Finite-field calculation of static polarizabilities and hyperpolarizabilities of In$^+$ and Sr

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The dipole polarizabilities, dipole hyperpolarizabilities, quadrupole moments, and quadrupole polarizabilities of the $5s^2\,^1S$ and $5s5p\,^3P^o$ states of In$^+$ and Sr are calculated by using the finite-field method. The electron correlation effect and the basis set convergence are investigated in the relativistic coupled-cluster and configuration interaction calculations in order to obtain polarizabilities of high accuracy. Comparative study of the fully and scalar relativistic calculations reveals the effect of the spin-orbit coupling on the dipole polarizabilities of In$^+$ and Sr. The blackbody-radiation shifts of the clock transition $5s^2\,^1S_0$-$5s5p\,^3P_0^o$ due to the dipole polarizabilities, quadrupole polarizabilities, and dipole hyperpolarizabilities are evaluated to be 0.017, 8.33×10^{-10}, and 1.93×10^{-17} Hz for In$^+$ and 2.09 and 5.82×10^{-8}, and 1.69×10^{-15} Hz for Sr. The blackbody-radiation shifts from the quadrupole polarizabilities and dipole hyperpolarizabilities are significantly less than that from the dipole polarizabilities and therefore can be safely omitted for the quoted 10^{-18} uncertainty of the optical frequency standard of In$^+$ and Sr.

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I. INTRODUCTION

In recent years, tremendous progresses of optical clocks have stimulated a great deal of interest in performing precision calculations of atomic polarizabilities and hyperpolarizabilities [1–5]. The highly accurate data of atomic polarizabilities and hyperpolarizabilities are very useful for the estimation of the energy shifts in an optical clock. For example, the difference in the static dipole polarizabilities between two states of a clock transition determines the blackbody-radiation (BBR) shift that is one of important sources of the frequency uncertainty budget of an optical clock [6,7]. The dipole polarizabilities and the BBR shifts of the optical clock transitions of Al$^+$, Ca$^+$, Sr, Yb, In$^+$, Sr$^+$, Hg$^+$, Mg, and Ca and so on have been calculated [8–11]. The higher multipolar polarizabilities, like the magnetic dipole and electric quadrupole polarizabilities, are also related to the energy shift of the optical clock transitions through the multipolar radiation channels. The multipolar BBR shifts have been studied for Mg, Ca, Sr, Yb, and Ca$^+$ [12,13]. The energy shifts due to the multipolar and higher-order polarizabilities are generally small but not necessarily negligible, for example, the energy shifts caused by the multipolar polarizabilities and dipole hyperpolarizabilities have been analyzed in detail for a Sr optical clock [14,15].

Among the current atomic optical clock candidates, an important category is the $ns^2\,^1S_0$-$nsnp\,^3P_0^o$ optical transition for the two valence electrons atoms or ions [3,6,7], where the upper state is one of the triplet states $^3P^o$, with $J = 0$, 1, and 2. Two good examples are In$^+$ and Sr optical clocks using the $5s^2\,^1S_0$-$5s5p\,^3P_0^o$ transition. The Sr optical clock is one of the most accurate atomic clock to date, for which the fractional frequency uncertainty has recently been estimated as 2.1×10^{-18} [5]. The BBR shift of the In$^+$ $5s^2\,^1S_0$-$5s5p\,^3P_0^o$ optical transition has also been calculated to be very small [9], which makes In$^+$ a good candidate for development of optical clock with the fractional frequency uncertainty at the 10^{-18}

level. The polarizabilities of such systems have been targeted with increasing theoretical efforts to perform precision calculations. For example, Sahoo and Das have calculated the ground-state dipole polarizability of Sr by using the relativistic coupled-cluster (CC) method [16]. Safronova *et al.* have given high-accuracy data for the dipole polarizabilities of the $5s^2\,^1S_0$ and $5s5p\,^3P_0^o$ states of In$^+$ and Sr using the configuration interaction (CI) + all-order method [9,11]. Mitroy *et al.* have calculated the $5s^2\,^1S_0$ and $5s5p\,^3P_1^o$ states of Sr by using the CI method with a semiempirical core polarization potential (CICP) [17,18]. Porsev *et al.* have calculated the Sr $5s^2\,^1S_0$ and $5s5p\,^3P_{0,1}^o$ states using the CI method with many-body perturbation theory (CI + MBPT) [19] and the CI + all-order method [20]. From these works, one can see that the most currently available data of the dipole polarizabilities of In$^+$ and Sr are concentrated on the $5s^2\,^1S_0$ and $5s5p\,^3P_0^o$ states, while the data for the $5s5p\,^3P_2^o$ state of Sr and the $5s5p\,^3P_1^o$ and $^3P_2^o$ states of In$^+$ have never been calculated. Besides, the quadrupole moment of the $5s5p\,^3P^o$ state and the quadrupole polarizabilities of the $5s^2\,^1S$ and $5s5p\,^3P^o$ states of Sr have been calculated in earlier works [17,20–22]. However, the recommended data for the quadrupole moment and the quadrupole polarizabilities of In$^+$ remain very scarce.

