PHYSICAL REVIEW A **83**, 012503 (2011)

Blackbody radiation shift, multipole polarizabilities, oscillator strengths, lifetimes, hyperfine constants, and excitation energies in Ca$^+$

M. S. Safronova[1] and U. I. Safronova[2,3]

[1]*Department of Physics and Astronomy, 217 Sharp Lab, University of Delaware, Newark, Delaware 19716, USA*
[2]*Physics Department, University of Nevada, Reno, Nevada 89557, USA*
[3]*Institute of Spectroscopy, Russian Academy of Science, Troitsk, Moscow, Russia*

(Received 26 November 2010; published 7 January 2011)

A systematic study of Ca$^+$ atomic properties is carried out using a high-precision relativistic all-order method where all single, double, and partial triple excitations of the Dirac-Fock wave functions are included to all orders of perturbation theory. Reduced matrix elements, oscillator strengths, transition rates, and lifetimes are determined for the levels up to $n = 7$. Recommended values and estimates of their uncertainties are provided for a large number of electric-dipole transitions. Electric-dipole scalar polarizabilities for the $5s$, $6s$, $7s$, $8s$, $4p_j$, $5p_j$, $3d_j$, and $4d_j$ states and tensor polarizabilities for the $4p_{3/2}$, $5p_{3/2}$, $3d_j$, and $4d_j$ states in Ca$^+$ are calculated. Methods are developed to accurately treat the contributions from highly excited states, resulting in significant (factor of 3) improvement in the accuracy of the $3d_{5/2}$ static polarizability value, $31.8(3)a_0^3$, in comparison with the previous calculation [Arora *et al.*, Phys. Rev. A **76**, 064501 (2007).]. The blackbody radiation shift of the $4s$ -$3d_{5/2}$ clock transition in Ca$^+$ is calculated to be 0.381(4) Hz at room temperature, $T = 300$ K. Electric-quadrupole $4s$-nd and electric-octupole $4s$-nf matrix elements are calculated to obtain the ground-state multipole $E2$ and $E3$ static polarizabilities. Excitation energies of the ns, np, nd, nf, and ng states with $n \leqslant 7$ in are evaluated and compared with experiment. Recommended values are provided for the $7p_{1/2}$, $7p_{3/2}$, $8p_{1/2}$, and $8p_{3/2}$ removal energies for which experimental measurements are not available. The hyperfine constants A are determined for the low-lying levels up to $n = 7$. The quadratic Stark effect on hyperfine structure levels of ^{43}Ca$^+$ ground state is investigated. These calculations provide recommended values critically evaluated for their accuracy for a number of Ca$^+$ atomic properties for use in planning and analysis of various experiments as well as theoretical modeling.

DOI: 10.1103/PhysRevA.83.012503 PACS number(s): 31.15.ac, 06.30.Ft, 31.15.ap, 31.15.ag

I. INTRODUCTION

This work presents a systematic study of atomic properties of Ca$^+$ ion motivated by its importance for the development of optical frequency standards and quantum-information processing.

The current definition of a second in the International System of Units (SI) is based on the microwave transition between the two hyperfine levels of the ground state of ^{133}Cs. The present relative standard uncertainty of Cs microwave frequency standard is around 4×10^{-16} [1]. More precise frequency standards will open ways to more sensitive quantum-based standards for applications such as measurements of the fundamental constants and testing of physics postulates, inertial navigation, magnetometry, gravity gradiometry, and tracking of deep-space probes. Optical frequency standards may achieve even smaller relative uncertainties owing to superior resonance line quality factors, allowing shorter averaging times and higher stability. Significant recent progress in optical spectroscopy and measurement techniques has led to the achievement of relative standard uncertainties in optical frequency standards that are comparable to the Cs microwave benchmark. With extremely low systematic perturbations and better stability and accuracy, such optical frequency standards can reach a systematic fractional uncertainty of the order of 10^{-18} [2,3].

Prospects of optical frequency standard based on the metastable $4s$-$3d_{5/2}$ transition in Ca$^+$ ion have been studied in [4–6]. In 2009, the first absolute transition frequency measurement at the 10^{-15} level with a single, laser-cooled ^{40}Ca$^+$ ion in a linear Paul trap has been reported [7]. The development of an ion clock based on Ca$^+$ has the technological advantage that all necessary wavelengths for laser cooling and state manipulation including lasers for photoionization can be generated by commercially available and easy-to-handle solid-state lasers [5,7]. The operation of atomic clocks is generally carried out at room temperature, whereas the definition of the second refers to the clock transition in an atom at absolute zero. This implies that the clock transition frequency should be corrected in practice for the effect of finite temperature, of which the leading contributor is the blackbody radiation (BBR) shift. Recent experimental work [5] notes that uncertainty due to BBR shift is particularly difficult to improve by experimental means. This uncertainty results from both the uncertainty in the stability and accuracy of trap temperature measurement, as well as the uncertainty in the evaluation of the BBR shift coefficient (i.e., BBR shift at 300 K). In the present paper, we improve the accuracy of the BBR shift value at 300 K by a factor of 3.

Ca$^+$ ions have been used for a number of quantum-information-processing experiments (see Refs. [8,9] and references therein). Most of the elementary building blocks for quantum-information processing such as state initialization, long quantum-information storage times, universal set of quantum logic gates, and readout have been realized with high fidelity with trapped ion systems such as Ca$^+$ [10–15]. Recently, the merits of a high-fidelity entangling operation on an optical transition (optical qubit) were combined with the long coherence times of two clock states in the hyperfine ground state (hyperfine qubit) by mapping between these two qubits [9]. Precise understanding of the ion qubit and gate operation decoherence properties is aided by precise knowledge of atomic properties of this system.

Properties of Ca^+ are also of interest to astrophysics as the absorption spectrum of the Ca^+ ion is used to explore the structure and properties of interstellar dust clouds [16,17]. In what follows, we briefly review previous studies of Ca^+ atomic properties.

The lifetime of the metastable $3d_{3/2}$ and $3d_{5/2}$ levels in Ca^+ was a subject of many theoretical and experimental studies owing to the importance of these states for the optical frequency standards and quantum-information applications. Early theoretical calculations and measurements of the $3d_{3/2}$ and $3d_{5/2}$ lifetimes in Ca^+ were reviewed in Ref. [18]. Both high-precision measurements and calculations of the $3d_j$ lifetimes were presented by Kreuter *et al.* in Ref. [18]. A measurement technique was based on high-efficiency quantum state detection after coherent excitation to the $3d_{5/2}$ state or incoherent shelving in the $3d_{3/2}$ state, and subsequent free, unperturbed spontaneous decay. The calculation of the $3d_j$-$4s$ electric-quadrupole matrix elements was carried out using an *ab initio* relativistic all-order method which sums infinite sets of many-body perturbation theory terms. These matrix elements were used to evaluate the $3d$ radiative lifetimes and their ratio [18]. In Refs. [19,20], the relativistic coupled-cluster theory was used to perform the calculations of these lowest excited $3d_{3/2}$ and $3d_{5/2}$ state lifetimes.

The BBR shift of the $4s$-$3d_{5/2}$ clock transition, accurate to 3%, and the $3d_{5/2}$ tensor polarizability were presented by Arora *et al.* in Ref. [21]. The calculations were based on the relativistic all-order single-double method, where all single and double excitations of the Dirac-Fock wave function are included to all orders of perturbation theory. The largest contribution to the uncertainty of the BBR shift originated from the contribution of the highly excited $nf_{7/2}$ states to the $3d_{5/2}$ static polarizability.

Relativistic coupled-cluster studies of ionization potentials, lifetimes, and polarizabilities in singly ionized calcium was recently presented by Sahoo *et al.* in Ref. [22]. Numerical results were given for the $4p_j$ lifetime and the $4s$ and $3d_j$ polarizabilities. The polarizabilities of the $4s$, $5s$, $4p$, $5p$, $3d$, and $4d$ of the Ca^+ ions were recently evaluated by Mitroy and Zhang [23] using the nonrelativistic configuration interaction with semiempirical core potential (CICP) method.

The first measurement of the $4p_{3/2}$ lifetime in Ca^+ was presented by Smith and Gallagher [24] using the Hanle-effect method with optical excitation from the $4s$ ground state. The same technique was used by Gallagher [25] to measure the branching ratio of the $4p_{3/2}$ decay [17.6(2.0)]. The beam-foil technique was used by Andersen *et al.* [26] to measure the oscillator strengths for the $4s$-$4p$, $4p$-$5s$, $4p$-$4d$, and $4p$-$5d$ transitions. The same technique was used by Emmoth *et al.* [27]. Additionally, the effects of cascades were analyzed and corrected for lifetime measurements. The first pulsed laser excitation measurements of the $4p_{1/2}$ and $4p_{3/2}$ level lifetime (6.96 ± 0.35 and 6.71 ± 0.25 ns, respectively) were reported by Ansbacher *et al.* [28]. Gosselin *et al.* presented precision $4p_{1/2}$ and $4p_{3/2}$ lifetime measurements in Refs. [29,30]. Two sets of results (6.95 ± 0.18 and 6.87 ± 0.17 ns [29]) and (7.07 ± 0.07 and 6.87 ± 0.06 ns [30]) agree within their uncertainties. The mean lifetimes of the $4p_{1/2}$ and $4p_{3/2}$ levels in Ca^+ were measured by Jin and Church [31,32] to 0.3% precision using a variant of the collinear laser-beam-ion-beam spectroscopy technique (7.098 ± 0.020 and 6.924 ± 0.019 ns, respectively). Lifetime of the $4p_{3/2}$ level (6.94 ± 0.18 ns) was measured by Rosner *et al.* [33] using the cascade-photon-coincidence technique with a sputtered-atom source. We note that recent linearized coupled-cluster calculation [21] disagrees with 0.3% Jin and Church measurement by 3%. The accuracy of the calculations should be better than 1% owing to excellent agreement of similar calculations for all alkali-metal atoms from Li to Fr [34], Mg^+ [35], Sr^+ [36], and Ba^+ [37] with all recent experimental values.

Precision measurement of the branching ratios of the $4p_{3/2}$ decay of Ca^+ was performed recently by Gerritsma *et al.* in Ref. [38]. High precision was achieved by a novel technique based on monitoring the population transfer when repeatedly pumping the ion between different internal states. Authors emphasized that 40-fold improvement was achieved for the $A(4p_{3/2}\text{-}4s)/\sum_J A(4p_{3/2}\text{-}nd_j) = 14.31(5)$ branching ratio in comparison with the best previous measurement [38].

Warner reported [39] oscillator strengths for the ns-$n'p$, np-$n'd$, and nd-$n'f$ transitions with $ns = 4s$-$9s$, $np = 4p$-$9p$, $nd = 3d$-$7d$, and $nf = 4f$-$7f$. The radial wave functions were calculated using scaled Thomas-Fermi-Dirac wave functions with spin-orbit interaction included [39]. The relativistic pseudopotential approach was applied by Hafner and Schwarzt [40] to the calculation of the ns-$n'p$ electric-dipole transition probabilities for $n = 4$-7 and $n' = 4$-6. Semiemerical wave functions were used by Theodosiou [41] to evaluate oscillator strengths and lifetimes of the $5s$, $6s$, $7s$, $4p$, $5p$, $6p$, $4d$, $5d$, and $4f$ levels. Relativistic many-body theory was applied by Guet and Johnson [42] to determine amplitudes for the $4p$-$4s$ and $4p$-$3d$ transitions and the $4p$ lifetime. Multiconfiguration Hartree-Fock wave functions were used by Vaeck *et al.* [43] to evaluate oscillator strengths for the $4p$-$4s$ and $4p$-$3d$ transitions and the $4p$ lifetime in Ca^+. Liaw [44] performed *ab initio* calculations based on the Brueckner approximation for the amplitudes of the $4p$-$4s$ and $4p$-$3d$ transitions and the $4p$ lifetime in Ca^+. The lifetimes of the $5s$, $6s$, $4p$, $5p$, $6p$, $4d$, $5d$, and $4f$ levels in Ca^+ were evaluated by Meléndez *et al.* [45] using the Thomas-Fermi-Dirac central potential method in the frozen core approximation and including the polarization interaction between the valence electron and the core using a model potential. Recently, nonrelativistic CICP method was used by Mitroy *et al.* [46] to evaluate the $4s$-np, $4p$-ns, and $3d$-np oscillator strengths with $n = 4$, 5.

The hyperfine structure of the $4s$, $4p$, and $3d$ states was evaluated by Mårtensson-Pendrill and Salomonson [47] using many-body perturbation theory. Numerical values were given for the $A(4s)$, $A(4p)$, and $A(3d)$ magnetic-dipole hyperfine constants and for the $B(4p_{3/2})$ and $B(3d)$ electric-quadrupole hyperfine constants [47]. First measurements published several years later [48] confirmed theoretical predictions [47]. The experimental and theoretical results for the $A(4s_{1/2})$ and $A(4p_j)$ hyperfine constants agreed at the 3% level [48]. Additional correlation contributions were added to the method used in [47] by Mårtensson-Pendrill *et al.* [49] to recalculate all of the preceding magnetic-dipole hyperfine constants. The hyperfine structure splittings of the $4s$, $4p_{1/2}$, and $4p_{3/2}$ levels in $^{43}\mathrm{Ca}^+$ were measured by fast-ion-beam collinear laser spectroscopy in [50]. Precise determination of the $4s$ ground-state hyperfine structure splitting of $^{43}\mathrm{Ca}^+$ [3225.608 286 4(3) MHz] was reported by Arbes *et al.* [51]. The Doppler-free and potentially very narrow resonances were used in Ref. [52] to determine the magnetic dipole hyperfine interaction constant A for the $4p_{1/2}$ and $3d_{3/2}$ states of $^{43}\mathrm{Ca}^+$. Hyperfine structure in the three $3d_{3/2,5/2} \Rightarrow 4p_{1/2,3/2}$ transitions were studied by fast-ion-beam collinear laser spectroscopy for all stable Ca isotopes in [53]. Hyperfine structure parameters $A(4p)$, $A(3d)$, $B(4p_{3/2})$, and $B(3d_j)$ for the odd isotope $^{43}\mathrm{Ca}^+$, as evaluated from the splittings observed, agreed well with theoretical predictions from relativistic many-body perturbation theory [47,49]. Recently, relativistic many-body calculations were performed to calculate the magnetic-dipole hyperfine constants $A(4s)$, $A(4p)$, and $A(3d)$ and the electric quadrupole constants $B(4p_{3/2})$ and $B(3d)$ in $^{43}\mathrm{Ca}^+$ [54,55]. The relativistic coupled-cluster theory was employed by Sahoo *et al.* [54] to calculate the hyperfine A constants of the low-lying states.

