# Calculation of the magnetic hyperfine structure constant of alkali metals and alkaline-earth-metal ions using the relativistic coupled-cluster method

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The $Z$-vector method in the relativistic coupled-cluster framework is used to calculate the magnetic hyperfine structure constant ($A_J$) of alkali metals and singly charged alkaline earth metals in their ground state electronic configuration. The $Z$-vector results are in very good agreement with the experiment. The $A_J$ values of Li, Na, K, Rb, Cs, Be$^+$, Mg$^+$, Ca$^+$, and Sr$^+$ obtained in the $Z$-vector method are compared with the extended coupled-cluster results taken from Phys. Rev. A **91**, 022512 (2015). The same basis and cutoff are used for the comparison purpose. The comparison shows that the $Z$-vector method with the single and double approximation can produce a more precise wave function in the nuclear region than the ECC method.

## I. INTRODUCTION

The interaction of an electromagnetic field of electrons with the nuclear moments of the nucleus, known as hyperfine structure interaction, causes a small shift and splitting of energy levels [1]. Therefore, it is very important for the accurate description of energy levels of the atom, molecule, and ion. The precise measurements of the energy levels of alkali metals play an important role in various areas of atomic and nuclear physics as they are extensively used in high-precision spectroscopy, laser cooling and trapping of atoms, ultracold collision studies, photo-association spectroscopy, Bose-Einstein condensation, and more recently, tests for parity and time reversal violation. Currently, the hyperfine transition of the Cs atom [[Xe]$6S(^2S_{1/2}, F = 3, m_F = 0) \leftrightarrow$ [Xe]$6S(^2S_{1/2}, F = 4, m_F = 0)$] is used as the frequency standard, which is accurate up to 1 per $10^{15}$ [2]. Singly ionized alkaline earth metal ions are insensitive to the perturbation of the environment arising form collisions and Doppler shift and thus, have been considered as potential candidates for the optical frequency standard [3–6]. The $^2S_{1/2}$ ground state of these ions is regarded for quantum information processing studies to encode quantum bits into hyperfine levels because of their long phase coherence due to their small energy gap and relatively large spontaneous decay lifetime [7,8].

Recently, experiments for parity nonconservation (PNC) have become a cutting-edge topic as it can test the accuracy of fundamental physics and explore new physics beyond the standard model. However, the PNC amplitudes, which are very essential to determine the value of PNC constants, cannot be measured experimentally and thus, have to be obtained theoretically. Therefore, it is extremely important to have a reliable way of determining the accuracy of such theoretical calculations. The PNC amplitudes are very sensitive to the accuracy of the wave function in the near nuclear region [9,10]. The same is true for HFS constants [11]. Therefore, one can assess the accuracy of PNC amplitudes by comparing theoretically obtained HFS constants with corresponding experimental values [12–14].

Relativistic effects are very important for the precise calculation of the wave function in the near nuclear region. For a single determinant theory, the best way to include the relativistic effect is to solve the four-component Dirac-Hartree-Fock (DHF) equation. However, the DHF method misses the instantaneous interaction of opposite spin electrons. Coupled-cluster (CC) [15–17] is the most elegant method to include this dynamic electron correlation.

The coupled-cluster equation can be solved either variationally or nonvariationally. Although the nonvariational coupled cluster, also known as the normal coupled cluster (NCC), is the most familiar, the variational coupled cluster (VCC) has several advantages over the NCC. The VCC, being variational, has upper boundedness in energy and satisfies the generalized Hellmann-Feynman (GHF) theorem, which simplifies the calculations for higher order properties. The unitary coupled cluster (UCC) [18–23], expectation value coupled cluster (XCC) [24–27], and extended coupled cluster (ECC) [28,29] are the most familiar VCCs [30] in the literature. Recently, ECC has been extended to the relativistic regime to calculate magnetic HFS constants of atoms and molecules [31]. ECC uses dual space of right and left vectors in a double linked form where the left vector is not complex conjugate of the right vector. Although the ECC functional is a terminating series, the natural termination leads to very expensive terms. Thus, for practical purposes, one needs to use some truncation scheme to avoid computationally expensive terms.

