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Nuclear quadrupole moment of ^{43}Ca and hyperfine-structure studies of its singly charged ion

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By combining our theoretical calculation and the recently measured electric quadrupole hyperfine-structure constant of the $3d\ ^2D_{5/2}$ state in the singly ionized ^{43}Ca, we determine its nuclear quadrupole moment to 1% accuracy. The obtained result, $-0.0444(6)b$, is about 10% more accurate over its current accepted value. We have employed the relativistic coupled-cluster theory at the single and double excitations level to calculate the atomic wave functions. The accuracy of these wave functions is estimated by comparing our calculated magnetic dipole hyperfine constants with their corresponding available experimental results of many low-lying states. We also present hyperfine-structure constants for other higher excited states where experimental results are not reported. The role of the Breit interaction has been investigated in these properties.

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I. INTRODUCTION

Advanced modern techniques of laser cooling and trapping have enabled experimentalists to carry out precision measurements of hyperfine-structure constants in atomic systems [1,2]. Theoretical studies of these quantities require accurate many-body methods, inclusion of relativistic effects, and the knowledge of nuclear moments [3–6]. Precise measurements of nuclear moments are difficult, especially the quadrupole and octupole moments. The prominent examples of techniques to measure them are NMR, atomic beams, optical pumping, recoil methods, etc. [7,8]. However, their absolute results are of great interest for the nuclear physicists to be able to test different nuclear models [9,10]. The quadrupole moment of the stable isotope ^{43}Ca is also of particular interest in the evaluation of the nuclear magnetic resonance measurements in biological systems [11,12]. Investigating properties of nuclei in the region of magic numbers is challenging because the valence nucleons can be strongly affected by the close shell configuration. ^{43}Ca has mass number between the double magic numbers ^{40}Ca and ^{48}Ca suggesting a peculiar nuclear charge distribution. It is possible to obtain accurate electronic wave functions and hence properties of single valence atomic systems using the relativistic coupled-cluster (RCC) theory [6,13–15].

It has been shown that electron correlation effects exhibit spectacular behavior in the studies of the magnetic dipole hyperfine-structure constant in the $^2D_{5/2}$ states of the singly ionized alkaline-earth-metal atoms. The coupled-cluster singles and doubles (CCSD) method with contributions from the leading order triple excitations [CCSD(T) method] is able to yield results that are in very good agreement with the precisely measured values of these quantities [15–17]. In this work, we have used this method to evaluate the electronic matrix elements due to the hyperfine interaction operators.

^{43}Ca$^+$ is an interesting candidate for quantum computation [18] and optical frequency standard [19,20]. Accurate values of hyperfine-structure constants are useful in estimating shifts in the energy levels due to the stray electromagnetic fields for certain experiments [21,22]. Again, theoretical estimations of these quantities are used to test the correct behavior of wave functions in the nuclear region [23,24]. The nuclear magnetic moment of ^{43}Ca is known within sub-1% accuracy [25], but its reported nuclear quadrupole moment values vary from $-0.0408(8)b$ to $-0.065(20)b$ [26–30]. Using the accurate matrix element of the electric quadrupole hyperfine interaction operator and the precisely measured [31] electric quadrupole hyperfine-structure constant of the $3d\ ^2D_{5/2}$ state in ^{43}Ca$^+$, it is possible to determine its nuclear quadrupole moment. The accuracy of the calculations is estimated from an analysis of the accuracy of the wave functions which reproduce the magnetic dipole hyperfine-structure constants in a few low-lying states where experimental results are available. We also present hyperfine-structure constants of other excited states and they can be compared with the results of high precision experiments if they become available in the future.

II. THEORY AND METHOD OF CALCULATIONS

The detailed theory of hyperfine structure has been given earlier in a classic paper by Schwartz [5]. Here, we have mentioned only the relevant formulas in explicit form. The relativistic hyperfine interaction Hamiltonian is given by

$$H_{hfs} = \sum_k \mathbf{M}^{(k)} \cdot \mathbf{T}^{(k)}, \tag{2.1}$$

where $\mathbf{M}^{(k)}$ and $\mathbf{T}^{(k)}$ are spherical tensor operators of rank k. In the first-order perturbation theory, the hyperfine interaction energy W_F of the hyperfine state $|F;I,J\rangle$ with angular momentum $F=I+J$ for I and J being the nuclear spin and electronic angular momentum of the associated fine structure state $|J,M_J\rangle$, respectively, after neglecting terms beyond $k=2$ is given by

$$W_F = \frac{1}{2}A_{hfs}K + B_{hfs}\frac{\frac{3}{2}K(K+1) - 2I(I+1)J(J+1)}{2I(2I-1)2J(2J-1)}, \tag{2.2}$$

where $K=F(F+1)-I(I+1)-J(J+1)$, A_{hfs} is the magnetic dipole structure constant for $k=1$, and B_{hfs} is the electric quad-