Despite many previous studies, no reliable recommended values exist for a number of properties of low-lying states of Ca^+. In many cases, only semiempirical calculations are available. In this work, we carry out a systematic study of Ca^+ energies; $E1$, $E2$, and $E3$ matrix elements; transition rates; lifetimes; A and B hyperfine constants; $E2$ and $E3$ ground-state polarizabilities; scalar $E1$ polarizabilities of the $5s$, $6s$, $7s$, $8s$, $4p_j$, $5p_j$, $3d_j$, and $4d_j$ states; and tensor polarizabilities of the $4p_{3/2}$, $5p_{3/2}$, $3d_j$, and $4d_j$ states using a high-precision all-order approach [56] in several different approximations. We evaluate the uncertainties of our calculations for most of the values listed in this work. We also re-evaluated the blackbody-radiation shift in a Ca^+ ion optical frequency standard and improved its accuracy by a factor of 3. The quadratic Stark effect on the hyperfine structure levels of $^{43}\mathrm{Ca}^+$ ground state is investigated. The methodologies for evaluating the uncertainties of theoretical values calculated in the framework of the all-order approach are developed. The calculation of uncertainties involved estimation of missing high-order effects and *ab initio* calculations in different approximations to establish the size of the higher-order corrections and approximate missing contributions. We evaluated the uncertainties of the recommended values for the transition matrix elements, oscillator strengths, transition rates, lifetimes, polarizabilities, BBR shift, and the Stark shift coefficient.

The main motivation for this work is to provide recommended values, critically evaluated for their accuracy, for a number of atomic properties via a systematic high-precision study for use in planning and analysis of various experiments as well as theoretical modeling.

II. ENERGY LEVELS

Energies of the nl_j states in Ca^+ are evaluated for $n \leqslant 7$ and $l \leqslant 3$ using both third-order relativistic many-body perturbation theory (RMBPT) and the single-double (SD) all-order method. The all-order (linearized coupled-cluster) method and its applications are discussed in detail in review [56] and references therein. Therefore, we do not repeat the method description in this work, with the exception of the details needed to discuss the evaluation of uncertainties in the transition matrix elements carried out in the next section. The comparison of the calculated energy levels with the experimental values gives an excellent indication of the accuracy of the approach and identifies states with particularly large correlation corrections. Moreover, a number of highly excited energy levels that we need for the polarizability calculations appear to be not known and are missing from the National Institute of Standards and Technology (NIST) database [57]. Results of our energy calculations are summarized in Table I. Columns 2–7 of Table I give the lowest-order DF energies $E^{(0)}$, second-order and third-order Coulomb correlation energies $E^{(2)}$ and $E^{(3)}$, first-order and second-order Breit corrections $B^{(1)}$ and $B^{(2)}$, and an estimated Lamb-shift contribution, $E^{(\mathrm{LS})}$. The Lamb shift $E^{(\mathrm{LS})}$ is calculated as the sum of the one-electron self-energy and the first-order vacuum-polarization energy. The vacuum-polarization contribution is calculated from the Uehling potential using the results of Fullerton and Rinker [58]. The self-energy contribution is estimated for the s, $p_{1/2}$, and $p_{3/2}$ orbitals by interpolating among the values obtained by Mohr [59–61] using Coulomb wave functions. For this purpose, an effective nuclear charge Z_{eff} is obtained by finding the value of Z_{eff} required to give a Coulomb orbital with the same average $\langle r \rangle$ as the DF orbital. We find that the values of $E^{(\mathrm{LS})}$ are very small. For states with $l > 0$, the Lamb shift is estimated to be smaller than 0.1 cm^{-1} using scaled Coulomb values and is negligible at the present level of accuracy. We list the all-order SD energies in the column labeled E^{SD} and the part of the third-order energies missing from E^{SD} in the column labeled $E^{(3)}_{\mathrm{extra}}$. The sum of the six terms $E^{(0)}$, E^{SD}, $E^{(3)}_{\mathrm{extra}}$, $B^{(1)}$, $B^{(2)}$, and $E^{(\mathrm{LS})}$ gives our final all-order result $E^{\mathrm{SD}}_{\mathrm{tot}}$, listed in the 11th column of Table I. Recommended energies from the NIST database [57] are given in the column labeled E_{NIST}. Differences between our third-order and all-order calculations and experimental data, $\delta E^{(3)} = E^{(3)}_{\mathrm{tot}} - E_{\mathrm{NIST}}$ and $\delta E^{\mathrm{SD}} = E^{\mathrm{SD}}_{\mathrm{tot}} - E_{\mathrm{NIST}}$, are given in the two final columns of Table I, respectively.

As expected, the largest correlation contribution to the valence energy comes from the second-order term $E^{(2)}$. Therefore, we calculate $E^{(2)}$ with higher numerical accuracy. The second-order energy includes partial waves up to $l_{\max} = 8$ and is extrapolated to account for contributions from higher partial waves (see, for example, Refs. [62,63] for details of the extrapolation procedure). As an example of the convergence of $E^{(2)}$ with the number of partial waves l, consider the ground $4s$ state. Calculations of $E^{(2)}$ with $l_{\max} = 6$ and 8 yield $E^{(2)}(4s) = -4726.2$ and -4743.7 cm^{-1}, respectively. Extrapolation of these calculations yields -4786.3 and -4786.9 cm^{-1}, respectively. Therefore, the numerical uncertainty in the second-order value $E^{(2)}(4s)$ is 0.6 cm^{-1}. It should be noted that the 17.5 cm^{-1} contribution from partial waves with $l > 6$ for the $4s$ state is the largest among all states considered in Table I; smaller (about 4–6 cm^{-1}) contributions are obtained for the $3d$, $4p$, and $4d$ states and much smaller contributions (0.5–1.5 cm^{-1}) are obtained for the $n = 6$ states.

Owing to complexity of the all-order calculations, we restrict $l \leqslant l_{\max} = 6$ in the E^{SD} calculation. The second-order contribution dominates E^{SD}; therefore, we can use the

TABLE I. Zeroth- (DF), second-, and third-order Coulomb correlation energies $E^{(n)}$, single-double Coulomb energies E^{SD}, $E^{(3)}_{\mathrm{extra}}$, and first-order Breit and second-order Coulomb-Breit corrections $B^{(n)}$ to the energies of Ca$^+$. The total energies ($E^{(3)}_{\mathrm{tot}} = E^{(0)} + E^{(2)} + E^{(3)} + B^{(1)} + B^{(2)} + E^{(\mathrm{LS})}$, $E^{\mathrm{SD}}_{\mathrm{tot}} = E^{(0)} + E^{\mathrm{SD}} + E^{(3)}_{\mathrm{extra}} + B^{(1)} + B^{(2)} + E^{(\mathrm{LS})}$) of Ca$^+$ are compared with experimental energies E_{NIST} [57] and $\delta E = E_{\mathrm{tot}} - E_{\mathrm{NIST}}$. Units, cm^{-1}. Energy is given in units of cm^{-1}.

nlj	$E^{(0)}$	$E^{(2)}$	$E^{(3)}$	$B^{(1)}$	$B^{(2)}$	$E^{(\mathrm{LS})}$	$E^{(3)}_{\mathrm{tot}}$	E^{SD}	$E^{(3)}_{\mathrm{extra}}$	$E^{\mathrm{SD}}_{\mathrm{tot}}$	E_{NIST}	$\delta E^{(3)}$	δE^{SD}
$4s_{1/2}$	−91 440	−4786.3	857.6	23.8	−23.2	3.5	−95 364	−4697.6	520.2	−95 600	−95 752	387	139
$4p_{1/2}$	−68 037	−2675.3	411.7	19.7	−12.3	0.0	−70 293	−2752.7	271.8	−70 506	−70 560	267	50
$4p_{3/2}$	−67 837	−2642.5	406.0	14.2	−13.3	0.0	−70 073	−2719.4	268.2	−70 283	−70 337	265	50
$3d_{3/2}$	−72 617	−10333.3	1989.7	34.1	−99.8	0.0	−81 027	−10578.5	1010.7	−82 206	−82 102	1075	−149
$3d_{5/2}$	−72 593	−10277.7	1978.0	21.0	−97.8	0.0	−80 970	−10520.6	1003.4	−82 142	−82 041	1071	−146
$4d_{3/2}$	−37 034	−2209.5	395.1	8.0	−21.7	0.0	−38 862	−1938.7	216.3	−38 761	−38 913	51	143
$4d_{5/2}$	−37 018	−2200.9	393.5	5.0	−21.4	0.0	−38 841	−1932.8	215.1	−38 743	−38 893	52	142
$4f_{5/2}$	−27 473	−224.8	22.2	0.0	−0.1	0.0	−27 676	−237.6	22.8	−27 688	−27 695	19	7
$4f_{7/2}$	−27 473	−224.7	22.2	0.0	−0.1	0.0	−27676	−237.6	22.8	−27 688	−27 695	19	7
$5s_{1/2}$	−42 428	−1314.5	242.8	7.4	−7.0	0.5	−43 499	−1246.8	145.2	−43 525	−43 585	86	56
$5p_{1/2}$	−34 406	−877.1	140.2	7.3	−4.5	0.0	−35 140	−868.4	90.0	−35 180	−35 219	79	37
$5p_{3/2}$	−34 333	−868.4	138.6	5.3	−4.9	0.0	−35 062	−860.1	89.0	−35 102	−35 141	78	37
$5d_{3/2}$	−22 244	−910.4	156.6	3.3	−8.8	0.0	−23 003	−809.7	89.2	−22 967	−23 030	26	60
$5d_{5/2}$	−22 236	−907.7	156.1	2.1	−8.7	0.0	−22 994	−807.8	88.8	−22 958	−23 021	27	59
$5f_{5/2}$	−17 589	−129.7	13.4	0.0	−0.1	0.0	−17 706	−137.2	13.1	−17 713	−17 717	12	4
$5f_{7/2}$	−17 589	−129.6	13.3	0.0	−0.1	0.0	−17 706	−137.2	13.0	−17 713	−17 717	12	4
$6s_{1/2}$	−24 589	−556.3	103.9	3.3	−3.1	0.1	−25 041	−521.3	61.7	−25 046	−25 074	34	26
$6p_{1/2}$	−20 894	−405.0	65.4	3.5	−2.2	0.0	−21 232	−401.5	41.7	−21 252	−21 267	35	15
$6p_{3/2}$	−20 859	−401.4	64.8	2.5	−2.3	0.0	−21 195	−398.0	41.3	−21 215	−21 230	35	15
$6d_{3/2}$	−14 820	−472.5	79.6	1.7	−4.5	0.0	−15 215	−423.2	46.3	−15 198	−15 230	15	31
$6d_{5/2}$	−14 815	−471.2	79.4	1.1	−4.5	0.0	−15 211	−422.4	46.1	−15 193	−15 226	15	31
$6f_{5/2}$	−12 215	−79.6	8.3	0.0	0.0	0.0	−12 286	−84.2	8.0	−12 291	−12 294	7	2
$6f_{7/2}$	−12 215	−79.6	8.3	0.0	0.0	0.0	−12 286	−84.2	8.0	−12 291	−12 294	7	2
$7s_{1/2}$	−16 053	−288.7	54.1	1.7	−1.6	0.0	−16 287	−268.8	32.1	−16 289	−16 304	16	14
$7p_{1/2}$	−14 051	−221.0	35.8	1.9	−1.2	0.0	−14 236	−218.3	22.8	−14 246			
										−14 253[a]			
$7p_{3/2}$	−14 032	−219.2	35.5	1.4	−1.3	0.0	−14 215	−216.6	22.6	−14 225			
										−14 232[a]			
$7d_{3/2}$	−10 576	−278.3	46.3	1.0	−2.6	0.0	−10 809	−250.2	27.3	−10 799	−10 818	9	18
$7d_{5/2}$	−10 573	−277.6	46.2	0.6	−2.6	0.0	−10 806	−249.7	27.2	−10 796	−10 815	9	18
$7f_{5/2}$	−8974	−51.8	5.5	0.0	0.0	0.0	−9 020	−54.9	5.2	−9 023	−9 025	5	2
$7f_{7/2}$	−8974	−51.8	5.5	0.0	0.0	0.0	−9 020	−54.8	5.2	−9 023	−9 025	5	1

[a] Recommended values.

extrapolated value of the $E^{(2)}$ described earlier to account for the contributions of the higher partial waves. The partial waves $l \leqslant 6$ are also used in the calculation of $E^{(3)}$. Since the asymptotic l dependence of the second- and third-order energies are similar (both fall off as l^{-4}), we use the second-order remainder as a guide to estimate the remainder in the third-order contribution. The term $E^{(3)}_{\mathrm{extra}}$ in Table I, which accounts for the part of the third-order MBPT energy missing from the SD expression for the energy, is smaller than $E^{(3)}$ by an order of magnitude for the states considered here.

The column labeled δE^{SD} in Table I gives differences between our *ab initio* results and the experimental values [57]. The SD results agree significantly better with measured values than do the third-order MBPT results (the ratio of $\delta E^{(3)}/\delta E^{\mathrm{SD}}$ is about 10 for some of cases), illustrating the importance of fourth- and higher-order correlation corrections.

We provide recommended values for the $7p_{1/2}$ and $7p_{3/2}$ energies in Table I in the separate rows. We estimate these values to be accurate to about 3 cm^{-1}. Our recommended values for the $8p_{1/2}$ and $8p_{3/2}$ energies are $-10\,221$ cm^{-1} and $-10\,209$ cm^{-1}, respectively.

III. ELECTRIC-DIPOLE MATRIX ELEMENTS, OSCILLATOR STRENGTHS, TRANSITION RATES, AND LIFETIMES IN Ca$^+$

A. Electric-dipole matrix elements

In Table II, we list our recommended values for 58 $E1$ ns-$n'p$ and nd-$n'p$ transitions. We note that we have calculated over 500 $E1$ matrix elements to evaluate polarizabilities and BBR shift presented in this work. We refer to these values as "best set" of the matrix elements. We list only the matrix elements that give significant contributions to the atomic properties calculated in the other sections. To evaluate the uncertainties of these values, we carried out several calculations in different approximations. To demonstrate the size of the second-, third-, and higher-order correlation corrections, we list the lowest-order Dirac-Fock (DF) Z^{DF}, second-order

TABLE II. Recommended values of the reduced electric-dipole matrix elements in atomic units. The first-order, second-order, and third-order MBPT and all-order SD and SDpT values are listed; the label "sc" indicates the scaled values. Final recommended values and their uncertainties are given in the Z^{final} column. The last column gives relative uncertainties of the final values in percentages. Absolute values are given.