The finite-field method has been implemented in many computational codes for atomic and molecular property calculations [23–25]. In this method the employed external field breaks the degeneracy of multiple states and thus the J- and M_J-resolved polarizabilities of the $nsnp\,^3P_J^o$ states can be obtained directly, where J and M_J are the total angular momentum and the magnetic quantum number, respectively [26]. In particular, the effect of the spin-orbit coupling on the J-resolved polarizability can be revealed through comparative studies between fully and scalar relativistic calculations. The polarizabilities of high accuracy of the $3s^2\,^1S_0$ and $3s3p\,^3P_J^o$ states of Al$^+$ have been calculated successfully by using the finite-field method [27,28]. However, the finite-field method has not been widely applied to calculate the polarizabilities of heavy atoms and ions. Polarizability studies of sufficient accuracy for heavy atoms and ions require careful treatment of electron correlation arising from core shells. The contribution

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of the high-order excitations also needs to be evaluated strictly. All of these factors pose a great challenge for the finite-field calculations of In$^+$ and Sr.

In this work, the dipole polarizabilities, dipole hyperpolarizabilities, quadrupole moments, and quadrupole polarizabilities for the $5s^2\,{}^1S$ and $5s5p\,{}^3P^o$ states of In$^+$ and Sr are calculated by applying the finite-field method. The effects of the hierarchies of electron correlation and the basis sets of the increasing sizes are investigated in the relativistic CC and CI calculations in order to obtain polarizabilities of high accuracy. Our results of the dipole polarizabilities of the $5s^2\,{}^1S_0$ and $5s5p\,{}^3P_0^o$ states of In$^+$ and Sr are in good agreement with previously reported data. The effect of the spin-orbit coupling is analyzed through comparing the L- and J-resolved values of the $5s5p\,{}^3P^o$ states, where L is the total orbital angular momentum. Besides, we recommend the values of the dipole hyperpolarizabilities, quadrupole moments, and quadrupole polarizabilities of $5s^2\,{}^1S$ and $5s5p\,{}^3P^o$ states of In$^+$ and Sr. Based on these data, the BBR shifts of the clock transition $5s^2\,{}^1S_0$-$5s5p\,{}^3P_0^o$ due to the quadrupole polarizabilities and dipole hyperpolarizabilities are evaluated to be 8.33×10^{-10} and 1.93×10^{-17} Hz, respectively, for In$^+$ and 5.82×10^{-8} and 1.69×10^{-15} Hz, respectively, for Sr. The BBR shifts due to the quadrupole polarizabilities and dipole hyperpolarizabilities are shown to be far less than that due to the dipole polarizabilities and, hence, can be safely omitted for the quoted 10^{-18} uncertainty of the optical frequency standard of In$^+$ and Sr.

II. THEORY

The energy shift of an atom or ion in a homogeneous electric field can be expressed as [29]

$$\Delta E_d(F_z) = -\alpha F_z^2/2 - \gamma F_z^4/24 - \cdots, \tag{1}$$

where F_z is the electric-field strength along the z direction, and α is the dipole polarizability, and γ is the dipole hyperpolarizability, respectively.

In a pure quadrupole electric field, the corresponding energy shift is

$$\Delta E_d(F_{zz}) = -\theta F_{zz}/2 - \alpha_2 F_{zz}^2/8 - \cdots, \tag{2}$$

where F_{zz} is the electric-field gradient in the z direction, θ is the quadrupole moment, and α_2 is the quadrupole polarizability, respectively.

