Relativistic coupled-cluster studies of ionization potentials, lifetimes and polarizabilities in singly ionized calcium

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Using the relativistic coupled-cluster method, we have calculated ionization potentials, E1 matrix elements and dipole polarizabilities of many low-lying states of Ca++. Contributions from the Breit interaction are given explicitly for these properties. Polarizabilities of the ground and the first excited d-states are determined by evaluating the wave functions that are perturbed to first order by the electric dipole operator and the black-body radiation shifts are estimated from these results.

We also report the results of branching ratios and lifetimes of the first excited p-states using both the calculated and experimental wavelengths and compare them with their measured values.

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I. INTRODUCTION

Singly ionized calcium (Ca++) is an interesting candidate in many areas of physics. It is especially important in astrophysics for investigating the radiative properties of stellar objects [1, 2]. Its transition wavelengths and electric dipole amplitudes are required to find out isotopic abundances [3] and the energy transfers in stars [1, 2]. They are also used for obtaining information on emission and absorption lines of the electric dipole transitions between the low-lying states in galaxies, interstellar gas clouds and gas disks surrounding the stars [1, 2, 4, 5]. Ca++ is also suitable for laboratory physics. Using the techniques of laser cooling and ion trapping, it has been subjected to many precision measurements, optical frequency methodology, quantum processing and accurate fine structure constant measurements [6, 7, 8, 9, 10, 11, 12]. In these measurements, the knowledge of polarizabilities is necessary to estimate the black-body shift (BBS) and the Stark shift due to the external electromagnetic fields. In our recent works, we have reported the hyperfine structure constants and quadrupole moments in Ca++ using the relativistic coupled-cluster (RCC) method [13, 14, 15]. The determination of electric dipole polarizabilities requires electric dipole (E1) matrix elements and excitation energies of all the allowed transitions. Due to the importance of these quantities, a number of calculations based on various many-body methods including the sum-over-states approach in the framework of the RCC theory are employed to evaluate them [17, 18, 19, 36]. There are also measurements of the static dipole polarizability of the ground state in Ca++ [20, 21], but the results do not agree with each other. In fact, all the calculations [17, 18, 19, 36] differ from the recent measured value [20]. Therefore, it is necessary to carry out thorough investigations of the role of electron correlation, higher order relativistic effects and contributions from the two hole-two particle and the neglected one hole-one particle excited states in the calculations of polarizabilities using an all order ab initio approach like the RCC theory. We have developed a novel technique to account for the importance of different correlation effects in these properties for closed-shell and one-valence atomic systems by directly obtaining the atomic wave functions perturbed to first order by the electric dipole operator in the framework of the RCC theory [22, 23]. This method avoids the sum-over-states approach and thereby includes different types of correlation effects in a rigorous manner. This theory has been employed to determine the ground state polarizabilities in a few alkali atoms and singly ionized alkaline earth ions including Ca++ to check the validity of the theory [22]. Although, the theory for the tensor polarizabilities has been developed, it has not been applied to excited states. In this work, we calculate the E1 matrix elements and excitation energies and employ the above approach to determine scalar and tensor polarizabilities of the 4S and 3D states of Ca++. The role of the Breit interaction had not been studied in the earlier works which we investigate here using this ab initio method.

There have been recent measurements on the branching ratios from the 4p^2P_3/2 state and the corresponding transition probabilities in Ca++ [24] which need to be theoretically investigated. We carry out these studies using our ab initio approach and by combining our E1 matrix
elements with the experimental wavelengths and compare
with their corresponding experimental results. We also
evaluate the lifetimes of the 4P-states using these results.

The remaining part of the paper is organized as follows:
In Sec. II, we present a brief outline of the theory. This
is followed in Sec. III by a discussion of the method to
evaluate the unperturbed and the first order perturbed
atomic wave functions using the RCC method. We then
present the results and discuss the effect of correlation
on various properties in Sec. IV and in the final section
we make some concluding remarks.

II. THEORETICAL APPROACH

The static dipole polarizability of a state \(|J_0, M_0\rangle\) is
given by

\[
\alpha_0 = \alpha_0^1 + \frac{3M_0^2 - J_0(J_0 + 1)}{J_0(2J_0 - 1)} \alpha_0^2
\]

where \(\alpha_0^1\) and \(\alpha_0^2\) are the scalar and tensor polarizabilities.