Transition		Z^{DF}	$Z^{(\text{DF}+2)}$	$Z^{(\text{DF}+2+3)}$	Z^{SD}	$Z^{(\text{SD})}_{\text{sc}}$	Z^{SDpT}	$Z^{\text{SDpT}}_{\text{sc}}$	Z^{final}	Unc. (%)
$4s_{1/2}$	$4p_{1/2}$	3.2012	3.0045	2.8826	2.8978	2.9071	2.9131	2.9071	2.898(13)	0.45
$4s_{1/2}$	$4p_{3/2}$	4.5269	4.2499	4.0773	4.0989	4.1119	4.1204	4.1119	4.099(18)	0.45
$5s_{1/2}$	$4p_{1/2}$	2.1084	2.1458	2.0799	2.0660	2.0735	2.0706	2.0717	2.073(11)	0.51
$5s_{1/2}$	$4p_{3/2}$	3.0142	3.0653	2.9752	2.9551	2.9647	2.9614	2.9622	2.965(14)	0.46
$5s_{1/2}$	$5p_{1/2}$	6.4426	6.3777	6.1965	6.2195	6.2297	6.2392	6.2287	6.23(1)	0.16
$5s_{1/2}$	$5p_{3/2}$	9.1006	9.0095	8.7523	8.7850	8.7999	8.8130	8.7984	8.80(1)	0.17
$6s_{1/2}$	$4p_{1/2}$	0.5798	0.6002	0.5837	0.5817	0.5820	0.5825	0.5827	0.582(1)	0.18
$6s_{1/2}$	$4p_{3/2}$	0.8239	0.8522	0.8291	0.8264	0.8267	0.8276	0.8278	0.826(2)	0.18
$6s_{1/2}$	$5p_{1/2}$	4.4346	4.4565	4.3672	4.3504	4.3606	4.3529	4.3529	4.361(8)	0.18
$6s_{1/2}$	$5p_{3/2}$	6.3311	6.3601	6.2388	6.2144	6.2267	6.2177	6.2159	6.23(1)	0.17
$6s_{1/2}$	$6p_{1/2}$	10.7169	10.6885	10.4530	10.4853	10.4977	10.5108	10.4952	10.50(1)	0.12
$6s_{1/2}$	$6p_{3/2}$	15.1300	15.0906	14.7554	14.8016	14.8201	14.8379	14.8166	14.82(2)	0.12
$7s_{1/2}$	$4p_{1/2}$	0.3140	0.3276	0.3193	0.3183	0.3182	0.3186	0.3187	0.3183(6)	0.20
$7s_{1/2}$	$4p_{3/2}$	0.4456	0.4644	0.4530	0.4515	0.4514	0.4520	0.4520	0.4515(9)	0.20
$7s_{1/2}$	$5p_{1/2}$	1.1176	1.1301	1.1057	1.1056	1.1061	1.1075	1.1073	1.106(1)	0.12
$7s_{1/2}$	$5p_{3/2}$	1.5845	1.6020	1.5676	1.5675	1.5681	1.5702	1.5699	1.568(2)	0.13
$7s_{1/2}$	$6p_{1/2}$	7.4782	7.4912	7.3825	7.3492	7.3629	7.3587	7.3582	7.363(5)	0.06
$7s_{1/2}$	$6p_{3/2}$	10.6693	10.6877	10.5391	10.4913	10.5071	10.5040	10.5009	10.507(6)	0.06
$7s_{1/2}$	$7p_{1/2}$	16.0333	16.0184	15.7262	15.7723	15.7894	15.8043	15.7856	15.79(1)	0.09
$7s_{1/2}$	$7p_{3/2}$	22.6281	22.6084	22.1909	22.2570	22.2812	22.3027	22.2758	22.28(2)	0.10
$8s_{1/2}$	$5p_{1/2}$	0.5862	0.5941	0.5827	0.5829	0.5830	0.5840	0.5839	0.583(1)	0.17
$8s_{1/2}$	$5p_{3/2}$	0.8299	0.8411	0.8248	0.8252	0.8253	0.8267	0.8265	0.825(1)	0.17
$8s_{1/2}$	$6p_{1/2}$	1.7969	1.8017	1.7732	1.7738	1.7743	1.7770	1.7767	1.774(3)	0.15
$8s_{1/2}$	$6p_{3/2}$	2.5448	2.5547	2.5112	2.5123	2.5129	2.5167	2.5163	2.513(4)	0.15
$8s_{1/2}$	$7p_{1/2}$	11.2499	11.2611	11.1339	11.0842	11.0946	11.0951	11.0879	11.095(7)	0.06
$8s_{1/2}$	$7p_{3/2}$	16.0443	16.0563	15.8877	15.8166	15.8313	15.8309	15.8219	15.831(9)	0.06
$8s_{1/2}$	$8p_{1/2}$	22.3941	22.3854	22.0348	22.0969		22.1359		22.14(4)	0.18
$8s_{1/2}$	$8p_{3/2}$	31.5981	31.5878	31.0854	31.1745		31.2302		31.23(6)	0.18
$3d_{3/2}$	$4p_{1/2}$	3.0825	2.9296	2.2998	2.4173	2.4636	2.4677	2.4503	2.464(13)	0.54
$3d_{3/2}$	$4p_{3/2}$	1.3764	1.3088	1.0260	1.0788	1.0996	1.1014	1.0937	1.100(6)	0.54
$3d_{3/2}$	$4f_{5/2}$	2.6059	2.5228	1.6763	1.8660	1.9265	1.9265	1.9051	1.927(21)	1.11
$3d_{3/2}$	$5f_{5/2}$	1.5216	1.4530	1.1073	1.1655	1.1917	1.1937	1.1846	1.192(7)	0.59
$3d_{5/2}$	$4p_{3/2}$	4.1348	3.9311	3.0882	3.2452	3.3063	3.3127	3.2884	3.306(18)	0.54
$3d_{5/2}$	$4f_{5/2}$	0.6976	0.6751	0.4502	0.5005	0.5163	0.5166	0.5106	0.516(6)	1.10
$3d_{5/2}$	$4f_{7/2}$	3.1201	3.0192	2.0134	2.2382	2.3090	2.3102	2.2835	2.309(25)	1.10
$3d_{5/2}$	$5f_{5/2}$	0.4072	0.3888	0.2970	0.3124	0.3192	0.3199	0.3174	0.319(2)	0.59
$3d_{5/2}$	$5f_{7/2}$	1.8214	1.7388	1.3284	1.3972	1.4278	1.4308	1.4193	1.428(8)	0.59
$4d_{3/2}$	$4p_{1/2}$	4.2159	4.1495	4.4121	4.2636	4.2818	4.2565	4.2821	4.28(3)	0.59
$4d_{3/2}$	$4p_{3/2}$	1.8990	1.8686	1.9867	1.9203	1.9280	1.9171	1.9281	1.93(1)	0.57
$4d_{3/2}$	$4f_{5/2}$	11.9755	11.8972	11.3300	11.3461	11.3552	11.4033	11.3479	11.36(5)	0.42
$4d_{3/2}$	$5p_{1/2}$	8.0685	8.0369	7.2981	7.4342	7.4325	7.4916	7.4704	7.43(6)	0.79
$4d_{3/2}$	$5p_{3/2}$	3.6014	3.5878	3.2554	3.3168	3.3162	3.3426	3.3320	3.32(3)	0.79
$4d_{5/2}$	$4p_{3/2}$	5.6913	5.6015	5.9527	5.7547	5.7786	5.7451	5.7791	5.78(3)	0.58
$4d_{5/2}$	$5p_{3/2}$	10.8150	10.7724	9.7806	9.9632	9.9600	10.0403	10.0091	9.96(8)	0.81
$4d_{5/2}$	$4f_{5/2}$	3.2020	3.1809	3.0300	3.0342	3.0364	3.0494	3.0345	3.04(1)	0.43
$4d_{5/2}$	$4f_{7/2}$	14.3198	14.2254	13.5508	13.5696	13.5793	13.6376	13.5707	13.58(6)	0.43
$5d_{3/2}$	$5p_{1/2}$	7.1941	7.1786	7.6248	7.4598	7.4916	7.4316	7.4808	7.49(6)	0.80
$5d_{3/2}$	$5p_{3/2}$	3.2436	3.2357	3.4371	3.3630	3.3763	3.3503	3.3715	3.38(3)	0.77
$5d_{3/2}$	$4f_{5/2}$	7.9026	7.9162	8.7463	8.5477	8.5564	8.4871	8.5512	8.56(7)	0.81
$5d_{5/2}$	$5p_{3/2}$	9.7176	9.6962	10.2951	10.0746	10.1162	10.0367	10.1018	10.12(8)	0.79
$5d_{5/2}$	$4f_{5/2}$	2.1094	2.1135	2.3342	2.2815	2.2841	2.2653	2.2828	2.28(2)	0.82
$5d_{5/2}$	$4f_{7/2}$	9.4333	9.4515	10.4388	10.2029	10.2149	10.1307	10.2088	10.21(8)	0.82
$5d_{3/2}$	$5f_{5/2}$	20.4001	20.3664	19.0555	19.1963	19.2049	19.3158	19.1938	19.2(1)	0.58
$5d_{5/2}$	$5f_{5/2}$	5.4558	5.4462	5.0977	5.1350	5.1367	5.1668	5.1337	5.14(3)	0.59
$5d_{5/2}$	$5f_{7/2}$	24.3991	24.3564	22.7979	22.9645	22.9721	23.1067	22.9588	23.0(1)	0.59
$6d_{3/2}$	$5p_{1/2}$	2.3088	2.2923	2.2439	2.2293	2.2284	2.2369	2.2368	2.228(9)	0.39
$6d_{3/2}$	$5p_{3/2}$	1.0338	1.0263	1.0032	0.9969	0.9965	1.0005	1.0004	0.996(4)	0.40
$6d_{5/2}$	$5p_{3/2}$	3.1018	3.0793	3.0112	2.9922	2.9908	3.0027	3.0025	2.99(1)	0.40

$Z^{(\mathrm{DF}+2)}$, and third-order $Z^{(\mathrm{DF}+2+3)}$ values in the first three numerical columns of Table II. The absolute values in atomic units (a_0e) are given in all cases. The many-body perturbation theory (MBPT) calculations are carried out following the method described in Ref. [64]. The values $Z^{(\mathrm{DF}+2)}$ are obtained as the sum of the second-order correlation correction $Z^{(2)}$ and the DF matrix elements Z^{DF}. The second-order Breit corrections $B^{(2)}$ are very small in comparison with the second-order Coulomb corrections $Z^{(2)}$ (the ratio of $B^{(2)}$ to $Z^{(2)}$ are about 1%–2%). The third-order matrix elements $Z^{(\mathrm{DF}+2+3)}$ include the DF values, the second-order $Z^{(2)}$ results, and the third-order $Z^{(3)}$ correlation correction. $Z^{(3)}$ includes random-phase-approximation (RPA) terms iterated to all orders, Brueckner orbital (BO) corrections, the structural radiation, and normalization terms (see [64] for definition of these terms).

The next four columns contain four different all-order calculations. *Ab initio* electric-dipole matrix elements evaluated in the all-order SD and SDpT approximations (SD all-order method including partial triple excitations [34]) are given in columns labeled Z^{SD} and Z^{SDpT} of Table II. The SD and SDpT matrix elements Z^{SD} include $Z^{(3)}$ completely, along with important fourth- and higher-order corrections. The fourth-order corrections omitted from the SD matrix elements were discussed by Derevianko and Emmons [65]. The difference between the Z^{SD} and the Z^{SDpT} values is about 0.5%–2.0%.

We have developed some general criteria to establish the final values for all transitions and evaluate uncertainties owing to the need to analyze a very large number of transitions. To evaluate the uncertainties of our matrix element values and to provide recommended values, we carried out a semiempirical evaluation of the missing correlation corrections using the scaling procedure described in what follows.

The matrix elements of any one-body operator $Z = \sum_{ij} z_{ij}\ a_i^\dagger a_j$ are obtained within the framework of the SD all-order method as

$$Z_{wv} = \frac{\langle \Psi_w | Z | \Psi_v \rangle}{\sqrt{\langle \Psi_v | \Psi_v \rangle \langle \Psi_w | \Psi_w \rangle}}, \tag{1}$$

where $|\Psi_v\rangle$ and $|\Psi_w\rangle$ are given by the expansion

$$|\Psi_v\rangle = \left[1 + \sum_{ma} \rho_{ma} a_m^\dagger a_a + \frac{1}{2} \sum_{mnab} \rho_{mnab} a_m^\dagger a_n^\dagger a_b a_a \right. \\ \left. + \sum_{m \neq v} \rho_{mv} a_m^\dagger a_v + \sum_{mna} \rho_{mnva} a_m^\dagger a_n^\dagger a_a a_v \right] |\Psi_v^{(0)}\rangle, \tag{2}$$

and $|\Psi_v^{(0)}\rangle$ is the lowest-order atomic state vector. In Eq. (2), the indices m and n range over all possible virtual states while indices a and b range over all occupied core states. The quantities ρ_{ma}, ρ_{mv} are single-excitation coefficients for core and valence electrons and ρ_{mnab} and ρ_{mnva} are double-excitation coefficients for core and valence electrons, respectively. In the SD approximation, the resulting expression for the numerator of Eq. (1) consists of the sum of the DF matrix element z_{wv} and 20 other terms that are linear or quadratic functions of the excitation coefficients. The all-order method yielded results for the properties of alkali-metal atoms and many other monovalent systems [34–37,56] in excellent agreement with experiment. For example, the SD results for the primary ns-np_j $E1$ matrix elements of alkali-metal atoms agree with experiment to 0.1%–0.5% [34]. However, triple corrections are important for many of the nd-$n'p$ matrix elements and have to be included. Our *ab initio* SDpT values include corrections to the equations for the valence excitation coefficients ρ_{mv} and valence energy. These corrections arise from the addition of the valence triple excitations to the wave function given by Eq. (2).

We find that only two terms give dominant contributions for all matrix elements considered in this work:

$$Z^{(a)} = \sum_{ma} (z_{am} \tilde{\rho}_{wmva} + z_{ma} \tilde{\rho}^*_{vmwa}) \tag{3}$$

or

$$Z^{(c)} = \sum_{m} \left(z_{wm} \rho_{mv} + z_{mv} \rho^*_{mw} \right), \tag{4}$$

where $\tilde{\rho}_{mnab} = \rho_{mnab} - \rho_{nmab}$ and z_{wv} are lowest-order matrix elements of the electric-dipole operator. For most of the transitions considered in this work, the term $Z^{(c)}$ is the dominant term. In many cases, it is overwhelmingly dominant (by a factor of 3 or more). To evaluate missing corrections to this term, we need to improve the values of the valence single-excitation coefficients ρ_{mv} [66]. These excitation coefficients are closely related to the correlation energy δE_v. If we introduce the self-energy operator Σ_{mv} (also referred to as correlation potential in some works) as

$$\Sigma_{mv} = (\tilde{\epsilon}_v - \epsilon_m)\, \rho_{mv}, \tag{5}$$

then the correlation energy would correspond to the diagonal term Σ_{vv} [67]. Therefore, the omitted correlation correction can be estimated by adjusting the single-excitation coefficients ρ_{mv} to the experimentally known value of the valence correlation energy and then recalculating the matrix elements using Eq. (1) with the modified coefficients [66]

$$\rho'_{mv} = \rho_{mv} \frac{\delta E_v^{\mathrm{expt}}}{\delta E_v^{\mathrm{theory}}}. \tag{6}$$

The $\delta E_v^{\mathrm{expt}}$ is defined as the experimental energy [57] minus the lowest-order DF energy ϵ_v. We note that it is a rather complicated procedure that involves complete recalculation of the matrix elements with new values of the valence excitation coefficients. The scaling factors depend on the correlation energy given by the particular calculation. Therefore, the scaling factors are different for the SD and SDpT calculations, and these values have to be scaled separately. Generally, scaled SD and SDpT values are close together, as expected. The corresponding results are listed in Table II with subscript “sc”.

