation can also be solved variationally. The variational coupled-cluster approach satisfies the generalized Hellmann-Feynman theorem, which is very important for higher-order property calculations. The expectation value coupled-cluster [12,13], unitary coupled-cluster [14,15], and extended coupled-cluster [16–18] are well-known variational CC methods in the literature.

The above-mentioned coupled-cluster CC-based methods have been well developed as well as implemented in the nonrelativistic framework to calculate various properties of atoms, ions, and molecules. However, these methods need to be introduced into the relativistic domain for accurate calculation of the properties of heavy systems as well as for study of properties such as parity nonconservation effects and the electric dipole moment of the electron. Parity nonconservation and the electric dipole moment can only be explained with the help of relativistic theory. In recent times, many groups have successfully extended these methods to the relativistic regime for accurate investigation of the structure and properties of many-electron atomic and molecular systems. For example,

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the Kramers-restricted closed-shell CC method with single and double excitation (CCSD) developed by Visscher *et al.* [19], Kramers-unrestricted open-shell CCSD method with the inclusion of partial triple excitation [CCSD(T)] by Visscher *et al.* [20], relativistic multi-reference Fock-space CC theory [21], relativistic coupled-cluster-based linear response theory [22], two-component Kramers-resticted CCSD and CCSD(T) method using the effective core potential [23], and relativistic Fock-space CC theory developed by Ishikawa and coworkers [24–26] are widely used relativistic CC-based methods in the literature. Moreover, a two-step relativistic correlation method was also developed by Petrov *et al.* [27] especially to calculate the symmetry-violating effects in heavy systems. This method is primarily based on the generalized relativistic effective core potential and relativistic CC methods. On the other hand, Sasmal *et al.* recently implemented the relativistic extended coupled-cluster method [28] and the *Z*-vector technique in the relativistic coupled-cluster framework [29] to calculate various first-order properties of atoms, ions, and molecules in their ground states. Similarly, Saue and coworkers [30] have reported the orbital-unrelaxed four-component relativistic SRCC analytical technique based on the Lagrange multiplier method of Helgaker, to calculate first-order one-electron properties. So, it is evident from the literature that the relativistic CC method in recent times has emerged as the most reliable and efficient method to precisely investigate the structure of atoms and molecules and their properties, especially the hyperfine structure (HFS) interaction constant and various symmetry violations [31–39]. Moreover, it is noteworthy that accurate theoretical calculation of the magnetic HFS coupling constant using relativistic CC-based methods has been a gateway to study various important and interesting properties, especially the parity nonconservation and electric dipole moment in atoms and molecules.

The phenomenon of magnetic HFS interaction arises due to the interaction of the nuclear magnetic moment with the electromagnetic field generated by electrons. It plays a very significant role in the accurate description of energy levels of atoms, ions, and molecules. Accurate measurements of HFS constants are essential from the point of view of atomic and nuclear physics, as the knowledge of accurate energy levels helps physicists enormously to study high-precision spectroscopy, laser cooling, atomic clock and atom-trapping experiments, ultracold collision, Bose-Einstein condensation, and many more subjects [40–42]. Like the HFS constant, the theoretical investigation of parity and time-reversal symmetry violation (*P*,*T*-odd properties) requires precise wave function in the near-nuclear region [43–45]. Explicit study of *P*,*T*-odd interactions in atoms and molecules can explore "new physics" beyond the standard model. As various *P*,*T*-odd constants cannot be measured directly from the experiment, they have to be calculated theoretically and the accuracy of these calculations can be assessed by comparing the theoretically calculated HFS constant with the available experimental value. Most alkali metal atoms and monopositive alkaline earth metal ions are considered to be potential candidates in many of the above-mentioned experiments. Thus, accurate calculation of the magnetic HFS constants of these atomic systems as well as study of the role of electron correlation in these calculations is significantly important. As the hyperfine structure interaction is very sensitive to the wave function near the nuclear region, simultaneous inclusion of relativistic effects and the electron correlation is extremely important for precise calculation of the HFS constant. Therefore, theoretical methods based on the coupled-cluster theory extended in the relativistic regime would be the proper choice to deal with HFS constant calculation. Angom and coworkers recently calculated the HFS constants of Mg^+, Ca^+, Sr^+, and Ba^+ using the relativistic coupled-cluster theory [46]. The HFS constant of alkali metals and alkaline earth metal monopositive ions has also been successfully calculated using the relativistic extended coupled-cluster method [28] and *Z*-vector technique [47] in the relativistic CC framework.