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rupole structure constant for $k=2$. These constants are defined as

$$A_{hfs} = \mu_N g_I \frac{\langle J||\mathbf{T}^{(1)}||J\rangle}{\sqrt{J(J+1)(2J+1)}}, \tag{2.3}$$

and

$$B_{hfs} = Q_{nuc}\left\{\frac{8J(2J-1)}{(2J+1)(2J+2)(2J+3)}\right\}^{1/2}\langle J||\mathbf{T}^{(2)}||J\rangle, \tag{2.4}$$

where we have used atomic units (a.u.). In the above expressions, μ_N is the Bohr magneton and we use $g_I=[\frac{\mu_I}{I}]$ with μ_I and $I(=7/2)$ are the nuclear magnetic dipole moment and spin, respectively, as $-0.376\,469\,43$ from the measurement [25] to evaluate A_{hfs}. Since the nuclear quadrupole moment, Q_{nuc}, is not known accurately, we calculate

$$\frac{B_{hfs}}{Q_{nuc}} = \left\{\frac{8J(2J-1)}{(2J+1)(2J+2)(2J+3)}\right\}^{1/2}\langle J||\mathbf{T}^{(2)}||J\rangle. \tag{2.5}$$

The reduced matrix elements of the electronic spherical operators, $\mathbf{T}^{(k)}=\Sigma t^{(k)}$, in terms of single orbitals are given by [5]

$$\langle\kappa_f||t^{(1)}||\kappa_i\rangle = -(\kappa_f+\kappa_i)\langle-\kappa_f||C^{(1)}||\kappa_i\rangle\int_0^\infty dr\frac{(P_fQ_i+Q_fP_i)}{r^2} \tag{2.6}$$

and

$$\langle\kappa_f||t^{(2)}||\kappa_i\rangle = -\langle\kappa_f||C^{(2)}||\kappa_i\rangle\int_0^\infty dr\frac{(P_fP_i+Q_fQ_i)}{r^3}, \tag{2.7}$$

where i and f represent initial and final orbitals, respectively. The reduced matrix elements of the spherical tensors ($C^{(k)}$) are given by

$$\begin{aligned}\langle\kappa_f||C^{(k)}||\kappa_i\rangle &= (-1)^{j_f+1/2}\sqrt{(2j_f+1)(2j_i+1)}\\ &\quad\times\begin{pmatrix} j_f & k & j_i\\ 1/2 & 0 & -1/2\end{pmatrix}\pi(l_f,k,l_i)\end{aligned} \tag{2.8}$$

with the angular momentum selection rule $\pi(l_f,k,l_i)=1$ when $l_f+k+l_i=$even for the orbital angular momenta l_f and l_i, otherwise zero.

We calculate the above electronic matrix elements of the hyperfine interaction operators by the CCSD(T) method. It is obvious from the single particle expressions that these matrix elements are sensitive to the nuclear region. As a starting point, we consider kinetically balanced Gaussian type of orbitals (GTOs) which seem to be an ideal choice for obtaining the correct behavior of the single particle wave functions in the nuclear region [32,33] to calculate the mean-field wave functions $|\Phi_0\rangle$ of the closed-shell configuration in the Dirac(Hartree)-Fock (DF) approach. To calculate the atomic state function of a single valence system with closed-shell configurations, we express it in the RCC ansatz as

$$|\Psi_v\rangle = e^T\{1+S_v\}|\Phi_v\rangle, \tag{2.9}$$

where $|\Phi_v\rangle$ is the new reference state which is defined as $|\Phi_v\rangle=a_v^\dagger|\Phi_0\rangle$ and will give the DF wave function for the above single valence system. In the above expression, we call T and S_v as the closed-shell core and the core with valence electron excitation operators, respectively, which in the second quantization notation in the CCSD approximation are given by

$$T = T_1 + T_2 = \sum_{a,p} a_p^\dagger a_a t_a^p + \frac{1}{4}\sum_{ab,pq} a_p^\dagger a_q^\dagger a_b a_a t_{ab}^{pq}, \tag{2.10}$$

$$S_v = S_{1v} + S_{2v} = \sum_{p\neq v} a_p^\dagger a_v s_v^p + \frac{1}{2}\sum_{b,pq} a_p^\dagger a_q^\dagger a_b a_v s_{vb}^{pq}, \tag{2.11}$$