The term $Z^{(a)}$ is not corrected by the scaling procedure. However, it is dominant for very few transitions that give significant contributions to the atomic properties considered in this work. Essentially, the only large matrix elements where term $Z^{(c)}$ is not dominant are $4s$-$4p$ and $5s$-$5p$. In both of these cases, term $Z^{(c)}$ is still of the same order magnitude as the term $Z^{(a)}$. Therefore, we can establish the recommended set of values and their uncertainties based on the ratio $R = Z^{(c)}/Z^{(a)}$. We take the final value to be SD scaled if $R > 1$. Otherwise, we use SD as the final value. If $0.5 < R < 1.5$, we evaluate the uncertainty in term $Z^{(c)}$ as the maximum difference of the final value and the other three all-order values from the SD, SDpT, SDsc, and SDpTsc set. Then we assume that the uncertainty of all the other terms does not exceed this value and add two uncertainties in quadrature. If $1.5 < R < 3$, we evaluate the final uncertainty as the max(SDsc-SD, SDsc-SDpT, SDsc-SDpTsc). If the term $Z^{(c)}$ strongly dominates and $R > 3$, we evaluate the final uncertainty as max(SDsc-SDpT, SDsc-SDpTsc). We note that we have conducted numerous comparisons of all available data on various properties of many different monovalent systems with different types of experiments in many other works (see [18,21,34–37,56,66,68–75] and references therein) and found that such procedures do not underestimate the uncertainties. If fact, they may somewhat overestimate the uncertainties in some cases.

The last column of Table II gives relative uncertainties of the final values Z^{final} in percentages. We find that the uncertainties are 0.2%–0.5% for most of the transitions. Larger uncertainties (0.8%) occur for some of the transitions such as $5d_j$-$4f_{j'}$. Our final results and their uncertainties are used to calculate the recommended values of the transition rates, oscillator strengths, lifetimes, and polarizabilities, as well as evaluate the uncertainties of these results.

The two most recent calculations of the $E1$ matrix elements between the low-lying states were carried out by Sahoo *et al.* [22] using the relativistic coupled-cluster (RCC) method and by Mitroy and Zhang [23] using a nonrelativistic CICP approach. Reference [22] includes comparison with earlier MBPT calculations [42,44]. Since [42,44] only include low-order MBPT corrections, these calculations are substantially less complete than the all-order coupled-cluster method used in our work and Ref. [22]. Therefore, we focus our discussion on the comparison of the present results with those of [22]. Since Ref. [23] presents nonrelativistic calculations and lists oscillator strengths rather than matrix elements, we compare their results with our j-averaged oscillator strengths in the next section. We note that we use the same method as [21] and our results for the transitions listed in [21] are the same. Therefore, we do not include a separate comparison with that work.

Our final values are compared with RCC calculations of Sahoo *et al.* [22] in Table III. We discuss this comparison in significant detail since both calculations are carried out using the coupled-cluster method but differ significantly in its implementation. All $E1$ transitions listed in [22] are included. The results of [22] listed in columns labeled "STOs" and "GTOs" are obtained by two different calculations, one with Slater-type orbitals and another with Gaussian-type orbitals, respectively. In both cases, the number of partial waves was restricted to $l_{\max} = 4$; that is, only s, p, d, f, and g orbitals were included. Table III illustrates significant basis-set dependence in the results of Sahoo *et al.* [22], 1.4%–1.7% for the $4s$-$4p$ transitions and 2.4%–3.8% for the $3d$-$4p$ transitions. Moreover, different fine-structure components have different basis-set dependencies. It is not clear how that may be possible unless some additional basis-set optimization was carried out in a different way for all transitions. The final results from [22] include corrections from higher-symmetry orbitals carried out using MBPT(2); the changes between the GTOs-STOs values and final recommended results range from 0.7% to 4.3%. Unfortunately, Ref. [22] does not explicitly state what terms are accounted for by MBPT(2). In the standard formulation of the perturbation theory [64], second-order perturbation theory contains only RPA terms which are relatively small for the $3d$-$4p$ transitions. The main contribution of the higher partial waves only appears starting from the third order and comes from BO terms [64]. Therefore, using the MBPT(2) to evaluate higher-symmetry contributions should severely underestimate these terms. The uncertainties of the final values from [22] are numerical uncertainties that are estimated from higher-symmetry orbital corrections and consistency of results carried out with different basis sets. They range from 0.2% to 1.4%. We note that these are only numerical uncertainties and do not include estimates of missing theory (such as other triple- and higher-excitation contributions). The uncertainties in our values represent our best estimate of all possible sources of uncertainties; that is, they give estimated boundary values of the recommended results. We refer the reader to a recent review [76] for further discussion of the differences between numerical and complete uncertainties.

TABLE III. Comparison of the present values of $E1$ dipole matrix elements with RCC calculations of Ref. [22]. The uncertainties in our values represent our best estimate of all possible sources of uncertainties; that is, they give estimated boundary values of these recommended results. The uncertainties in Ref. [22] values are numerical uncertainties resulting from the use of incomplete basis sets. Absolute values in atomic units are given.

		Ref. [22]		
Transition	Present	STOs	GTOs	Final
$4p_{1/2}$-$4s$	2.898(13)	2.86	2.90	2.88(1)
$4p_{3/2}$-$4s$	4.099(18)	4.02	4.09	4.03(1)
$4p_{1/2}$-$3d_{3/2}$	2.464(13)	2.50	2.41	2.40(2)
$4p_{3/2}$-$3d_{3/2}$	1.100(6)	1.12	1.09	1.09(1)
$4p_{3/2}$-$3d_{5/2}$	3.306(18)	3.36	3.28	3.22(4)

The same very large basis is used in all calculations carried out in this work. We use 70 basis-set functions for all partial waves with $l_{\max} \leqslant 6$. Use of such a large basis set results in negligible numerical errors in our values. The contribution of the $l > 6$ partial waves to the $4s$-$4p$ transitions is expected to be at the 0.05% level. The contribution of the $l > 6$ partial waves to the $3d$-$4p$ transitions is accounted for by the scaling procedure. The correction is small since the entire scaling of the *ab initio* SDpT values (that also accounts for the corrections due to higher-order and nonlinear excitations) is 0.7%.

The other major differences between the present work and Ref. [22] include treatment of nonlinear contributions, triple excitations, and higher-excitation terms. The Breit correction calculated in [22] is negligible for the $E1$ matrix elements. Reference [22] includes nonlinear terms at the SD level. While we have not explicitly included nonlinear terms in this work, they were estimated by adjustment of the correlation potential described earlier along with contributions from higher excitations. We have demonstrated in Ref. [66] that correcting correlation potential staring from either linearized SD coupled-cluster (LCCSD) or CCSD approximation leads to the same results within the expected accuracy of the calculations. Our *ab initio* inclusion of the valence triple excitation (SDpT) is more complete than that of [22] since

TABLE IV. Comparison of the ratios $R = d_1^2/d_2^2$ of the squares of the $E1$ matrix elements calculated in the present work in several approximations with results of Ref. [22].

		Present work							Ref. [22]		
d_1	d_2	DF	MBPT2	MBPT3	SD	SDsc	SDpT	SDpTsc	STOs	GTOs	Final
$4s$-$4p_{3/2}$	$4s$-$4p_{1/2}$	2.000	2.001	2.001	2.001	2.001	2.001	2.001	1.976	1.989	1.958(17)
$4p_{1/2}$-$3d_{3/2}$	$4p_{3/2}$-$3d_{3/2}$	5.02	5.01	5.02	5.02	5.02	5.02	5.02	4.98	4.89	4.85(12)
$4p_{3/2}$-$3d_{5/2}$	$4p_{3/2}$-$3d_{3/2}$	9.02	9.02	9.06	9.05	9.04	9.05	9.04	9.00	9.06	8.73(27)

we included triple corrections to both δE_v and ρ_{mv} equations while only δE_v was corrected in [22]. We also estimated other higher-excitation corrections as described earlier while no such estimates were done in Ref. [22].

Our values are in agreement with results of [22] for the $4p_{1/2}$-$4s$ and $4p_{3/2}$-$3d_{3/2}$ transitions but disagree well beyond the uncertainties for the $4p_{3/2}$-$4s$, $4p_{1/2}$-$3d_{3/2}$, and $4p_{3/2}$-$3d_{5/2}$ transitions. We find this to be rather irregular since the correlation corrections are known to contribute nearly the same relative amount for the different fine-structure transitions for such light ions as Ca$^+$.

To clarify this issue, we calculated the ratios $R = d_1^2/d_2^2$ of the squares of all three relevant pairs of matrix elements in the lowest, second, and third order of MBPT and all all-order approximations used in this work. The values of the matrix elements used in calculating the ratios are listed in Table II. The comparison of all values is given in Table IV. As we expected, all ratios of our values calculated in all approximations, including the lowest-order DF values, are nearly identical to the nonrelativistic (NR) values (2, 5, and 9, respectively), which are simply the ratios of the corresponding angular factors. The effect of the entire correlation correction to the ratio is negligible. We see no feasible explanation of the anomalous ratios in [22] and significant changes between their GTOs-STOs and final-value ratios. In the case of the $4s$-$4p$ transitions, the ratio of the final values from [22] is 3σ away from the NR value. The values of the other ratios are only slightly outside of the numerical error but it is not clear what could cause such changes in ratios from initial values to the final ones. The contributions from the higher-symmetry orbitals cannot change these ratios when the same basis set is used for the nl states with different j.

In summary, we expect our results for all of the properties listed in this work to be more accurate than those of Ref. [22] based on the preceding detailed analysis.

B. Transition rates and oscillator strengths

We combine recommended NIST energies [57] and our final values of the matrix elements listed in Table II to calculate transition rates A and oscillator strengths f. The transition rates are calculated using

$$A_{ab} = \frac{2.026\,13 \times 10^{18}}{\lambda^3} \frac{S}{2j_a + 1}\ \mathrm{s}^{-1}, \qquad (7)$$

where the wavelength λ is in Å and the line strength $S = d^2$ is in atomic units.

Transition rates $A(\mathrm{s}^{-1})$ and oscillator strengths (f) for the 55 np-$n's$, np-$n'd$, and nd-$n'f$ transitions in Ca$^+$ are summarized in Table V. Vacuum wavelengths obtained from NIST energies are also listed for reference. The relative uncertainties of the transition rates and oscillator strengths are twice that of the corresponding matrix element uncertainties since these properties are proportional to the squares of the matrix elements. The uncertainties in percent are listed in the column labeled "Unc.".

The values of the j-averaged oscillator strengths obtained using our final values of the matrix elements and NIST energies are compared with theoretical results from Refs. [23,41] in Table VI. The values of the Ref. [41] are obtained with a semiempirical approach that uses experimental energy levels and experimental or theoretical core polarizabilities as an input and approximates the core potential by the Hartree-Slater method. In recent work, Mitroy and Zhang [23] used a nonrelativistic CICP approach. The CICP values are in good agreement with our results, taking into account the accuracy of both calculations. The earlier and significantly less sophisticated semiempirical calculations of [41] appear to be less accurate, as expected.

C. Lifetimes and branching ratios

We calculated lifetimes of the $5s, 6s, 7s, 4p_j, 5p_j, 6p_j, 4d_j$, $5d_j$, and $4f_j$ states in Ca$^+$ using our final values of the dipole matrix elements and NIST energies [57]. The uncertainties in the lifetime values are obtained from the uncertainties in the matrix elements listed in Table II. The present values are compared with available experimental [26,27,31,32] and theoretical [22,41] results in Table VII.

The value of the branching ratio of the $4p_{3/2}$ decay of Ca$^+$ calculated from transition rates given in Table V $A(4p_{3/2}\text{-}4s)/\sum_j A(4p_{3/2}\text{-}3d_j) = 14.15(20)$ agrees with the 2008 measurement, 14.31(5), reported in Ref. [38] within our uncertainty. As we noted earlier, our values for the $4s$-$4p$ and $4p$-$3d_{3/2}$ matrix elements are the same as in Ref. [21] since the same method is used. Therefore, the agreement of our values for the three branching fractions measured in [38] remains the same as listed in the experimental work [38]: $R(4p_{3/2}\text{-}4s) = 0.9347(3)^{\mathrm{expt}}$ vs 0.9340^{th}, $R(4p_{3/2}\text{-}3d_{3/2}) = 0.006\,61(4)^{\mathrm{expt}}$ vs $0.006\,67^{\mathrm{th}}$, $R(4p_{3/2}\text{-}3d_{3/2}) = 0.005\,87(2)^{\mathrm{expt}}$ vs $0.005\,93^{\mathrm{th}}$. The uncertainties in our values of the transition rates are about 1% for all three transitions. Therefore, the agreement of our central values with experiment is significantly better than expected from our uncertainty estimates (the uncertainty in the ratio is about twice that of the uncertainties in the individual transition rates). In fact, the $4s$-$4p_{3/2}$ branching fraction agrees with experiment to 0.07%, making the substantial (3%) disagreement of our $4p$ lifetime values with those of a 1993 experiment that lists 0.3% accuracy even more puzzling.

TABLE V. Wavelengths λ (Å), transition rates A (s^{-1}), and oscillator strengths (f) for transitions in Ca^+ calculated using our recommended values of reduced electric-dipole matrix elements Z^{final} and their uncertainties. The relative uncertainties in the values of transition rates and oscillator strengths are the same. They are listed in the column labeled "Unc." in percentages. Numbers in brackets represent powers of 10.

