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Electron-correlation trends in the hyperfine *A* and *B* constants of the Na isoelectronic sequence

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In this paper, we have described electron-correlation trends in the calculations of the hyperfine A and B constants for a few elements belonging to the Na isoelectronic sequence. The hyperfine A and B/Q values of the ground state $3s\ ^2S_{1/2}$ and the excited states $3p\ ^2P_{1/2}$, $3p\ ^2P_{3/2}$, $3d\ ^2D_{3/2}$, and $3d\ ^2D_{5/2}$ of the ions from Si^{3+} to V^{12+} are presented. The influence of the Breit interaction in the unretarded approximation to these hyperfine values is reported briefly. With increasing atomic number of this sequence, the variations of the different correlation contributing terms such as core correlations, core polarizations, and pair correlations are discussed in the framework of the relativistic coupled-cluster theory. The electron-correlation effect relative to the Dirac-Fock value in the hyperfine A constants of the $3d\ ^2D_{3/2,5/2}$ states follows unusual trends with increasing ionization. The relative pair-correlation effect influences the hyperfine constants of the fine-structure states of a term in an identical way at each species of this sequence. The presented relativistic coupled-cluster results are found to agree excellently with the other available results for a few ions.

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I. INTRODUCTION

Elements belonging to the isoelectronic sequences of lighter and heavier atoms are being considered as ideal species to investigate the electron-correlation trends with increasing ionization in different atomic properties [1–9]. In particular, research on the isoelectronic sequences of alkali-metal atoms is a subject of considerable interest to observe the correlation effects on the hyperfine properties in various levels of ionization [3–6]. In the calculations of the hyperfine fields or hyperfine constants, it was noticed earlier that the electron correlation relative to the single-particle approximation decreases rapidly for the first few elements with increasing atomic number (Z) in an isoelectronic sequence [2–6]. The linked-cluster many-body perturbation theory was applied in relativistic (RLCMBPT) and nonrelativistic (LCMBPT) forms to analyze these correlation effects in some Li-like [3,6] and K-like systems [4]. In their work, they gave detailed descriptions of the different correlation mechanisms such as exchange core polarization and other many-body effects with respect to the single-particle approximation in the hyperfine properties of these systems [3,4,6]. Calculations on the ground-state hyperfine constants of a few Li-like species were also performed by the relativistic many-body perturbation theory (RMBPT) [5]. This work included the estimations of Dirac-Fock contribution, complete polarization, and first- and higher-order correlations to these constants [5].

The hyperfine calculations associated with the LCMBPT, RLCMBPT, and RMBPT were carried out mainly on the ground states of the species considered there [3–6]. There are some calculations on a few excited states of Li-like F^{6+} only [6]. However, the correlations in the hyperfine calculations of the excited states of the elements that are isoelectronic to alkali-metal atoms are very interesting. In particular, the A constants of $^2D_{5/2}$ states of such singly ionized ions are abnormally correlated, as observed in some earlier calculations [10,11]. For the alkali-metal-like singly ionized ions, it was demonstrated earlier by Mani *et al.* and Sahoo *et al.* that the relativistic coupled-cluster (RCC) theory has the potential to exhaust even such an abnormal correlation in the most accurate way [10,11]. This theory has been used successfully to analyze the correlation contributions to the hyperfine A constants of a few low-lying states of these ions [10–12]. The correlations arising from the different coupled-cluster terms were discussed there extensively [10–12]. But, to the best of our knowledge, using the coupled-cluster theory, there are no discussions on the correlation trends for a series of species which are isoelectronic to an alkali-metal atom.

In the work of Mani *et al.*, the discussions were aimed at the hyperfine A constants only [10]. Also, with $^2S_{1/2}$ states as the ground states of Li-like and K-like systems, there was no scope in the LCMBPT, RLCMBPT, and RMBPT calculations to understand the correlation trends in the hyperfine B constants, as their values are zero there [13]. The work of Sahoo *et al.* presented the exhaustiveness of the electron correlations in the hyperfine B constants of $^2D_{5/2}$ states using the RCC theory through several singly ionized alkali-metal-like ions [11]. In this work, more than 150% correlation contribution is observed for the B constant of the Na-like $^{25}\mathrm{Mg}^+$ [11]. However, no work has been done yet on the isoelectronic trend in the B constants to the best of our knowledge.

The stripped ions of the Na isoelectronic sequence are very important elements in various astronomical bodies. The ultraviolet emission lines of these ions from the solar atmosphere, transition regions, and coronae of active stars have been identified using advanced high-resolution spectroscopy [14–16]. With the availability of wavelengths [17] and oscillator strengths [18] from the literature, the analysis of these high-resolution spectra requires the inclusion of hyperfine splitting for proper modeling of line profiles [19]. Hence, one can get a more accurate picture of abundance analysis [19,20]. Therefore, it is necessary to provide more hyperfine data in the literature for such ions. Hyperfine data for stripped ions can be considered as an excellent benchmark comparison between experiment and theory [3,6,21]. Also, these data may be used for nuclear quadrupole moment estimations using experimental techniques such as laser spectroscopy [22].

In the present work, we use RCC theory in a nonlinear form [12,23,24] to study the correlation trends in the hyperfine A and B constants of a few elements of the sodium isoelectronic sequence. In the present method, the Breit interaction is implemented in the atomic Hamiltonian in the unretarded approximation [2]. The earlier coupled-cluster calculations [10–12] did not consider this interaction. However, in the present work, we treat this in an all-order way. The coupled-cluster theory has the advantage to incorporate all of the important correlation contributing terms, such as core correlation, core polarization, and pair correlation, exhaustively [11,25]. These terms arise from the Goldstone diagrams [11,26] obtained from the contractions of different one-body and two-body cluster operators with the hyperfine operators [11]. Our present work contains all of the detailed analysis of these correlation contributions to a few low-lying states, including the ground state. Both the hyperfine A and B/Q values are presented at the RCC levels for the ionic species from Si^{3+} to V^{12+}. The separate presentation of these values is performed from the point of view of various applications, as mentioned in the previous paragraph. The hyperfine A constants for the first six elements of the Na isoelectronic sequence were calculated by employing the relativistic all-order many-body perturbation theory (RAOMBPT) [7]. Therefore, it is a good opportunity to compare these results with our RCC calculations for the three elements $^{29}\mathrm{Si}^{3+}$, $^{31}\mathrm{P}^{4+}$, and $^{33}\mathrm{S}^{5+}$. However, in the RAOMBPT calculations, the hyperfine B constants are presented for the neutral Na only.