In this paper, we demonstrate the correlation trends in the HFS calculation of atoms or ions. We calculated the HFS constant of alkali metal and alkaline earth metal monopositive ions using the *Z*-vector technique in the relativistic coupled-cluster regime. The calculated HFS values are compared with the available experimental values to check the reliability of our method in producing precise wave functions near the nuclear region. The paper is organized as follows. A brief overview of the *Z*-vector method in the CC framework including concise details of the magnetic HFS constant is given in Sec. II. Computational details are reported in Sec. III. We present and discuss our calculated results in Sec. IV, before the conclusion in Sec. V. Atomic units are used throughout unless otherwise stated.

II. THEORY

A. *Z*-vector method

The Dirac-Hartree-Fock method is the most elegant way to incorporate the relativistic effect in many-electron systems and also to describe the ground state in a single-determinant theory. Hence, the four-component DHF wave function is used as a reference function for treatment of the dynamic electron correlation. We have used the Dirac-Coulomb (DC) Hamiltonian, where the interelectronic repulsion term is approximated as the Coulomb interaction and is given by

$$H_{\mathrm{DC}} = \sum_i \Big[-c(\vec{\alpha}\cdot\vec{\nabla})_i + (\beta - \mathbb{1}_4)c^2 + V^{\mathrm{nuc}}(r_i) + \sum_{j>i} \frac{1}{r_{ij}} \mathbb{1}_4 \Big]. \tag{1}$$

Here, $\boldsymbol{\alpha}$ and β are the conventional Dirac matrices, c is the speed of light, and $\mathbb{1}_4$ is the 4×4 identity matrix. $V^{\mathrm{nuc}}(r_i)$ is the nuclear potential function and here we have used the Gaussian-type charge distribution. The DHF method misses the correlation between opposite-spin electrons, as it approximates the interelectronic repulsion in an average way.

In this work, we have employed the SRCC (with the singles and doubles approximation) method to include the missing dynamic electron correlation. The SRCC wave function is given by $|\Psi_{\mathrm{cc}}\rangle = e^T|\Phi_0\rangle$, where Φ_0 is the DHF determinant and T is the CC excitation operator, which can be defined as

$$T = T_1 + T_2 + \cdots + T_N = \sum_n^N T_n, \tag{2}$$

with

$$T_m = \frac{1}{(m!)^2} \sum_{ij\ldots ab\ldots} t_{ij\ldots}^{ab\ldots} a_a^\dagger a_b^\dagger \ldots a_j a_i. \tag{3}$$

Here, i, j and a, b are the occupied and unoccupied spinor indices, respectively. $t_{ij\ldots}^{ab\ldots}$ is the cluster amplitude of the cluster operator T_m. In the case of the coupled-cluster method within the singles and doubles (CCSD) approximation, $T = T_1 + T_2$. The respective amplitude equations for T_1 and T_2 are given by

$$\langle \Phi_i^a | (H_N e^T)_c | \Phi_0 \rangle = 0, \quad \langle \Phi_{ij}^{ab} \big| (H_N e^T)_c | \Phi_0 \rangle = 0. \tag{4}$$

Here, H_N is the normal-ordered DC Hamiltonian. The subscript c in the expression means only that the connected terms exist in the contraction between H_N and T. This connectedness ensures the size extensivity of the CCSD model. Once the amplitude equations are solved, the correlation energy can be calculated by the following equation:

