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Fock-space multireference coupled-cluster calculations of the hyperfine structure of isoelectronic $^{33}S^{-}$ and $^{35,37}Cl$

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Due to its flexibility and possible systematic improvement, the Fock-space (FS) multireference coupled-cluster (MRCC) method remains a very important tool for the computation of energy differences of spectroscopic interest. In the present work, the FS MRCC method for the electron detachment process has been applied to determine the magnetic hyperfine constant A_J and nuclear quadrupole moments Q (related to electric hyperfine constant B_J) for the lowest multiplets of $^{33}S^{-}$, ^{35}Cl, and ^{37}Cl with Dirac-Fock orbitals. In addition, we also report $^2P_{3/2}([Ne]3s^2 3p^5) \rightarrow {}^2P_{1/2}([Ne]3s^2 3p^5)$ magnetic dipole transition matrix element and electron affinity of ^{35}Cl (i.e., ionization energy of Cl^-). Calculated properties are in very good agreement with the available new standard or reference values.

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I. INTRODUCTION

The study of magnetic dipole hyperfine structures (related to A_J) are of considerable interest in atomic, molecular, and nuclear physics as these kind of studies not only provide the foundation for a wide range of experiments and precision measurements but also can be used as stringent tests of our fundamental concepts and theories. In fact, some recent studies of frequency standards have yielded sensitive probes of possible temporal variation of the fundamental constants [1–3]. Likewise, the knowledge of reliable nuclear quadrupole moments (NQM) [4–7] is very useful in chemical and solid-state spectroscopy.[1] Accurate estimation of the NQMs (termed as Q) is also pertinent in nuclear physics for testing nuclear models. It is also important to note that as the ratio of the quadrupole splittings (act as a gauge of the electron distribution) for two isotopes can be directly measured by spectroscopic methods, the Q value for one isotope can help determine the value for the other isotopes. As emphasized in the previous articles due to Pyykkö [6,7], during the past two decades the best way to estimate the NQMs has been by combining the experimental quadrupole coupling constants (also known as the electric quadrupole hyperfine interaction constant, B) [8] with calculated electric field gradients (EFG) at the nucleus. Therefore, the accurate determination of NQM relies on both the precise measurement of the nuclear quadrupole coupling constant from spectroscopic methods and the accurate calculation of the EFG (identified here as b) for atoms, molecules, or the solid state. Atomic experiments yield nuclear quadrupole coupling constants, usually with high accuracy and, hence, the reliability of the derived NQM values depends mainly on the accuracy of the EFG calculation. Although, traditionally, EFGs have been estimated from magnetic hyperfine structure along with the correction for quadrupole shielding by Sternheimer's formulation [9], in recent times, the EFGs have been calculated by robust and accurate quality *ab initio* calculations without any further corrections [7]. The error in the measured NQM is determined by the uncertainty in the measurement of EFG. It is worth mentioning that the EFG is very sensitive to changes of the electron distribution. Relativistic effect is as important as electron correlation in the calculation of EFGs. In addition, calculations aiming at high accuracy should include large basis sets (it is important to go to the basis-set limit to get stable EFGs) and high-order treatment of electron correlations [7]. Over the past years, high-level computational methods of quantum chemistry have been employed for the theoretical determination of EFG in small or moderate sized systems and these have led to significantly improved data for NQMs. This molecular method has also resolved some discrepancies between the NQMs computed by different techniques or schemes [5,7]. It is well known that the properties such as magnetic dipole and electric quadrupole hyperfine structures are described by the operators that are prominent in the nuclear region. On the other hand, properties like electronic dipole-quadrupole transition matrix elements (both electric and magnetic) are described by the operators that are prominent at large distance. Thus, accurate determination of hyperfine interaction constants and transition matrix elements require wave functions which can describe the atomic and molecular system(s) over the entire range. *Ab initio* methods like the multireference coupled-cluster scheme within the framework of the four-component Dirac-Coulomb Hamiltonian is very promising in the calculation of both relativistic and electron correlation effects in an effective manner.