II. THEORY

The details for the coupled-cluster theory are given in some earlier publications [23,26–28]. According to this theory, the correlated wave function $|\Psi_v\rangle$ of a single-valence system can be derived from the corresponding reference-state wave function $|\Phi_v\rangle$ using the following relation:

$$|\Psi_v\rangle = e^T\{1 + S_v\}|\Phi_v\rangle. \tag{1}$$

Here, v indicates the valence orbital. The reference state $|\Phi_v\rangle$ is generated at the single-particle (Dirac-Fock) level of the closed-shell system [23]. This closed-shell system is obtained by removing the valence electron from the single-valence system. T and S_v are the closed-shell and open-shell cluster operators, respectively [23], and are solved from the energy eigenvalue equations associated with the closed-shell and open-shell atomic Hamiltonians, respectively [2].

The Breit interaction is the correction to the Coulomb interaction due to the exchange of a transverse photon [29]. The magnetic part of this interaction is called the Gaunt interaction. The other part, called the retardation part, contributes little with respect to the Gaunt part [29,30]. Therefore, the Gaunt part can be treated as a good approximation of the Breit interaction. The inclusion of the Gaunt interaction in the atomic Hamiltonian at the Dirac-Fock and coupled-cluster levels is discussed descriptively in Ref. [2].

The expectation value of a hyperfine operator $\hat{O}$ [13] in the state $|\Psi_v\rangle$ can be written by using the coupled-cluster theory as

$$\begin{aligned} O_v &= \frac{\langle\Psi_v|\hat{O}|\Psi_v\rangle}{\langle\Psi_v|\Psi_v\rangle} = \frac{\langle\Phi_v|\{1+S_v^\dagger\}e^{T^\dagger}\hat{O}e^T\{1+S_v\}|\Phi_v\rangle}{\langle\Phi_v|\{1+S_v^\dagger\}e^{T^\dagger}e^T\{1+S_v\}|\Phi_v\rangle} \\ &= \frac{\langle\Phi_v|\{1+S_v^\dagger\}\overline{O}\{1+S_v\}|\Phi_v\rangle}{N}, \end{aligned} \tag{2}$$

where $\overline{O} = e^{T^\dagger}\hat{O}e^T$. Here, $N = \langle\Phi_v|\{1+S_v^\dagger\}e^{T^\dagger}e^T\{1+S_v\}|\Phi_v\rangle$ is the factor which is associated with the normalization of the wave function $|\Psi_v\rangle$. The different correlation contributing many-body terms arise from the $\overline{O}$ and from the contractions of $\overline{O}$ with S at the numerator of Eq. (2) [11]. These terms such as core correlation, pair correlation, and core polarization are defined from $\overline{O} - O$, $S_{1v}^\dagger\overline{O} + \overline{O}S_{1v}$ and $S_{2v}^\dagger\overline{O} + \overline{O}S_{2v}$, respectively [11,25]. Here, 1 and 2 stand for single and double excitations, respectively.

The detailed descriptions of the hyperfine A and B constants along with their corresponding single-particle operator forms are given in Refs. [13,31].

III. RESULTS AND DISCUSSIONS

Our calculations start from the generation of Dirac-Fock (DF) reference states. These reference-state wave functions are generated from the Gaussian-type orbital (GTO) basis functions [25]. These GTO basis functions have two parameters, α_0 and β, which are considered the same for all of the s, p, d, and f symmetries of an element. The parameters α_0 and β are optimized with respect to the numerical energies and radial expectation values of r and $1/r$ of the bound orbitals, as obtained from the GRASP 92 code [32]. These optimized parameters for the ions from Si^{3+} to V^{12+} are presented in Table I. The Fermi-type distribution is used here to describe the nuclear potential function [10]. We use 33, 28, 25, and 21 number of GTOs for the s, p, d, and f symmetries, respectively, to calculate the hyperfine constants at the DF levels. However, at the coupled-cluster levels, the number of active orbitals are considered as 12, 11, 10, and 9, respectively, for the symmetries mentioned above. These numbers of active orbitals, which include all of the bound orbitals and the first few unbound orbitals, follow the convergence criteria of the core correlation energies [25].

In Tables II and III, the hyperfine A and B/Q values, respectively, are presented with the correlation and Gaunt contributions. Here, Q is the nuclear quadrupole moment. In order to calculate the A constants, the magnitudes of the g_I (g factor of nucleus) values for most stable isotopes are taken from Ref. [33]. For some of these isotopes, we could not find any Q value from Ref. [33]. This is the reason for choosing B/Q values instead of B constants in Table III. In both of these

TABLE I. Basis parameters α_0 and β.

	Si^{3+}	P^{4+}	S^{5+}	Cl^{6+}	Ar^{7+}	K^{8+}	Ca^{9+}	Sc^{10+}	Ti^{11+}	V^{12+}
α_0	0.00500	0.00725	0.00975	0.01250	0.01550	0.01875	0.02250	0.02675	0.03150	0.03675
β	2.73	2.73	2.73	2.73	2.73	2.73	2.73	2.73	2.73	2.73

TABLE II. Calculated hyperfine A constants (in MHz) with the correlation (Corr) and Gaunt contribution and their comparisons with the RAOMBPT calculations (Other) [7]. Total = DF + Corr + Gaunt.