$$E^{\mathrm{corr}} = \langle \Phi_0 | (H_N e^T)_c | \Phi_0 \rangle. \tag{5}$$

As we have adopted the nonvariational approach to solve the CCSD energy equation, the CC energy is not optimized with respect to C_D and C_M for a fixed nuclear geometry [8]. Here, C_D and C_M are the determinantal coefficient and the molecular orbital coefficient, respectively, in the expansion of the many-electron correlated wave function. Therefore, for calculation of the derivative of energy with respect to any external field of perturbation, we must include both the derivative of the energy with respect to C_D and C_M and the derivative of these two parameters with respect to the external perturbation. The equations for these derivative terms are linear but perturbation dependent. However, in the so-called Z-vector technique, the derivative terms which involve the determinantal coefficient can be included by introducing a perturbation-independent linear operator, Λ [10]. Thus, in the Z-vector approach, any number of properties can be calculated with the solution of just one set of T and Λ amplitudes. The second quantized form of the deexcitation operator, Λ, is given as

$$\Lambda = \Lambda_1 + \Lambda_2 + \cdots + \Lambda_N = \sum_n^N \Lambda_n, \tag{6}$$

with

$$\Lambda_m = \frac{1}{(m!)^2} \sum_{ij\ldots ab\ldots} \lambda_{ab\ldots}^{ij\ldots} a_i^\dagger a_j^\dagger \ldots a_b a_a, \tag{7}$$

where $\lambda_{ab\ldots}^{ij\ldots}$ is the cluster amplitude of the operator Λ_m. Within the CCSD framework, $\Lambda = \Lambda_1 + \Lambda_2$ and the explicit equations for the amplitudes of the Λ_1 and Λ_2 operators are given by

$$\langle \Phi_0 | [\Lambda (H_N e^T)_c]_c \big| \Phi_i^a \big\rangle + \langle \Phi_0 | (H_N e^T)_c \big| \Phi_i^a \big\rangle = 0, \tag{8}$$

$$\begin{aligned} &\langle \Phi_0 | [\Lambda (H_N e^T)_c]_c \big| \Phi_{ij}^{ab} \big\rangle + \langle \Phi_0 | (H_N e^T)_c \big| \Phi_{ij}^{ab} \big\rangle \\ &+ \langle \Phi_0 | (H_N e^T)_c \big| \Phi_i^a \big\rangle \big\langle \Phi_i^a \big| \Lambda \big| \Phi_{ij}^{ab} \big\rangle = 0. \end{aligned} \tag{9}$$

Finally, the energy derivative can be obtained as

$$\Delta E' = \langle \Phi_0 | (O_N e^T)_c | \Phi_0 \rangle + \langle \Phi_0 | [\Lambda (O_N e^T)_c]_c | \Phi_0 \rangle, \tag{10}$$

where O_N is nothing but the derivative of the normal-ordered perturbed Hamiltonian with respect to the external field of perturbation.

B. Magnetic hyperfine structure constant

The magnetic moment of the nucleus interacts with the internally generated electromagnetic field of electrons in an atom, ion, or molecule. This interaction, which causes small shifts and splitting of energy levels, is known as the magnetic hyperfine structure interaction [48]. The magnetic vector potential ($\vec{A}$) of a nucleus (k) at a distance $\vec{r}$ is given by

$$\vec{A} = \frac{\vec{\mu}_k \times \vec{r}}{r^3}, \tag{11}$$

where $\vec{\mu}_k$ is the magnetic moment of the nucleus. The perturbed HFS Hamiltonian of an atom or ion due to $\vec{A}$ is defined in Dirac

TABLE I. Effect of core-correlation functions in the calculation of the magnetic HFS constant, A_J (in MHz), of atoms in the ground electronic state. Basis used in the present work: dyall.ae3z for Rb, Fr, Sr$^+$, and Ra$^+$; dyall.ae4z for Li, Na, K, Cs, Be$^+$, Mg$^+$, Ca$^+$, Ba$^+$, and the basis used in Ref. [47]: aug-cc-pCVQZ for Li, Na, Be$^+$, and Mg$^+$; dyall.cv3z for Rb, Fr, Sr$^+$, and Ra$^+$; and dyall.cv4z for K, Cs, Ca$^+$, and Ba$^+$.