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[1] Atomic nuclei with the nuclear spin $I \geqslant 1$ have nuclear electric quadrupole moments.

In this paper, we study the hyperfine interactions in isoelectronic S^- and Cl systems using Fock-space (FS) multireference coupled-cluster (MRCC) method, a multireference variant of the coupled-cluster method, within the framework of the four-component Dirac-Coulomb Hamiltonian. The study of hyperfine interactions for these systems is particularly important as the experimental [10–12] and theoretical studies (at *ab-initio* level) are scarce [9,13–17]. The first *ab initio* study on the NQM of ^{35,37}Cl and ^{33}S (on S^-) was carried out by Sundholm and Olsen [13,18]. Using the multiconfiguration Hartree-Fock (MCHF) method, they estimated the NQM of ^{35}Cl, ^{37}Cl, and $^{33}S^-$ to be −81.65 mb [13], −64.35 mb [13], and −67.8 mb [18], respectively. Alonso *et al.* [14] obtained a value of −85.5(1.1) mb from the *ab initio* full-potential linear-augmented plane-wave method. In their scheme, the EFG was estimated by using the generalized gradient approximation (for exchange and correlation effects). Their solid-state-based value for ^{35}Cl was later revised to −85.0(1.1) mb [7]. The calculated $Q(^{35}\mathrm{Cl})$ from to Kellö and Sadlej [15] is −81.6 mb. In their calculation, the electron correlation contribution has been accounted for at the level of the coupled-cluster method with singles, doubles, and perturbative triples [CCSD(T)] approximation and the spin-averaged no-pair approximation to the Dirac-Coulomb Hamiltonian has been used for the evaluation of the relativistic contribution. A full-blown relativistic MRCC calculation on the NQM of ^{35}Cl was later carried out by Yakobi *et al.* [16]. They used the relativistic FS MRCC method to calculate the EFG at the atomic nuclei by the finite-field approach. Their best estimated Q (^{35}Cl) after incorporating the Gaunt corrections (main part of the Breit interaction) is −81.1 mb. This value is accepted as the new standard value for Q (^{35}Cl) [7]. Recently, Carette *et al.* [17] re-examined these two systems using the multireference configuration interaction (MRCI) method with nonrelativistic spinors in which the relativistic corrections were incorporated via Pauli approximation. With this scheme, they obtained a value of −65.7, −81.764, and −64.438 mb for the NQM of $^{33}S^-$, ^{35}Cl, and ^{37}Cl, respectively. Carette *et al.* [17] also obtained a reliable estimate of magnetic dipole hyperfine constants (A_J) for these systems. However, their assignment of magnetic dipole hyperfine constants for ^{35}Cl and ^{37}Cl appears to be inverted [19]. Since the nuclear magnetic moment of ^{35}Cl is higher than that of ^{37}Cl, the magnetic dipole hyperfine constant of ^{35}Cl should also be higher than that of ^{37}Cl (magnetic dipole hyperfine constant is directly proportional to the nuclear magnetic moment). Thus, these systems merit reinvestigation with full-blown relativistic many-body methods for proper assignments of magnetic dipole hyperfine constants of Cl isotopes and other spectroscopic constants.

It has now been widely accepted that the FS MRCC [20–22] method is a compact, efficient, and balanced formulation for the energy differences relative to a closed-shell reference state. The FS MRCC method can have many versions [20,21]. Guided by a general idea of having a single Fermi vacuum for all references, one can formulate different versions of the FS MRCC method. The critical feature of FS MRCC formulation is it size extensivity which is fulfilled by the exponential definition of the wave operator. By construction, the FS MRCC method has been tailored to treat differential correlation effects and orbital relaxation accompanying ionization, electron attachment, or excitation. Both effects play a crucial role in shaping diverse structural and spectroscopic properties. Thus, the FS MRCC method is the natural method of choice for the computation of energy differences of spectroscopic interest. Its wide use in high-precision theoretical spectroscopic calculations or predictions is well documented in the literature [21,23,24]. The FS MRCC method starts with the CC solution for a closed-shell parent state (termed a *core*), generally, the ground state, and then the higher valence sectors are hierarchically addressed until the desired valence sector is reached (since equations for the Fock space excitation operator in a given sector do not involve amplitudes from the higher valence sectors). To improve the convergence behavior of the traditional FS MRCC equations in the presence of intruder states,[2] various methodologies have been developed and implemented [23–25]. It is worth mentioning that in recent times various attempts have been made to extend the FS MRCC method to various relativistic systems [26–28].