Ions	States	DF	Corr	Gaunt	Total	Other
^{29}Si^{3+}	$3s\ ^2S_{1/2}$	5102.09	945.43	2.82	6050.34	6060.00
	$3p\ ^2P_{1/2}$	1140.08	235.65	0.38	1376.11	1388.00
	$3p\ ^2P_{3/2}$	224.62	18.80	0.06	243.48	245.20
	$3d\ ^2D_{3/2}$	40.01	−0.10	0.03	39.94	39.65
	$3d\ ^2D_{5/2}$	17.14	−20.11	−0.02	−2.99	−3.24
^{31}P^{4+}	$3s\ ^2S_{1/2}$	15865.43	2547.08	9.48	18421.99	18407.00
	$3p\ ^2P_{1/2}$	3785.60	675.70	1.26	4462.56	4488.00
	$3p\ ^2P_{3/2}$	743.97	35.30	0.18	779.45	783.40
	$3d\ ^2D_{3/2}$	164.75	1.47	0.15	166.37	165.40
	$3d\ ^2D_{5/2}$	70.56	−72.89	−0.05	−2.38	−2.52
^{33}S^{5+}	$3s\ ^2S_{1/2}$	4308.64	610.97	2.74	4922.35	4910.00
	$3p\ ^2P_{1/2}$	1075.90	169.21	0.36	1245.47	1250.00
	$3p\ ^2P_{3/2}$	210.88	5.01	0.06	215.95	216.80
	$3d\ ^2D_{3/2}$	54.55	0.68	0.06	55.29	55.02
	$3d\ ^2D_{5/2}$	23.35	−21.07	−0.02	2.26	2.36
^{35}Cl^{6+}	$3s\ ^2S_{1/2}$	7530.66	957.34	5.07	8493.07	
	$3p\ ^2P_{1/2}$	1944.55	273.68	0.66	2218.89	
	$3p\ ^2P_{3/2}$	380.06	2.97	0.10	383.13	
	$3d\ ^2D_{3/2}$	110.27	1.41	0.12	111.80	
	$3d\ ^2D_{5/2}$	47.19	−37.39	−0.03	9.77	
^{39}Ar^{7+}	$3s\ ^2S_{1/2}$	6757.32	778.81	4.78	7540.91	
	$3p\ ^2P_{1/2}$	1790.54	228.17	0.61	2019.32	
	$3p\ ^2P_{3/2}$	348.92	−1.17	0.10	347.85	
	$3d\ ^2D_{3/2}$	110.52	1.29	0.12	111.93	
	$3d\ ^2D_{5/2}$	47.27	−33.16	−0.02	14.09	
^{41}K^{8+}	$3s\ ^2S_{1/2}$	3359.19	354.27	2.49	3715.95	
	$3p\ ^2P_{1/2}$	908.59	105.84	0.31	1014.74	
	$3p\ ^2P_{3/2}$	176.49	−1.98	0.05	174.56	
	$3d\ ^2D_{3/2}$	59.89	0.61	0.07	60.57	
	$3d\ ^2D_{5/2}$	25.60	−16.05	−0.01	9.54	
^{43}Ca^{9+}	$3s\ ^2S_{1/2}$	11146.61	1076.86	8.60	12232.07	
	$3p\ ^2P_{1/2}$	3065.63	328.05	1.06	3394.74	
	$3p\ ^2P_{3/2}$	593.50	−9.98	0.17	583.69	
	$3d\ ^2D_{3/2}$	212.87	1.82	0.26	214.95	
	$3d\ ^2D_{5/2}$	90.96	−51.41	−0.02	39.53	
^{45}Sc^{10+}	$3s\ ^2S_{1/2}$	49926.47	4452.30	39.37	54418.14	
	$3p\ ^2P_{1/2}$	13922.11	1369.14	4.55	15295.80	
	$3p\ ^2P_{3/2}$	2685.82	−56.20	0.72	2630.34	
	$3d\ ^2D_{3/2}$	1008.08	7.11	1.26	1016.45	
	$3d\ ^2D_{5/2}$	430.52	−221.12	−0.07	209.33	
^{47}Ti^{11+}	$3s\ ^2S_{1/2}$	14164.11	1180.02	11.52	15355.65	
	$3p\ ^2P_{1/2}$	3995.88	367.00	1.31	4364.19	
	$3p\ ^2P_{3/2}$	768.02	−18.28	0.21	749.95	
	$3d\ ^2D_{3/2}$	299.38	1.66	0.39	301.43	
	$3d\ ^2D_{5/2}$	127.79	−60.07	−0.02	67.70	
^{51}V^{12+}	$3s\ ^2S_{1/2}$	79740.39	6234.51	66.49	86041.39	
	$3p\ ^2P_{1/2}$	22721.34	1957.85	7.53	24686.72	
	$3p\ ^2P_{3/2}$	4350.11	−112.53	1.25	4238.83	
	$3d\ ^2D_{3/2}$	1750.88	6.90	2.29	1760.07	
	$3d\ ^2D_{5/2}$	746.89	−323.39	−0.06	423.44	

TABLE III. Calculated hyperfine B/Q values (in MHz/b) with the correlation (Corr) and Gaunt contributions. Total = DF + Corr + Gaunt.

Ions	States	DF	Corr	Gaunt	Total
^{29}Si^{3+}	$3p\ ^2P_{3/2}$	374.38	78.05	−0.50	451.93
	$3d\ ^2D_{3/2}$	22.20	7.86	−0.02	30.04
	$3d\ ^2D_{5/2}$	31.68	11.25	−0.02	42.91
^{31}P^{4+}	$3p\ ^2P_{3/2}$	608.74	102.64	−0.85	710.53
	$3d\ ^2D_{3/2}$	44.87	7.37	−0.05	52.19
	$3d\ ^2D_{5/2}$	64.00	10.58	−0.04	74.54
^{33}S^{5+}	$3p\ ^2P_{3/2}$	910.26	128.53	−1.35	1037.44
	$3d\ ^2D_{3/2}$	78.37	5.23	−0.08	83.52
	$3d\ ^2D_{5/2}$	111.70	7.60	−0.06	119.24
^{35}Cl^{6+}	$3p\ ^2P_{3/2}$	1285.76	155.89	−2.01	1439.64
	$3d\ ^2D_{3/2}$	124.17	1.63	−0.12	125.68
	$3d\ ^2D_{5/2}$	176.83	2.57	−0.09	179.31
^{39}Ar^{7+}	$3p\ ^2P_{3/2}$	1742.25	184.78	−2.88	1924.15
	$3d\ ^2D_{3/2}$	183.68	−3.28	−0.18	180.22
	$3d\ ^2D_{5/2}$	261.34	−4.29	−0.13	256.92
^{41}K^{8+}	$3p\ ^2P_{3/2}$	2286.94	215.32	−3.97	2498.29
	$3d\ ^2D_{3/2}$	258.30	−9.39	−0.26	248.65
	$3d\ ^2D_{5/2}$	367.17	−12.81	−0.18	354.18
^{43}Ca^{9+}	$3p\ ^2P_{3/2}$	2927.56	247.50	−5.33	3169.73
	$3d\ ^2D_{3/2}$	349.50	−16.65	−0.37	332.48
	$3d\ ^2D_{5/2}$	496.30	−22.88	−0.25	473.17
^{45}Sc^{10+}	$3p\ ^2P_{3/2}$	3671.65	278.15	−6.96	3942.84
	$3d\ ^2D_{3/2}$	458.70	−24.99	−0.50	433.21
	$3d\ ^2D_{5/2}$	650.69	−34.44	−0.34	615.91
^{47}Ti^{11+}	$3p\ ^2P_{3/2}$	4526.91	313.87	−8.98	4831.80
	$3d\ ^2D_{3/2}$	587.38	−34.38	−0.67	552.33
	$3d\ ^2D_{5/2}$	832.31	−47.40	−0.46	784.45
^{51}V^{12+}	$3p\ ^2P_{3/2}$	5501.16	351.48	−11.41	5841.23
	$3d\ ^2D_{3/2}$	737.02	−44.50	−0.88	691.64
	$3d\ ^2D_{5/2}$	1043.13	−61.72	−0.60	980.81

tables, the DF results are calculated using the Dirac-Coulomb (DC) Hamiltonian. The correlations (Corr) are also defined here by the Coulomb correlation among the electrons. The Gaunt contributions are added to the overall DC results to obtain the total results, which are the RCC results based on the Dirac-Coulomb-Gaunt (DCG) Hamiltonian. Except for the A constants of the $3d\ ^2D_{5/2}$ states, the approximate theoretical uncertainty is estimated around ±1% for the total values presented in Tables II and III, whereas in the total values of the former cases this uncertainty is calculated around ±6%. Here, in determining these uncertainties approximately, we have considered the noninclusion of the retardation part of the Breit interaction, other quantum electrodynamic effects, higher-order coupled-cluster terms, and more numbers of orbitals and orbital symmetries in the calculations of the hyperfine constants. The RAOMBPT calculations [7] of the hyperfine A constants are presented in the last column of Table II. Safronova *et al.* obtained these results using the B-spline basis set [34], whereas our results are based on the GTO basis. The present coupled-cluster method incorporates the single, double, and partial triple excitations in linear and nonlinear forms [CCSD(T)] [12,24]. The CCSD(T) method was used earlier in the correlation descriptions for the hyperfine constants of a few low-lying states of Mg$^+$ [12]. However, the calculations performed by Safronova *et al.*