where the $(a,b,c\ldots)$, $(p,q,r\ldots)$ and (v) subscripts of the second quantized operators represent core, particle (virtual) and valence orbitals, respectively. The t and s_v coefficients are the corresponding excitation amplitudes which are determined using the following equations:

$$\langle\Phi^L|\{\widehat{H_Ne^T}\}|\Phi_0\rangle = 0, \tag{2.12}$$

$$\langle\Phi_v^L|\{\widehat{H_Ne^T}\}S_v|\Phi_v\rangle = -\langle\Phi_v^L|\{\widehat{H_Ne^T}\}|\Phi_v\rangle + \langle\Phi_v^L|S_v|\Phi_v\rangle\Delta E_v, \tag{2.13}$$

with the superscript $L(=1,2)$ representing the single and double excited states from the corresponding reference states and the wide-hat symbol denotes the linked terms. Subscript N with the Hamiltonian H represents its normal order form. ΔE_v is the corresponding valence electron affinity energy which is evaluated by

$$\Delta E_v = \langle\Phi_v|\{\widehat{H_Ne^T}\}\{1+S_v\}|\Phi_v\rangle. \tag{2.14}$$

In our CCSD(T) approach, we consider effects of the leading order triple excitations through ΔE_v by constructing the triple excitation operator (S_{3v}) with amplitude s_{vbc}^{pqr} as

$$S_{3v}(s_{vbc}^{pqr}) = \frac{\widehat{H_NT_2}+\widehat{H_NS_{2v}}}{\epsilon_b+\epsilon_c-\epsilon_q-\epsilon_r}, \tag{2.15}$$

and contracting it with the Hamiltonian to get contributions to the corresponding ΔE_v, where ϵ_i is the DF energy of the electron in the ith orbital.

We consider the Dirac-Coulomb-Breit Hamiltonian in the above equations that is given by

$$\begin{aligned}H &= c\vec{\alpha}\cdot\vec{p} + (\beta-1)c^2 + V_{nuc}(r) + \frac{1}{r_{12}} - \frac{\vec{\alpha}_1\cdot\vec{\alpha}_2}{r_{12}}\\ &\quad + \frac{1}{2}\left\{\frac{\vec{\alpha}_1\cdot\vec{\alpha}_2}{r_{12}} - \frac{(\vec{\alpha}_1\cdot\vec{r}_{12})(\vec{\alpha}_2\cdot\vec{r}_{12})}{r_{12}^3}\right\},\end{aligned} \tag{2.16}$$

where c is the velocity of light, α and β are the Dirac matrices, and $V_{nuc}(r)$ is the nuclear potential. We solve the wave functions of the above Hamiltonian in the DF and RCC methods self-consistently with a tolerance of below 10^{-7} to obtain precise results.

TABLE I. Results of A_{hfs}, B_{hfs}/Q_{nuc}, and B_{hfs} of many states in ^{43}Ca^{+}.

State	A_{hfs} Calc. (MHz)	A_{hfs} Expt. (MHz)	B_{hfs}/Q_{nuc} Calc. (MHz b^{-1})	B_{hfs} Expt. (MHz)
$4s\ ^2S_{1/2}$	−806.4(2.5)[a]	−797.5(2.4)[b]		
	−805.348[c]	−805(2)[d]		
	−819[e]	−817(15)[f]		
	−794.7[g]	−806.402 071 60(8)[h]		
$5s\ ^2S_{1/2}$	−234.0(2.0)[a]			
$4p\ ^2P_{1/2}$	−145.4(4)[a]	−158.0(3.3)[b]		
	−143.068[c]	−145.5(1.0)[d]		
	−148[e]	−142(8)[i]		
	−144.8[g]	145.4(0.1)[j]		
$5p\ ^2P_{1/2}$	−49.7(5)[a]			
$4p\ ^2P_{3/2}$	−30.4(4)[a]	−29.7(1.6)[b]	151.3(7)[a]	
	−30.498[c]	−31.9(2)[d]	151.798[c]	−6.7(1.4)[d]
	−30.9[e]	−31.0(2)[j]	155[e]	−6.9(1.7)[j]
	−29.3[g]			
$5p\ ^2P_{3/2}$	−10.335(112)[a]		50.904(571)[a]	
$3d\ ^2D_{3/2}$	−47.3(3)[a]	−48.3(1.6)[i]	67.3(7)[a]	
	−47.824[c]	−47.3(2)[j]	68.067[c]	−3.7(1.9)[j]
	−52[e]		68[e]	
	−49.4[g]			
	−47.27[k]		72.06[k]	
$4d\ ^2D_{3/2}$	−9.5(1)[a]		17.5(2)[a]	
$3d\ ^2D_{5/2}$	−3.6(3)[a]	−3.8(6)[j]	95.5(1.3)[a]	−3.9(6.0)[j]
	−3.552[c]	−3.8931(2)[l]	100.208[c]	−4.241(4)[l]
	−5.2[e]		97[e]	
	−4.2[g]			
	−4.84[k]		102.45[k]	
$4d\ ^2D_{4/2}$	−3.0(1)[a]		24.7(2)[a]	