\[
\alpha_0^1 = 2 \sum_{n \neq 0} C_n \frac{|\langle J_0 || D || J_n \rangle|^2}{E_0 - E_n},
\]

with

\[
C_n = -\frac{1}{3(2J_0 + 1)}.
\]

\[
C_2 = \left[ \frac{10J_0(2J_0 - 1)}{3(J_0 + 1)(2J_0 + 1)(2J_0 + 3)} \right]^2
\]

and the Es are the energies of the atomic states. In a
single valence system, \(\alpha_0\) can be divided into three parts
in general as follows:

\[
\alpha_0^i = \alpha_0^i(v) + \alpha_0^i(cv) + \alpha_0^i(c),
\]

where \(v, cv\) and \(c\) inside the parenthesis represent
valence, core-valence and core correlation contributions,
respectively. In the sum-over-states approach, it is customary
to evaluate \(\alpha_0^i(v)\) by calculating the important
dipole excited states. However, contributions from \(\alpha_0^i(cv)\)
and \(\alpha_0^i(c)\) are generally taken approximately in such
an approach. On the otherhand, it is possible to calculate
\(\alpha_0\) exactly in a particular configuration space by evaluat-
ing the wave function that is perturbed by the electric
dipole operator \(D\) in the following manner:

Let us rewrite Eq. (2.2) as

\[
\alpha_0^i = 2 \sum_{n \neq 0} C_n (-1)^{J_0 - J_n} \frac{\langle J_0 || D || J_n \rangle \langle J_n || D || J_0 \rangle}{E_0 - E_n}
\]

which in Dirac notation can be expressed as

\[
\alpha_0^i = 2 \sum_{n \neq 0} C_n (-1)^{J_0 - J_n} \frac{\langle \Psi(0)(J_0, \gamma) || D || \Psi(0)(J_n, \gamma') \rangle \langle \Psi(0)(J_n, \gamma') || D || \Psi(0)(J_0, \gamma) \rangle}{E_0 - E_n}
\]

where \(\gamma\) represents parity eigenvalue of the state \(|J_0, M_0\rangle\) and \(\gamma'\) is its opposite eigenvalue and we define an effective

dipole operator as \(\tilde{D}_i = C_i (-1)^{J_0 - J_n} D\). Here, \(|\Psi(1)(J_0, \gamma')\rangle\) is the first order perturbation correction to the wave
function \(|\Psi(0)(J_0, \gamma)\rangle\) due to the dipole operator \(D\) and given by

\[
|\Psi(1)(J_0, \gamma')\rangle = \sum_{n \neq 0} |\Psi(0)(J_n, \gamma')\rangle \frac{\langle \Psi(0)(J_n, \gamma') || D || \Psi(0)(J_0, \gamma) \rangle}{E_0 - E_n}
\]

It can be equivalently written as

\[
|\Psi(1)(J_0, \gamma')\rangle = \frac{1}{E_0 - H} \sum_{n \neq 0} |\Psi(0)(J_n, \gamma')\rangle \langle \Psi(0)(J_n, \gamma') || D || \Psi(0)(J_0, \gamma) \rangle
\]

\[
= \frac{1}{E_0 - H} \sum_{n, \phi = \gamma, \gamma'} |\Psi(0)(J_n, \phi)\rangle \langle \Psi(0)(J_n, \phi) || D || \Psi(0)(J_0, \gamma) \rangle,
\]
since the matrix elements between the same parity states vanish. Applying the completeness condition, we get

\[(H - E_0)|\Psi^{(1)}(J_0, \gamma')\rangle = -D|\Psi^{(0)}(J_n, \gamma)\rangle; \quad (2.8)\]

and

\[A^{M1}_{f \rightarrow i} = \frac{2.69735 \times 10^{13}}{(2J_f + 1)\lambda^3_{f \rightarrow i}} |\langle J_f || M1 || J_i \rangle|^2, \quad (2.13)\]

respectively. In the above equations, \(\lambda_{f \rightarrow i}\) is the wavelength of the corresponding transition and it is the reciprocal of the excitation energy (EE).

### III. METHOD OF CALCULATIONS

The RCC method which is equivalent to all order perturbation theory has been recently used to obtain precise results and account for the correlation effects in single valence systems \[13 \quad 14 \quad 15\]. Atomic wave functions for single valence systems can be expressed in the framework of RCC theory as

\[|\Psi_v^{(0)}\rangle = e^T (1 + S_v)|\Phi_v\rangle, \quad (3.1)\]

where \(|\Phi_v\rangle\) is the reference state constructed from the Dirac-Fock wave function \(|\Phi_0\rangle\) of the closed-shell configuration \([1s^22s^22p^63s^23p^6] (\equiv |3p^6\rangle)\) of Ca\(^+\) by defining \(|\Phi_v\rangle = a_v^\dagger |\Phi_0\rangle\) with \(a_v^\dagger\) representing addition of a valence electron \(v\). Here \(T\) and \(S_v\) are the RCC excitation operators which excite electrons from \(|3p^6\rangle\) and \(a_v^\dagger |3p^6\rangle\) for the corresponding valence electron \(v\), respectively. The amplitudes of these excitation operators are solved by

\[(\Phi_v^L | (H_{\text{NeT}}) | \Phi_0) = 0 \quad (3.2)\]