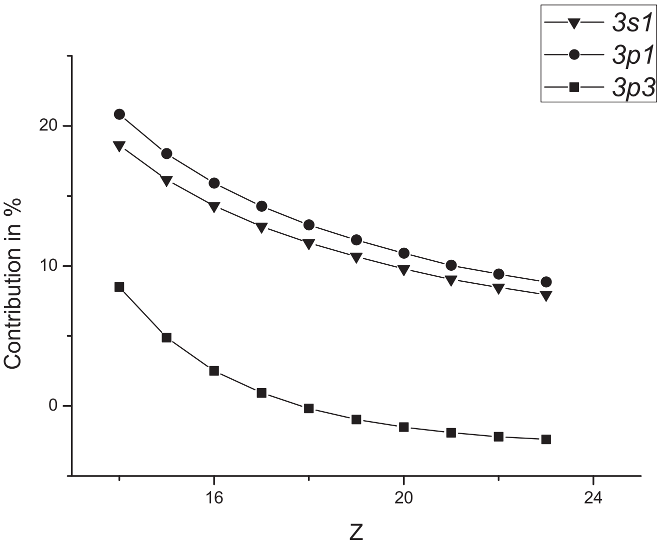

FIG. 1. Percentage correlation contributions to the hyperfine A constants of the $3s\ ^2S_{1/2}$ ($3s1$), $3p\ ^2P_{1/2}$ ($3p1$), and $3p\ ^2P_{3/2}$ ($3p3$) states.

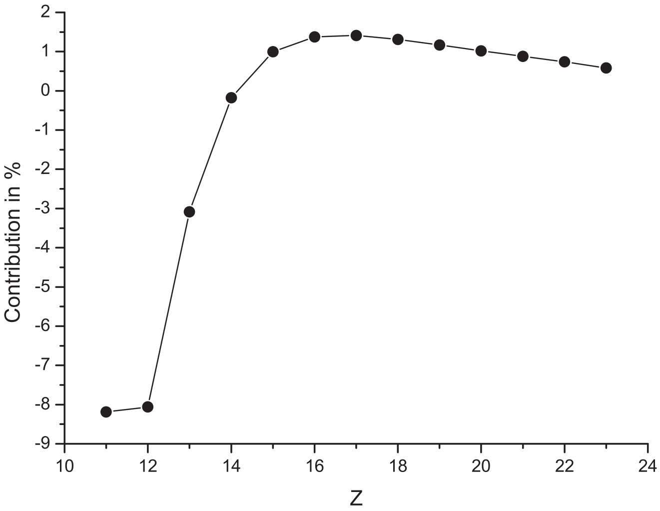

FIG. 2. Percentage correlation contributions to the hyperfine A constants of the $3d\ ^2D_{3/2}$ state.

used single and double excitations (SD) in linear form only. Theoretically, CCSD(T) is more accurate with respect to the linearized SD [12,24,35]. However, inclusion of the higher-order excitations is expected to improve the accuracy of the present calculations [24], which are not considered here. Nevertheless, the results of Safronova *et al.* agree excellently with our RCC results, which is evident from this table. As seen from both tables, with respect to the Coulomb correlations, the Gaunt effects are found to be small in the determination of the hyperfine constants. Our calculated values of these Gaunt contributions to the A constants of the $3s\ ^2S_{1/2}$ states are found to be consistent with the analytical expression of the Breit contribution $\delta A = 0.68 Z A \alpha^2$ as derived by Sushkov [36]. For example, according to this analytical expression, the Breit contributions to the $3s\ ^2S_{1/2}$ states of $^{29}\mathrm{Si}^{3+}$, $^{39}\mathrm{Ar}^{7+}$, and $^{51}\mathrm{V}^{12+}$ should be 3.07, 4.91, and 71.64 MHz, respectively. These values are calculated to be 2.82, 4.78, and 66.49 MHz, respectively, by our present all-order treatment of the Gaunt interaction. The good agreements among these contributions ensure the accuracy of our correlated treatment of the Gaunt interaction using the coupled-cluster theory.

The trends of percentage correlation contributions to the hyperfine A constants are presented in Figs. 1–3 and those to the hyperfine B constants are presented in Fig. 4 for the states as indicated there. These percentage values are calculated with respect to the corresponding DF results. The percentage correlations have the same significance in the B constants and B/Q values, as Q is entirely a nuclear property. Here, we include the Gaunt interaction at the DF levels as well as in the correlation contributions. The inclusion of this interaction provides a more accurate representation of the percentage electron correlation. In order to show the Z dependence of the percentage correlation, we consider the ions from $Z = 14$ to $Z = 23$ in Figs. 1 and 4. This is due to the fact that the trends which are depicted there have been found to follow general trends of rapid decreases in percentage correlations with increasing ionization between the elements from $Z = 11$ to $Z = 14$. This behavior is expected because, with increasing ionization of an isoelectronic sequence, the core electrons and valence electron become more tightly bound and hence are less perturbed by the correlation [4]. But, in the A constants of the $3d\ ^2D_{3/2,5/2}$ states, we have found unusual pictures inside the region of $Z = 11$ to $Z = 14$. Therefore, here we extend the curves depicting the trends in Figs. 2 and 3 from $Z = 14$ to $Z = 11$. In estimating the correlation contributions of Na and Mg^+, we have considered 13, 12, 12, and 9 number of active orbitals for the s, p, d, and f symmetries, respectively, in order to satisfy the convergence of core correlation energies, as mentioned earlier.

As seen from Fig. 1, the correlation contributions to the $3s\ ^2S_{1/2}$, $3p\ ^2P_{1/2}$, and $3p\ ^2P_{3/2}$ states decrease monotonically from 18.6% to 8.0%, 20.8% to 8.8%, and 8.5% to -2.4% with increasing Z. Also, the percentage correlations to the $3s\ ^2S_{1/2}$ and $3p\ ^2P_{1/2}$ states fall in an almost similar way with increasing ionization and remain positive everywhere. However, for the $3p\ ^2P_{3/2}$ state, these percentage values become negative at $Z \geqslant 18$.