II. METHODOLOGY

In this section we want to discuss in brief the important and essential theoretical aspects which are pertinent for our present work.

A. Basic preliminaries

The calculations reported here are carried out in the framework of the four-component Dirac-Coulomb Hamiltonian

$$\mathrm{H} = \sum_i h_D(i) + \sum_{i<j} e^2/r_{ij}, \tag{1}$$

where h_D is the one-electron Dirac Hamiltonian. Here, the nuclei are described by the Fermi nucleus model to capture the effect arising from finite-size nuclear correction.

In the FS MRCC theory, we seek the solution of the Schrödinger equation $H\Psi_K = E_K\Psi_K$ for the K^{th} state of the system. The wave function Ψ_K is constructed by operating with the valence universal wave operator Ω on the model function. We start by assuming that there exists a set of model functions spanning a model space of dimension M with the projector $\mathcal{P} = \sum_I^M |\Phi_I\rangle\langle\Phi_I|$ while the complementary functions (virtual) spanning the complement of the model space are characterized by the projector $\mathcal{Q}$. The union of $\mathcal{P}$ and $\mathcal{Q}$ defines the entire space. The ansatz [20,21] used is $\Omega = \Omega_c\Omega_v = \exp(T)\{\exp(S)\}$ (which is *valence universal* in the sense that the same Ω is used for all solutions),

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[2] The Fock-space approach is plagued by divergence problems in the iterative process when intruder states occur. The intruders originate from situations where some high-lying model functions come close in energy with some low-lying virtual functions, spoiling the convergence of the MRCC equations and hence of the quality of the all computed roots. That situation is more likely to occur when large model spaces are used. Intruder states cause problems with converging the desired physical solution of the MRCC equations and are blamed for the significant deterioration of the quality of the results, when the ground state becomes nondegenerate. Intruder states or solutions constitute a serious limitation of the MRCC approach.

where {} denotes the normal-ordered form. The Fock space excitation operator is defined with respect to a reference determinant, which we take to be a closed shell (this restriction makes application more convenient, but a single open-shell determinant may also be employed). The starting point of the FS MRCC method involves solution of cluster equations for the (0,0) valence sector. This is the usual single reference problem; its implementation in the framework of two- and four-component relativistic functions has been described nicely in Ref. [29]. Calling the similarity transformed Hamiltonian $\exp(-T)H\exp(T)$ as $\bar{H}$, the closed-shell CC equations determining the amplitudes of T can be compactly written as

$$\langle \Phi_l^* | \overline{H} | \Phi \rangle = 0 \;\; \forall \;\; l, \tag{2}$$

where T consists of hole-particle excitations from Φ and $\langle \Phi_l^* | \Phi \rangle = 0$.

The FS Bloch equation for k-hole and l-particle valence sector can be written as [20,21]

$$\begin{aligned} \mathcal{Q}^{(k,l)}\overline{H\Omega_v}\mathcal{P}^{(k,l)} &= \mathcal{Q}^{(k,l)}\overline{\Omega_v H}_{\text{eff}}\mathcal{P}^{(k,l)}, \\ \mathcal{P}^{(k,l)}\overline{H\Omega_v}\mathcal{P}^{(k,l)} &= \mathcal{P}^{(k,l)}\overline{\Omega_v H}_{\text{eff}}\mathcal{P}^{(k,l)}. \end{aligned} \tag{3}$$