	Virtual	Z vector			$\delta\%$	
Atom	cutoff (a.u.)	This work	Ref. [47]	Expt.	This work	Ref. [47]
^{7}Li		399.1	391.6	401.7 [55]	0.6	2.6
^{23}Na		875.6	861.4	885.8 [55]	1.2	2.8
^{39}K	500	226.6	226.6	230.8 [55]	1.9	1.9
^{85}Rb	500	986.5	986.5	1011.9 [56]	2.6	2.6
^{133}Cs	40	2218.2	2218.4	2298.1 [57]	3.6	3.6
^{223}Fr	50	7584.5	7537.4	7654(2) [58]	0.9	1.5
^{9}Be$^+$		−622.9	−612.9	−625.0 [59]	0.3	2.0
^{25}Mg$^+$		−594.4	−584.8	−596.2 [60]	0.3	1.9
^{43}Ca$^+$	500	−801.4	−801.5	−806.4 [61]	0.6	0.6
^{87}Sr$^+$	100	−978.0	−977.9	−1000.5(1.0) [62]	2.3	2.3
^{137}Ba$^+$	40	3930.7	3930.2	4018.9 [63]	2.2	2.3
^{223}Ra$^+$	50	3464.8	3446.3	3404(2) [64,65]	1.7	1.2

theory as

$$H_{\text{hyp}} = \sum_{i}^{n} \vec{\alpha}_i . \vec{A}_i . \tag{12}$$

Here, n is the total number of electrons and $\vec{\alpha}_i$ denotes the Dirac α matrices for the ith electron.

The magnetic HFS constant (A_J) of an atom or ion in the Jth electronic state can be obtained as

$$A_J = \frac{\vec{\mu}_k}{IJ} \cdot \langle \Psi_J | \sum_{i}^{n} \left(\frac{\vec{\alpha}_i \times \vec{r}_i}{r_i^3} \right) | \Psi_J \rangle, \tag{13}$$

where Ψ_J is the wave function of the Jth electronic state and I is the nuclear spin quantum number.

III. COMPUTATIONAL DETAILS

The DHF equation is solved by using the locally modified version of the DIRAC10 [49] program package, and one- and two-electron integrals along with the HFS property integrals are extracted by using a locally modified version of the same package. A finite-size nucleus with a Gaussian charge distribution is considered in our calculation. The default values of DIRAC10 are used for the nuclear parameters of the respective atom [50]. The restricted kinetic balance condition [51] is used to generate a small component basis from the large component basis. The "no virtual pair approximation" is considered when solving the DHF equation to remove the negative-energy solutions. We have used the following uncontracted all-electron multiple-zeta basis sets in our calculations: triple-zeta (TZ) basis, dyall.ae3z [52–54]; and quadruple-zeta (QZ) basis, dyall.ae4z [52–54].

IV. RESULTS AND DISCUSSION

The purpose of the present work is the precise calculation of the magnetic HFS constant of alkali metal atoms as well as monopositive alkaline earth metal ions in their ground-state electronic configuration and the study of electron-correlation trends in the hyperfine structure of these systems using the Z-vector method in the relativistic CC framework. Recently, Sasmal calculated the magnetic HFS constant of these systems using the same method [47]. However, in his study the core-valence multiple-zeta (cvNz) basis was used, which lacks some important core-correlating functions. That is why in this study we have used the all-electron multiple-zeta (aeNz) basis, which is designed for all-electron calculation and can treat the core-polarization effect more efficiently than the cvNz basis.

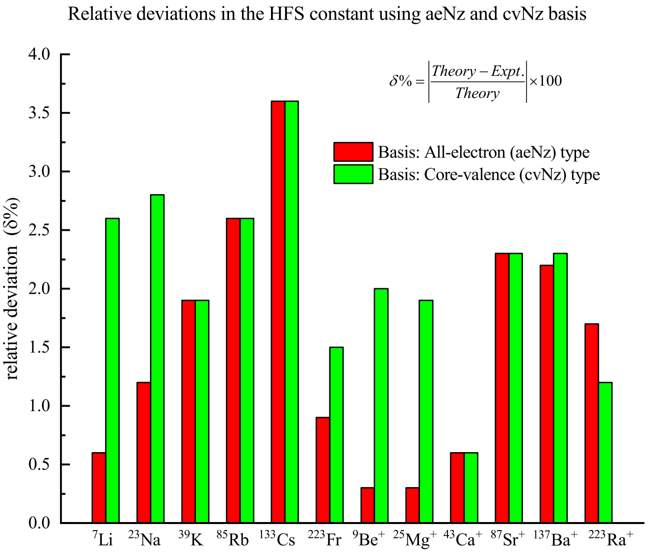

FIG. 1. Relative deviations of the HFS constant using the aeNz and cvNz basis.