On the other hand, the NCC is nonvariational and, thus, does not satisfy the GHF theorem. Therefore, the expectation value and first order energy derivative yield different results [32,33]. However, the energy derivative method is superior than the expectation value method as the property value obtained in the energy derivative method can be expressed as the corresponding expectation value plus some additional terms which make it closer to the full configuration interaction property value. The NCC energy is not optimized with respect to determinantal coefficients ($C_d$) in the expansion of many electron wave function [32]. Thus, the derivative of energy with respect to external perturbation requires the derivative of energy with respect to $C_d$ times the derivative of $C_d$ with respect to external perturbation. The derivative terms involving $C_d$ can be included in the $Z$-vector [34,35] method by

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introducing a perturbation independent de-excitation operator where the equation for this operator is linear. Thus, for any number of property calculation, one needs to calculate only one set of coupled-cluster amplitudes. The advantage of the $Z$-vector method over the ECC method is that unlike ECC, the equations for excitation operators are decoupled from the de-excitation operators. This saves enormous computational cost. Recently the $Z$-vector method has been extended to the relativistic region for the calculation of ground state properties of atomic and molecular systems [36].

In this paper, we have calculated the magnetic HFS constant of alkali metal atoms and singly charged alkaline earth metal cations using the $Z$-vector technique in the relativistic coupled-cluster framework. We have compared the $Z$-vector values with the ECC values calculated in Ref. [31] to show that the $Z$-vector method with single and double approximation can produce a much better wave function in the nuclear region of the atomic nucleus than the ECC method with the approximation stated in the paper and, thus, is capable of providing the precise value of the types of property like PNC amplitudes, which are prominent in the nuclear region. The paper is organized as follows. A brief introduction and the workable equations for the $Z$-vector method are given in Sec. II followed by the matrix elements for the magnetic HFS constant of the atomic system. The computational details are given in Sec. III. In Sec. IV we present our results and discuss these before making our final remarks in Sec. V.

## II. THEORY

### A. Z-vector method

The study of hyperfine interaction helps us to understand the nuclear structure of an atom and its impact on the electronic wave function in the nuclear and near nuclear region. Therefore, for the accurate calculation of magnetic HFS constant, which demands a very precise wave function in the short range of the nucleus, we need to incorporate both relativistic and electron correlation effects. In this work, the four-component Dirac-Hartree-Fock (DHF) method is used to include the effect of relativity where the electron-electron repulsion term is approximated as a Coulomb interaction. The Dirac-Coulomb Hamiltonian is given by

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

where $\boldsymbol{\alpha}$ and $\beta$ are the usual Dirac matrices, $c$ is the speed of light, $\mathbb{1}_4$ is the $4 \times 4$ identity matrix, and $V^{\text{nuc}}(r_i)$ is the nuclear potential function; the Gaussian charge distribution is used in this work. The DHF method misses the instantaneous dynamic correlation of opposite spin electrons. Among various many-body theories, the single reference coupled cluster (SRCC) is the most elegant technique to incorporate dynamic correlation. The SRCC wave function is given as

$$|\Psi_{cc}\rangle = e^T |\Phi_0\rangle, \quad (2)$$

where $\Phi_0$ is the DHF wave function and $T$ is the coupled-cluster excitation operator, which is given by

$$T = T_1 + T_2 + \cdots + T_N = \sum_n^N T_n \quad (3)$$

with

$$T_m = \frac{1}{(m!)^2} \sum_{ij...ab...} t_{ij...}^{ab...} a_a^\dagger a_b^\dagger \cdots a_j a_i. \quad (4)$$

Here $i, j(a, b)$ are the hole (particle) indices and $t_{ij...}^{ab...}$ are the cluster amplitudes corresponding to the cluster operator $T_m$. In the coupled-cluster single and double (CCSD) approximation, $T = T_1 + T_2$. The equations for $T_1$ and $T_2$ are given as

$$\langle \Phi_i^a | (H_N e^T)_c | \Phi_0 \rangle = 0,$$
$$\langle \Phi_{ij}^{ab} | (H_N e^T)_c | \Phi_0 \rangle = 0, \quad (5)$$

where $H_N$ is the normal ordered DC Hamiltonian and the subscript $c$ means only the connected terms exist in the contraction between $H_N$ and $T$. Size extensivity is ensured by this connectedness. The coupled-cluster correlation energy can be obtained as

$$E^{\text{corr}} = \langle \Phi_0 | (H_N e^T)_c | \Phi_0 \rangle. \quad (6)$$

However, the SRCC energy is not optimized with respect to the determinantal coefficients and the molecular orbital coefficients in the expansion of the many electron correlated wave function [32]. Therefore, the calculation of the SRCC energy derivative with respect to external perturbation requires one to include these derivative terms. The equation for these terms is linear but, in general, perturbation dependent. However, in the $Z$-vector method, the derivative terms containing the determinantal coefficients can be incorporated by the introduction of a perturbation-independent operator $\Lambda$ [35]. Thus, in the $Z$-vector method, any number of property calculations can be done by solving only one set of $T$ and $\Lambda$ amplitudes. $\Lambda$ is a deexcitation operator, and the second quantized form is given by

$$\Lambda = \Lambda_1 + \Lambda_2 + \cdots + \Lambda_N = \sum_n^N \Lambda_n, \quad (7)$$

where

$$\Lambda_m = \frac{1}{(m!)^2} \sum_{ij..ab..} \lambda_{ab..}^{ij..} a_i^\dagger a_j^\dagger \cdots a_b a_a. \quad (8)$$