The hierarchical structure of the wave operator as well as the resulting equations is a characteristic feature of the FS MRCC approach. Here, H_{eff} defined as $\mathcal{P}H\Omega\mathcal{P}$ (in terms of the matrix elements, $H_{\text{eff}}^{IJ} = \langle \Phi_I | H\Omega | \Phi_J \rangle$). The energy difference with respect to the reference state can be obtained directly by removing the term $H_{\text{eff}}^{(0,0)} = E_{\text{ref}}$ from Eq. (3). Here, $\overline{H\Omega_v}$ denotes all the connected terms in which Ω_v are joined to $\overline{H}$. After convergence is achieved in a particular sector, H_{eff} is diagonalized to yield all energies of $\mathcal{P}^{(k,l)}$ states in that sector relative to the correlated energy of the reference determinant. This amounts to obtaining a large number of states simultaneously. The energies obtained by diagonalizing H_{eff} are size extensive [21]. This, in contrast to the single reference approach, enjoys an obvious advantage of bypassing the computationally expensive four-component HF and four-index transformation steps prior to the calculation of every CC energy. The method is additionally meritorious in the sense that full spatial and spin symmetries remain embedded in this approach through the inclusion of all pertinent determinants in $\mathcal{P}$, alleviating the possibilities of symmetry breaking which deters the single determinant open-shell approaches. The ease of evaluating the full manifold of excited states via a single run is definitely a remarkable asset of the method.

The FS MRCC equations for the one-hole valence sector (corresponds to electron detachment process, i.e., ionization process) can be expressed as

$$\begin{aligned} \mathcal{Q}^{(1,0)}[\overline{H} + \overline{\overline{H}S^{(1,0)}} - \overline{S^{(1,0)}\overline{H}_{\text{eff}}}]\mathcal{P}^{(1,0)} &= 0, \\ \mathcal{P}^{(1,0)}[\overline{H} + \overline{\overline{H}S^{(1,0)}}]\mathcal{P}^{(1,0)} &= \overline{H}_{\text{eff}}^{(1,0)}. \end{aligned} \tag{4}$$

The effective Hamiltonian constructed from H, T, and $S^{(1,0)}$ is then diagonalized within the model space to obtained the desired eigenvalues and eigenvectors. In the implementation of the method we mainly exploit diagrammatic forms of the FS equations to efficiently organize the calculations presented here.

The closed-shell S^{2-} and Cl^- systems are used as reference states. The Dirac-Hartree-Fock (DHF) functions are first obtained and correlated by the CC approach with singles and doubles approximation (CCSD). An electron is then removed, and the functions of the S^- and Cl are then recorrelated following the FS scheme:

$$\begin{aligned} \mathrm{S}^{2-}(0,0) - e &\rightarrow \mathrm{S}^-(1,0) \\ \mathrm{Cl}^-(0,0) - e &\rightarrow \mathrm{Cl}(1,0). \end{aligned}$$

There have been many implementations of the standard effective Hamiltonian formulation of the basic FS MRCCSD model [22]. Since the full-blown coupled cluster with single, double, and triple excitations is computationally expensive, the effect of triples in the calculation of electron removal energy is included in an approximate way [30]. In passing, to increase the efficacy and potentiality of the FS MRCCSD scheme, inclusion of triples has also been studied by various workers [31].

Once the cluster amplitudes T and S are known, the transition/hyperfine matrix elements between the initial $|\Psi_i^{(1,0)}\rangle$ and final $|\Psi_f^{(1,0)}\rangle$ states are computed using the following expression

$$\langle Z \rangle_{fi} = \frac{\langle \Psi_f^{(1,0)} | Z | \Psi_i^{(1,0)} \rangle}{\sqrt{\langle \Psi_f^{(1,0)} | \Psi_f^{(1,0)} \rangle \langle \Psi_i^{(1,0)} | \Psi_i^{(1,0)} \rangle}} \tag{5}$$