In Table I, we compare our aeNz basis results with the core-valence basis results obtained from Ref. [47] using the same cutoff as in the said reference. We also present the relative deviation of the calculated magnetic HFS value from the experimental value as $\delta\%$. A comparison of $\delta\%$ values is shown in Fig. 1. From Table I and Fig. 1, it is clear that the inclusion of core-correlating functions does not show any significant effect in the cases of ^{39}K, ^{43}Ca$^+$, ^{85}Rb, ^{87}Sr$^+$, ^{133}Cs, and ^{137}Ba$^+$. But it is noticeable that relativistic all-electron multiple-zeta-basis calculations significantly improve our results compared to those in Ref. [47] in the cases of ^{7}Li, ^{9}Be$^+$, ^{23}Na, and ^{25}Mg$^+$. Also, in the heaviest atoms in our study, *viz.*, ^{223}Fr and ^{223}Ra$^+$, HFS values are affected by the inclusion of some core-correlating functions. Use of the

TABLE II. Magnetic HFS constant, A_J (in MHz), of atoms in the ground electronic state.

Atom	Basis	Virtual cutoff (a.u.)	Z vector	DHF	Expt.	$\delta\%$ (Z vector)
^{7}Li	dyall.ae4z		399.1	288.2	401.7 [55]	0.6
^{23}Na	dyall.ae4z		875.6	633.4	885.8 [55]	1.2
^{39}K	dyall.ae4z	5000	227.9	151.0	230.8 [55]	1.3
^{85}Rb	dyall.ae4z	4000	1001.0	666.9	1011.9 [56]	1.0
^{133}Cs	dyall.ae4z	1000	2266.1	1495.5	2298.1 [57]	1.4
^{223}Fr	dyall.ae3z	1000	7761.0	5518.0	7654(2) [58]	1.4
^{9}Be$^+$	dyall.ae4z		−622.9	−506.6	−625.0 [59]	0.3
^{25}Mg$^+$	dyall.ae4z		−594.4	−471.7	−596.2 [60]	0.3
^{43}Ca$^+$	dyall.ae4z	7000	−805.3	−606.2	−806.4 [61]	0.1
^{87}Sr$^+$	dyall.ae4z	3000	−1000.2	−760.9	−1000.5(1.0) [62]	0.02
^{137}Ba$^+$	dyall.ae3z	1000	4028.3	3061.9	4018.9 [63]	0.2
^{223}Ra$^+$	dyall.ae3z	1000	3538.0	2843.4	3404(2) [64,65]	3.8

TABLE III. Effect of inner-core electrons at different cutoffs of virtual spinors.