\[\langle \Phi_v^L | (H_{\text{NeT}}) S_v | \Phi_v \rangle = -\langle \Phi_v^L | (H_{\text{NeT}}) | \Phi_v \rangle + \langle \Phi_v^L | S_v | \Phi_v \rangle \Delta E_v, \quad (3.3)\]

with the superscript \(L (= 1, 2)\) representing the single and double excited states from the corresponding reference states and the wide-hat symbol over \(H_{\text{NeT}}\) represent the linked terms of normal order atomic Hamiltonian \(H_{\text{Ne}}\) and RCC operator \(T\). \(\Delta E_v\) is the corresponding valence electron affinity (negative of the ionization potential (IP)) energy which is evaluated by

\[\Delta E_v = (\Phi_v | (H_{\text{NeT}}) \{1 + S_v\} | \Phi_v) \quad (3.4)\]

The EE between two different states are determined from the difference of their \(\Delta E_v\). In Eqs. \[5.2\] and \[5.3\] we have considered only the single and double excitations, however we have incorporated contributions from important triple excitations to the \(\Delta E_v\) calculations. After obtaining the amplitudes for \(T\), the core excitation operator, we solve Eqs. \[5.3\] and \[5.4\] simultaneously to
represent the single and double excitations, respectively. The modified operators as
\[
|\Psi^{(0)}\rangle = -\langle \Phi | \hat{D} \hat{e}^T | \Phi \rangle
\]
where \( \hat{D} \) and \( \hat{e} \) represent the single and double excitations, respectively.

Now, separating the above wave function as \( |\Psi_0^{(0)}\rangle \) and \( |\Psi_1^{(1)}\rangle \), we get
\[
|\Psi_0^{(1)}\rangle = -e^{T\Omega} \{ 1 + S_v + \Omega(1 + S_v) + \Lambda_v \} |\Phi_0\rangle
\]
where \( \Omega \) and \( \Lambda_v \) are the modified RCC operators to the \( T \) and \( S_v \) operators, respectively. Since Eq. (3.3) is first order in the \( D \) operator, the above expression will reduce to
\[
|\Psi_0\rangle = e^{T\Omega} \{ 1 + S_v + \Omega(1 + S_v) + \Lambda_v \} |\Phi_0\rangle
\]
Now, separating the above wave function as \( |\Psi_0^{(0)}\rangle \) and \( |\Psi_1^{(1)}\rangle \), we get
\[
|\Psi_1^{(1)}\rangle = e^{T\Omega} \{ 1 + S_v + \Lambda_v \} |\Phi_0\rangle
\]

Following Eq. (2.3), we solve again the amplitudes for the modified operators as
\[
\langle \Phi | \hat{D} \hat{e}^T | \Phi \rangle = -\langle \Phi | \hat{D} \hat{e}^T | \Phi \rangle
\]
and
\[
\Lambda_v = \Lambda_1 v + \Lambda_2 v
\]
where the subscripts \{1,2\} represent the single and double excitations, respectively.

Now the expression for the dipole polarizability follows as
\[
\alpha_0 = \frac{\langle \Phi_0 | \hat{D}_1 | \Psi_0 \rangle + \langle \Psi_0 | \hat{D}_1 | \Psi_0 \rangle}{\langle \Phi_0 | \Psi_0 \rangle}
\]
where we define \( \hat{D}_1 = (e^{T\Omega} \hat{D}_1 e^T) \) and \( \hat{N}_0 = e^{T\Omega} e^T \). Generally, both \( \hat{D}_1 \) and \( \hat{N}_0 \) in the RCC approach are each represented by a non-terminating series. However, we have devised a procedure motivated by physical considerations to deal with them using the Wick’s generalized theorem. We evaluate first the effective zero-body, one-body, two body terms etc. systematically and then sand-

### TABLE I: Ionization potentials (in au) of Ca\(^+\) from different works.

| State   | This work | Others | Expt. [25] |
|---------|-----------|--------|------------|
| 4s \(^2\)S\(_{1/2}\) | -0.43627757 | -0.43836\(^a\) | -0.43627767 |
|         | -0.436287\(^b\) |        |            |
| 3d \(^2\)D\(_{3/2}\) | -0.37396663 | -0.37407\(^a\) | -0.37408278 |
|         | -0.37485\(^b\) |        |            |
| 3d \(^2\)D\(_{3/2}\) | -0.37361011 | -0.37379 | -0.37380626 |
|         | -0.37448\(^b\) |        |            |
| 4p \(^2\)P\(_{1/2}\) | -0.32123958 | -0.32217\(^a\) | -0.32149667 |
|         | -0.32224\(^b\) |        |            |
| 4p \(^2\)P\(_{3/2}\) | -0.32025203 | -0.32111\(^a\) | -0.32048108 |
|         | -0.32118\(^b\) |        |            |
| 5s \(^2\)S\(_{1/2}\) | -0.19786845 | -0.198293\(^c\) | -0.19858760 |
| 4d \(^2\)D\(_{3/2}\) | -0.17674718 | -0.175144\(^c\) | -0.17729894 |
| 4d \(^2\)D\(_{3/2}\) | -0.17665912 | -0.175144\(^c\) | -0.17721142 |
| 5p \(^2\)P\(_{1/2}\) | -0.15978307 | -0.160060\(^c\) | -0.16046888 |
| 5p \(^2\)P\(_{3/2}\) | -0.15944054 | -0.160060\(^c\) | -0.16011231 |