which can be further simplified to

$$\langle Z \rangle_{fi} = \frac{\langle \Phi_f^{(1,0)} | \overline{\{1+S^\dagger\}\overline{Z}\{1+S\}} | \Phi_i^{(1,0)} \rangle}{[\langle \Phi_f^{(1,0)} | \overline{\{1+S^\dagger\}\overline{O}\{1+S\}} | \Phi_f^{(1,0)} \rangle \langle \Phi_i^{(1,0)} | \overline{\{1+S^\dagger\}\overline{O}\{1+S\}} | \Phi_i^{(1,0)} \rangle]^{1/2}}, \tag{6}$$

where $\overline{Z} = \overline{e^{T^\dagger} Z e^T}$, $\overline{O} = \overline{e^{T^\dagger} e^T}$, and $|\Phi^{(1,0)}\rangle$ is the model-space function for the (1,0) valence sector. In the actual computations, terms higher than $\overline{T^\dagger Z T}$ and $\overline{T^\dagger T}$ are not included in computation of $\overline{Z}$ and $\overline{O}$, respectively.

B. Electric quadrupole hyperfine structure

The NQM, Q cannot be computed directly. In the present work, expectation value of the EFG operator is used to calculate the electric field gradient at the nuclei which are needed to obtain the NQMs from experimental quadrupole coupling constants via the following relation [17,32]:

$$B = 2eQb. \tag{7}$$

Here, we compute the EFG b from the magnetic hyperfine structure and estimate Q via

$$eQ = \frac{B_{\text{expt}}}{2b_{\text{theor}}}. \tag{8}$$

The EFG can be calculated from the magnetic hyperfine structure which for the jj-coupled state $|IJFM_F\rangle$ is of the form:

$$b = \left[\frac{2J(2J-1)}{(2J+1)(2J+2)(2J+3)}\right]^{1/2} \langle J||\mathcal{T}^{(2)}||J\rangle, \tag{9}$$

where I and J are the total angular momentum of the nucleus and electron state, respectively, and $F = I + J$. The operator $\mathcal{T}^{(2)}$ is given by

$$\mathcal{T}^{(2)} = \sum t_i^{(2)}, \tag{10}$$

where the sum runs over all electrons. The single-particle matrix element of $t_i^{(2)}$ can be factored out into angular part and radial integrals as [32]

$$\langle n\kappa m|t_i^{(2)}|n'\kappa' m'\rangle = -\langle n\kappa m|C_i^{(2)}|n'\kappa' m'\rangle \times \int r^{-3}[P_\kappa(r)P_{\kappa'}(r) + Q_\kappa(r)Q_{\kappa'}(r)]dr, \tag{11}$$

where n, κ, and m are the principal, angular, and magnetic quantum numbers, respectively. The angular-momentum operator $\kappa = \mp(j + 1/2)$ for $j = l \pm 1/2$, with l and j being the orbital and total angular-momentum operator. The functions $P(r)$ and $Q(r)$ are the large and the small components of the radial functions.

C. Magnetic dipole hyperfine structure

The magnetic dipole hyperfine constant A is defined as

$$A = \mu_N\left[\frac{\mu_I}{I}\right]\frac{\langle J||\mathcal{T}^{(1)}||J\rangle}{\sqrt{J(J+1)(2J+1)}}, \tag{12}$$

where μ_I and μ_N are the nuclear dipole moment and nuclear magneton, respectively, and $\mathcal{T}^{(1)} = \sum t_i^{(1)}$. Like $t_i^{(2)}$, the single-particle matrix element of $t_i^{(1)}$ can be written as

$$\langle \kappa m|t_i^{(1)}|\kappa' m'\rangle = -\langle -\kappa m|C_i^{(1)}|\kappa' m'\rangle(\kappa + \kappa') \times \int r^{-2}[P_\kappa(r)Q_{\kappa'}(r) + Q_\kappa(r)P_{\kappa'}(r)]dr. \tag{13}$$