Basis		Cutoff (a.u.)		Spinor		Correlation	A_J	$\delta\%$
Name	Nature	Occupied	Virtual	Occupied	Virtual	energy (a.u.)	(MHz)	
^{85}Rb								
dyall.ae3z	TZ		50.0	37	213	−1.1605359	961.8	5.2
dyall.ae3z	TZ		1000.0	37	283	−1.5014829	990.9	2.1
dyall.ae3z	TZ		10000.0	37	327	−1.5374646	996.1	1.6
dyall.ae3z	TZ	−50.0	50.0	27	213	−1.0159187	952.4	6.2
dyall.ae3z	TZ	−50.0	1000.0	27	283	−1.0512570	959.7	5.4
dyall.ae3z	TZ	−50.0	10000.0	27	327	−1.0513454	959.8	5.4
dyall.ae3z	TZ	−6.0	50	19	213	−0.68818907	922.7	9.7
dyall.ae3z	TZ	−6.0	1000	19	283	−0.69450181	925.9	9.3
dyall.ae3z	TZ	−6.0	10000	19	327	−0.69450430	925.9	9.3
^{87}Sr$^+$								
dyall.ae3z	TZ		50.0	37	215	−1.14620563	−968.0	3.3
dyall.ae3z	TZ		1000.0	37	289	−1.51939462	−990.2	1.0
dyall.ae3z	TZ		10000.0	37	329	−1.5577899	−998.5	0.2
dyall.ae3z	TZ	−50.0	50.0	27	215	−1.01635428	−958.8	4.3
dyall.ae3z	TZ	−50.0	1000.0	27	289	−1.06899997	−963.7	3.8
dyall.ae3z	TZ	−50.0	10000.0	27	329	−1.0691097	−963.9	3.8
dyall.ae3z	TZ	−7.0	50.0	19	215	−0.70568002	−928.9	7.7
dyall.ae3z	TZ	−7.0	1000.0	19	289	−0.71484442	−931.1	7.4
dyall.ae3z	TZ	−7.0	10000.0	19	329	−0.71484786	−931.1	7.4
^{133}Cs								
dyall.ae3z	TZ		40.0	55	221	−1.47336828	2190.4	4.9
dyall.ae3z	TZ		500.0	55	307	−2.23544909	2246.1	2.3
dyall.ae3z	TZ		1000.0	55	339	−2.37355408	2256.1	1.9
dyall.ae3z	TZ	−100.0	40.0	45	221	−1.44526106	2186.1	5.1
dyall.ae3z	TZ	−100.0	500.0	45	307	−1.91396340	2223.9	3.3
dyall.ae3z	TZ	−100.0	1000.0	45	339	−1.92641235	2225.2	3.3
dyall.ae3z	TZ	−30.0	40.0	37	221	−1.32223526	2165.9	6.1
dyall.ae3z	TZ	−30.0	500.0	37	307	−1.55549141	2185.6	5.1
dyall.ae3z	TZ	−30.0	1000.0	37	339	−1.55955339	2186.0	5.1
^{137}Ba$^+$								
dyall.ae3z	TZ		40.0	55	219	−1.43005838	3926.0	2.4
dyall.ae3z	TZ		500.0	55	315	−2.28562448	4012.9	0.1
dyall.ae3z	TZ		1000.0	55	337	−2.38526100	4028.3	0.2
dyall.ae3z	TZ	−100.0	40.0	45	219	−1.41292899	3917.6	2.6
dyall.ae3z	TZ	−100.0	500.0	45	315	−1.94880958	3964.1	1.4
dyall.ae3z	TZ	−100.0	1000.0	45	337	−1.95870556	3965.8	1.3
dyall.ae3z	TZ	−35.0	40.0	37	219	−1.30837365	3877.9	3.6
dyall.ae3z	TZ	−35.0	500.0	37	315	−1.58809244	3895.7	3.2
dyall.ae3z	TZ	−35.0	1000.0	37	337	−1.59176867	3896.1	3.1

dyall.aeNz basis improves the result for ^{223}Fr, whereas for ^{223}Ra$^+$, the HFS value deviates more from the experiment. However, the cutoffs for the virtual spinors considered in the above calculations are small in most cases. Therefore, for proper correlation treatment of the inner-core electrons we have performed another set of calculations using the all-electron multiple-zeta (dyall.aeNz) basis at very high cutoffs for virtual spinors. We have summarized these results in Table II. It is clearly shown in this table that the HFS values obtained by the Z-vector method are in excellent agreement with the experiment. The relative deviations in our calculation are less than 1.5% in all cases considered except for ^{223}Ra$^+$. As we have used the all-electron multiple-zeta basis and explicitly correlated all the electrons in our calculations, accuracy of this kind is expected. However, it is worth mentioning that various other effects such as a higher-order correlation, Breit and QED effects, a negative energy spectrum, and the Bohr-Weisskopf effect have not been taken into account, which could yield some error in our calculations. This might be the reason that the HFS value calculated in the better basis set deviates more from the experiment, especially in the ^{223}Ra$^+$ case.