\(^a\)Relativistic MBPT(2) [28],
\(^b\)Brueckner approximation [27],
\(^c\)Non-relativistic Coulomb approximation [19].
TABLE II: Transition matrix elements (in au) from different calculations. Recommended values from our work is given as reco.

| Transition | This work | Others |
|------------|-----------|--------|
| $4p^2 3p/2 \rightarrow 4s^2 S_{1/2}$ | 2.86 | 2.90 | 2.88 | 2.890$^a$ |
| | | | | 2.866$^{b, l}$ |
| | | | | 2.861$^{b, v}$ |
| | | | | 2.898$^c$ |
| $4p^2 3p/2 \rightarrow 3d^2 D_{3/2}$ | 2.50 | 2.41 | 2.40 | 2.373$^d$ |
| | | | | 2.410$^{b, l}$ |
| | | | | 2.244$^{b, v}$ |
| $4p^2 3p/2 \rightarrow 4s^2 S_{1/2}$ | 4.02 | 4.09 | 4.03 | 4.088$^e$ |
| | | | | 4.060$^{b, l}$ |
| | | | | 4.055$^{b, v}$ |
| | | | | 4.099$^c$ |
| $4p^2 3p/2 \rightarrow 4p^2 P_{3/2}$ | 1.15 | 1.15 | 1.15 | 1.059$^e$ |
| | | | | 1.076$^{b, l}$ |
| | | | | 1.029$^{b, v}$ |
| $4p^2 3p/2 \rightarrow 3d^2 D_{3/2}$ | 1.12 | 1.09 | 1.09 | 3.186$^e$ |
| | | | | 3.234$^{b, l}$ |
| | | | | 2.995$^{b, v}$ |
| | | | | 3.306$^c$ |
| $4p^2 3p/2 \rightarrow 3d^2 D_{5/2}$ | 3.36 | 3.28 | 3.22 | 3.306$^c$ |

$^a$Relativistic MBPT(2) $^{[26]}$

$^b, l$Length gauge result with Brueckner approximation $^{[27]}$

$^b, v$Velocity gauge result with Brueckner approximation $^{[27]}$

$^c$Linearized RCC method $^{[14]}$.

We have employed two different types of the basis functions to generate the atomic orbitals; Slater type orbitals (STOs) and Gaussian type orbitals (GTOs). These orbitals are defined on a grid given by

$$r_i = r_0 \left[ e^{h(i-1)} - 1 \right],$$

where $i$ represents the grid points which we have taken as 750 in total, the step size $h$ is taken as 0.03 in the present case and $r_0$ is the starting point of the radial distribution from where the electron orbitals become finite and taken as $2 \times 10^{-6}$. The STOs and GTOs are given by

$$F^{STO}(r_i) = r_i^n e^{-\alpha_i r_i},$$

and

$$F^{GTO}(r_i) = r_i^n e^{-\alpha_i r_i^2},$$

respectively. Here $n_\kappa$ is the radial quantum number of the orbitals and $\alpha_i$ is a parameter whose value is chosen to obtain orbitals with proper behavior inside and outside the nucleus of an atomic system. We further define $\alpha_i$ as

$$\alpha_i = \alpha_0 \beta^i - 1.$$  

We have considered $\alpha_0 = 0.0975$ and $\beta = 1.77$ for STOs and $\alpha_0 = 0.00525$ and $\beta = 2.83$ for GTOs. However, we have taken 35, 35, 30, 30 and 25 STO and GTO basis functions to construct the s, p, d, f and g orbitals respectively. For RCC calculations, we have included all the core orbitals and virtual orbitals are considered up to 3500 au for s, p and d symmetries and 1500 au for f and g symmetries in the present calculations. In fact, it is observed that number of virtual orbitals obtained using STOs are more in a given upper energy limit than GTOs while bound orbital energies match well in both the cases. To account for the contributions from the high lying orbitals in some of the properties that we have considered, we have estimated contributions from virtual orbitals using the second order many-body perturbation theory (MBPT(2)) and recommended (reco) results are given by taking into account all these contributions.