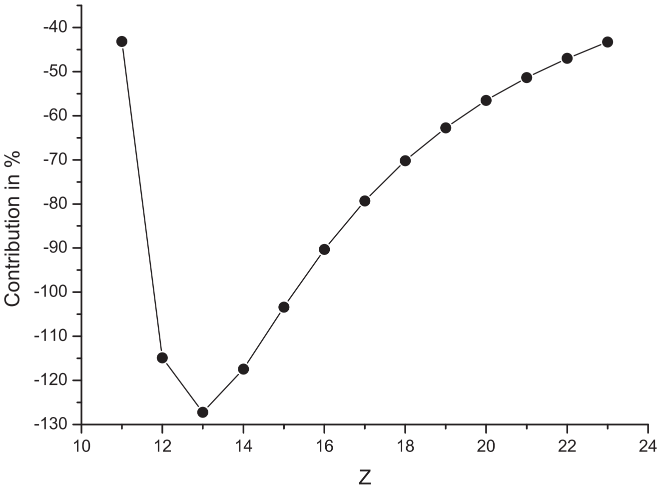

FIG. 3. Percentage correlation contributions to the hyperfine A constants of the $3d\ ^2D_{5/2}$ state.

One can see from Fig. 2 that with increasing Z, the curve depicting the percentage correlation contribution to the $3d\ ^2D_{3/2}$ state rises sharply from -8.1% at Mg^+ and finds a maximum at Cl^{6+} (about 1.4%), from where it falls relatively very slowly to 0.6% at V^{12+}. From $Z = 14$ to $Z = 23$, the correlation is seen to have little impact on the hyperfine constants. Therefore, in order to ensure this unusual picture of Z dependence, we have increased the number of orbitals and orbital symmetries. But we have not found any change in this trend. The reason behind this picture can be understood from the behaviors of the different correlation mechanisms at different regions of Z, which is discussed later in the present section. The percentage negative correlation contribution to Na ($Z = 11$) is seen to be slightly more then Mg^+ ($Z = 12$). However, with the consideration of orbital symmetries beyond f states, we have found the opposite case, i.e., the point at $Z = 11$ is shifted slightly above with respect to the point at $Z = 12$.

From Table II, one can see very large changes in the A constants from the DF to the total values due to abnormal correlation contributions in the $3d\ ^2D_{5/2}$ states of all the ions. Due to this very large correlation, the signs of Si^{3+} and P^{4+} are changed from the DF to the coupled-cluster levels. The trend of the percentage value of this abnormal correlation with increasing ionization is presented in Fig. 3. This trend is seen to be unusual in the lower Z region. From $Z = 11$, the magnitude of the total percentage correlation increases from 43.2% and becomes maximum with value 127.2% at $Z = 13$. From $Z = 13$, it decreases with increasing ionization and finds a value 43.3% at $Z = 23$.

Figure 4 shows that in the B constants, the correlations decrease gradually from 20.8% to 6.4%, 35.4% to -6.1%, and 35.5% to -5.9% for the $3p\ ^2P_{3/2}$, $3d\ ^2D_{3/2}$, and $3d\ ^2D_{5/2}$ states, respectively, with increasing Z. The B constants of the $3d\ ^2D_{3/2}$ and $3d\ ^2D_{5/2}$ states follow almost exactly the same percentage correlation trend with increasing Z, which is obvious in Fig. 4. Also, the percentage correlations to the $3d\ ^2D_{3/2,5/2}$ states vary in a relatively wider range with respect to those of the $3p\ ^2P_{3/2}$ state.

The effects of the important many-body terms, i.e., core correlation (CC), pair correlation (PC), and core polarization (CP), to the hyperfine A and B constants are discussed in the next few paragraphs. Here, also, the percentage values of these terms are calculated with respect to the corresponding DF results and within the framework of the Dirac-Coulomb-Gaunt Hamiltonian. Besides these important terms, some small contributions from the term $S^\dagger \overline{O} S$, the other effective two-body terms, and normalization correction [11,25] are expected and are accounted for in the total correlation. But these terms are not discussed later in the present section. However, the CC contributions are plotted for both the A and B constants of all the states; these contributions rarely have any significance with respect to the PC and CP contributions at any value of Z. The CC effect is accounted for by the modification of the valence orbital due to the correlation among the core electrons. The tightly bound core electrons are perturbed little by this correlation [4] and hence are responsible for the negligible CC effect. Therefore, in the following discussions, we focus mainly on the PC and CP mechanisms to observe their responsibilities in the Z dependence of the total percentage correlations. Like the trends of the total percentage correlations, the trends of these different contributing terms between the elements from $Z = 11$ to $Z = 14$ have been found to follow general trends of rapid decreases in percentage correlations with increasing ionization for the A constants of the $3s\ ^2S_{1/2}$, $3p\ ^2P_{1/2}$, and $3p\ ^2P_{3/2}$ states and the B constants of the $3p\ ^2P_{3/2}$ state.

$3s\ ^2S_{1/2}$ state. For the ground state $3s\ ^2S_{1/2}$, the percentage correlation contributions from the different many-body terms to the A constants are plotted in Fig. 5. All of these contributions show trends of decreasing with increasing Z. The maximum core correlation contribution is seen to be slightly less than 1%. The dominant correlation mechanism

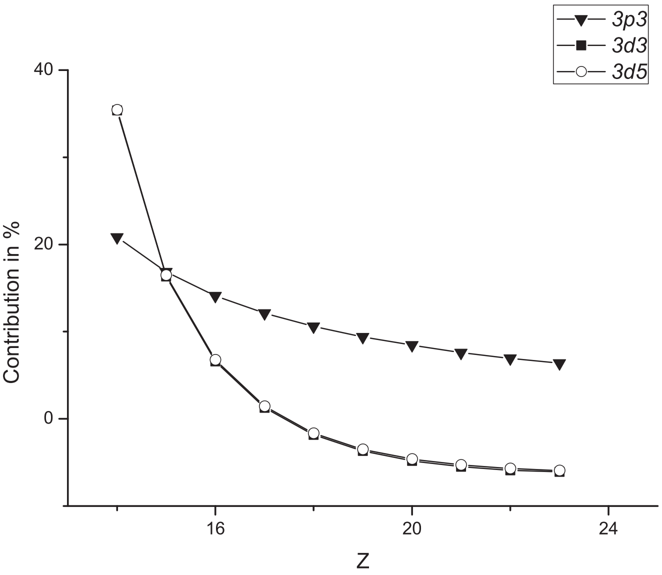

FIG. 4. Percentage correlation contributions to the hyperfine B constants of the $3p\ ^2P_{3/2}$ ($3p3$), $3d\ ^2D_{3/2}$ ($3d3$) and $3d\ ^2D_{5/2}$ ($3d5$) states.