Transition		λ	A	f	Unc.	Transition		λ	A	f	Unc.
$4s_{1/2}$	$4p_{1/2}$	3969.6	1.360[8]	3.213[−1]	0.90	$4d_{3/2}$	$4f_{5/2}$	8914.5	6.146[7]	1.098[0]	0.84
$4s_{1/2}$	$4p_{3/2}$	3934.8	1.397[8]	6.485[−1]	0.90	$4d_{5/2}$	$4f_{5/2}$	8929.8	4.372[6]	5.227[−2]	0.86
$5s_{1/2}$	$5p_{1/2}$	11953.0	2.302[7]	4.931[−1]	0.32	$4d_{5/2}$	$4f_{7/2}$	8929.8	6.559[7]	1.045[0]	0.86
$5s_{1/2}$	$5p_{3/2}$	11842.2	2.362[7]	9.932[−1]	0.34	$5d_{3/2}$	$5f_{5/2}$	18824.7	1.867[7]	1.488[0]	1.16
$6s_{1/2}$	$6p_{1/2}$	26265.3	6.161[6]	6.372[−1]	0.24	$5d_{5/2}$	$5f_{5/2}$	18855.6	1.329[6]	7.084[−2]	1.18
$6s_{1/2}$	$6p_{3/2}$	26013.7	6.320[6]	1.282[0]	0.24	$5d_{5/2}$	$5f_{7/2}$	18855.6	1.994[7]	1.417[0]	1.18
$4p_{1/2}$	$5s_{1/2}$	3707.1	8.550[7]	1.761[−1]	1.02	$4p_{1/2}$	$4d_{3/2}$	3159.8	2.944[8]	8.812[−1]	1.18
$4p_{3/2}$	$5s_{1/2}$	3738.0	1.705[8]	1.786[−1]	0.92	$4p_{3/2}$	$4d_{3/2}$	3182.2	5.843[7]	8.871[−2]	1.14
$4p_{1/2}$	$6s_{1/2}$	2198.5	3.226[7]	2.338[−2]	0.36	$4p_{3/2}$	$4d_{5/2}$	3180.3	3.506[8]	7.973[−1]	1.16
$4p_{3/2}$	$6s_{1/2}$	2209.3	6.416[7]	2.347[−2]	0.36	$4p_{1/2}$	$5d_{3/2}$	2103.9	8.102[7]	1.075[−1]	2.58
$4p_{1/2}$	$7s_{1/2}$	1843.1	1.639[7]	8.349[−3]	0.40	$4p_{3/2}$	$5d_{3/2}$	2113.8	1.592[7]	1.067[−2]	2.62
$4p_{3/2}$	$7s_{1/2}$	1850.7	3.258[7]	8.365[−3]	0.40	$4p_{3/2}$	$5d_{5/2}$	2113.4	9.580[7]	9.623[−2]	2.62
$4p_{1/2}$	$8s_{1/2}$	1691.8	9.528[6]	4.088[−3]	0.42	$5p_{1/2}$	$5d_{3/2}$	8204.0	5.149[7]	1.039[0]	1.60
$4p_{3/2}$	$8s_{1/2}$	1698.2	1.893[7]	4.092[−3]	0.42	$5p_{3/2}$	$5d_{3/2}$	8257.0	1.026[7]	1.048[−1]	1.54
$5p_{1/2}$	$6s_{1/2}$	9857.5	2.011[7]	2.930[−1]	0.36	$5p_{3/2}$	$5d_{5/2}$	8251.1	6.152[7]	9.419[−1]	1.58
$5p_{3/2}$	$6s_{1/2}$	9934.1	4.007[7]	2.964[−1]	0.34	$5p_{1/2}$	$6d_{3/2}$	5002.9	2.009[7]	1.508[−1]	0.78
$5p_{1/2}$	$7s_{1/2}$	5286.7	8.388[6]	3.515[−2]	0.24	$5p_{3/2}$	$6d_{3/2}$	5022.5	3.970[6]	1.501[−2]	0.80
$5p_{3/2}$	$7s_{1/2}$	5308.7	1.665[7]	3.517[−2]	0.26	$5p_{3/2}$	$6d_{5/2}$	5021.4	2.386[7]	1.353[−1]	0.80
$5p_{1/2}$	$8s_{1/2}$	4207.4	4.623[6]	1.227[−2]	0.34						
$5p_{3/2}$	$8s_{1/2}$	4221.3	9.173[6]	1.225[−2]	0.34	$3d_{3/2}$	$4p_{1/2}$	8664.5	9.452[6]	5.319[−2]	1.08
$5p_{1/2}$	$9s_{1/2}$	3740.4	2.859[6]	5.997[−3]	0.38	$3d_{3/2}$	$4p_{3/2}$	8500.4	9.972[5]	1.080[−2]	1.08
$5p_{3/2}$	$9s_{1/2}$	3751.4	5.670[6]	5.982[−3]	0.38	$3d_{5/2}$	$4p_{3/2}$	8544.4	8.876[6]	6.477[−2]	1.08
$5p_{1/2}$	$10s_{1/2}$	3486.6	1.899[6]	3.462[−3]	0.54	$4d_{3/2}$	$5p_{1/2}$	27072.6	2.820[6]	1.550[−1]	1.58
$5p_{3/2}$	$10s_{1/2}$	3496.2	3.768[6]	3.453[−3]	0.54	$4d_{3/2}$	$5p_{3/2}$	26510.9	2.990[5]	3.150[−2]	1.58
$6p_{1/2}$	$7s_{1/2}$	20147.6	6.715[6]	4.087[−1]	0.12	$4d_{5/2}$	$5p_{3/2}$	26646.6	2.656[6]	1.885[−1]	1.60
$6p_{3/2}$	$7s_{1/2}$	20298.3	1.337[7]	4.130[−1]	0.12						
$6p_{1/2}$	$8s_{1/2}$	10187.5	3.016[6]	4.693[−2]	0.30	$4f_{5/2}$	$5d_{3/2}$	21434.8	3.766[6]	1.729[−1]	1.62
$6p_{3/2}$	$8s_{1/2}$	10225.8	5.983[6]	4.689[−2]	0.30	$4f_{5/2}$	$5d_{5/2}$	21394.9	1.799[5]	1.235[−2]	1.64
						$4f_{7/2}$	$5d_{5/2}$	21394.9	3.598[6]	1.852[−1]	1.64

Our calculation of the $4p$ lifetimes in K [34] agrees with experimental values [77] to 0.13%. Moreover, our primary np_j lifetime values agree with recent experiments for all other alkali metals [34], Sr^+ [36], and Ba^+ [37]. Our values for the ground-state polarizabilities that are completely dominated by the primary ns-np matrix element contributions agree with all recent experiments in Li, Na, Cs [76], Mg^+ [35], Si^{3+}, and Ba^+ [37]. This issue already have been discussed in detail in both [21] and [38]. It would be very interesting to see new measurements of the $4p_j$ lifetimes, $4s$-$4p_j$ transition rates, ground-state polarizability, or other properties that make it possible to infer $4s$-$4p_j$ matrix elements in Ca^+.

All other experimental values listed in Table VII are much older (1970–1975) measurements with low precision. The values of the metastable $3d_j$ state lifetimes calculated with our approach agree within the uncertainties with the recent experimental values [18]. This calculation and comparison with experiment was already discussed in detail in [18], and we do not repeat it here. We note that 1% RCC theoretical value for the $3d_{5/2}$ lifetime, 1.110(9)s [20], calculated by the same group as work [22] that we discussed at length in the matrix element section, disagrees with both our value and experiment by 6%. Nevertheless, their $3d_{3/2}$ lifetime is in agrement with both our theoretical value and experimental [18] result. This demonstrates another significant inconsistency of the approach used in [20,22] in calculations of properties of the levels from the same fine-structure multiplet. The ratio of these lifetimes is affected very weakly by the correlation, as discussed in detail in [18]. Our value of this ratio is 1.0259(9) [20], while the ratio between Ref. [20] $3d$ lifetimes is 1.068. We note that

TABLE VI. Comparison of the j-averaged oscillator strengths with theoretical results from Refs. [23,41]. Numbers in brackets represent powers of 10.

Transitions	Present	Ref. [41]	Ref. [23]
$4s$-$4p$	0.970(9)	0.9523	0.9606
$4s$-$5p$	1.25[−3]	3.3[−4]	1.72[−3]
$5s$-$5p$	1.486(5)	1.4736	
$4p$-$5s$	0.178(2)	0.168	
$4p$-$4d$	0.884(10)	0.8741	0.8685
$4p$-$5d$	0.107(3)	0.1076	
$3d$-$4p$	0.0645(7)	0.0572	0.0660
$3d$-$5p$	5.1(1.8)[−4]	6.9[−4]	3.8[−4]
$4d$-$5p$	0.188(3)	0.1865	
$3d$-$4f$	0.154(3)		0.1599
$4d$-$4f$	1.098(9)		

TABLE VII. Comparison of the lifetimes (in ns) of nl_j states with other theory and experiment. Uncertainties are given in parentheses. References are given in square brackets.

Level	Present	Expt.	Theory
$5s_{1/2}$	3.91(4)	4.3(4) [26]	4.153 [41]
$6s_{1/2}$	6.39(2)		6.766 [41]
$7s_{1/2}$	10.63(3)		11.262 [41]
$4p_{1/2}$	6.88(6)	7.098(20) [31]	6.978(56) [22]
$4p_{3/2}$	6.69(6)	6.924(19) [31]	6.926(36) [22]
$5p_{1/2}$	35.4(7)		36.200 [41]
$5p_{3/2}$	34.8(7)		35.249 [41]
$6p_{1/2}$	89(2)		100.254 [41]
$6p_{3/2}$	90(2)		99.675 [41]
$4d_{3/2}$	2.83(3)	2.9(3) [27]	2.868 [41]
$4d_{5/2}$	2.85(3)	3.1(2) [26]	2.886 [41]
$5d_{3/2}$	6.16(13)	4.3(2) [26]	6.148 [41]
$5d_{5/2}$	6.21(14)		6.199 [41]
$4f_{5/2}$	3.55(7)		3.895 [41]
$4f_{7/2}$	3.54(7)		3.897 [41]

TABLE VIII. Contributions to dipole, α^{E1}, quadrupole, α^{E2}, and octupole, α^{E3}, polarizabilities (a.u.) of the Ca$^+$ ground states. All values are in atomic units. The uncertainties are given in parentheses.

	α^{E1}		α^{E2}		α^{E3}
$4p_{1/2}$	24.4(2)	$3d_{3/2}$	203(2)	$4f_{5/2}$	3017(31)
$4p_{3/2}$	48.4(4)	$4d_{3/2}$	125(1)	$5f_{5/2}$	469(4)
$np_{1/2}$	0.08(2)	$5d_{3/2}$	10.6(2)	$6f_{5/2}$	141(1)
$np_{3/2}$	0.14(3)	$6d_{3/2}$	2.7(1)	$7f_{5/2}$	59.5(4)
Core	3.26(3)	$7d_{3/2}$	1.1(0)	$8f_{5/2}$	30.7(1)
$\alpha_{\rm vc}$	$-0.12(1)$	$nd_{3/2}$	4.0(2)	$nf_{5/2}$	131(19)
Total	76.1(5)	$3d_{5/2}$	304(3)	$4f_{7/2}$	4023(41)
		$4d_{5/2}$	187(2)	$5f_{7/2}$	625(5)
		$5d_{5/2}$	15.9(2)	$6f_{7/2}$	188(1)
		$6d_{5/2}$	4.1(1)	$7f_{7/2}$	79.3(5)
		$7d_{5/2}$	1.6(0)	$8f_{7/2}$	41.0(1)
		$nd_{5/2}$	5.0(3)	$nf_{7/2}$	175(24)
		Core	6.9(3)	Core	34(4)
		Total	871(4)	Total	9012(60)
Ref. [23]	75.49	Ref. [23]	875.1	Ref. [23]	8990
Ref. [22]	73.0(1.5)				

lowest-order DF ratio of these lifetimes is 1.0245. Therefore, no difference in the treatment on the correlation correction can explain such anomalous ratio of these lifetimes.

IV. STATIC GROUND-STATE MULTIPOLE POLARIZABILITIES OF Ca$^+$

The static multipole polarizability α^{Ek} of Ca$^+$ in its $4s$ ground state can be separated to a valence polarizability and a polarizability of an ionic core. For the $4s$ state, the dominant valence contribution is calculated using the sum-over-state approach,

$$\alpha_v^{Ek} = \frac{1}{2k+1}\sum_{nlj}\frac{|\langle nl_j||r^k C_{kq}||4s\rangle|^2}{E_{nl_j}-E_{4s}}, \qquad (8)$$

where $C_{kq}(\hat{r})$ is a normalized spherical harmonic and nl_j is np_j, nd_j, and nf_j for $k = 1, 2$, and 3, respectively [35]. The $E2$ and $E3$ matrix elements and their uncertainties are calculated following the same approach that we used in calculating electric-dipole matrix elements (see Sec. III A).

Contributions to the ground-state state dipole, quadrupole, and octupole polarizabilities are presented in Table VIII. Dominant contributions are listed separately. The remainders of the sums are listed together. For example, the row labeled "$nd_{3/2}$" gives the combined contribution of all $nd_{3/2}$ terms with $n > 7$. The first terms ($4p$, $3d$, and $4f$, respectively) in the sum-over-states for α^{E1}, α^{E2}, and α^{E3} contribute 99.7%, 59%, and 79%, respectively, of the total valence polarizabilities. The rapid convergence of the sum over states for α^{E1} has been emphasized in many publications (for example, Refs. [34,78]). The sums in Eq. (8) converge much slower for the $E2$ and $E3$ polarizabilities. Therefore, accurate evaluation of a large number of terms in the sums (8) is needed for these states. We use NIST energies from [57] and our final recommended values of the matrix elements to evaluate terms with $n \leqslant 13$. We use theoretical SD energies and matrix elements to evaluate terms with $13 \leqslant n \leqslant 26$. The remaining contributions to α^{Ek} from basis functions with $27 \leqslant n \leqslant 70$ are evaluated in the DF approximation. These remainders are very small. Even in the case of the $E3$ polarizability, which is the slowest one to converge, the tail remainder with $n > 26$ contributes only 13 a.u., which is 0.14% of the total valence polarizability.

The electric-dipole core polarizability is taken to be 3.26(3) a.u. based on the comparison of the coupled-cluster and experimental values listed in the review [76]. This value is essentially the same as the RPA result of 3.25 a.u.. Since this value is the polarizability of the ionic Ca^{2+} core, we need to account for the presence of the valence electron by adding a term $\alpha_{\rm vc}$, which in this case is equal to half of the core polarizability contribution from the excitation to the valence $4s$ shell. In the cases of the $E2$ and $E3$ polarizabilities, we evaluate core contributions in the RPA [79]. The core polarizabilities are small in comparison with the valence ones and their uncertainties are negligible. We note that $\alpha_{\rm vc}$ terms are zero for the $E2$ and $E3$ polarizabilities since Ca$^+$ core contains no nd or nf states.

Our final results for the ground-state multipole polarizabilities are compared with other theoretical values [22,23] in Table VIII. The CICP values of Ref. [23] are in remarkably good agreement with our results in all three cases. Interestingly, we differ by 3% in the main $4s$-$3d_j$ contribution to the $E2$ polarizabilities (which is 523 a.u. in [23]), but agree in the final value. The difference between the present and Ref. [22] $E1$ polarizability value results from the differences in the $4s$-$4p_j$ matrix elements, which we discussed in detail in Sec. III A.