In Table III, we present the A_J and $\delta\%$ values for ^{85}Rb, ^{87}Sr$^+$, ^{133}Cs, and ^{137}Ba$^+$ systems with different numbers of correlating electrons and virtual cutoffs to understand the effect of virtual orbitals on the core-correlation effect. For this purpose, we have performed three sets of calculations: first, by correlating all the electrons; second, by freezing the 10 lowest-occupied spinors ($1s$-$2p$); and, finally, by freezing the 18 lowest-occupied spinors ($1s$-$3p$). Furthermore, in each set, we have performed calculations with three different cutoffs

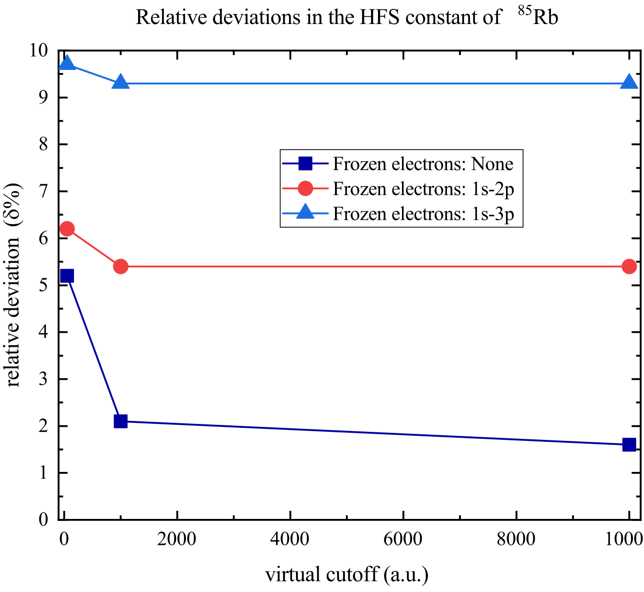

FIG. 2. Relative deviations of the HFS constant of ^{85}Rb.

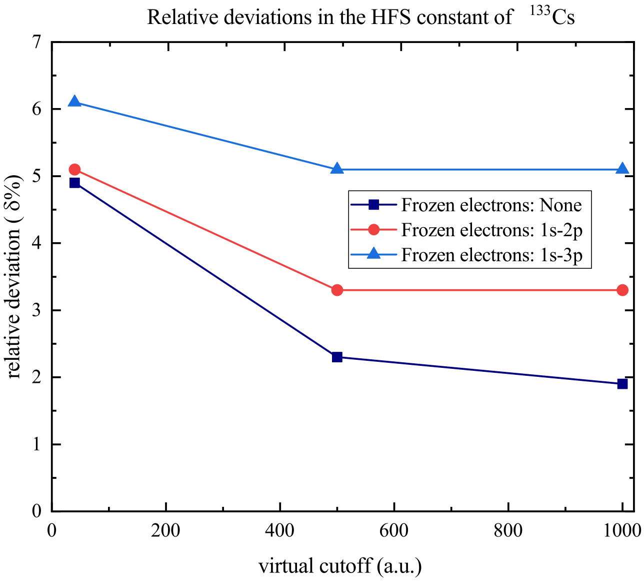

FIG. 4. Relative deviations of the HFS constant of ^{133}Cs.

for the virtual spinor. The $\delta\%$ of the magnetic HFS value for ^{85}Rb, ^{87}Sr$^+$, ^{133}Cs, and ^{137}Ba$^+$ of these calculations is shown in Figs. 2, 3, 4, and 5, respectively. Now, from Table III and Figs. 2–5 it is clear that when we increase the cutoff of the virtual orbital while keeping the number of electrons in the correlation calculation constant, the $\delta\%$ decreases. This is due to the fact that by increasing the virtual cutoff, we are adding more and more correlation space, and thus, the associated error decreases. It is also evident that with the same cutoff, as we correlate more core electrons, the $\delta\%$ decreases. This is expected as, by correlating more core electrons, we are treating the core-polarization effect more explicitly, and hence, this results in a better agreement with the experimental result.