The angular part of Eqs. (11) and (13) can be written as

$$\langle \kappa m|C_i^{(k)}|\kappa' m'\rangle = (-1)^{j-m}\begin{pmatrix} j & k & j' \\ -m & i & m' \end{pmatrix}\langle \kappa||C^{(k)}|\kappa'\rangle, \tag{14}$$

where

$$\langle \kappa||C^{(k)}||\kappa'\rangle = (-1)^{j+1/2}\sqrt{(2j+1)(2j'+1)} \times \begin{pmatrix} j & k & j' \\ 1/2 & 0 & -1/2 \end{pmatrix}\pi(l,k,l') \tag{15}$$

with

$$\pi(l,k,l') = \begin{cases} 1 & \text{if } l+k+l' \text{ even} \\ 0 & \text{otherwise} \end{cases}. \tag{16}$$

III. RESULTS AND DISCUSSION

The calculations for the S$^-$ and Cl systems have been carried out using a $26s20p16d13f11g7h$ uncontracted well-tempered basis set of Huzinaga and Klobukowski [33] of the form

$$\zeta_N = \alpha; \quad \zeta_{N-k+1} = \zeta_{N-k+2}\beta\left[\gamma + \left(\frac{k}{N}\right)^{\delta}\right] \quad k = 2,\ldots,N. \tag{17}$$

The basis set used here for the Cl atom is very similar to that used by Yakobi *et al.* [16] except that we have added some additional h functions. Kinetically balanced single-particle DHF orbitals for S^{2-} (Cl$^-$) are generated using $\alpha = 0.05804$ (0.07536), $\beta = 1.9310$ (1.9242), $\gamma = 1.5034$ (1.4932), and $\delta = 5.7796$ (5.6771), respectively. The high-lying virtual orbitals are discarded at the CC stage of calculations. The s and p orbitals having orbital energies (ϵ) greater than 500 a.u. are kept frozen in the CC calculation. Likewise, the cut-off energies for the d, f, g, h orbitals are set at 100, 50, 50,

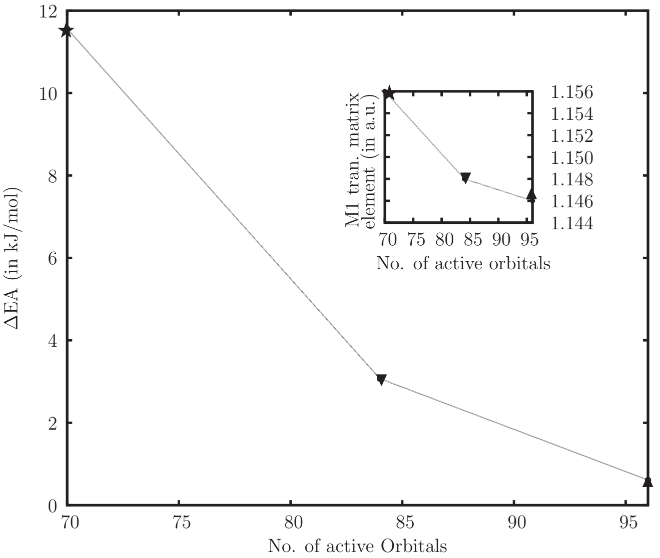

FIG. 1. Plot of error in the computed electron affinity (in kJ/mol) with respect to experiment [ΔEA = EA(theory) − EA(experiment)] vs. the number of active orbitals at the CC stage. The figure in the inset depicts the variation of $M1$ transition matrix elements against the number of active orbitals. In the figure, ★, ▼, and ▲ represent the $26s20p16d13f$ (70 active orbitals), $26s20p16d13f11g$ (84 active orbitals), and $26s20p16d13f11g7h$ (96 active orbitals) basis sets, respectively.

TABLE I. Comparison of magnetic hyperfine A_J constants (in MHz) and nuclear quadrupole moments Q (mb) for the lowest multiplets of ${}^{33}\mathrm{S}^-$, ${}^{35}\mathrm{Cl}$, and ${}^{37}\mathrm{Cl}$. To illustrate the influence of correlation effects on the NQMs, the zeroth-order (uncorrelated) values are shown in the parentheses. As per our estimation, the average absolute error bars are about 1% (see text for details).