V. SCALAR AND TENSOR EXCITED-STATE POLARIZABILITIES

The valence scalar $\alpha_0(v)$ and tensor α_2 polarizabilities of Ca$^+$ in an excited state v are given by

$$\alpha_0(v) = \frac{2}{3(2j_v+1)}\sum_{nlj}\frac{|\langle v||d||nlj\rangle|^2}{E_{nlj}-E_v}, \qquad (9)$$

$$\alpha_2 = (-1)^{j_v}\sqrt{\frac{40 j_v(2j_v-1)}{3(j_v+1)(2j_v+1)(2j_v+3)}} \times \sum_{nlj}(-1)^{j}\begin{Bmatrix} j_v & 1 & j \\ 1 & j_v & 2 \end{Bmatrix}\frac{|\langle v||d||nlj\rangle|^2}{E_{nlj}-E_v}. \qquad (10)$$

The ionic core polarizability discussed in the previous section has to be added to the valence term given by Eq. (9) and corrected for the presence of the respective valence electron (term α_{vc}). This core correction α_{vc} term is negligible for all excited states that we considered with the exception of the $3d_{3/2}$ and $3d_{5/2}$ states. It is calculated in the RPA.

The dipole polarizability calculations are carried out in the same way as the calculations of the multipole polarizabilities discussed in the previous section. We list the contributions to the $5s$, $6s$, $7s$, $8s$, $4p_j$, $5p_j$, $3d_j$, and $4d_j$ scalar polarizabilities of Ca$^+$ in Table IX. The dominant contributions are listed separately. The remaining contributions are grouped together. For example, "$nd_{3/2}$" contribution includes all of the $nd_{3/2}$ terms excluding only the terms that were already listed separately.

Table IX illustrates very fast convergence of the ns level polarizabilities which are dominated by the corresponding np contributions. The $(n$-$1)p$ term contributions are significant, while all of the other contributions are very small owing to fast convergence of the sums. We use our recommended values for the $7p$ and $8p$ energy levels, for which we did not find the experimental values. The uncertainties in these recommended energy values are included when the polarizability uncertainties are calculated. The uncertainties of the final polarizability values are obtained by adding the uncertainties of the individual terms in quadarture.

When calculating polarizabilities of the np and nd states, we calculated the terms with $n \leqslant 26$ using the all-order approach. The terms with $n > 10$ are calculated using our calculated recommended values of the $E1$ matrix elements and the experimental energies [57]. The terms with $10 < n < 27$ are calculated using SD energies and matrix elements. The remainders are evaluated in the DF or RPA approximations. The remainders in the $3d$-nf sums are treated more accurately as described in what follows.

We find that the scalar polarizabilities of the $4p_{3/2}$ and $4p_{1/2}$ states are anomalously small owing to a very precise cancellations of the various contributions. This fact was already pointed out by Mitroy and Zhang [23]. Our uncertainties of these polarizability values are very large because of these severe cancellations. Such cancellations are not observed for the $5p$ polarizabilities, where $5p$-$4d$ contributions strongly dominate.

The case of the $3d_{5/2}$ polarizability is particularly interesting owing to its importance for the calculation of the blackbody radiation shift in the optical frequency standard with Ca$^+$ ion. Reference [21] points out that the sum over the $nf_{7/2}$ states converges very slowly, making accurate calculation of these contributions difficult. In this work, we have explored several different approaches to the accurate calculation of this sum and obtained consistent results in all cases.

First, we calculated terms with $n \leqslant 26$ in the all-order approximation and determined that these terms contribute 5.41(16) a.u. We find that even with so many terms included, the remainder is still 0.43 a.u. in DF approximation and 0.32 a.u. in the RPA, which is a significant fraction of the total $nf_{7/2}$ contribution. Therefore, we estimate the accuracy of the DF approximation by calculating the main terms with $n \leqslant 26$ in the DF approximation as well. We find that DF approximation overestimates the polarizability contributions from highly excited state by about 38% and adjust the DF value accordingly. The entire adjustment is taken to be the uncertainty of the $n > 26$ remainder. Therefore, our final value for $n > 26$ $nf_{7/2}$ terms is 0.27(15), and the total $nf_{7/2}$ sum is equal to 5.67(22) a.u..

Second, we carry out the calculation of the highly excited states by a different approach to verify that the all-order calculation of such highly excited states does not introduce unexpected errors. We compare the contributions with $6 < n < 13$ calculated in DF, RPA, and all-order approximations. The wave functions of all these states fit inside of our 220 a.u. cavity, and the all-order method is definitely reliable for these states. We establish that DF overestimates the results by 40%–44% and RPA overestimates the results by 37%–41%. Then we use these percentages to adjust the contributions for the $n > 12$ states calculated in the DF and RPA approximations. Adding these adjusted remainders to the all-order terms with $n < 13$ gives 5.63 a.u. (DF) and 5.53 a.u. (RPA) for the total $nf_{7/2}$ sum. These values are consistent with our result 5.67(22) obtained earlier. Such accurate evaluation of this sum allows us to reduce the uncertainty of the $3d_{5/2}$ polarizability by a factor of 3 in comparison with the previous calculation of this quantity using the all-order sum-over-states approach [21]. The calculation of the $nf_{5/2}$ contribution to the $3d_{3/2}$ polarizability is carried out using the same method. In all the other cases, the contributions of the terms with $n > 26$ are very small in comparison with the other terms and DF approximation is sufficiently accurate.

We compare our values of the scalar polarizabilities for the $3d_{3/2}$ and $3d_{5/2}$ states with RCC [22] and CICP [23] theoretical calculations in Table IX. Reference [22] estimates their numerical (basis-set truncation) uncertainty to be 3.5%. This estimate does not account for the uncertainty owing to the missing correlation correction. Our $3d_j$ polarizabilities differ from values of [22] by 7% and 11%. It is well known (see [76] and references therein) that the polarizabilities are very sensitive to the problems with the basis-set completeness in the coupled-cluster calculations such as the RCC calculation of Ref. [22]. We note that Ref. [22] STO values (31.6 and 32.5) are very close to our results.

Since the CICP calculation [23] is nonrelativistic, we list its values for both fine-structure states. Our $5s$ and $3d$ results are in good agreement with CICP calculation. The agreement is rather poor for the $4p$, $4d$, and $5p$ states. It is expected for the $4p$ states owing to severe cancellations discussed earlier but somewhat surprising for the other two states.

We list the contributions to the tensor polarizabilities of the Ca$^+$ in $4p_{3/2}$, $5p_{3/2}$, $3d_j$, and $4d_j$ states in Table X. Tensor-polarizability calculations are carried our in the same way as the scalar-polarizability ones. The same designations are used in Table X as in the scalar-polarizability Table IX. The final values are compared with RCC [22] and CICP [23] theoretical calculations. We multiply the $3d$ and $4d$ nonrelativistic values

TABLE IX. Contributions to the $5s$, $6s$, $7s$, $8s$, $4p_j$, $5p_j$, $3d_j$, and $4d_j$ scalar polarizabilities of Ca^+ in a_0^3. Uncertainties are given in parentheses. The final results are compared with other theory [22,23].

Contribution	α_0	Contribution	α_0	Contribution	α_0	Contribution	α_0
$5s$		$6s$		$7s$		$8s$	
$4p_{1/2}$	−11.7(1)	$5p_{1/2}$	−137.1(5)	$6p_{1/2}$	−799(1)	$7p_{1/2}$	−3214(4)
$4p_{3/2}$	−24.0(2)	$5p_{3/2}$	−282(1)	$6p_{3/2}$	−1639(2)	$7p_{3/2}$	−6593(8)
$5p_{1/2}$	339(1)	$6p_{1/2}$	2118(5)	$7p_{1/2}$	8894(21)	$8p_{1/2}$	29153(125)
$5p_{3/2}$	671(2)	$6p_{3/2}$	4180(10)	$7p_{3/2}$	17532(42)	$8p_{3/2}$	57432(248)
Other	3.6	Other	3.8	Other	5	Other	−22
Total	978(3)	Total	5882(11)	Total	23 990(50)	Total	76 760(280)
Ref. [23]	983.5						
$4p_{1/2}$		$5p_{1/2}$		$4d_{3/2}$		$4d_{5/2}$	
$4s$	−24.39(22)	$5s$	−339(1)	$4p_{1/2}$	−21.2(3)	$4p_{3/2}$	−25.9(3)
$5s$	11.66(12)	$6s$	137	$5p_{1/2}$	547(9)	$5p_{3/2}$	645(10)
$6s$	0.54	$7s$	5	$4p_{3/2}$	−4.3	$np_{3/2}$	0
ns	0.46(1)	ns	3	$5p_{3/2}$	107(2)	$4f_{5/2}$	20.1(2)
$3d_{3/2}$	−38.47(41)	$4d_{3/2}$	−1094(17)	np	0	$nf_{5/2}$	0.1
$4d_{3/2}$	42.38(50)	$5d_{3/2}$	337(5)	$4f_{5/2}$	421(4)	$4f_{7/2}$	402(3)
$5d_{3/2}$	2.29(6)	$6d_{3/2}$	18	$5f_{5/2}$	0.1	$5f_{7/2}$	0.1
$nd_{3/2}$	1.51(8)	$nd_{3/2}$	11(1)	$nf_{5/2}$	2.3(1)	$nf_{7/2}$	2.2(1)
Core	3.26(3)	Core	3	Core	3.3	Core	3.3
Total	−0.75(70)	Total	−920(18)	Total	1054(10)	Total	1046(11)
Ref. [23]	−2.032	Ref. [23]	−1135	Ref. [23]	1209	Ref. [23]	1209
$4p_{3/2}$		$5p_{3/2}$		$3d_{3/2}$		$3d_{5/2}$	
$4s$	−24.18(22)	$5s$	−335(1)	$4p_{1/2}$	19.24(21)	$4p_{3/2}$	22.78(25)
$5s$	12.02(11)	$6s$	141	$np_{1/2}$	0.02	$np_{3/2}$	0.03
$6s$	0.55	$7s$	5	$4p_{3/2}$	3.76(4)	$4f_{5/2}$	0.12
ns	0.46(1)	ns	3	$np_{3/2}$	0.01	$nf_{5/2}$	0.17
$3d_{3/2}$	−3.76(4)	$4d_{3/2}$	−107(2)	$4f_{5/2}$	2.50(6)	$4f_{7/2}$	2.39(5)
$4d_{3/2}$	4.33(5)	$5d_{3/2}$	34(1)	$5f_{5/2}$	0.81(1)	$5f_{7/2}$	0.77(1)
$5d_{3/2}$	0.23(1)	$6d_{3/2}$	2	$6f_{5/2}$	0.37(1)	$6f_{7/2}$	0.35(1)
$nd_{3/2}$	0.15(1)	$nd_{3/2}$	1	$7f_{5/2}$	0.20(1)	$7f_{7/2}$	0.19(1)
$3d_{5/2}$	−34.17(37)	$4d_{5/2}$	−967(16)	(8-12)$f_{5/2}$	0.33(1)	(8-12)$f_{7/2}$	0.31(1)
$4d_{5/2}$	38.85(45)	$5d_{5/2}$	309(5)	$(13-26)f_{5/2}$	1.42(4)	(13-26)$f_{7/2}$	1.39(4)
$5d_{5/2}$	2.07(5)	$6d_{5/2}$	16	$nf_{5/2}$	0.32(19)	$nf_{7/2}$	0.27(15)
$nd_{5/2}$	1.22(6)	$nd_{5/2}$	9	Core	3.26(3)	Core	3.26(3)
Core	3.26(3)	Core	3	α_{vc}	−0.23(1)	α_{vc}	−0.23(1)
Total	1.02(64)	Total	−886(16)	Total	32.0(3)	Total	31.8(3)
Ref. [23]	−2.032	Ref. [23]	−1135	Ref. [23]	32.73	Ref. [23]	32.73
				Ref. [22]	28.5(1.0)	Ref. [22]	29.5(1.0)

of [23] by 7/10 to compare these values to our $3d_{3/2}$ and $4d_{3/2}$ tensor polarizabilities (see [76] for explanation of this conversion factor). The differences between the present and [22,23] theoretical tensor-polarizability values are similar to those for the scalar polarizabilities for these states.

VI. BLACKBODY RADIATION SHIFT IN Ca$^+$ OPTICAL FREQUENCY STANDARD

The electrical field E radiated by a blackbody at temperature T, as given by Planck's law,

$$E^2(\omega)\,d\omega = \frac{8\alpha^3}{\pi}\frac{\omega^3 d\omega}{\exp(\omega/k_B T) - 1}, \tag{11}$$

induces a nonresonant perturbation of the optical transition at room temperature [80]. The frequency shift of an atomic state due to such an electrical field is related to the static electric-dipole polarizability α_0 by (see Ref. [81])

$$\Delta\nu = -\frac{1}{2}(831.9\ \mathrm{V/m})^2 \left(\frac{T\ (\mathrm{K})}{300}\right)^4 \alpha_0(1+\eta), \tag{12}$$

where η is a small dynamic correction due to the frequency distribution. Only the electric-dipole transition part of the contribution is considered in the preceding formula because the contributions from $M1$ and $E2$ transitions are suppressed by a factor of α^2 [81]. The overall BBR shift of the Ca$^+$ $4s$-$3d_{5/2}$ clock transition frequency is then calculated as the difference between the BBR shifts of the individual levels involved in the transition:

$$\Delta_{\mathrm{BBR}}(4s\text{-}3d_{5/2}) = -\frac{1}{2}[\alpha_0(3d_{5/2}) - \alpha_0(4s_{1/2})] \times (831.9\ \mathrm{V/m})^2 \left(\frac{T(\mathrm{K})}{300}\right)^4. \tag{13}$$

TABLE X. Contributions to the $4p_{3/2}$, $5p_{3/2}$, $3d_j$, and $4d_j$ tensor polarizabilities of Ca$^+$ in a_0^3. Uncertainties are given in parentheses. The final results are compared with other theory [22,23].