For a state with nonzero angular momentum J, the scalar and tensor polarizabilities are defined as

$$\bar{Q}^J = \frac{1}{2J+1}\sum_{M_J} Q(J,M_J), \tag{3}$$

$$Q_a^J = Q(J,|M_J|=J) - \bar{Q}^J, \tag{4}$$

where Q denotes α, γ, and α_2; $Q(J,M_J)$ denotes polarizabilities for each M_J component; and $\bar{Q}$ and Q_a denote the scalar and tensor polarizabilities. In the L representation, the scalar and tensor polarizabilities are defined by expressions of identical form to Eqs. (3) and (4) with J replaced with L. The quadrupole moment θ is generally defined with $M_L = L$ or $M_J = J$. In details, θ^L is taken from the $5s5p\,{}^3P^o$ state with $M_L = 1$, and θ^J is taken from the $5s5p\,{}^3P_2^o$ state with $M_J = 2$. Upon the approximation known as LS coupling, the L- and

J-resolved polarizabilities have a relationship like $\bar{\alpha}^L = \bar{\alpha}^J$ when the spin-orbit coupling interaction is not strong and then can be treated as a perturbation [26].

III. METHOD OF CALCULATION

First, the self-consistent field (SCF) calculation is carried out for a given electric field to generate the reference state as well as the optimized atomic orbitals by using the SCF module in the relativistic quantum chemistry calculation package DIRAC [30]. Either the Dirac-Coulomb Hamiltonian or spin-free Dyall Hamiltonian [31] is employed in the SCF calculations. The Dirac-Coulomb Hamiltonian gives a full description of the relativistic effects. The spin-free Dyall Hamiltonian is based on the Dirac formalism by Dyall that decomposes the Dirac operator into a spin-free part and a spin-dependent part that represents the spin-orbit operators. The spin-free Dyall Hamiltonian neglects the spin-dependent part. Next, the electron correlation calculation is performed based on the SCF reference state and optimized atomic orbitals. The relativistic CC calculation is implemented by applying the quantum chemistry calculation package MRCC [32], and the relativistic CI calculation is implemented by applying the LUCIAREL module in the DIRAC package. The scalar relativistic CI calculation is carried out by applying the LUCITA module in the DIRAC package that is built on the spin-free Dyall Hamiltonian.

In DIRAC and MRCC, the wave function can be specified by an arbitrary number of active orbital spaces with arbitrary electron occupation constraints, thus providing maximum flexibility for the treatment of electron correlations by taking advantage of the concept of generalized active spaces [32,33]. In our calculations, the Dirac-Fock orbitals are divided into the inner-core, outer-core, valence, and virtual shells. No excitation is allowed in the inner-core shells, but the excitation in the outer-core and valence shells can be defined to any order. The outer-core shells are designed to contain more and more core orbitals in order to investigate the convergence of the calculated results with the increasingly correlated core shells. In details, the $(4d)$, $(4s,4p,4d)$, and $(3d,4s,4p,4d)$ core orbitals that contain 10, 18, and 28 electrons, which are labeled as (core10), (core18), and (core28), respectively, are taken as the outer-core shells for In$^+$. Similarly, the $(4s,4p)$, $(3d,4s,4p)$, and $(3s,3p,3d,4s,4p)$ core orbitals that contain 8, 18, and 26 electrons, which are labeled as (core8), (core18), and (core26), respectively, are taken as the outer-core shells for Sr. The $(5s,5p)$ orbitals constitute the valence shells of In$^+$ and Sr. The virtual orbitals with the orbital energy larger than a given cutoff value are neglected in our CC and CI calculations. We have carried out the calculations of the different cutoff values in order to check the influence of the truncation of the virtual orbitals on the results.

In the following, the CC calculation is referred to as (core n)SD and (core n)SDT that include single and double (SD) excitations and single, double, and triple (SDT) excitations from the outer-core and valence shells into the virtual orbitals, where n means the number of outer-core electrons that are involved in the CC calculations. The CI calculation is referred to as (core n)SD(2in4)SDT and (core n)SD(2in4)SDTQ, where (core n)SD means that the outer-core shells are restricted

to single and double (SD) excitations and (2in4) means that two valence electrons are distributed in four $(5s,5p)$ valence shells with the addition of excited electrons from the outer-core to valence shells, for which all single, double, and triple (SDT) excitations and single, double, triple, and quadruple (SDTQ) excitations into virtual orbitals are taken into account.