[a] This work.
[b] Reference [40].
[c] Reference [37].
[d] Reference [30].
[e] Reference [38].
[f] Reference [41].
[g] Reference [39].
[h] Reference [42].
[i] Reference [43].
[j] Reference [44].
[k] Reference [22].
[l] Reference [31].

We evaluate expectation values due to the hyperfine interaction operators using our RCC method by

$$\langle O\rangle = \frac{\langle\Psi_v|O|\Psi_v\rangle}{\langle\Psi_v|\Psi_v\rangle} = \frac{\langle\Phi_v|\{1+S_v^{\dagger}\}\bar{O}\{1+S_v\}|\Phi_v\rangle}{\{1+S_v^{\dagger}\}\bar{N}_0\{1+S_v\}}$$
$$= \frac{\langle\Phi_v|\{1+S_{1v}^{\dagger}+S_{2v}^{\dagger}\}\bar{O}\{1+S_{1v}+S_{2v}\}|\Phi_v\rangle}{\{1+S_{1v}^{\dagger}+S_{2v}^{\dagger}\}\bar{N}_0\{1+S_{1v}+S_{2v}\}}, \quad (2.17)$$

where O is any of the operator, $\bar{O}=(e^{T^{\dagger}}Oe^{T})$ and $\bar{N}_0=e^{T^{\dagger}}e^{T}$. Generally, both $\bar{O}$ and $\bar{N}_0$ in the RCC approach are nonterminating series. However, we use a special trick to obtain the leading order contributions using Wick's generalized theorem [34]. In this procedure, we evaluate first the effective one-body, two-body terms, etc. step by step and at the end sandwich them between the S_v and its conjugate operators. This procedure has already been demonstrated in our earlier works [15,23,35]. We also explicitly present contributions from the normalization factors evaluating them in the following way:

$$\text{Norm} = \langle\Psi_v|O|\Psi_v\rangle\left\{\frac{1}{1+N_v}-1\right\}, \quad (2.18)$$

where $N_v=\{1+S_{1v}^{\dagger}+S_{2v}^{\dagger}\}\bar{N}_0\{1+S_{1v}+S_{2v}\}$.

III. RESULTS AND DISCUSSIONS

Earlier, we have studied the behavior of the electron correlation effects in the magnetic dipole hyperfine-structure

TABLE II. Contributions from higher symmetry orbitals to the A_{hfs} and B_{hfs}/Q_{nuc} using MBPT(2) method in MHz and MHz b^{-1}, respectively. Here l represents the orbital quantum number.

$\vert JM_J\rangle$ l	$4s\ ^2S_{1/2}$	$5s\ ^2S_{1/2}$	$4p\ ^2P_{1/2}$	$5p\ ^2P_{1/2}$	$4p\ ^2P_{3/2}$	$5p\ ^2P_{3/2}$	$3d\ ^2P_{3/2}$	$4d\ ^2P_{3/2}$	$3d\ ^2P_{5/2}$	$4d\ ^2D_{5/2}$
A_{hfs}										
0–3	−784.612	−228.708	−127.789	−45.226	−26.782	−9.426	−39.139	−8.593	−3.613	−1.666
4	−787.468	−229.294	−127.922	−45.265	−26.808	−9.434	−39.579	−8.562	−3.800	−1.652
5	−787.681	−229.338	−128.148	−45.327	−26.852	−9.446	−39.852	−8.532	−3.916	−1.640
6	−788.096	−229.426	−128.165	−45.331	−26.855	−9.447	−39.910	−8.527	−3.941	−1.638
7	−788.154	−229.438	−128.209	−45.344	−26.863	−9.449	−39.951	−8.523	−3.959	−1.636
$8-\infty$	−788.200	−229.480	−128.215	−45.365	−26.870	−9.475	−39.960	−8.540	−3.965	−1.640
B_{hfs}/Q_{nuc}										
0–3					135.285	47.001	63.513	15.463	90.358	22.019
4					135.413	47.037	64.237	15.412	91.384	21.948
5					135.628	47.096	64.686	15.362	92.020	21.879
6					135.645	47.101	64.783	15.356	92.157	21.869
7					135.687	47.113	64.850	15.348	92.253	21.859
$8-\infty$					135.705	47.120	64.880	15.355	92.260	21.865