Here $\lambda_{ab..}^{ij..}$ are the cluster amplitudes corresponding to the cluster operator $\Lambda_m$. In the CCSD approximation, $\Lambda = \Lambda_1 + \Lambda_2$. The explicit equations for the amplitudes of $\Lambda_1$ and $\Lambda_2$ operators are given by

$$\langle \Phi_0 | [\Lambda (H_N e^T)_c]_c | \Phi_i^a \rangle + \langle \Phi_0 | (H_N e^T)_c | \Phi_i^a \rangle = 0, \quad (9)$$

$$\langle \Phi_0 | [\Lambda (H_N e^T)_c]_c | \Phi_{ij}^{ab} \rangle + \langle \Phi_0 | (H_N e^T)_c | \Phi_{ij}^{ab} \rangle$$
$$+ \langle \Phi_0 | (H_N e^T)_c | \Phi_i^a \rangle \langle \Phi_i^a | \Lambda | \Phi_{ij}^{ab} \rangle = 0. \quad (10)$$

The energy derivative is given by

$$\Delta E' = \langle \Phi_0 | (O_N e^T)_c | \Phi_0 \rangle + \langle \Phi_0 | [\Lambda (O_N e^T)_c]_c | \Phi_0 \rangle. \quad (11)$$

TABLE I. Basis and cutoff used for the atomic calculation.

| Atom | Basis | Virtual cutoff (a.u.) |
|---|---|---|
| Li | aug-cc-pCVQZ | |
| Na | aug-cc-pCVQZ | |
| K | dyall.cv4z | 500 |
| Rb | dyall.cv3z | 500 |
| Cs | dyall.cv4z | 40 |
| Fr | dyall.cv3z | 50 |
| $Be^+$ | aug-cc-pCVQZ | |
| $Mg^+$ | aug-cc-pCVQZ | |
| $Ca^+$ | dyall.cv4z | 500 |
| $Sr^+$ | dyall.cv3z | 100 |
| $Ba^+$ | dyall.cv4z | 40 |
| $Ra^+$ | dyall.cv3z | 50 |

Here $O_N$ is the derivative of a normal ordered perturbed Hamiltonian with respect to an external field of perturbation. It is clear from the above formulation that the derivative terms containing only the determinantal coefficients are included here, i.e., the orbital relaxation terms that are required to make energy functional stationary with respect to molecular orbital coefficients are not considered here. It is worth mentioning that recently Saue and coworkers [37] have implemented the orbital-unrelaxed analytical method in the four-component relativistic SRCC framework based on the Lagrangian multiplier method of Helgaker and coworkers [38], which is similar to the $Z$-vector method for the ground state first order properties.

### B. Magnetic hyperfine structure constant

The magnetic HFS interaction arises due to the coupling of the nuclear magnetic moment with the angular momentum of electrons and, thus, can be treated as a one-body interaction from the electronic structure point of view. The magnetic

vector potential due to a nucleus is given by

$$\vec{A} = \frac{\vec{\mu}_k \times \vec{r}}{r^3}, \tag{12}$$

where $\vec{\mu}_k$ is the magnetic moment of nucleus $K$. In Dirac theory, the HFS interaction Hamiltonian due to $\vec{A}$ can be given as

$$H_{\mathrm{hfs}} = \sum_i^n \vec{\alpha}_i \cdot \vec{A}_i, \tag{13}$$

where $\alpha_i$ denotes the Dirac $\alpha$ matrices for the $i$th electron and $n$ is the total number of electrons. The magnetic hyperfine constant of the $J$th electronic state of an atom can be given as

$$A_J = \frac{1}{IJ} \langle \Psi_J | H_{\mathrm{hfs}} | \Psi_J \rangle$$
$$= \frac{\vec{\mu}_k}{IJ} \cdot \langle \Psi_J | \sum_i^n \left( \frac{\vec{\alpha}_i \times \vec{r}_i}{r_i^3} \right) | \Psi_J \rangle, \tag{14}$$

where $I$ is the nuclear spin quantum number and $\Psi_J$ is the wave function of the $J$th electronic state.