In Table II, we present our IP results for the low-lying states and compare them with the corresponding experimental results. These results using STOs and GTOs were consistent. Some IPs from the excited states deviate from the experimental results and it might be possible to improve them by increasing the virtual space. We also compare our results with other theoretical results. Guet and Johnson had employed the relativistic MBPT(2) method to obtain their results $^{[26]}$. Liaw had employed the Brueckner approximation method to evaluate these energies $^{[27]}$ and his results match with the above MBPT(2) results. In a recent work, Mitroy and Zhang have used a one electron semi-empirical core potential in the non-relativistic framework $^{[14]}$ to estimate these energies which cannot distinguish the fine structure levels. Our method in contrast is $ab initio$ and electron correlation effects are included to all orders in perturbation theory in the residual Coulomb and Breit interaction in the one hole-one particle, two hole-two particle and partial three hole-three particle approximation.

We present the E1 and M1 matrix elements in Table III. As can be seen, results from our STOs and GTOs differ for different transitions. We have considered contributions from virtual orbitals from both the basis functions

IV. RESULTS AND DISCUSSIONS

We have employed two different types of the basis functions to generate the atomic orbitals; Slater type orbitals (STOs) and Gaussian type orbitals (GTOs). These orbitals are defined on a grid given by
TABLE III: Transition probabilities (in $\times 10^6$ s$^{-1}$) in Ca$^+$.  

| Transition | This work $\lambda^{cal}$ | $\lambda^{exp}$ | Others |
|------------|----------------|-------------|--------|
| $4p^2P_{3/2} \rightarrow 4s^2S_{1/2}$ | 135.240 | 134.333 | 135.26$^a$ |
| | | | 132.9$^b$ |
| | | | 132.5$^c$ |
| | | | 136.0$^d$ |
| $4p^2P_{3/2} \rightarrow 3d^2D_{3/2}$ | 9.0431 | 8.971 | 8.77$^a$ |
| | | | 9.0$^b$ |
| | | | 7.8$^c$ |
| | | | 9.452$^d$ |
| $4p^2P_{3/2} \rightarrow 4s^2S_{1/2}$ | 135.842 | 135.036 | 138.95$^a$ |
| | | | 136.9$^b$ |
| | | | 136.9$^c$ |
| | | | 139.7$^d$ |
| $4p^2P_{3/2} \rightarrow 4p^2P_{1/2}$ | $\sim 10^{-10}$ | $\sim 10^{-10}$ | 0.93$^a$ |
| | | | 0.95$^b$ |
| | | | 0.87$^c$ |
| | | | 0.997$^d$ |
| $4p^2P_{3/2} \rightarrow 3d^2D_{3/2}$ | 1.055 | 0.962 | 8.24$^a$ |
| | | | 8.5$^b$ |
| | | | 7.2$^c$ |
| | | | 8.87$^d$ |
| $4p^2P_{3/2} \rightarrow 3d^2D_{5/2}$ | 8.435 | 8.419 | 10 |

$^a$Relativistic MBPT(2) is used $^{26}$
$^b$Length gauge result with Brueckner approximation $^{27}$
$^c$Velocity gauge result with Brueckner approximation $^{27}$
$^d$Linearized RCC method is employed $^{17}$

using MBPT(2) and finally given the consistent results as reco values. Guet and Johnson $^{26}$ have used B-spline basis based MBPT to obtain these results. Again, Arora et al. $^{17}$ have also used a B-spline basis but a linearized RCC method to obtain their results. Liaw $^{27}$ has used the Brueckner approximation method to get E1 matrix elements in both the length and velocity gauge expressions. Our method intrinsically contains all these many-body effects. We have also evaluated M1 matrix element between the $4p^2P_{3/2}$ $\rightarrow$ $4p^2P_{1/2}$ transition which is around 1.15 au; almost same with the $3d^2D_{5/2}$ $\rightarrow$ $3d^2D_{3/2}$ transition $^{29}$.

Using the above matrix elements, we determine the transition probabilities and present them in Table III. We have followed two approaches to determine them. First we have considered energies from our calculations and derived wavelengths ($\lambda^{cal}$) to obtain the $ab\ initio$ results. In the other case, we use our matrix elements with the experimental wavelengths ($\lambda^{exp}$). Although the M1 transition amplitude from the $4p^2P_{3/2}$ state is finite due to a very small fine structure splitting, the corresponding transition probability is almost negligible. We have also compared our results with other $ab\ initio$ and semi-empirical results in the same table. In a recent work, Gerritsma et al. $^{24}$ have measured BRs (we discuss these results below in detail) from the $4p^2P_{3/2}$ state and obtain various transition probabilities from this state by combining their results with the lifetime measurements as given by Eq. (2.11). Our results with $\lambda^{exp}$ match well with their results.