Contribution	α_2	Contribution	α_2
$4p_{3/2}$		$5p_{3/2}$	
$4s$	24.18(22)	$5s$	335(1)
$5s$	−12.02(11)	$6s$	−141
$6s$	−0.55	$7s$	−5
ns	−0.46(1)	ns	−3
$3d_{3/2}$	−3.01(3)	$4d_{3/2}$	−85(1)
$4d_{3/2}$	3.46(4)	$5d_{3/2}$	28
$5d_{3/2}$	0.18	$6d_{3/2}$	1
$nd_{3/2}$	0.12	$nd_{3/2}$	1
$3d_{5/2}$	6.83(7)	$4d_{5/2}$	193(3)
$4d_{5/2}$	−7.77(9)	$5d_{5/2}$	−62(1)
$5d_{5/2}$	−0.41(1)	$6d_{5/2}$	−3
$nd_{5/2}$	−0.24(1)	$nd_{5/2}$	−2
Total	10.31(28)	Total	258(4)
Ref. [23]	10.47	Ref. [23]	286.2
$3d_{3/2}$		$3d_{5/2}$	
$4p_{1/2}$	−19.24(21)	$4p_{3/2}$	−22.78(25)
$np_{1/2}$	−0.01	$np_{3/2}$	−0.02
$4p_{3/2}$	3.01(3)	$4f_{5/2}$	0.18
$np_{3/2}$	0.00	$nf_{5/2}$	0.15
$4f_{5/2}$	−0.50(1)	$4f_{7/2}$	−0.85(2)
$5f_{5/2}$	−0.16	$5f_{7/2}$	−0.28
$6f_{5/2}$	−0.07	$6f_{7/2}$	−0.12
$nf_{5/2}$	−0.46(2)	$nf_{7/2}$	−0.79(4)
Total	−17.43(23)	Total	−24.51(29)
Ref. [22]	−15.8(7)	Ref. [22]	−22.45(5)
Ref. [23]	−17.64	Ref. [23]	−25.20
$4d_{3/2}$		$4d_{5/2}$	
$4p_{1/2}$	21.2(3)	$4p_{3/2}$	25.9(3)
$5p_{1/2}$	−547(9)	$5p_{3/2}$	−645(10)
$4p_{3/2}$	−3.46(4)	$np_{3/2}$	−0.02
$5p_{3/2}$	85(1)	$4f_{5/2}$	23.0(2)
np	−0.01	$nf_{5/2}$	0.13
$4f_{5/2}$	−84.1(7)	$4f_{7/2}$	−143(1)
$5f_{5/2}$	−0.03(1)	$5f_{7/2}$	−0.05(2)
$nf_{5/2}$	−0.46	$nf_{7/2}$	−0.79
Total	−529(9)	Total	−740(10)
Ref. [23]	−615.9	Ref. [23]	−879.8

The tensor part of polarizability is averaged out due to the isotropic nature of the electric field radiated by the blackbody. Substituting out values for the $4s$ and $3d_{5/2}$ static polarizabilities into Eq. (13), we obtain 0.3815(44) Hz for the BBR shift. We note that atomic units for α are converted to SI units via α/h [Hz/(V/m)^2] $= 2.48832 \times 10^{-8}\alpha$ [a.u.], where the conversion coefficient is $4\pi\epsilon_0 a_0^3/h$ and Planck constant h is factored out.

We estimate the dynamic corrections to be $\eta = 0.0012$ and $\eta = 0.0044$ for the $4s$ and $3d_{5/2}$ states, respectively, following Ref. [81]. The resulting dynamic correction to the BBR shift is −0.0004 Hz and our final value is

$$\Delta_{\mathrm{BBR}}(4s - 3d_{5/2}) = 0.3811(44)\mathrm{Hz}.$$

The value is the same for different Ca$^+$ isotopes within its accuracy. The third-order F-dependent polarizability of the ground state is evaluated in the final section of this paper. Its contribution is several orders of magnitudes smaller than the second-order value and can be omitted in evaluating BBR shift in the optical standard.

The present value is consistent with other calculations, 0.380(14) Hz [21], 0.37(1) Hz [22], and 0.368 Hz [23], but is three times more accurate.

VII. HYPERFINE CONSTANTS FOR ^{43}Ca$^+$

Calculations of hyperfine constants are carried out using the SD and SDpT all-order methods described in Sec. III A. A number of terms other than terms $Z^{(a)}$ and $Z^{(c)}$ give significant contributions to the hyperfine constants. Therefore, the scaling procedure described in Sec. III A is not expected to produce more accurate values and is not carried out for the hyperfine constants. In Table XI, we list hyperfine constants A for ^{43}Ca$^+$ and compare our values with available theoretical [55] and experimental data [48,53].

In this table, we present the lowest-order A^{DF}, all-order A^{SD}, and A^{SDpT} values for the ns, np, nd, and nf levels up to $n = 7$. The magnetic moment of ^{43}Ca$^+$ used here ($I = 7/2$, $\mu = -1.31727$) is taken from [82]. Our SDpT results are in

TABLE XI. Hyperfine constants A (in MHz) in ^{43}Ca$^+$ ($I = 7/2$, $\mu = -1.31727$). The SD and SDpT all-order results are compared with theoretical [55] and experimental [51,53] values.

Level	A^{DF}	A^{SD}	A^{SDpT}	Th. [55]	Expt. [51,53]
$4s$	−587.39	−818.82	−801.28	−805.348	−806.402 072
$5s$	−183.99	−239.19	−236.30		
$6s$	−81.25	−103.29	−102.33		
$7s$	−42.91	−53.96	−53.53		
$4p_{1/2}$	−101.48	−148.26	−144.96	−143.068	−145.4(1)
$5p_{1/2}$	−37.43	−51.28	−50.71		
$6p_{1/2}$	−17.91	−24.14	−23.81		
$7p_{1/2}$	−9.94	−13.25	−13.08		
$4p_{3/2}$	−19.64	−31.04	−30.34	−30.498	−31.0(2)
$5p_{3/2}$	−7.25	−10.69	−10.58		
$6p_{3/2}$	−3.47	−5.04	−4.97		
$7p_{3/2}$	−1.93	−2.76	−2.73		
$3d_{3/2}$	−33.20	−48.83	−47.63	−47.824	−47.3(2)
$4d_{3/2}$	−8.01	−9.32	−9.35		
$5d_{3/2}$	−3.36	−3.86	−3.88		
$6d_{3/2}$	−1.75	−1.99			
$7d_{3/2}$	−1.03	−1.17			
$3d_{5/2}$	−14.14	−4.71	−4.24	−3.553	−3.8(6)
$4d_{5/2}$	−3.41	−3.12	−3.06		
$5d_{5/2}$	−1.43	−1.51	−1.49		
$6d_{5/2}$	−0.748	−0.831			
$7d_{5/2}$	−0.441	−0.502			
$4f_{5/2}$	−0.151	−0.165	−0.163		
$5f_{5/2}$	−0.079	−0.089			
$6f_{5/2}$	−0.046	−0.053			
$7f_{5/2}$	−0.029	−0.034			
$4f_{7/2}$	−0.084	−0.044	−0.044		
$5f_{7/2}$	−0.044	−0.011			
$6f_{7/2}$	−0.026	−0.002			
$7f_{7/2}$	−0.016	0.000			

TABLE XII. Hyperfine constants B (in MHz) in ^{43}Ca$^+$. Nuclear quadrupole moment Q is taken to be equal to $-0.044(9)$ barns (1b = 10^{-24} cm^2) [55]. The SD and SDpT values are compared with theory [55] and experiment [53].

Level	$\frac{B^{\mathrm{DF}}}{Q}$	$\frac{B^{\mathrm{SD}}}{Q}$	$\frac{B^{\mathrm{SDpT}}}{Q}$	B^{DF}	B^{SD}	B^{SDpT}	$\frac{B^{\mathrm{th}}}{Q}$ [55]	B^{expt} [53]
$4p_{3/2}$	96.69	153.99	150.81	−4.25	−6.78	−6.64	−151.798	−6.9(1.7)
$5p_{3/2}$	35.58	52.40	51.82	−1.57	−2.31	−2.28		
$6p_{3/2}$	16.93	24.37	24.06	−0.75	−1.07	−1.06		
$3d_{3/2}$	54.24	67.01	65.24	−2.39	−2.95	−2.87	−68.067	−3.7(1.9)
$4d_{3/2}$	12.93	17.37	17.24	−0.57	−0.76	−0.76		
$5d_{3/2}$	5.31	7.28	7.24	−0.23	−0.32	−0.32		
$3d_{5/2}$	76.86	95.19	92.69	−3.38	−4.19	−4.08	−100.208	−3.9(6.0)
$4d_{5/2}$	18.33	24.70	24.51	−0.81	−1.09	−1.08		
$5d_{5/2}$	7.54	10.35	10.30	−0.33	−0.46	−0.45		

very good agreement with experimental results for the ns and $np_{1/2}$ states when experimental uncertainties are taken into account. The contributions from valence triple excitations are large for the hyperfine constants and have to be included for an accurate calculation.

Hyperfine constants B (in MHz) in ^{43}Ca$^+$ are given in Table XII. Nuclear quadrupole moment Q is taken to be equal to $-0.044(9)$ b (1 b = 10^{-24} cm^2) [55]. The SD and SDpT values are compared with theory [55] and experiment [53].

VIII. HYPERFINE-INDUCED TRANSITION POLARIZABILITY OF THE ^{43}Ca$^+$ GROUND STATE

We now turn to the calculation of the quadratic Stark shift of the ground-state hyperfine interval ($F = 4 - F = 3$) in ^{43}Ca$^+$. The quadratic Stark shift is closely related to the blackbody radiation shift in the microwave frequency standards discussed, for example, in Refs. [83–85]. Our calculation follows the methodology outlined in those works.

The dominant second-order contribution to the polarizability cancels for the transition between the two hyperfine components of the $4s$ state. Therefore, the Stark shift of the hyperfine interval is governed by the the third-order F-dependent polarizability $\alpha_F^{(3)}(0)$. The expression for the $\alpha_F^{(3)}(0)$ is [83]

$$\alpha_F^{(3)}(0)=\frac{1}{3}\sqrt{(2I)(2I+1)(2I+2)}\begin{Bmatrix} j_v & I & F\\ I & j_v & 1\end{Bmatrix}\times g_I\mu_n(-1)^{F+I+j_v}(2T+C+R), \tag{14}$$

where g_I is the nuclear gyromagnetic ratio, μ_n is the nuclear magneton equal to 0.392 465 8 in ^{43}Ca$^+$, $I = 7/2$ is the nuclear spin, and $j_v = 1/2$ is the total angular momentum of the atomic ground state. The formulas for the F-independent terms T, C, and R are given in Ref. [83]. These terms are similar to the polarizability sum-over-state expression but are more complicated.

First, we calculate these values in the DF approximation (in atomic units):

$$2T^{\mathrm{DF}} = 2.0018\times10^{-4},\quad C^{\mathrm{DF}} = 3.9507\times10^{-7},\quad R^{\mathrm{DF}} = 3.8838\times10^{-4}. \tag{15}$$

Since the value of C^{DF} is smaller than the T^{DF} and R^{DF} by three orders of magnitude, we do not recalculate the C term using the all-order method.

The expression for R is similar to that for α^{E1} but contains diagonal hyperfine matrix element:

$$\langle 4s\|\mathcal{T}\|4s\rangle^{\mathrm{SDpT}} = 3.9629\times10^{-7}\ \text{a.u.}$$

We use our all-order recommended values for the reduced electric-dipole matrix elements described in Sec. III A and their uncertainties to calculate the main terms in the T and

TABLE XIII. Contributions to the mp sums of term $2T$, m = 4–26. The main contribution $\sum_{n=5}^{26}$ calculated in the DF approximation is given in the column labeled "Main$^{\mathrm{DF}}$" in 10^4 a.u. The final values of the main contributions to the mp sums are given in the column labeled "Main$^{\mathrm{final}}$" in 10^4 a.u.. Accumulated values are given for both DF and final results. The ratio of the final and DF values for the main terms is given in the fourth column in percentages. The relative tail contribution $\sum_{n=27}^{70}$ calculated in the DF approximation is given in the last column.

mp	Main$^{\mathrm{DF}}$	Main$^{\mathrm{final}}$	Dif. (%)	Tail (%)
$4p$	1.965	2.060(12)	4.6	1.8
$5p$	1.965	2.079(12)	5.5	1.8
$6p$	1.969	2.089(12)	5.7	1.6
$7p$	1.971	2.094(12)	5.9	1.5
$8p$	1.972	2.097(12)	5.9	1.5
$9pp$	1.973	2.098(11)	6.0	1.4
$10p$	1.974	2.100(12)	6.0	1.4
$11p$	1.974	2.101(12)	6.0	1.4
$12p$	1.974	2.102(13)	6.1	1.4
$13p$	1.975	2.102(13)	6.1	1.4
$14p$	1.975	2.102(13)	6.1	1.4
$15p$	1.975	2.102(13)	6.1	1.4
$16p$	1.975	2.102(13)	6.1	1.4
$17p$	1.975	2.103(13)	6.1	1.3
$18p$	1.976	2.104(13)	6.1	1.3
$19p$	1.976	2.104(13)	6.1	1.3
$20p$	1.976	2.104(13)	6.1	1.3
$21p$	1.979	2.109(13)	6.2	1.2
$22p$	1.979	2.109(13)	6.2	1.2
$23p$	1.983	2.118(13)	6.4	0.9
$24p$	1.986	2.124(13)	6.5	0.8
$25p$	1.988	2.129(13)	6.6	0.7
$26p$	1.990	2.129(13)	6.5	0.6

R sums. We refer to these values as the "best-set" values. Available recommended NIST energies [57] are used for $nl = 4s$-$10s,4p$-$6p$, and SD energies are used for the other states up to $n = 26$. The sum of R terms with $n \leqslant 26$ is equal to $R = 3.772(34) \times 10^{-4}$. The remainder of the R sum is evaluated in the DF approximation, $R_{n>26} = 3.0 \times 10^{-8}$, and is less than 0.01%.

Term T contains two sums, over ns and over mp_j. We evaluate main contributions, which include $n \leqslant 26$ and $m \leqslant 26$ using all-order matrix elements and NIST or all-order energies as described earlier. We find that the remaining contributions with $n > 26$ and $m > 26$ are very small. Table XIII illustrates the size of the remainders and accuracy of the DF approximation. We break down each mp term as

$$\sum_{mp}\left(\sum_{5s}^{26s}[\cdots]+\sum_{27s}^{70s}[\cdots]\right)$$

and list contributions to the mp sums of term T, $m = 4$–26 in Table XIII. Each mp term is given by

$$\sum_{n=5}^{26} A_T \frac{\langle 4s\|D\|mp_j\rangle\langle mp_j\|D\|ns\rangle\langle ns\|\mathcal{T}\|4s\rangle}{(E_{mp}-E_{4s})(E_{ns}-E_{4s})}, \qquad (16)$$

where A_T is an angular factor. The main contribution $\sum_{n=5}^{26}[\cdots]$ calculated in the DF approximation is given in the column labeled "Main$^{\rm DF}$" in 10^4 a.u.. The final values of the main contributions to the mp sums are given in the column labeled "Main$^{\rm final}$" in 10^4 a.u.. Accumulated values are given for both DF and final results to illustrate the convergence of the mp sum. The ratio of the final and DF values for the main terms is given in the fourth column in pecentages. The relative tail contribution $\sum_{n=27}^{70}[\cdots]$ calculated in the DF approximation is given in the last column. The remainder is 0.6% of the main term and is equal to 0.013×10^{-4} a.u.. Our final value for this term is $2T^{\rm final} = 2.142(13) \times 10^{-4}$. Combining these contributions, we obtain

$$2T^{\rm final} + C^{\rm DF} + R^{\rm final} = 5.918(36) \times 10^{-4}\ \text{a.u.} \qquad (17)$$

The F-dependent factor in Eq. (14) is equal to 0.4609 for $F = 3$ and -0.3585 for $F = 4$. Using these values and the result from Eq. (17), we obtain

$$\alpha_{\rm hf}(4s) = \alpha^{(3)}_{F=4}(0) - \alpha^{(3)}_{F=3}(0) = -4.850(29) \times 10^{-4}\ \text{a.u.}$$

The Stark shift coefficient k defined as $\Delta\nu = kE^2$ is $k = -\frac{1}{2}[\alpha^{(3)}_{F=4}(0) - \alpha^{(3)}_{F=3}(0)]$. Converting from atomic units, we obtain

$$k = -2.425(15) \times 10^{-4}\ \text{a.u.} = 6.03(4) \times 10^{-12}\ \text{Hz}/(\text{V/m})^2.$$

We note that the lowest-order DF value is $k^{\rm (DF)} = 6.00 \times 10^{-12}$ Hz$/(\text{V/m})^2$. While values of both R and T terms change with the inclusion of the correlation correction, it essentially cancels when these terms are added.