The Dyall's uncontracted correlation-consistent double-, triple-, and quadruple-ζ basis sets are used, which are called $X\zeta$ with $X = 2$, 3, and 4, respectively [34,35]. Each shell is augmented by two additional diffused functions. The exponential coefficients of the augmented functions are determined according to

$$\zeta_{N+1} = \left[\frac{\zeta_N}{\zeta_{N-1}}\right]\zeta_N, \tag{5}$$

where ζ_N and ζ_{N-1} are the two most diffused exponents for the respective atomic shells in the original basis set. Four to eight arbitrary finite-field strengths are chosen in the range of $F_z = (0, 4.5 \times 10^{-3})$ and of $F_{zz} = (0, 4.5 \times 10^{-5})$ in atomic units. The fitting is checked to remove the dependence of the properties studied on sampling. In our calculations, the criterion for energy convergence is set to be 10^{-10} hartree.

We use the composite scheme [27] to give the final value, P_{final}, of a studied property. In the CC calculation,

$$P_{\text{final}} = P_{SD} + \Delta P_T + \Delta P_{\text{core}}, \tag{6}$$

where P_{SD} is the value calculated for property P using the (core10)SD method with the $X = 4$ basis set, ΔP_T and ΔP_{core} are the corrections due to the triple excitation and more outer-core shells. In the CI calculation,

$$P_{\text{final}} = P_{SDT} + \Delta P_Q + \Delta P_{\text{core}}, \tag{7}$$

where P_{SDT} is the value calculated for property P using the (core10)SD(2in4)SDT method with the $X = 4$ basis set, and ΔP_Q is the correction due to the quadruple excitation. In the following CC and CI calculations, the virtual orbitals with the orbital energy larger than 20 a.u. for In$^+$ and 10 a.u. for Sr are neglected. The calculations of the cutoff value of the virtual orbitals being 100 a.u. have also been carried out. Increasing the cutoff value to 100 a.u. causes only 0.5% change in α^J in comparison to the cases of cutoff value being 20 a.u. for In$^+$ and 10 a.u. for Sr. Therefore, the influence of the truncation of the virtual orbitals on our results is expected to be small and then neglected in the composite scheme.

We consider the possible error sources that cause the uncertainty in P_{final}. The first error is due to the finite basis set used for calculating P_{SD} and P_{SDT}, i.e., the errors in P_{SD} and P_{SDT}. The convergence of the value of P with respect to the basis set is very quick when the basis set is larger than $X = 3$, as shown by the Al$^+$ results [28]. Thus, we assume empirically that the errors in P_{SD} and P_{SDT} are equal to half of the difference of the P values obtained by using $X = 3$ and 4 basis sets. This error can be regarded as the possible correction with respect to the value computed in the complete basis-set limit. The second error comes from estimations of ΔP_T and ΔP_Q. Previous experience [28] has shown that the ΔP_T and ΔP_Q corrections computed even with the much small basis set of $X = 2$ are never in error by more than 50% with respect to the complete basis-set limit, and hence the errors of ΔP_T

and ΔP_Q are taken to be half of themselves, i.e., $0.5\Delta P_T$ and $0.5\Delta P_Q$. The third error is due to the estimation of ΔP_{core}. This error is determined as the difference of the results obtained with the increasing outer-core shells. Finally, the overall uncertainty in P_{final} is evaluated by root-mean-square of the above three errors.

Throughout this paper, atomic units (a.u.) are used, unless otherwise stated. The atomic units of α, α_2, γ, F_z, and F_{zz} are, respectively, $1.648\,778 \times 10^{-41}$ C^2 m^2 J^{-1}, $4.617\,048 \times 10^{-62}$ C^2 m^4 J^{-1}, $6.235\,378 \times 10^{-65}$ C^4 m^4 J^{-3}, $5.142\,250 \times 10^9$ V/cm, and $5.142\,250 \times 10^{11}$ V/cm^2.

IV. RESULTS AND DISCUSSION

A. Dipole polarizability and hyperpolarizability

Table I summarizes the results of α^J for the $5s^2\,^1S_0$ and $5s5p\,^3P^o_{0,1,2}$ states of In$^+$ calculated by using the relativistic CC method. First, the obtained values of α^J in the (core10)SD calculation with the $X = 2$, 3, and 4 basis sets show a good convergence with the increasing size of the basis set. The error in P_{SD} is only about 0.01–0.06. Then, the ΔP_{core} correction is estimated with the $X = 3$ basis set. The α^J value decreases upon inclusion of the more core shells, $4s$ and $4p$, in the (core18)SD calculation. Including more core shells, $3d$, in the (core28)SD calculation leads to rather small changes of α^J. This means that α^J has entered the convergence region with the increasing correlated core shells; then ΔP_{core} is estimated to be the difference of the α^J values obtained by the (core28)SD and (core10)SD calculations, being about -0.09 to -0.30. Next, ΔP_T is estimated to be the difference of the α^J values obtained by the (core10)SD and (core10)SDT calculations with the $X = 2$ basis set, being around -0.08 to -0.46. The magnitudes of the ΔP_T and ΔP_{core} corrections are obviously larger than the error in P_{SD}. The reference data for the $5s^2\,^1S_0$ and $5s5p\,^3P^o$ states of In$^+$ are also given in Table I, as calculated by Safronova *et al.* by using the CI + all-order method [9]. Our results are consistent with their data with a discrepancy of around 1%. Finally, we recommend that $\bar{\alpha}^J = 27.31$ for $5s5p\,^3P^o_1$, with $|M_J| = 1$, and $\bar{\alpha}^J = 28.78$ and $\alpha^J_a = -1.53$ for $5s5p\,^3P^o_2$.