Using the above transition probabilities, we determine BRs from different calculations and present them in Table IV. These results are compared with the recently measured values of the $4p^2P_{3/2}$ state $^{24}$. As presented in this table, our results with $\lambda^{exp}$ match well the measurements. When we evaluate BRs for the $4p^2P_{1/2}$ and $4p^2P_{3/2}$ states due to 3d states using the relation

$$\Gamma_{f\rightarrow i} = \frac{A_{f\rightarrow i}}{\sum_{i=3d} A_{f\rightarrow i}},$$

it gives as 14.97 and 14.40, respectively, which are not within the error bar of the existing experimental result $^{28}$, and hence require further measurements for verification.

There are a number of experimental lifetime measurements available for the $4p^2P_{1/2}$ and $4p^2P_{3/2}$ states $^{30,31,32,33,34,35}$ using beam laser, beam foil, beam foil with cascade correction and Hanle techniques. Among them the laser-beam-ion-beam spectroscopy by Jin and Church $^{30}$ results are the most precise. Substituting our transition probabilities in Eq. (2.11), we obtain the lifetimes of the $4p^2P_{1/2}$ and $4p^2P_{3/2}$ states as 6.931s and 6.881s with $\lambda^{cal}$, respectively, which as 6.979s and 6.924s with $\lambda^{exp}$, respectively. Other calculations based on the above discussed results also predict results close to ours. In fact, our result 6.924s of lifetime of the $4p^2P_{3/2}$ state is in good agreement with the experimental results.

Using the same wave functions used to obtain the above properties and solving Eq. (2.8), we obtain the static dipole polarizabilities of the $4s^2S_{1/2}$, $3d^2D_{3/2}$ and $3d^2D_{5/2}$ states with STOs and GTOs and they are presented in Table VI. The dipole polarizabilities for the ground state from STOs and GTOs are in good agreement, but the 3d state dipole polarizabilities differ by 4%. Since we were able to generate less number of virtuals using GTOs in a given energy upper bound, the convergence of these results were checked with virtual orbitals with higher energies which was not possible for STOs due to the computational limitation. Therefore, we consider our results from GTOs are more accurate than results from STOs. There are also a number of theoretical calculations available on both the ground and 3d excited states including our previous work and references therein $^{17,19,20,22,36,37}$. We had just carried out the ground state polarizability calculation in Ca$^+$ along with other atomic systems in the earlier work $^{22}$ to verify the validity of the method that was proposed for the first time. In the present case, we have investigated the accuracy of the wave functions in Ca$^+$ to obtain IPs and E1 matrix elements which are the ingredients to evaluate
TABLE IV: BRs of 4p $^2P_{1/2}$ and 4p $^2P_{3/2}$ states in Ca$^+$.  

| Transition | This work $\lambda^{\text{cal}}$ | $\lambda^{\text{exp}}$ | Others | Expt [24] |
|------------|--------------------------------|-----------------|---------|-----------|
| 4p $^2P_{1/2} \rightarrow 4s^2S_{1/2}$ | 0.9373 | 0.9374 | 0.9391$^a$ | |
| | | | 0.9366$^b$ | |
| | | | 0.9444$^c$ | |
| | | | 0.9350$^d$ | |
| 4p $^2P_{1/2} \rightarrow 3d^2D_{3/2}$ | 0.0627 | 0.0626 | 0.0609$^a$ | |
| | | | 0.0634$^b$ | |
| | | | 0.0556$^c$ | |
| | | | 0.0650$^d$ | |
| 4p $^2P_{3/2} \rightarrow 4s^2S_{1/2}$ | 0.9347 | 0.9350 | 0.9381$^a$ | 0.9347(3) |
| | | | 0.9354$^b$ | |
| | | | 0.9443$^c$ | |
| | | | 0.9340$^d$ | |
| | | | 0.9357$^e$ | |
| 4p $^2P_{3/2} \rightarrow 4p^2P_{1/2}$ | $\sim 0$ | | | |
| 4p $^2P_{3/2} \rightarrow 3d^2D_{5/2}$ | 0.00726 | 0.00666 | 0.00628$^a$ | 0.00661(4) |
| | | | 0.00649$^b$ | |
| | | | 0.00600$^c$ | |
| | | | 0.00667$^d$ | |
| 4p $^2P_{3/2} \rightarrow 3d^2D_{5/2}$ | 0.0581 | 0.0583 | 0.0556$^a$ | 0.0587(2) |
| | | | 0.0581$^b$ | |
| | | | 0.0497$^c$ | |
| | | | 0.0593$^d$ | |
| | | | 0.0643$^e$ | |