### III. COMPUTATIONAL DETAILS

The DIRAC10 program package [39] is used to solve the DHF equation and to construct the one- and two-electron matrix elements. The magnetic HFS integrals are extracted from a locally modified version of DIRAC10. Gaussian charge distribution is considered for the finite size of the nucleus where the the nuclear parameters are taken from Ref. [40]. The restricted kinetic balance [41] condition is used to link small and large component basis functions. No virtual pair approximation (NVPA) is used to solve the DHF equation. This means that the negative energy solutions are removed by using a projection operator and only positive energy solutions are included in the correlation calculations. However, how to go

TABLE II. Magnetic hyperfine coupling constant (in MHz) of ground state of atoms.

| Atom | SCF | ECC [31] | $Z$-vector | Expt. | $\delta\%$ ECC | $\delta\%$ $Z$-vector |
|---|---|---|---|---|---|---|
| $^6$Li | 107.2 | 149.3 | 148.3 | 152.1 [48] | 1.9 | 2.6 |
| $^7$Li | 283.2 | 394.3 | 391.6 | 401.7 [48] | 1.9 | 2.6 |
| $^{23}$Na | 630.6 | 861.8 | 861.4 | 885.8 [48] | 2.8 | 2.8 |
| $^{39}$K | 151.0 | 223.5 | 226.6 | 230.8 [48] | 3.3 | 1.9 |
| $^{40}$K | −187.7 | −277.9 | −281.8 | −285.7 [49] | 2.8 | 1.4 |
| $^{41}$K | 82.9 | 122.7 | 124.4 | 127.0 [48] | 3.5 | 2.1 |
| $^{85}$Rb | 666.9 | 972.5 | 986.5 | 1011.9 [50] | 4.1 | 2.6 |
| $^{87}$Rb | 2260.1 | 3295.7 | 3343.3 | 3417.3 [51] | 3.7 | 2.2 |
| $^{133}$Cs | 1495.5 | 2179.1 | 2218.4 | 2298.1 [52] | 5.5 | 3.6 |
| $^{223}$Fr | 5518.0 | | 7537.4 | 7654(2)[53] | | 1.5 |
| $^9$Be$^+$ | −498.8 | −614.6 | −612.9 | −625.0 [54] | 1.7 | 2.0 |
| $^{25}$Mg$^+$ | −466.7 | −581.6 | −584.8 | −596.2 [55] | 2.5 | 1.9 |
| $^{43}$Ca$^+$ | −606.2 | −794.9 | −801.5 | -806.4 [56] | 1.4 | 0.6 |
| $^{87}$Sr$^+$ | −761.0 | −969.9 | −977.9 | −1000.5(1.0) [57] | 3.2 | 2.3 |
| $^{135}$Ba$^+$ | 2737.4 | | 3513.3 | 3591.7 [58] | | 2.2 |
| $^{137}$Ba$^+$ | 3062.1 | | 3930.2 | 4018.9 [58] | | 2.3 |
| $^{223}$Ra$^+$ | 2842.8 | | 3446.3 | 3404(2) [59,60] | | 1.2 |
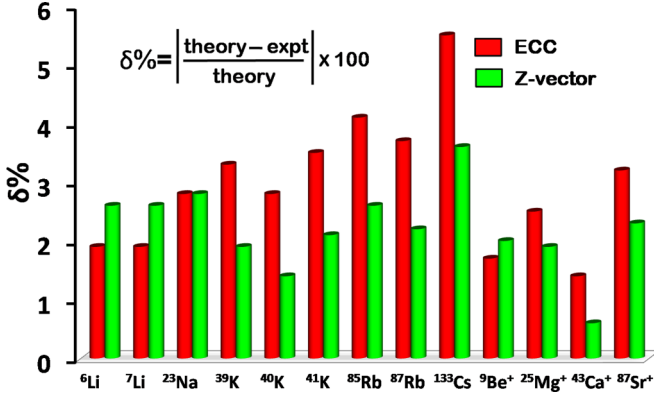
FIG. 1. Comparison of relative deviations between $Z$-vector and ECC values of the magnetic HFS constant of atoms.

beyond the no-pair approximation by accounting for correlation contributions of negative energy states has been discussed in depth in Refs. [42–44]. In our calculation, we have used aug-cc-pCVQZ basis [45,46] for Li, Na, Be, and Mg atoms and dyall.cv3z basis [47] for Rb, Sr, Fr, and Ra atoms and dyall.cv4z [47] basis for K, Ca, Cs, and Ba atoms. All electrons are considered for the correlation calculation of all systems. The cutoff used for the virtual orbitals is compiled in Table I.