The results of γ^J are summarized in Table II for the $5s^2\,^1S_0$ and $5s5p\,^3P^o_{0,1,2}$ states of In$^+$. Similar to the case of α^J, the γ^J values show a good convergence trend with respect to the size of basis set, and the magnitudes of the ΔP_T and ΔP_{core} corrections are also larger than the error in P_{SD}. The P_{final} values are recommended as $\gamma^J = 2989$, $13\,467$, and $19\,679$ for the $5s^2\,^1S_0$, $5s5p\,^3P^o_0$, and $5s5p\,^3P^o_1$, $|M_J| = 1$ states, respectively, and $\bar{\gamma}^J = 16\,531$ and $\gamma^J_a = -9052$ for the $5s5p\,^3P^o_2$ state. The uncertainties for the P_{final} values of γ^J are slightly larger than those for α^J, which is comprehensible because the hyperpolarizability is a higher-order response that is more sensitive to a small energy variation and thus various contributions bring substantial corrections to γ^J.

We also give the results of the relativistic CI calculation that is implemented at the level of (core10)SD(2in4)SD < 2 with the $X = 3$ basis set, where "<2" means the cutoff for the virtual orbitals being 2 a.u. in energy, in the footnotes of Tables I and II for comparison. In the relativistic CI calculations, we neglect the triple excitation, cut off more

TABLE I. Values of the dipole polarizabilities α^J of the $5s^2\,{}^1S_0$ and $5s5p\,{}^3P^o_{0,1,2}$ states of In$^+$ obtained by the relativistic CC calculations.

| | | | ${}^3P^o_1$ | ${}^3P^o_2$ | | | | |
Level of excitation[a]	${}^1S_0$	${}^3P^o_0$	$\lvert M_J\rvert=1$	$\lvert M_J\rvert=0$	$\lvert M_J\rvert=1$	$\lvert M_J\rvert=2$	$\bar\alpha^J$	α^J_a
Basis: $2\zeta(23s,17p,13d,4f)$								
(core10)SD	24.83	27.91	29.12	32.34	31.47	28.88	30.61	−1.73
(core10)SDT	24.54	27.50	28.75	32.26	31.13	28.42	30.27	−1.85
ΔP_T	−0.29	−0.41	−0.37	−0.08	−0.35	−0.46	−0.34	−0.12
Error in ΔP_T	±0.15	±0.21	±0.19	±0.04	±0.18	±0.23	±0.17	±0.06
Basis:$3\zeta(30s,23p,17d,5f,3g)$								
(core10)SD	24.90	27.01	27.98	30.75	30.09	28.10	29.42	−1.33
(core18)SD	24.71	26.81	27.83	30.68	30.09	27.84	29.31	−1.47
(core28)SD	24.67	26.77	27.79	30.63	29.93	29.79	29.21	−1.42
ΔP_{core}	−0.24	−0.25	−0.19	−0.12	−0.16	−0.30	−0.21	−0.09
Error in ΔP_{core}	±0.04	±0.04	±0.04	±0.05	±0.16	±0.05	±0.09	±0.05
Basis:$4\zeta(35s,29p,20d,7f,5g,3h)$								
(core10)SD, P_{SD}	24.86	26.91	27.87	30.64	29.98	28.01	29.32	−1.31
Error in P_{SD}	±0.03	±0.05	±0.06	±0.06	±0.05	±0.04	±0.05	±0.01
				$P_{\text{final}}=P_{SD}+\Delta P_{\text{core}}+\Delta P_T$				
Final data, P_{final}	24.33	26.25	27.31	30.44	29.48	27.25	28.78	−1.53
Uncertainty (%)	0.62	0.82	0.73	0.28	0.82	0.87	0.69	4.99
Ref. [9]	24.01	26.02						