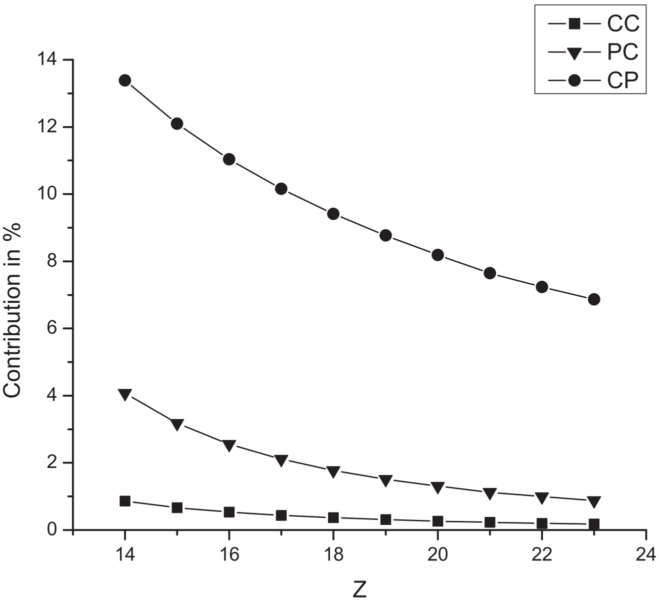

FIG. 5. Percentage correlation contributions from the CC, PC, and CP to the hyperfine A constants of the $3s\ ^2S_{1/2}$ state.

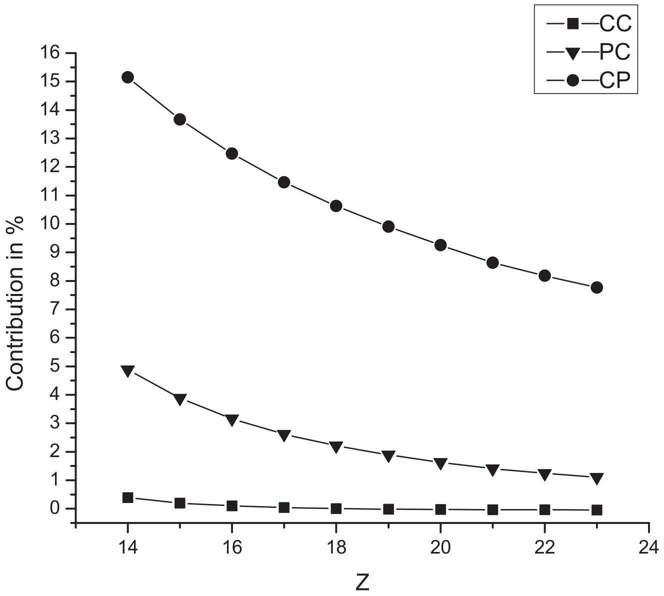

FIG. 6. Percentage correlation contributions from the CC, PC, and CP to the hyperfine A constants of the $3p\ ^2P_{1/2}$ state.

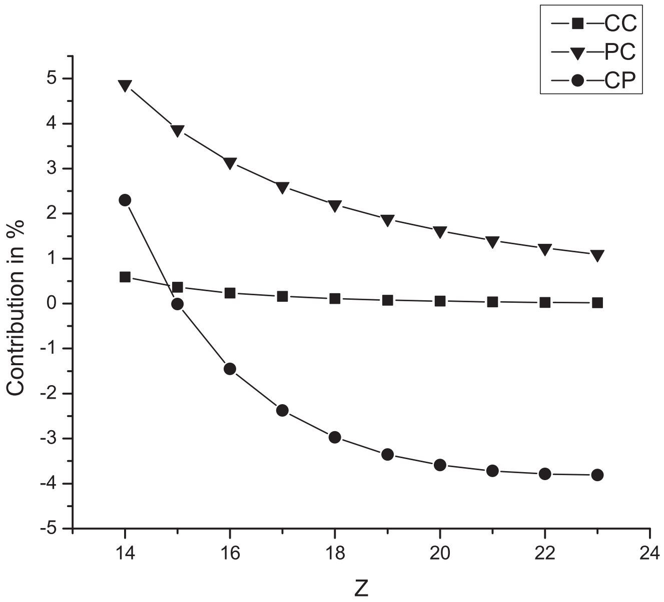

FIG. 7. Percentage correlation contributions from the CC, PC, and CP to the hyperfine A constants of the $3p\ ^2P_{3/2}$ state.

is the CP effect, which varies here from 13.4% to 6.9%. In the case of Ca^{9+}, this effect was estimated around 8.4% by the LCMBPT theory [6], which is found around 8.2% from our RCC calculation. The PC contribution is seen to vary from 4.1% to 0.9%. Here, one thing can be noticed: there is no negative contribution from any one of the three terms at any value of Z. Hence, the addition of all the percentage correlations from these terms ensures a systematic decrease of the total percentage correlation with increasing Z.

$3p\ ^2P_{1/2}$ *state*. The correlation contributions from the different terms to the A constants of the $3p\ ^2P_{1/2}$ states are plotted in Fig. 6. This figure also shows trends of decreasing percentage contributions for all of the terms with increasing ionization. However, for a few ions of higher atomic number, the CC contributions are negative. Here, the CP and PC contributions decrease from 15.1% to 7.8% and 4.9% to 1.1%, respectively, as Z increases. Like the $3s\ ^2S_{1/2}$ state, here also the behavior of the different correlation terms leads to a systematic decrease in the total percentage correlation with increasing atomic number.

$3p\ ^2P_{3/2}$ *state*. For the $3p\ ^2P_{3/2}$ state, we have the opportunity to discuss both the hyperfine A and B constants. The percentage correlation trends from the CC, PC, and CP effects to the A constants are plotted in Fig. 7, whereas those to the B constants are plotted in Fig. 8. In the A constants of this state, one can see a few distinct features which are not observed in the $3s\ ^2S_{1/2}$ and $3p\ ^2P_{1/2}$ states. The first is the greater correlations from the PC effects compared to the CP effects for a few ions ($Z = 14$ to $Z = 17$). The second is the negative contributions from the CPs for the ions with $Z \geqslant 15$. At Cl^{6+} and Ar^{7+}, strong cancellations occur between the negative CPs and positive PCs, leading to the total results which are close to the DF results. As seen from Fig. 7, the PC varies from 4.9% to 1.1% and the CP varies in a relatively wider range from 2.3% to −3.8% with increasing atomic number. The percentage PC contributions to the A constants of the $3p\ ^2P_{1/2}$ and $3p\ ^2P_{3/2}$ states have been found to be identical to each other at every value of Z. Due to the relatively greater negative contribution of the CP with respect to the positive contribution of the PC, the total correlation becomes negative for the ions at $Z \geqslant 18$.