## IV. RESULTS AND DISCUSSION

In Table II we present the magnetic HFS constant of alkali metal atoms and mono-positive alkaline earth metal ions in their ground state ($^2S$) electronic configuration using the $Z$-vector technique in the relativistic coupled-cluster framework. We have compiled the experimental values for these systems in the same table, and the relative deviations of $Z$-vector results from the experimental values are presented as $\delta\%$. The results for different isotopes are calculated by using their corresponding nuclear magnetic moment values although the nuclear parameters in the nuclear model are taken as the same for each isotope, which is the default for the most stable isotopes in DIRAC10 [39]. Our calculated $Z$-vector results are in very good agreement with the experimental values. From the table, it is clear that the deviations of the $Z$-vector results from the experiments are well within 3% except for the $^{133}$Cs atom, where it is 3.6%. The $Z$-vector results are quite impressive, especially for the heavy atoms. The ECC values of magnetic HFS constant are taken from Ref. [31], and the deviations from the experiment are presented in the table. We have used the same basis and cutoff for those systems for comparison purposes. The deviations of ECC and $Z$-vector values from the experimental values are presented in Fig. 1. From the figure, it is clear that $Z$-vector results are far better

TABLE III. Comparison of full CI and $Z$-vector magnetic HFS values (in MHz) of $^7$Li.

| Basis | Full CI [31] | $Z$-vector |
|---|---|---|
| aug-cc-pCVDZ | 384.1 | 383.9 |
| aug-cc-pCVTZ | 402.0 | 401.3 |
| aug-cc-pCVQZ[a] | 386.0 | 385.2 |

[a]Considering three electrons and 189 virtual orbitals.

TABLE IV. Comparison of full CI and $Z$-vector magnetic HFS values (in MHz) of $^9$Be$^+$.

| Basis | Full CI [31] | $Z$-vector |
|---|---|---|
| aug-cc-pCVDZ | −586.6 | −586.5 |
| aug-cc-pCVTZ | −615.7 | −615.4 |
| aug-cc-pCVQZ[a] | −613.0 | −612.7 |

[a]Considering three electrons and 183 virtual orbitals.

than the ECC results except for two small systems like Li and Be$^+$. As the magnetic HFS constant is very sensitive to the near nuclear wave function, the above results show that the $Z$-vector method can produce a far better wave function in the nuclear region than the ECC method, and the results are quite impressive for the heavy atoms. Although ECC is a truncated series, in the CCSD model, the natural truncation leads to very expensive terms. In Ref. [31], the truncation scheme proposed by Vaval *et al.* is used to avoid the expensive terms in the ECC functional where the right exponential is full within the CCSD approximation and the higher-order double-linked terms within the CCSD approximation are taken in the left exponent. This approximation introduces an additional error, which may be the reason for the poor performance of ECC compared to the $Z$-vector method.

The HFS constant predominantly depends on the spin density of the valence electron in the nuclear region and thus is not very sensitive to the retardation and magnetic effects described by the Breit interaction [61,62]. It can be seen from the previous calculations that the higher order relativistic effects on these types of properties generally lie ~0.5%–1% [63–65]. It is worth mentioning that although we have correlated all electrons in our $Z$-vector calculations, the results are not completely free from the uncertainty associated with a core correlation as the cvNz ($N = 3$, 4) basis set misses some important core correlating functions. The $1s - 3d$ electrons also need much higher virtual energy orbitals for proper correlation functions as shown in Ref. [66,67]. A series of calculations are done to estimate the uncertainty associated with the $Z$-vector values of the magnetic HFS constant of these systems. A comparison between full configuration interaction (FCI) and $Z$-vector magnetic HFS constant values of $^7$Li and $^9$Be$^+$ has been made and is presented in Tables III and IV, respectively. By comparing $Z$-vector values with FCI values and considering all other sources of error like higher order relativistic effects, missing correlation effects, etc., it can be assumed that the overall uncertainty in our final results is less than 5%.

## V. CONCLUSION

We have calculated the magnetic HFS constant of alkali metal atoms (Li, Na, K, Rb, Cs, and Fr) and mono-positive alkaline earth metal ions (Be$^+$, Mg$^+$, Ca$^+$, Sr$^+$, Ba$^+$, and Ra$^+$) using the $Z$-vector technique in the relativistic coupled-cluster framework. We have compared the $Z$-vector values and the ECC values taken from Ref. [31] with experiment, and the comparison shows that the $Z$-vector method with single and double approximation can produce a much more accurate wave function in the nuclear region than the ECC method with the given approximation. A possible explanation for the poor performance of the ECC method is also given.

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