constants in this system using the CCSD(T) method and GTOs for a few low-lying states [35] and later only in the $3d\ ^2D_{5/2}$ state [15]. Due to the limitations of the available computational resources at that time, we had restricted our calculations by considering only up to f-symmetry (orbital quantum number l=3) orbitals. Subsequently, we had extended the basis to include g-symmetry orbitals where we found a peculiar behavior of the core-polarization effects in the $^2D_{5/2}$ states of the alkaline-earth-metal ions. However, detailed investigations of the accuracy of the wave functions for other low-lying states were not carried out in that work. In the present work, we use a large basis where functions up to g symmetry have been included. This basis reproduces the results of our calculations of other properties [36] including electron affinities of many low-lying states which agree well with the experimental results.

In Table I, we present our A_{hfs} and B_{hfs}/Q_{nuc} (or B_{hfs}) results of many states along with the available theoretical values and experimental measurements. Estimated errors in our calculations are given inside the parentheses. We have estimated two types of errors for all the states: (a) calculations with limited number of finite-size basis functions up to g symmetry and (b) approximations in the level of excitations that have been considered in the RCC approach. In the first case, we have tested our DF results for a set of basis functions to achieve consistent results and contributions from the higher orbitals are estimated as possible discrepancies in these results which are assumed as one of the sources of errors. In Table II, we present estimated results to both the A_{hfs} and B_{hfs}/Q_{nuc} calculations from the orbitals those belong to the higher symmetries. In fact, we start this study from f symmetry as our previous calculations [35] were reported by considering orbitals up to f symmetry. These estimated results are based on the second-order many-body perturbation theory [MBPT(2)]. Second, we approximate our excitations at the level of singles and doubles. However, equations to determine these amplitudes, in principle, should couple with the higher excitations for accurate calculations. Although our leading order triple excitations take care of most of these contributions, we estimate the contributions from the higher excitations by finding differences of the results between the CCSD and CCSD(T) methods and evaluating the lower order diagrams that may arise through the neglected triple excitations in the RCC approach. This procedure may not be very rigorous, but it explains their importance qualitatively. We have scaled these contributions to find the upper limit of the second source of errors. Again, both the QED and Bohr-Weisskopf (BW) effects are important in the hyperfine structures of the s states. Possible amount of contributions, which are discussed below, is also estimated and considered as another source of errors in the s states.

It is obvious that our A_{hfs} results agree quite well within the uncertainties of the available experimental values giving an indication that our calculated wave functions are suffi-

TABLE III. Breit contributions (Δ_{Br}) to the A_{hfs} and B_{hfs}/Q_{nuc} in MHz and MHz b^{-1}, respectively.

	Δ_{Br}	
State	A_{hfs}	B_{hfs}/Q_{nuc}
$4s\ ^2S_{1/2}$	−0.697	
$5s\ ^2S_{1/2}$	−0.214	
$4p\ ^2P_{1/2}$	−0.115	
$5p\ ^2P_{1/2}$	−0.063	
$4p\ ^2P_{3/2}$	0.048	−0.242
$5p\ ^2P_{3/2}$	0.014	−0.054
$3d\ ^2D_{3/2}$	−0.102	0.150
$4d\ ^2D_{3/2}$	0.135	−0.231
$3d\ ^2D_{5/2}$	−0.102	0.385
$4d\ ^2D_{5/2}$	−0.035	−0.298

TABLE IV. RCC contributions to the A_{hfs} calculations.