One can see, in Fig. 8, that the percentage correlations from the CP and PC terms to the B constants of the $3p\ ^2P_{3/2}$ state fall with increasing atomic number and remain positive everywhere. As mentioned earlier, the corresponding terms in the A constants of $3s\ ^2S_{1/2}$ and $3p\ ^2P_{1/2}$ states also behave like this. However, the percentage CP effect falls rapidly for the former case compared to the latter two cases. Here, the dominant CP effect and the relatively much less contributing

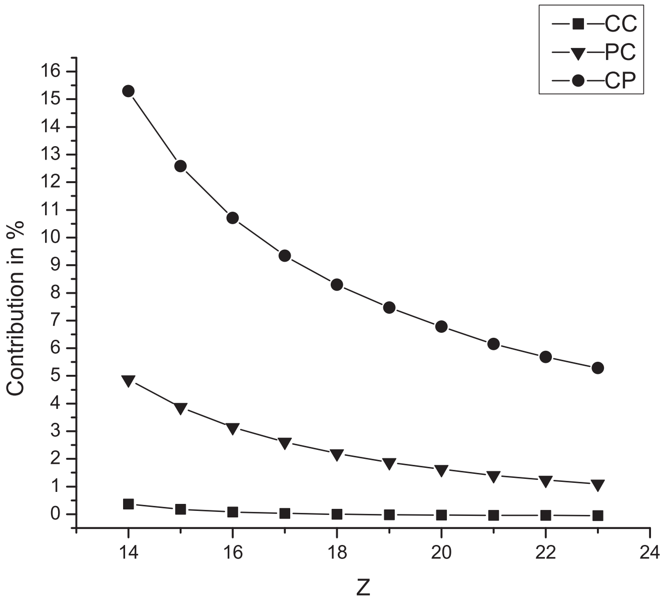

FIG. 8. Percentage correlation contributions from the CC, PC, and CP to the hyperfine B constants of the $3p\ ^2P_{3/2}$ state.

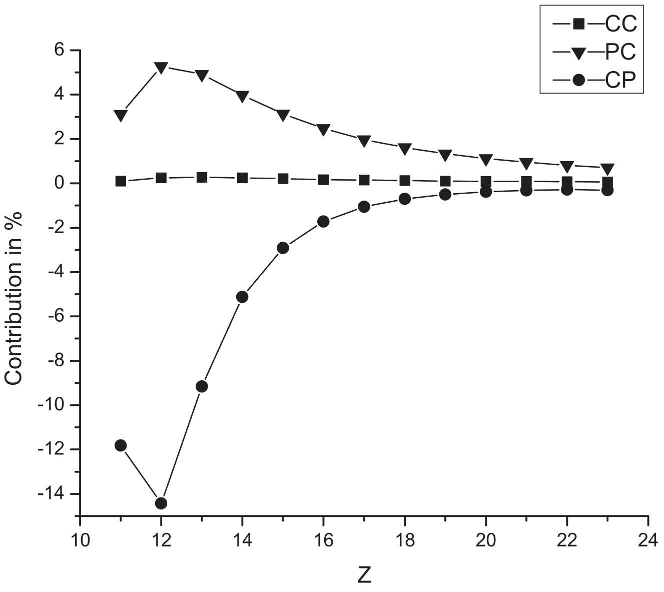

FIG. 9. Percentage correlation contributions from the CC, PC, and CP to the hyperfine A constants of the $3d\ ^2D_{3/2}$ state.

PC effect decreases from 15.3% to 5.3% and 4.9% to 1.1%, respectively, with increasing Z. Also, it has been observed that the percentage PC affects the B constant at a Z value identically to how it affects the A constant at the same Z.

$3d\ ^2D_{3/2}$ state. The contributions from the different correlation mechanisms to the hyperfine A constants of the $3d\ ^2D_{3/2}$ state are plotted in Fig. 9. Here, the competition between the CP and PC is interesting. As one can see from Fig. 9, the CP remains negative and the PC remains positive at every value of Z. From $Z = 14$, both of these effects systematically decrease with increasing ionization, but the former is from -5.1% to -0.3% and the latter is from 4% to 0.7%. As a consequence, one of the effects is largely canceled by the other one in the total correlation at all of the ions considered after $Z = 14$. Therefore, for these ions, the correlated values of the hyperfine A constants of this state can be approximated by the corresponding DF results. The negative CP effect dominates with respect to the positive PC effect from $Z = 11$ to $Z = 13$. As a result, the total correlation remains negative here. However, the PC values are seen to be greater with respect to the CP values at $Z \geqslant 15$ and hence the total correlations become positive here. A close observation of Fig. 9 explains the unusual picture of the total percentage correlation curve at the higher Z region as plotted in Fig. 2. In the region from $Z = 12$ to $Z = 17$, the negative CP effect decreases rapidly compared to the positive PC effect, resulting in a sharp increase in the total percentage correlation curve from $Z = 12$. In contrary, an opposite flow between these two correlation terms is seen to happen at $Z > 17$, leading to a fall in the total percentage correlation curve with increasing ionization. Unexpectedly, from $Z = 12$ to $Z = 11$, both the percentage PC and CP effects change their trends in opposite direction, i.e., both of these effects reduce their impacts with decreasing ionization.

In the B constants of the $3d\ ^2D_{3/2}$ state, as observed in Fig. 10, the CP is seen to dominate over the PC except in the region from $Z = 16$ to $Z = 18$. Here, the former decreases rapidly from $Z = 14$ to $Z = 19$ and then decreases very slowly for $Z > 19$, covering a wide range of 32.2% to -7% with increasing ionization. The PC remains positive everywhere. For this state also, we have found that the percentage PC contribution to the A and B constants is the same at every value of Z. Hence, the percentage PC effect to the B constants of this state also follows the unusual trend at the lower Z region, as depicted in Fig. 9. However, unlike the PC effect, the percentage values of the very strongly dominating CP effect (about 357% for Na, 163% for Mg^{+}, and 71% for Al^{2+}) have been found to decrease with increasing ionization in this region. As a consequence, the total percentage correlation for this case, which is almost determined by the CP effect, follows a general trend, as mentioned earlier in this section. Due to relatively more negative contributions of the CPs, the total correlations become negative for the ions at $Z \geqslant 18$.