The relative blackbody radiative shift β is defined as

$$\beta = -\frac{2}{15}\frac{1}{\nu_{\rm hf}}(\alpha\pi)^3 T^4 \alpha_{\rm hf}(4s_{1/2}), \qquad (18)$$

where $\nu_{\rm hf}$ is the ^{43}Ca$^+$ hyperfine ($F = 3 - F = 4$) splitting equal to 3225.608 286 4(3) MHz [51] and T is temperature taken to be 300 K. Using those factors and our value of $\alpha_{\rm hf}(4s)$, we obtain

$$\beta = -2.6696 \times 10^{-12}\ \alpha_{\rm hf}(4s) = 1.29(1) \times 10^{-15}.$$

IX. CONCLUSION

A systematic study of Ca$^+$ atomic properties is carried out using high-precision relativistic all-order method where all single, double, and partial-triple excitations of the Dirac-Fock wave function are included to all orders of perturbation theory. Energies, $E1$, $E2$, $E3$ matrix elements, transition rates; lifetimes; A and B hyperfine constants; $E1$, $E2$, and $E3$ ground-state polarizabilities; scalar $E1$ polarizabilities of the $5s$, $6s$, $7s$, $8s$, $4p_j$, $5p_j$, $3d_j$, and $4d_j$ states; and tensor polarizabilities of the $4p_{3/2}$, $5p_{3/2}$, $3d_j$, and $4d_j$ states are calculated. We evaluate the uncertainties of our calculations for most of the values listed in this work. The BBR shift of the $4s$-$3d_{5/2}$ clock transition in Ca$^+$ is calculated to be 0.381(4) Hz at room temperature, $T = 300$ K, improving its accuracy by a factor of 3. The quadratic Stark effect on hyperfine structure levels of ^{43}Ca$^+$ ground state is investigated. These calculations provide recommended values critically evaluated for their accuracy for a number of Ca$^+$ atomic properties useful for a variety of applications.

ACKNOWLEDGMENT

The work of M.S.S. was supported in part by National Science Foundation Grant No. PHY-07-58088.

---

[1] M. Lombardi, T. Heavner, and S. Jefferts, Measure: J. Meas. Sci. **2**, 74 (2007).
[2] H. S. Margolis, G. Barwood, G. Huang, H. A. Klein, S. N. Lea, K. Szymaniec, and P. Gill, Science **306**, 19 (2004).
[3] S. A. Diddams *et al.*, Science **293**, 825 (2001).
[4] C. Champenois, M. Houssin, C. Lisowski, M. Knoop, G. Hagel, M. Vedel, and F. Vedel, Phys. Lett. A **331**, 298 (2004).
[5] M. Kajita, Y. Li, K. Matsubara, K. Hayasaka, and M. Hosokawa, Phys. Rev. A **72**, 043404 (2005).
[6] C. Champenois, G. Hagel, M. Houssin, M. Knoop, M. Vedel, C. Zumsteg, and F. Vedel, Ann. Phys. (Paris) **32**, 25 (2007).
[7] M. Chwalla *et al.*, Phys. Rev. Lett. **102**, 023002 (2009).
[8] J. Benhelm *et al.*, Phys. Scr. T **137**, 014008 (2009).
[9] G. Kirchmair, J. Benhelm, F. Zähringer, R. Gerritsma, C. F. Roos, and R. Blatt, Phys. Rev. A **79**, 020304 (2009).
[10] D. Leibfried *et al.*, Nature (London) **422**, 412 (2003).
[11] C. Langer *et al.*, Phys. Rev. Lett. **95**, 060502 (2005).
[12] S. Olmschenk, K. C. Younge, D. L. Moehring, D. N. Matsukevich, P. Maunz, and C. Monroe, Phys. Rev. A **76**, 052314 (2007).
[13] J. Benhelm, G. Kirchmair, C. F. Roos, and R. Blatt, Nat. Phys. **4**, 463 (2008).

[14] A. H. Myerson, D. J. Szwer, S. C. Webster, D. T. C. Allcock, M. J. Curtis, G. Imreh, J. A. Sherman, D. N. Stacey, A. M. Steane, and D. M. Lucas, Phys. Rev. Lett. **100**, 200502 (2008).

[15] E. Knill, D. Leibfried, R. Reichle, J. Britton, R. B. Blakestad, J. D. Jost, C. Langer, R. Ozeri, S. Seidelin, and D. J. Wineland, Phys. Rev. A **77**, 012307 (2008).

[16] L. M. Hobbs, D. E. Welty, A. M. Lagrange-Henri, R. Ferlet, and A. Vidal-Madja, Astrophys. J. **334**, L41 (1988).

[17] D. E. Welty, D. C. Morton, and L. M. Hobbs, Astrophys. J. **106**, 533 (1996).

[18] A. Kreuter *et al.*, Phys. Rev. A **71**, 032504 (2005).

[19] C. Sur, K. V. P. Latha, Bijaya K. Sahoo, Rajat K. Chaudhuri, B. P. Das, and D. Mukherjee, Phys. Rev. Lett. **96**, 193001 (2006).

[20] B. K. Sahoo, M. R. Islam, B. P. Das, R. K. Chaudhuri, and D. Mukherjee, Phys. Rev. A **74**, 062504 (2006).

[21] B. Arora, M. S. Safronova, and C. W. Clark, Phys. Rev. A **76**, 064501 (2007).

[22] B. K. Sahoo, B. P. Das, and D. Mukherjee, Phys. Rev. A **79**, 052511 (2009).

[23] J. Mitroy and J. Y. Zhang, Eur. Phys. J. D **46**, 415 (2008).

[24] W. W. Smith and A. Gallagher, Phys. Rev. **145**, 26 (1966).

[25] A. Gallagher, Phys. Rev. **157**, 24 (1967).

[26] T. Andersen, J. Desesquelles, K. A. Jessen, and G. Sørensen, J. Quant. Spectrosc. Radiat. Transfer **10**, 1143 (1970).

[27] B. Emmoth, M. Braun, J. Bromander, and I. Martinson, Phys. Scr. **12**, 75 (1975).

[28] W. Ansbacher, A. S. Inamdar, and E. H. Pinnington, Phys. Lett. A **110**, 383 (1985).

[29] R. N. Gosselin, E. H. Pinnington, and W. Ansbacher, Nucl. Instrum. Methods Phys. Res. B **31**, 305 (1988).

[30] R. N. Gosselin, E. H. Pinnington, and W. Ansbacher, Phys. Rev. A **38**, 4887 (1988).

[31] J. Jin and D. A. Church, Phys. Rev. Lett. **70**, 3213 (1993).

[32] J. Jin and D. A. Church, Phys. Rev. A **49**, 3463 (1994).

[33] S. D. Rosner, R. A. Holt, and T. J. Scholl, Phys. Rev. A **55**, 3469 (1997).

[34] M. S. Safronova, W. R. Johnson, and A. Derevianko, Phys. Rev. A **60**, 4476 (1999).

[35] J. Mitroy and M. S. Safronova, Phys. Rev. A **79**, 012513 (2009).

[36] D. Jiang, B. Arora, M. S. Safronova, and C. W. Clark, J. Phys. B **42**, 154020 (2009).

[37] E. Iskrenova-Tchoukova and M. S. Safronova, Phys. Rev. A **78**, 012508 (2008).

[38] R. Gerritsma, G. Kirchmair, F. Zähringer, J. Benhelm, R. Blatt, and C. Roos, Eur. Phys. J. D **50**, 13 (2008).

[39] B. Warner, Mon. Not. R. Astron. Soc. **139**, 115 (1968).

[40] P. Hafner and W. H. Schwarz, J. Phys. B **11**, 2975 (1975).

[41] C. E. Theodosiou, Phys. Rev. A **39**, 4880 (1989).

[42] C. Guet and W. R. Johnson, Phys. Rev. A **44**, 1531 (1991).

[43] N. Vaeck, M. Godefroid, and C. Froese Fischer, Phys. Rev. A **46**, 3704 (1992).

[44] S.-S. Liaw, Phys. Rev. A **51**, 1723(R) (1995).

[45] M. Meléndez, M. A. Bautista, and N. R. Badnell, Astron. Astrophys. **469**, 1203 (2007).

[46] J. Mitroy, D. C. Griffin, D. W. Norcross, and M. S. Pindzola, Phys. Rev. A **38**, 3339 (1988).

[47] A.-M. Mårtensson-Pendrill and S. Salomonson, Phys. Rev. A **30**, 712 (1984).

[48] A. T. Goble and S. Maleki, Phys. Rev. A **42**, 649 (1990).

[49] A.-M. Mårtensson-Pendrill, A. Ynnerman, H. Warston, L. Vermeeren, R. E. Silverans, A. Klein, R. Neugart, C. Schulz, and P. Lievens, Phys. Rev. A **45**, 4675 (1992).

[50] R. E. Silverans, L. Vermeeren, R. Neugart, and P. Lievens, Z. Phys. D **18**, 352 (1991).

[51] F. Arbes, M. Benzing, Th. Gudjons, F. Kurth, and G. Werth, Z. Phys. D **31**, 27 (1994).

[52] F. Kurth, T. Gudjons, B. Hiblert, T. Reisinger, G. Werth, and A.-M. Martensson, Z. Phys. D **34**, 227 (1995).

[53] W. Nörtershäuser, K. Blaum, K. Icker, P. Müller, A. Schmitt, K. Wendt, and B. Wiche, Eur. Phys. J. D **2**, 33 (1998).

[54] B. K. Sahoo, R. K. Chaudhuri, B. P. Das, So. Majumder, H. Merlitz, U. S. Mahapatra, and D. Mukherjee, J. Phys. B **36**, 1899 (2003).

[55] K.-z. Yu, L.-j. Wu, B.-c. Gou, and T.-y. Shi, Phys. Rev. A **70**, 012506 (2004).

[56] M. S. Safronova and W. R. Johnson, Adv. At. Mol. Opt. Phys. **55**, 191 (2007).

[57] Yu. Ralchenko, F.-C. Jou, D. E. Kelleher, A. E. Kramida, A. Musgrove, J. Reader, W. L. Wiese, and K. Olsen, NIST Atomic Spectra Database (version 3.0.2) [http://physics.nist.gov/asd3 (2006, January 4)], National Institute of Standards and Technology, Gaithersburg, MD.

[58] L. W. Fullerton and G. A. Rinker, Jr., Phys. Rev. A **13**, 1283 (1976).

[59] P. J. Mohr, Ann. Phys. (NY) **88**, 26 (1974).

[60] P. J. Mohr, Ann. Phys. (NY) **88**, 52 (1974).

[61] P. J. Mohr, Phys. Rev. Lett. **34**, 1050 (1975).

[62] M. S. Safronova, W. R. Johnson, and U. I. Safronova, Phys. Rev. A **53**, 4036 (1996).

[63] M. S. Safronova, W. R. Johnson, and U. I. Safronova, J. Phys. B **30**, 2375 (1997).

[64] W. R. Johnon, Z. W. Liu, and J. Sapirstein, At. Data Nucl. Data Tables **64**, 279 (1996).

[65] A. Derevianko and E. D. Emmons, Phys. Rev. A **66**, 012503 (2002).

[66] D. Jiang, B. Arora, and M. S. Safronova, Phys. Rev. A **78**, 022514 (2008).

[67] M. S. Safronova, M. G. Kozlov, W. R. Johnson, and D. Jiang, Phys. Rev. A **80**, 012516 (2009).

[68] U. I. Safronova, Phys. Rev. A **82**, 022504 (2010).

[69] U. I. Safronova, Phys. Rev. A **81**, 052506 (2010).

[70] U. I. Safronova, M. S. Safronova, and W. R. Johnson, Phys. Rev. A **71**, 052506 (2005).

[71] B. Arora, M. S. Safronova, and C. W. Clark, Phys. Rev. A **76**, 052516 (2007).

[72] M. Gunawardena, D. S. Elliott, M. S. Safronova, and U. Safronova, Phys. Rev. A **75**, 022507 (2007).

[73] M. Auzinsh, K. Bluss, R. Ferber, F. Gahbauer, A. Jarmola, M. S. Safronova, U. I. Safronova, and M. Tamanis, Phys. Rev. A **75**, 022502 (2007).

[74] M. S. Safronova, W. R. Johnson, U. I. Safronova, and T. E. Cowan, Phys. Rev. A **74**, 022504 (2006).

[75] S. B. Bayram, M. D. Havey, M. S. Safronova, and A. Sieradzan, J. Phys. B **39**, 2545 (2006).

[76] J. Mitroy, M. S. Safronova, and C. W. Clark, J. Phys. B **43**, 202001 (2010).

[77] U. Volz and H. Schmoranzer, Phys. Scr. T **65**, 48 (1996).

[78] A. Derevianko, W. R. Johnson, M. S. Safronova, and J. F. Babb, Phys. Rev. Lett. **82**, 3589 (1999).

[79] W. R. Johnson, D. Kolb, and K.-N. Huang, At. Data Nucl. Data Tables **28**, 333 (1983).

[80] J. W. Farley and W. H. Wing, Phys. Rev. A **23**, 2397 (1981).

[81] S. G. Porsev and A. Derevianko, Phys. Rev. A **74**, 020502(R) (2006).

[82] [http://www.webelements.com].

[83] K. Beloy, U. I. Safronova, and A. Derevianko, Phys. Rev. Lett. **97**, 040801 (2006).

[84] W. R. Johnson, U. I. Safronova, A. Derevianko, and M. S. Safronova, Phys. Rev. A **77**, 022510 (2008).

[85] M. S. Safronova, D. Jiang, and U. I. Safronova, Phys. Rev. A **82**, 022510 (2010).