RCC terms	$4s\ ^2S_{1/2}$	$5s\ ^2S_{1/2}$	$4p\ ^2P_{1/2}$	$5p\ ^2P_{1/2}$	$4p\ ^2P_{3/2}$	$5p\ ^2P_{3/2}$	$3d\ ^2D_{3/2}$	$4d\ ^2D_{3/2}$	$3d\ ^2D_{5/2}$	$4d\ ^2D_{5/2}$
O (DF)	−587.902	−181.120	−101.559	−36.396	−19.669	−7.056	−33.409	−8.104	−14.235	−3.455
$O-\bar{O}$	−1.626	0.111	1.076	0.370	0.215	0.080	−0.604	−0.079	−0.283	−0.041
$\bar{O}S_{1v}$+c.c.	−103.321	−21.064	−21.032	−5.887	−4.089	−1.159	−8.373	−0.244	−3.554	−0.100
$\bar{O}S_{2v}$+c.c.	−102.224	−28.843	−19.997	−6.345	−5.386	−1.812	−3.120	−0.926	15.803	1.138
$S_{1v}^{\dagger}\bar{O}S_{1v}$	−4.527	−0.613	−1.113	−0.245	−0.217	−0.049	−0.571	−0.031	−0.241	−0.013
$S_{1v}^{\dagger}\bar{O}S_{2v}$+c.c.	−7.338	−0.873	−1.689	−0.313	−0.374	−0.048	−0.260	0.115	0.932	−0.112
$S_{2v}^{\dagger}\bar{O}S_{2v}$+c.c.	−9.615	−3.117	−1.108	−0.355	−0.837	−0.348	−2.017	−0.384	−2.125	−0.443
Norm	8.466	1.519	1.107	0.273	0.232	0.057	1.072	0.179	0.081	0.055

ciently accurate in the nuclear region. There are also experimental results available for B_{hfs} in many cases, but none of them are accurate enough except the recent measured value for the $3d\ ^2D_{5/2}$ state [31]. It is obvious from Table I that there is fairly good agreement between the different calculations of B_{hfs}/Q_{nuc} at least for the $4p\ ^2P_{3/2}$ and $3d\ ^2D_{3/2}$ states, but there are large discrepancies between the results for the $3d\ ^2D_{5/2}$ state. Due to consistency among the theoretical calculations in the $4p\ ^2P_{3/2}$ and $3d\ ^2D_{3/2}$ states, it would indeed be appropriate to combine these results with the measured B_{hfs} values of their corresponding states to determine the less accurately known Q_{nuc} in ^{43}Ca. In contrast, B_{hfs} of the $3d\ ^2D_{5/2}$ state is measured quite precisely and hence it is necessary to use its calculated B_{hfs}/Q_{nuc} result and combine with the measured B_{hfs} value to determine Q_{nuc} for the system that we have considered. Therefore, we would like to investigate the possible reasons for the discrepancies among the theoretical methods which are employed in these calculations. First, we investigate the role of the Breit interaction from which we can realize the effect of the higher relativistic effects in the above properties which was not considered in the previous works, then we proceed with describing differences in the inclusion of various electron correlation effects through the different theoretical methods that have been employed.

For high accuracy calculations, it is necessary to find the contributions from the higher order relativistic corrections. The most important of these contributions comes from the frequency-independent Breit interaction due to the transverse photon [45] which can be assumed as a benchmark test to estimate how large the neglected relativistic effects would be. Studies of the Breit interaction in the hyperfine-structure constants are also of great interest as discussed by Derevianko [46] for determining accuracy of the wave functions in the nuclear region especially to estimate matrix elements of the parity nonconserving amplitudes in the atomic systems. In that work the random phase approximation and Bruckner orbitals were employed to estimate the Breit interaction contribution, however, we have treated the frequency-independent Breit interaction self-consistently here both at DF and CCSD(T) methods. In Table III, we present contributions from the Breit interaction in the A_{hfs} and B_{hfs}/Q_{nuc} calculations in different states. There is an analytical expression as $dA_{hfs}/A_{hfs} \approx 0.68Z\alpha^2$ with Z and α denoting atomic number and fine structure constant, respectively, to estimate the Breit interaction contributions to the s electrons in many-body systems [48]. This result corresponds to 0.0007 for the present system which matches well with our results as 0.0008 and 0.0009 in the $4s\ ^2S_{1/2}$ and $5s\ ^2S_{1/2}$ states, respectively. The Breit interaction contributions in the considered system are not large and it is larger in the ground state than in the excited states. From the recent calculation [47] on the BW effect in lithium like ^{43}Ca shows that the relative corrections to the hyperfine constants for the s states are around −0.00120(60). The relative QED corrections to the s states from the same work are about −0.07%. By accounting these corrections, we estimate possible errors in our calculations due to both the neglected QED and BW corrections are

TABLE V. RCC contributions to the B_{hfs}/Q_{nuc} calculations.