$^a$Relativistic MBPT(2) is used [26]
$^b$Length gauge result with MCDF method [27]
$^c$Velocity gauge result with MCDF method [27]
$^d$Linearized RCC method is employed [17]
$^e$Semi empirical [19]

accurate dipole polarizabilities. In fact, the correlation behavior in the 3d state dipole polarizabilities is not discussed in the literature. Patil and Tang [36] had used multipolar-matrix elements based in the non-relativistic approximation to obtain the $4s^2S_{1/2}$ state dipole polarizability. This has got both the summation and integration approach over the intermediate states from different orbital quantum numbers. Using Coulomb approximation with the Hartree-Slater core calculations, Theodosiou et al. [20] had reported the dipole polarizability of the same state. Their result differs from ours and it seems as though they have not taken core-correlation into account. Recently, Arora et al. [17] and Mitroy and Zhang [19] have also evaluated dipole polarizabilities based on the sum-over E1 matrix elements and oscillator strengths between different states. The main differences in their results and ours is that they have estimated core (neglected for tensor polarizability) and core-valence correlation effects approximately whereas we have used the first order perturbed RCC method to evaluate them. Contributions from the continuum and doubly excited states with configurations like $[4p^5]nsms$ ($n \neq m$, with $n, m$ being principal quantum numbers) which are also important for the dipole polarizability calculations of the states have been considered by us. They are implicitly accounted for in the present work by evaluating the first order perturbed wave functions due to the electric dipole operator. We have also corrected our results due to the normalization of the wave functions. In Table VII, we present contributions from the DF and the individual RCC terms obtained using GTOs. The differences between these two results give the correlation contributions associated in evaluating these quantities. It is evident from our studies that correlation effects in the 3d-states are more than 50% while it is about 20% in the $4s^2S_{1/2}$ state. The $\alpha_0(c)$ and $\alpha_0(cv)$ contributions are found to be smaller for the scalar dipole polarizability than the previously estimated results. We also present these contributions for the tensor polarizabilities which were neglected earlier. Contributions due to the doubly excited states and normalization corrections cannot be neglected in precision calculations. There are three experimental results for the ground state dipole polarizability [20, 21], but they do not match with each other. Although the re-
TABLE V: Lifetimes (in s) of 4p $^2P_{1/2}$ and 4p $^2P_{3/2}$ states in Ca$^+$.  

| State | This work $\lambda^{\text{cal}}$ | $\lambda^{\text{exp}}$ | Others | Expt |
|-------|-----------------|-----------------|--------|------|
| 4p $^2P_{1/2}$ | 6.931 | 6.978 | 6.94$^a$ | 7.098(20)$^d$ |
| | | | 7.04$^{b,l}$ | 7.07(7)$^e$ |
| | | | 7.12$^{b,v}$ | 7.5(5)$^f$ |
| | | | 6.875$^c$ | 6.62(35)$^g$ |
| 4p $^2P_{3/2}$ | 6.881 | 6.924 | 6.75$^a$ | 6.924(19)$^d$ |
| | | | 6.83$^{b,l}$ | 6.87(6)$^e$ |
| | | | 6.89$^{b,v}$ | 7.4(6)$^f$ |
| | | | 6.686$^c$ | 6.68(35)$^g$ |
| | | | 6.61(30)$^i$ |

$^a$ Relativistic MBPT(2) \[17\]  
$^b$ Length gauge result with MCDF method \[27\]  
$^c$ Velocity gauge result with MCDF method \[27\]  
$^d$ Laser-beam-ion-beam technique \[31\]  
$^e$ Laser-beam techniques \[31\]  
$^f$ Beam foil technique \[32\]  
$^g$ Beam foil technique with cascade correction \[33\]  
$^h$ Hanle method \[34\]  
$^i$ Hanle method \[35\]  

The frequency shift (in Hz) due to a black-body (BBS) state This work Others Expt

\[ \Delta \nu = \frac{1}{2}(831.9 \text{V/m})^2 \left( \frac{T(K)}{300} \right)^4 \left[ \alpha_0(4s) - \alpha_0(3d_{5/2}) \right] \]  

By substituting our results in the above expression, we obtain $\Delta \nu = 0.376$Hz which is in agreement with 0.38(1)Hz by Arora et al. \[17\] and 0.368Hz by Mitroy and Zhang \[19\]. This also supports the measured value 0.39(27)Hz \[10\]. The agreement between different calculations is mainly due to the cancellation of the effects of $4s^2S_{1/2}$ and $3d^2D_{5/2}$ states.

In Table VIII we present the contributions from the Breit interaction to different properties. These contributions are smaller in these properties than in the hyperfine structure constants which were reported recently \[14\]. In contrast to the hyperfine constants where the Breit interaction contributes more to the $4s^2S_{1/2}$ state, it is larger in the $3d$ states than the ground state in the these properties.