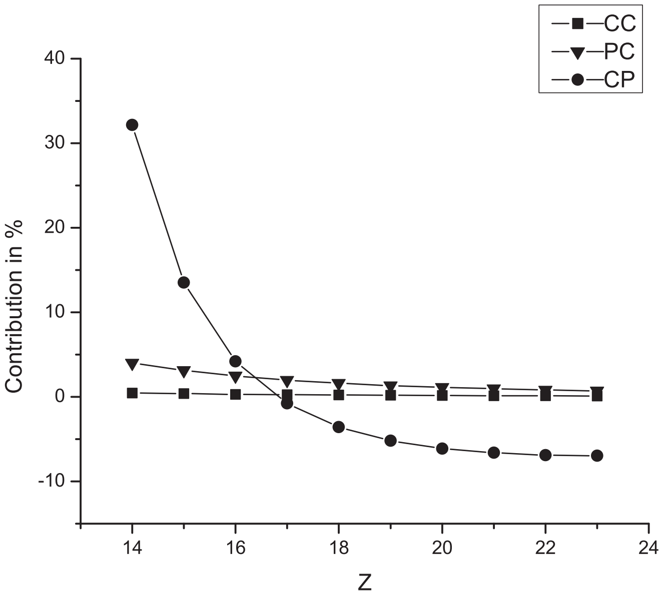

FIG. 10. Percentage correlation contributions from the CC, PC, and CP to the hyperfine B constants of the $3d\ ^2D_{3/2}$ state.

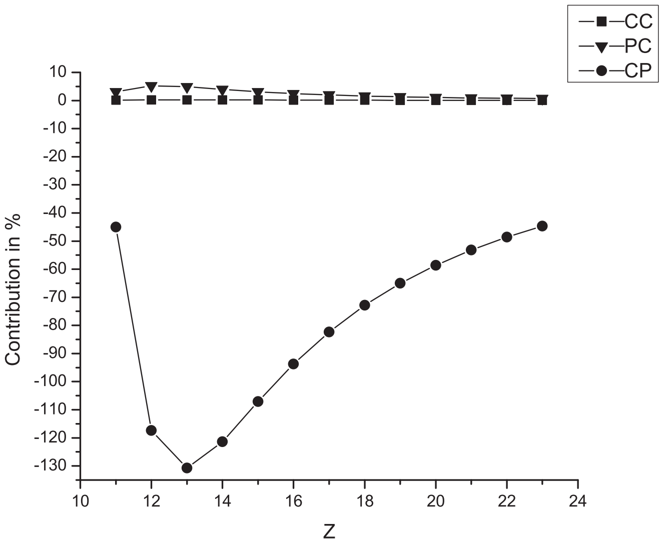

FIG. 11. Percentage correlation contributions from the CC, PC, and CP to the hyperfine A constants of the $3d\ ^2D_{5/2}$ state.

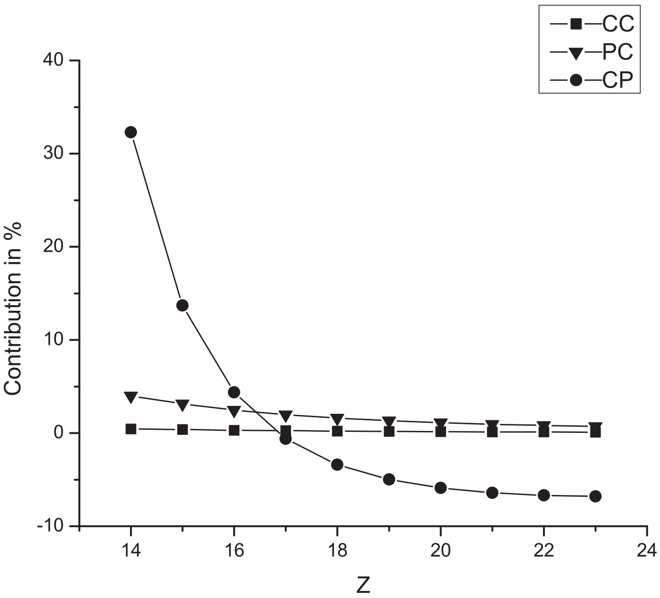

FIG. 12. Percentage correlation contributions from the CC, PC, and CP to the hyperfine *B* constants of the $3d\ ^2D_{5/2}$ state.

The combined effects of these two terms at Cl^{6+} and Ar^{7+} provide little correlation contributions due to large cancellations between them.

$3d\ ^2D_{5/2}$ state. Figure 11 represents the correlations from the different many-body terms to the *A* constants of the $3d\ ^2D_{5/2}$ state. As seen from this figure and Fig. 3, the CP effect can be treated excellently as a determinable factor to the total correlation. This effect itself accounts for the unusual trend of the total percentage correlation at the lower *Z* region in Fig. 3. It contributes a huge amount of negative correlation by more than -100% to Mg^+, Al^{2+}, Si^{3+}, and P^{4+}. But, as seen from Fig. 11, the percentage CP effect reduces its impact considerably at relatively highly ionized species. However, a close look at the curve shows that this reduction decreases consistently on consecutive *Z* values with increasing ionization from $Z = 14$. This is the reason that even for a highly stripped system like V^{12+}, this effect can hold total correlation of about -43%. From our investigation, we have found that here also, the percentage PC contributes equally to the hyperfine *A* constants of the $3d\ ^2D_{3/2}$ and $3d\ ^2D_{5/2}$ states at every value of *Z*.

The percentage correlations from the different contributing terms to the *B* constants of the $3d\ ^2D_{5/2}$ state can be observed in Fig. 12. A close look at Figs. 10 and 12 indicates the fact that the corresponding terms in the *B* constants of the $3d\ ^2D_{3/2}$ and $3d\ ^2D_{5/2}$ states follow almost exactly the same trends with increasing ionization. The differences between them are too small at every ion that it is very difficult to identify any difference between Figs. 10 and 12. This is the reason that both of the total percentage correlation plots of $3d\ ^2D_{3/2}$ and $3d\ ^2D_{5/2}$ states in Fig. 4 almost overlap each other. Therefore, the discussions in the context of the hyperfine *B* constants of the $3d\ ^2D_{3/2}$ state are also valid here, even for $Z = 11$ to $Z = 14$.

IV. CONCLUSION

The correlation trends in the hyperfine *A* and *B* constants of the ground and a few excited states of the Na-like systems have been described extensively. The responsibilities of the different correlation contributing terms for such trends have been analyzed using the coupled-cluster theory based on the Dirac-Coulomb-Gaunt Hamiltonian. The effects of the Gaunt interactions on these hyperfine constants have been presented separately. We have found different pictures of percentage correlation trends in the hyperfine *A* constants of the $3d\ ^2D_{3/2,5/2}$ states with respect to those of the other cases with increasing ionization. The percentage contributions of the corresponding many-body terms have been found to be almost the same for the hyperfine *B* constants of the $3d\ ^2D_{3/2}$ and $3d\ ^2D_{5/2}$ states at every element. The percentage pair-correlation contribution has been found to affect the hyperfine constants of the fine-structure states of a term in a similar way with increasing ionization. Our presented hyperfine data may be applied for astrophysical applications and nuclear quadrupole moment estimations. We hope that this kind of work will be continued in the near future on the several other group of elements, especially on elements that are isoelectronic to heavier atoms.

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