RCC terms	$4p\ ^2P_{3/2}$	$5p\ ^2P_{3/2}$	$3d\ ^2D_{3/2}$	$4d\ ^2D_{3/2}$	$3d\ ^2D_{5/2}$	$4d\ ^2D_{5/2}$
O (DF)	96.976	34.789	55.354	13.354	78.466	18.939
$O-\bar{O}$	−0.869	−0.307	3.208	0.493	4.456	0.680
$\bar{O}S_{1v}$+c.c.	20.220	5.736	15.275	0.306	21.509	0.451
$\bar{O}S_{2v}$+c.c.	32.885	10.217	−5.066	2.836	−6.843	4.067
$S_{1v}^{\dagger}\bar{O}S_{1v}$	1.076	0.243	1.155	0.060	1.619	0.084
$S_{1v}^{\dagger}\bar{O}S_{2v}$+c.c.	1.770	0.286	−1.586	0.456	−2.225	0.632
$S_{2v}^{\dagger}\bar{O}S_{2v}$+c.c.	0.341	0.220	0.621	0.308	0.844	0.432
Norm	−1.153	−0.280	−1.681	−0.371	−2.354	−0.516

TABLE VI. Comparison of Q_{nuc} values (in b) from different calculations.

Q_{nuc}	Reference
−0.0444(6)	This work
−0.040(8)	[10]
−0.0408(8)	[26]
−0.043(9)	[30]
−0.065(20)	[28]
−0.049(5)	[29,50]
−0.044 [a]	[37]
−0.062(12)	[51]

[a] Error has not been estimated, however, the uncertainty in the experimental result used in this work is about 20%.

TABLE VII. Calculations of B_{hfs} (in MHz) using new Q_{nuc} value and our B_{hfs}/Q_{nuc} results reported in Table I.

State	B_{hfs}
$4p\ ^2P_{3/2}$	−6.715(125)
$5p\ ^2P_{3/2}$	−2.260(56)
$3d\ ^2D_{3/2}$	−2.987(71)
$4d\ ^2D_{3/2}$	−0.774(16)
$3d\ ^2D_{5/2}$	−4.239(115)
$4d\ ^2D_{5/2}$	−1.100(24)

around 1.6(5)MHz and 0.5(1)MHz in the $4s\ ^2S_{1/2}$ and $5s\ ^2S_{1/2}$ states, respectively. As mentioned above, they are included in the error bars in Table I.

We now discuss the differences between the various calculations that account for correlation effects at different levels. As mentioned earlier, our previous and present calculations are carried out with the RCC method in the CCSD(T) approximation, but the main differences in the results are due to the inclusion of orbitals from the g symmetry and the Breit interaction in this work. Both Yu *et al.* [37] and Martensson *et al.* [38] have carried out their calculations in the framework of finite order MBPT, but they determine core-polarization effects to all orders and the Bruckner pair-correlation effects [34] to lowest order. In the work of Yu *et al.*, they have restricted the orbitals in the evaluation of the hyperfine-structure constants for individual states by selecting the configurations that make the largest contributions. However, contributions from all these orbitals are intrinsically accounted through the coupled-cluster amplitude equations in the RCC method. Recently, another calculation has been carried out using the multiconfigurational Dirac-Fock (MCDF) method [22]. In contrast to our RCC approach, this method incorporates less correlation effects at a given level of excitation.

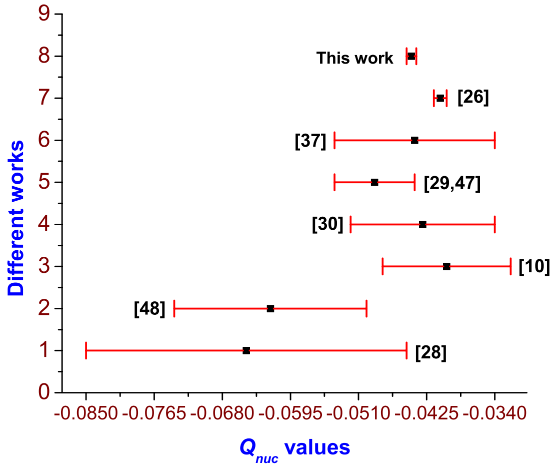

FIG. 1. (Color online) Comparison of nuclear quadrupole moments reported by different calculations (references are given beside the results) on ^{43}Ca. Error only from the corresponding experimental result is accounted in [37].

In Tables IV and V, we present contributions from individual RCC terms to our A_{hfs} and B_{hfs}/Q_{nuc} results, respectively. As seen from these tables, the trends of the correlation effects for A_{hfs} in the first five low-lying states are the same as those discussed in our previous works [15,35] except that the differences in the magnitudes are due to the new basis functions. The correlation effects in the higher excited states are comparatively smaller. Likewise for A_{hfs}, both the pair-correlation and core-polarization effects which arise through S_{1v} and S_{2v} RCC operators [15,35], respectively, play major roles in obtaining the final results of B_{hfs}/Q_{nuc}. The differences between our B_{hfs}/Q_{nuc} result of the $3d\ ^2D_{5/2}$ state with those of others can be attributed to the accurate treatment of these correlation effects in the present work.