[a]The relativistic CI calculation is performed using the 3ζ basis set at (core10)SD(2in4)SD <2 level, which yields $\alpha=25.06$ and 27.93 for the $5s^2\,{}^1S_0$ and $5s5p\,{}^3P^o_0$ states, $\bar\alpha^J=28.59$ and $\alpha^J_a=0.34$ for the $5s5p\,{}^3P^o_1$ state, and $\bar\alpha^J=30.30$ and $\alpha^J_a=-1.38$ for the $5s5p\,{}^3P^o_2$ state.

virtual orbitals, and use a small basis set of $X=3$, which reduces the computational cost but causes large errors in the results of α^J and γ^J. The errors of the relativistic CI results are about 10% compared with the P_{final} values obtained by the relativistic CC calculations shown in Tables I and II.

In Table III we summarize the results of α^L and γ^L for the $5s^2\,{}^1S$ and $5s5p\,{}^3P^o$ states of In$^+$ calculated by the scalar relativistic CI method. The P_{SDT} value is determined by the (core10)SD(2in4)SDT calculation with the $X=4$ basis set. Further, the ΔP_{core} and ΔP_Q corrections are estimated with $X=2$ basis set. The ΔP_{core} correction is equal to the difference of the results obtained by the (core10)SD(2in4)SDT and (core28)SD(2in4)SDT calculations, and the ΔP_Q correction is equal to the difference of the results obtained

TABLE II. Values of the dipole hyperpolarizabilities γ^J of the $5s^2\,{}^1S_0$ and $5s5p\,{}^3P^o_{0,1,2}$ states of In$^+$ obtained by the relativistic CC calculations.

| | | | ${}^3P^o_1$ | ${}^3P^o_2$ | | | | |
Level of excitation[a]	${}^1S_0$	${}^3P^o_0$	$\lvert M_J\rvert=1$	$\lvert M_J\rvert=0$	$\lvert M_J\rvert=1$	$\lvert M_J\rvert=2$	$\bar\gamma^J$	γ^J_a
Basis:$2\zeta(23s,17p,13d,4f)$								
(core10)SD	3695	14752	21119	27116	20729	7294	16632	−9338
(core10)SDT	3640	15134	21611	27546	20989	7773	17014	−9241
ΔP_T	−55	381	492	431	260	479	382	97
Error in ΔP_T	±28	±191	±246	±216	±130	±240	±191	±49
Basis:$3\zeta(30s,23p,17d,5f,3g)$								
(core10)SD	3143	13435	19265	26644	20951	6820	16437	−9617
(core18)SD	3072	13467	19368	26472	20755	6968	16384	−9645
(core28)SD	3065	13464	19327	26480	20703	7056	16400	−9344
ΔP_{core}	−78	28	62	−164	−248	236	−38	273
Error in ΔP_{core}	±7	±3	±42	±9	±52	±88	±16	±72
Basis:$4\zeta(35s,29p,20d,7f,5g,3h)$								
(core10)SD, P_{SD}	3122	13057	19125	26265	20571	6765	16187	−9422
Error in P_{SD}	±11	±189	±70	±190	±190	±28	±125	±97
				$P_{\text{final}}=P_{SD}+\Delta P_{\text{core}}+\Delta P_T$				
Final data, P_{final}	2989	13467	19679	26532	20583	7479	16531	−9052
Uncertainty (%)	1.01	1.99	1.32	1.08	1.15	3.43	1.38	1.44

[a]The relativistic CI calculation is performed using the 3ζ basis set at (core10)SD(2in4)SD <2 level, which yields $\alpha=2715$ and 16164 for the $5s^2\,{}^1S_0$ and $5s5p\,{}^3P^o_0$ states, $\bar\alpha^J=17247$ and $\alpha^J_a=4263$ for the $5s5p\,{}^3P^o_1$ state, and $\bar\alpha^J=18614$ and $\alpha^J_a=-8518$ for the $5s5p\,{}^3P^o_2$ state.