	Magnetic hyperfine constants (A_J)					
	${}^{33}\mathrm{S}^-$		${}^{35}\mathrm{Cl}$		${}^{37}\mathrm{Cl}$	
Method	$A_{3/2}$	$A_{1/2}$	$A_{3/2}$	$A_{1/2}$	$A_{3/2}$	$A_{1/2}$
MRCI[a] [17]	92.48	482.30	202.45	1016.46	168.52	846.09
MRCI + RC[b] [17]	91.43	496.28	201.25	1113.22	167.52	872.05
Present work	91.30	442.50	204.42	965.16	170.16	803.40
	(71.17)	(369.58)	(159.92)	(824.90)	(133.12)	(686.64)
Experiment	91.49 [10]		205.05 [11,12]		170.69 [11,12]	

	Nuclear quadruple moments (Q)		
	${}^{33}\mathrm{S}^-$	${}^{35}\mathrm{Cl}$	${}^{37}\mathrm{Cl}$
MRCI[a] [17]	−65.5	−82.265	−64.833
MRCI + RC[b] [17]	−65.7	−81.764	−64.438
MCHF	−67.8 [18]	−81.65 [13]	−64.35 [13]
FS MRCC [16]		−81.1	
Ref. [12]		−78.94	−62.13
Present work	−65.8	−79.5	−62.7
	(−76.3)	(−90.5)	(−71.3)

[a] Nonrelativistic results.
[b] MRCI with relativistic corrections.

and 20 a.u., respectively. The overall basis set used in the CC calculations comprises $12s$, $12p$, $9d$, $8f$, $7g$, and $6h$ functions.

Figure 1 depicts the error in our computed electron affinity of Cl (or ionization energy of Cl^{-1}) with respect to experiment [34] against the basis function. The variation of magnetic dipole matrix for the lowest ${}^2P_{3/2} \rightarrow {}^2P_{1/2}$ transition with respect to the number of basis functions is also shown in Fig. 1. As can be seen in the figure, the accuracy of our computed electron affinity increases with an increase in basis set size. It further demonstrates that the inclusion of g and h functions barely affects the magnetic dipole matrix element value.

The magnetic dipole hyperfine constants of ${}^{33}\mathrm{S}^-$, ${}^{35}\mathrm{Cl}$, and ${}^{37}\mathrm{Cl}$ computed[3] using the FS MRCC method with $26s20p16d13f11g7h$ basis functions are compared with experiment and earlier theoretical calculations in Table I. The NQMs estimated at the FS MRCC level of theory are also listed in Table I. The results presented in the table can be summarized as follows: (a) The FS MRCC estimates of hyperfine constants (A) for Cl are in better agreement with experiment (off by 0.5 MHz) than those resulting from the MRCI method (off by 3–4 MHz). (b) The MRCI estimate of A for ${}^{33}\mathrm{S}^-$ is slightly better (off by 0.06 MHz) than the FS MRCC value (off by 0.2 MHz). (c) The nuclear quadrupole moment of S^- obtained from FS MRCC is almost identical to that reported by Caratte and Godefroid (MCHF CI with relativistic corrections) [17]. (d) The present estimate of the nuclear quadrupole moment of ${}^{35}\mathrm{Cl}$ is 1.5 mb (2%) less than that obtained by Yakobi *et al.* from the finite-field FS MRCC scheme. It also differs by 2 mb from the MCHF and MRCI estimates. This difference (especially with respect to the previous FS MRCC value) clearly indicates that the uncertainty in our computed EFG b is almost 2%.