Combining our B_{hfs}/Q_{nuc} result with the measured B_{hfs} value of this state [31], we get $Q_{nuc}=-0.0444(6)b$. Following the same procedure when we combine B_{hfs}/Q_{nuc} results of the $4p\ ^2P_{3/2}$ and $3d\ ^2D_{3/2}$ states with their corresponding experimental B_{hfs} results, it gives less accurate values as $Q_{nuc}=-0.044(10)b$ and $Q_{nuc}=-0.059(29)b$, respectively. The associated larger errors are mainly due to the larger uncertainties in the experimental results. We compare the above accurately estimated Q_{nuc} value with the previously reported results in Table VI. Our result is an improvement of about 10% over the current accepted value −0.049(5)b [49] in this system. Recently Yu *et al.* [37] had evaluated this value as −0.044b, which is in reasonable agreement with our result, by combining their B_{hfs}/Q_{nuc} result of the $4p\ ^2P_{3/2}$ state with its experimental B_{hfs} value which has an uncertainty of around 20%. Sundholm and Olsen [26] had combined the precisely measured B_{hfs} result of the $3d\,4s\ ^1D_2$ state of ^{43}Ca with their calculated electric-field gradient result to obtain $Q_{nuc}=-0.0408(8)b$ for the same atom. In this work, they had employed the nonrelativistic multiconfigurational Hartree-Fock (MCHF) method in a restricted active space to calculate electric-field gradient. We have already discussed the difference between the RCC and MCDF/MCHF methods earlier in this section. Again, orbitals in their work were obtained using the molecular basis functions which in principle lose properties of atomic symmetry. There are also other works [10,28–30,50,51] which determine Q_{nuc} in ^{43}Ca, but all of them have used either experimental results with larger uncertainties or methods less rigorous than the present work like MBPT(2), results correcting for Sternheimer effects us-

TABLE VIII. Hyperfine interaction energies (W_F) for different $|F;I,J\rangle$ states in ^{43}Ca$^+$ in MHz.

$\vert JM_J\rangle$ F	$4s\ ^2S_{1/2}$	$5s\ ^2S_{1/2}$	$4p\ ^2P_{1/2}$	$5p\ ^2P_{1/2}$	$4p\ ^2P_{3/2}$	$5p\ ^2P_{3/2}$	$3d\ ^2P_{3/2}$	$4d\ ^2P_{3/2}$	$3d\ ^2P_{5/2}$	$4d\ ^2D_{5/2}$
1									38.477	32.834
2					201.400	68.551	317.553	63.535	32.444	27.207
3	1814.371	526.500	327.201	111.715	115.087	39.160	177.841	35.666	22.940	18.647
4	−1411.177	−409.500	−254.489	−86.889	−4.475	−1.534	−10.434	−2.009	9.421	7.015
5					−161.121	−54.824	−248.977	−49.932	−8.840	−7.880
6									−32.752	−26.271

ing the antishielding factor in the Hartree-Fock calculations, etc. In Fig. 1, we compare the uncertainties associated with various reported Q_{nuc} values in ^{43}Ca using different works as tabulated in Table VI.

Using our Q_{nuc} value, we determine B_{hfs} from our B_{hfs}/Q_{nuc} results presented in Table I and have given them in Table VII. The B_{hfs} results are well within the error bars of the experimental values with less uncertainties. We have also evaluated energies of different hyperfine states using the formula given by Eq. (2.2) corresponding to each fine structure level. In Table VIII, we have reported these results which can be verified by analyzing isotope shift measurements in future experiments on ^{43}Ca$^+$.

IV. CONCLUSION

We have employed the relativistic coupled-cluster method in the Dirac-Coulomb-Breit approximation to compute the atomic wave functions in ^{43}Ca$^+$. Using these wave functions, we were able to determine accurate results for A_{hfs} and B_{hfs}/Q_{nuc}. By combining our calculated result of B_{hfs}/Q_{nuc} for the $3d\ ^2D_{5/2}$ state of ^{43}Ca$^+$ with its measured value of B_{hfs} that is precisely available, we determine Q_{nuc} of ^{43}Ca$=-0.0444(6)b$ which is about 10% more accurate over the current accepted value. In the present work, we have given contributions from the Breit interaction to the hyperfine-structure constants and its interaction energies for a number of states. The Q_{nuc} value that we have obtained and the hyperfine interaction energies that we have reported would be useful to researchers in the fields of atomic, molecular, and nuclear physics.

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