TABLE III. Values of the dipole polarizabilities α^L and the dipole hyperpolarizabilities γ^L for the $5s^2\,^1S$ and $5s5p\,^3P^o$ states of In$^+$ obtained by the scalar relativistic CI calculations.

| Level of excitation | α^L | | | | | γ^L | | | | |
| | | $^3P^o$ | | | | | $^3P^o$ | | | |
	$^1S_0$	$|M_L|=0$	$|M_L|=1$	$\bar{\alpha}^L$	α_a^L	$^1S_0$	$|M_L|=0$	$|M_L|=1$	$\bar{\gamma}^L$	γ_a^L
Basis:$2\zeta(23s,17p,13d,4f)$										
(core10)SD(2in4)SDT	24.42	32.24	27.98	29.40	−1.42	2832	35528	7099	16576	−9476
(core18)SD(2in4)SDT	24.28	32.23	27.84	29.31	−1.46	2521	35712	6972	16552	−9580
(core28)SD(2in4)SDT	24.26	32.19	27.82	29.28	−1.46	2567	35679	6967	16538	−9571
(core10)SDT(2in4)SDTQ	24.41	32.17	27.82	29.27	−1.45	3650	35577	7381	16780	−9398
ΔP_Q	−0.015	−0.07	−0.16	−0.13	−0.03	789	49	282	204	78
Error in P_Q	±0.008	±0.035	±0.08	±0.065	0.015	±395	±25	±141	±102	±39
ΔP_{core}	−0.16	−0.05	−0.16	−0.12	−0.04	−294	151	−132	−38	−94
Error in P_{core}	±0.02	±0.05	±0.0.02	±0.03	±0.01	±46	±33	±5	±14	±9
Basis:$3\zeta(30s,23p,17d,5f,3g)$										
(core10)SD(2in4)SDT	24.38	30.43	27.17	28.26	−1.08	2182	34283	6742	15922	−9180
Basis:$4\zeta(35s,29p,20d,7f,5g,3h)$										
(core10)SD(2in4)SDT, P_{SDT}	24.34	30.35	27.12	28.20	−1.08	2270	34257	6761	15926	−9165
Error in P_{SDT}	±0.02	±0.04	±0.03	±0.03	±0.005	±44	±13	±9	±2	±8
					$P_{\text{final}} = P_{SDT} + \Delta P_{\text{core}} + \Delta P_Q$					
Final data, P_{final}	24.16	30.22	26.80	27.94	−1.14	2765	34457	6910	16092	−9182
Uncertainty(%)	0.13	0.23	0.33	0.28	1.56	14.46	0.13	2.05	0.64	0.44

by the (core10)SD(2in4)SDT and (core10)SDT(2in4)SDTQ calculations. We can find that the magnitudes of the ΔP_Q and ΔP_{core} corrections are also larger than the error in P_{SDT} in the scalar relativistic CI calculations. This trend is in accordance with that found in the relativistic CC calculations shown in Tables I and II.

The results shown in Tables I, II, and III have proven that the error in P_{SD} has decreased to be very small when expansion of the basis set goes to $X = 4$ in the calculation of α and γ of the $5s^2\,^1S$ and $5s5p\,^3P^o$ states of In$^+$. In this situation, the ΔP_{core} correction arising from more outer-core shells and the ΔP_T and ΔP_Q corrections arising from the higher-order excitations become crucial for the accuracy of the final α and γ values. In this work, the ΔP_T correction in the relativistic CC calculation and the ΔP_Q correction in the scalar relativistic CI calculation are calculated only with the $X = 2$ basis set in order to avoid very high computational demand in using larger basis sets. In Tables I, II, and III, our estimations of ΔP_T and ΔP_Q are reasonable for most of states of In$^+$, although the $X = 2$ basis set is small. However, there are a few anomalous cases, like the ΔP_T corrections for the α_a^J value of the $5s5p\,^3P_2^o$ state shown in Table I and the γ^J value of the $5s5p\,^3P_2^o$ state with $M_J = 2$ shown in Table II, as well as the ΔP_Q correction for the γ^L value of the $5s^2\,^1S_0$ state shown in Table III. For such above states the ΔP_T and ΔP_Q corrections are anomalously larger than the other states. This may be due to the incompleteness of the basis set at the $X = 2$ level that causes large errors in some states.