V. CONCLUSION

We have employed the relativistic coupled-cluster method with two different basis functions to study ionization potentials, electric dipole matrix elements and dipole polarizabilities in the singly ionized calcium. We have also evaluated transition probabilities, branching ratios and lifetimes of the first excited p-states using these results. By determining the first order perturbed wave function due to the electric dipole operator, we obtain ab initio results for the static dipole polarizabilities in the ground and first excited d-states. Black-body shift in the $4s^2S_{1/2} \rightarrow 3d^2D_{5/2}$ transition has been evaluated using these results and compared with the other available results. Contributions from the Breit interaction to the above properties have been studied for the first time in singly ionized calcium.

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TABLE VII: Contributions from DF and important RCC terms for the dipole polarizabilities.

| Terms       | 4s $^2 S_{1/2}$ | 3d $^2 D_{3/2}$ | 3d $^2 D_{5/2}$ |
|-------------|-----------------|-----------------|-----------------|
| DF          | 96.201          | 91.487          | -59.261         | 89.340          | -81.330         |
| $D_c$       | 2.730           | 2.730           | -0.178          | 2.730           | -0.178          |
| $D_c \Omega + cc$ | 0.038          | 0.151           | -0.245          | 0.268           | -0.268          |
| $D_c \Lambda_{1v} + cc$ | 77.283         | 32.427          | -18.317         | 33.162          | -27.573         |
| $D_c \Lambda_{2v} + cc$ | -1.865         | -0.927          | -0.271          | -0.910          | 0.618           |
| $S_{1v} D_c \Lambda_{1v} + cc$ | -2.543         | -5.097          | 2.876           | -5.161          | 4.277           |
| $S_{2v} D_c \Lambda_{2v} + cc$ | -2.017         | -0.298          | 0.105           | -0.289          | 0.132           |
| Others      | 0.130           | 0.161           | -0.226          | 0.161           | -0.050          |
| Norm        | -0.754          | -0.643          | 0.386           | -0.654          | 0.550           |

Note: Subscripts $1v$ and $2v$ represent the valence contributions due to the singly and doubly excited states, respectively.

TABLE VI: Polarizabilities (in au) of the 4s $^2 S_{1/2}$, 3d $^2 D_{3/2}$ and 3d $^2 D_{5/2}$ states in Ca$^+$. 

| State       | GTOs (reco) | STOs | Others | Expt |
|-------------|-------------|------|--------|------|
| 4s $^2 S_{1/2}$ | 73.002     | 74.342 | 76.1(1.1)$^a$ | 70.89(15)$^c$ |
| 3d $^2 D_{3/2}$ | 28.504     | -15.870 | 32.73$^c$ | -25.20$^c$ |
| 3d $^2 D_{5/2}$ | 29.307     | -22.492 | 32.0(1.1)$^a$ | -24.5(4)$^a$ |

$^a$Linearized RCC method is employed [17].
$^b$Non-relativistic sum-over-oscillator strengths approach [10].
$^c$Non-relativistic sum-over-oscillator strengths approach [21].
$^d$Non-relativistic sum-over-oscillator strengths approach [37].
$^e$Lifetime measurements and oscillator strengths of [5].

Note: Subscripts $i$ and $v$ represent the core-valence ($\alpha_i^c(v)$) correlation effects, respectively. The remaining terms except Norm represent the valence correlation contributions. Norm gives the correction due to the normalization of the wave functions.

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TABLE VIII: Breit interaction contributions to various properties.

| State | Results          |
|-------|------------------|
| IP (au) |                   |
| 4s $^2 S_{1/2}$ | 0.00003056 |
| 3d $^2 D_{3/2}$ | -0.00034491 |
| 3d $^2 D_{5/2}$ | -0.00027547 |
| 4p $^2 P_{1/2}$ | 0.00005439 |
| 4p $^2 P_{3/2}$ | 0.00002354 |
| 5s $^2 S_{1/2}$ | 0.00001018 |
| 4d $^2 D_{3/2}$ | 0.00003778 |
| 4d $^2 D_{5/2}$ | 0.00001114 |
| 5p $^2 P_{1/2}$ | 0.00001729 |
| 5p $^2 P_{3/2}$ | 0.00000674 |
| E1 elements (au) |       |
| 4s $^2 P_{1/2} \rightarrow 4s ^2 S_{1/2}$ | 0.001 |
| 4s $^2 P_{1/2} \rightarrow 3d ^2 D_{3/2}$ | -0.012 |
| 4s $^2 P_{3/2} \rightarrow 4s ^2 S_{1/2}$ | 0.001 |
| 4s $^2 P_{3/2} \rightarrow 3d ^2 D_{3/2}$ | -0.002 |
| 4s $^2 P_{3/2} \rightarrow 3d ^2 D_{5/2}$ | -0.005 |
| Polarizability (au) | $\alpha_0^1$ $\alpha_0^2$ |
| 4s $^2 S_{1/2}$ | -0.011 |
| 3d $^2 P_{3/2}$ | -0.384 0.226 |
| 3d $^2 D_{5/2}$ | -0.499 0.415 |

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