It is worth noting that the accuracy of the nuclear quadrupole coupling constant (B_{expt}) from which the NQM value has been estimated is quite high. The uncertainty in the theoretically computed EFG can arise due to the basis set size and/or level of treatment of electron correlation (a very important source of error is the neglect of triple and higher excitations in the CC expansion). This aspect has been discussed at length by Pyykkö [6,7] and Stralen *et al.* [35]. Since the basis set and level of theory used by us and also by Yakobi *et al.* [16] are almost same, the difference in the calculated NQM values can be solely attributed to the way the EFG has been estimated in these two calculations. It is pertinent to note that the numerator and the denominator of Eq. (6) (from which b has been estimated) are, by construction, nonterminating and, hence, can invite uncertainty or error in the computed EFG value. The truncation error, in principle, can be minimized by incorporating more terms in the numerator and the denominator which, however, is a nontrivial task. This problem can be alleviated or at least attenuated by invoking the analytical gradient approach for the computation of EFG and other related properties. The present calculation has more room for further improvement in accuracy. More extensive applications are underway and will be reported in our forthcoming articles.

At this juncture, it is worthwhile to mention the error bars of our computed values. As a matter of fact, the error bars (uncertainty estimates) of the atomic data are difficult to establish. We reiterate that they should combine both the inaccuracies in the determination of the EFG (from the method of calculation of the electron correlation) and B constants (from the atomic spectra) and the inaccuracies emerging from

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[3] The states for which A's ($A_{1/2}$ and $A_{3/2}$) have been computed here can be written explicitly as $[\mathrm{Ne}]3s^23p_{1/2}3p_{3/2}^4$ (${}^2P_{1/2}$, $I = 3/2$, $J = 1/2$, $F = 2$, $m_F = 0$) and $[\mathrm{Ne}]3s^23p_{1/2}^23p_{3/2}^3$ (${}^2P_{3/2}f$, $I = 3/2$, $J = 3/2$, $F = 3$, $m_F = 0$), respectively.

the incompleteness of the basis sets. Moreover, the source of error may also arise due to the exclusion of high-lying virtual orbitals all occupied orbitals are active in our CCSD calculations). To illustrate the uncertainty due to the omission of high-lying virtual orbitals, we have carried out the CCSD calculations for Cl atom with $16s15p15d13f11g7h$ (virtual orbitals with orbitals energy 5000 a.u. are kept frozen, which effectively means that all the orbitals remain active in the post Dirac-Fock treatment). The CCSD calculation with this 138 active orbitals yields the NQM values of ^{35}Cl and ^{37}Cl to be -78.8 mb and -62.1 mb, respectively. These results indicate that the uncertainty in our calculations with $12s12p9d8f7g6h$ active orbitals is $\sim$1%, which is quite small and can be taken into account by adding 1 mb to the error bar. Similar deviations have also been found for the magnetic hyperfine constants and ionization potential of Cl atom. We emphasize that from the computational point of view, CCSD calculations with this high cutoff (5000 a.u.) are extremely cost-effective for heavy atoms and that is why the low-lying occupied and high-lying virtual orbitals are generally kept frozen in the CCSD treatments.

IV. CONCLUSION

In this work, the state-of-the-art FS MRCC method with single and double excitations within the DHF framework has been used to study the properties of ^{35,37}Cl and ^{33}S$^-$ systems of spectroscopic interest. A closer inspection of the results presented here reveals that the magnetic hyperfine constants (A_J) obtained using the FS MRCC method are in acceptably good agreement with the available experiment and current generation theoretical estimates. The electron affinity provided by the relativistic FS MRCC is also in good agreement with experiment.

A closer look at the results shows that our estimated $Q(^{35}\text{Cl})$ show good overall agreement with the latest reference values [7]. Our computed value is off by 2% from the earlier FS MRCC estimate of Kaldor and coworkers [16], where the EFG value had been calculated via a finite-field approach (numerical gradient scheme). We reiterate that, in our opinion, this difference arises due to the uncertainty in our computed EFG value (via expectation value technique). The deviation of our computed values with respect to the accepted reference value can be removed or at least attenuated via a better treatment of relativity and electron correlation which may decrease the computed EFG and, therefore, increase the derived NQM toward the current generation standard value.

We end this paper by quoting Pyykkö, who, in a recent review, wrote [7]: "The study of nuclear quadrupole moments of the elements is in a sense a tiny science, having about hundred objects, each characterized by a single number, usually known with less than three-figure accuracy." These wise words can perfectly serve as a motivation and summary of our present work. We could not say it better.

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