It is interesting to see that the effect of virtual orbitals is more prominent when the core electrons are present in the correlation calculation. For example, the virtual orbitals having an energy between 1000 and 10 000 a.u. for ^{85}Rb and ^{87}Sr$^+$ and between 500 and 1000 a.u. for ^{133}Cs and ^{137}Ba$^+$ have no or a very insignificant effect on the electrons except for $1s$-$2p$ electrons. This is evident from the fact that $\delta\%$ does not change when we increase the virtual cutoff by the said amount of these systems except for all-electron calculations. On the other hand, this effect is significant when $1s$-$2p$ electrons are correlated in those systems. These observations lead us to conclude that to properly correlate $1s$-$2p$ electrons, we need high-energy virtual orbitals in the correlation calculation.

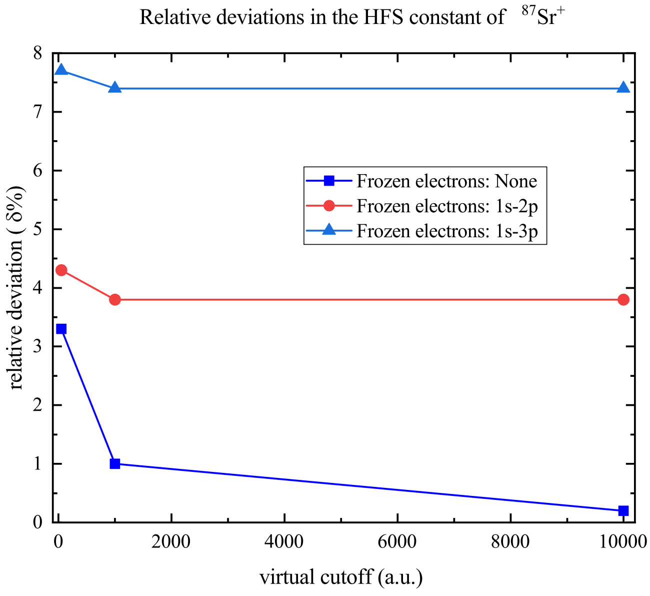

FIG. 3. Relative deviations of the HFS constant of ^{87}Sr$^+$.

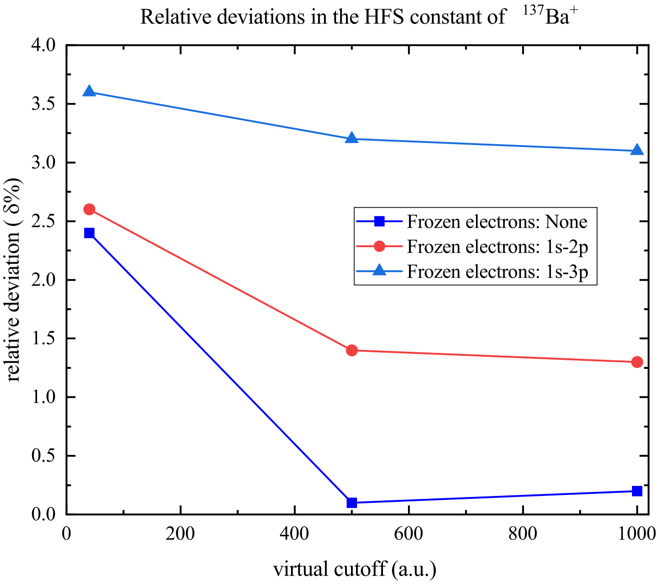

FIG. 5. Relative deviations of the HFS constant of ^{137}Ba$^+$.

V. CONCLUSION

In conclusion, we have implemented the *Z*-vector method in the relativistic coupled-cluster framework for calculation of the magnetic HFS constant of alkali metals and alkaline earth metal monopositive ions. We have demonstrated the importance of the electron correlation and studied the correlation trends in the hyperfine structure calculation. Our calculated values are in excellent agreement with the corresponding experimental values, which means that the *Z*-vector technique can produce a precise wave function near the nuclear region. Thus, this method is very reliable for studying parity and time-reversal symmetry violations in atomic systems to explore the physics beyond the standard model. Our calculation also shows that core-correlation effects of electrons play a very significant role in the calculation of the HFS constant of atoms and ions. Furthermore, our study infers that inner-core ($1s$-$2p$) electrons need higher-virtual-energy functions for proper correlation, which is obvious due to the fact that the higher-virtual-energy functions are localized in the same area as spanned by the inner-core ($1s$-$2p$) spinors.

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