Table IV summarizes the results of α^J for the $5s^2\,^1S_0$ and $5s5p\,^3P_{0,1,2}^o$ states of Sr calculated by using the relativistic CC method. The (core8)SD calculations are conducted with the $X = 2$, 3, and 4 basis sets. Upon the increasing sizes of the basis sets, the α^J value of the $5s^2\,^1S_0$ state shows very

rapid convergence, whereas the α^J values of the $5s5p\,^3P_{0,1,2}^o$ states converge slowly. The increments of the α^J values of the $5s5p\,^3P_{0,1,2}^o$ states are substantial when the basis set goes from $X = 3$ to 4 and consequently lead to the rather large error in P_{SD}, being about 12.1–15.7, except for the α_a^J value of the $^3P_2^o$ state. For the $^3P_2^o$ state, the α_a^J value is determined to be the $\bar{\alpha}^J$ value minus the α^J value of the $M_J = 2$ component. The error cancellation yields a small error in P_{SD} of the α_a^J value of the $^3P_2^o$ state. We also carry out the relativistic CI calculation at the (core8)SD(2in4)SD < 2 level with the $X = 3$ basis set for the $5s^2\,^1S_0$ and $5s5p\,^3P_{0,1,2}^o$ states of Sr. Its results are given in the footnote to Table IV for comparison. The error of these relativistic CI results are about 12% compared with the corresponding P_{final} values obtained by the relativistic CC calculations shown in Tables IV.

From Table IV we can see that the error in P_{SD} is basically larger than the magnitudes of the ΔP_T and ΔP_{core} corrections for the $5s5p\,^3P_J^o$ states of Sr. This indicates that the primary dominant factor that affects the accuracy of the P_{final} value of α^J for the $5s5p\,^3P_J^o$ states of Sr comes from the size of the basis set. This trend is different from that found for In$^+$. Note that the error in ΔP_{SD} is very small and is far less than ΔP_T and ΔP_{core} for the case of In$^+$. The possible reason can be ascribed to the different electron distribution of In$^+$ and Sr. As a positively charged ion, in general, In$^+$ has a compact electron distribution around the nucleus. However, as a neutral atom, Sr is expected to have more diffused electron distribution than In$^+$, indicating that larger basis sets are required for Sr.

The previously reported dipole polarizabilities of Sr are also listed in Table IV for comparison. It includes the calculation of Sahoo and Das using the relativistic couple cluster (RCC) method [16], the calculation of Porsev et al. using the CI + MBPT method [19], the calculation of Safronova et al.

TABLE IV. Values of the dipole polarizabilities α^J of the $5s^2\,^1S_0$ and $5s5p\,^3P^o_{0,1,2}$ states of Sr obtained by the relativistic CC calculations.

			$^3P^o_1$	$^3P^o_2$				
Level of excitation[a]	$^1S_0$	$^3P^o_0$	$\|M_J\|=1$	$\|M_J\|=0$	$\|M_J\|=1$	$\|M_J\|=2$	$\bar{\alpha}^J$	α^J_a
Basis:$2\zeta(23s,17p,12d,3f)$								
(core8)SD	205.1	349.3	377.1	418.7	397.1	331.7	375.3	–43.5
(core8)SDT	200.1	348.8	379.5	422.2	499.8	332.0	377.2	–45.2
ΔP_T	–5.0	–0.5	2.4	3.5	2.8	0.2	1.9	–1.7
Error in ΔP_T	±2.5	±0.3	±1.2	±1.8	±1.4	±0.1	±1.0	±0.9
Basis:$3\zeta(31s,22p,15d,7f,3g)$								
(core8)SD	204.8	423.8	460.8	515.1	490.5	415.7	465.5	–49.8
(core18)SD	204.6	415.3	450.3	503.8	478.8	406.3	454.8	–48.5
(core26)SD	204.7	418.8	454.4	509.0	486.9	410.1	460.6	–50.5
ΔP_{core}	–0.2	–5.0	–6.4	–6.2	–7.6	–5.6	–6.5	0.9
Error in ΔP_{core}	±0.01	±3.5	±4.0	±5.2	±4.1	±3.9	±4.2	±0.3
Basis:$4\zeta(35s,27p,17d,9f,7g,3h)$								
(core8)SD, P_{SD}	204.8	446.4	484.9	546.6	520.0	441.9	494.1	–52.2
Error in P_{SD}	0.0	±11.3	±12.1	±15.7	±14.8	±13.1	±14.3	±1.2
			$P_{\text{final}}=P_{SD}+\Delta P_{\text{core}}+\Delta P_T$					
Final data, P_{final}	199.7	444.1	480.9	543.9	519.2	436.5	491.1	–54.5
Uncertainty (%)	1.2	2.7	2.7	3.1	3.0	3.1	3.1	2.8
RCC [16]	199.7							
CI + MBPT [19]	197.2	457.0	498.8					
CI + all-order [11]	194.4	441.9						
CICP [17]	204.5		497.0 (27.7)[b]					
CI + all-order [20]			459.2 (26.0)[b]					
Expt. [36]			(24.5)[b]					

[a]The relativistic CI calculation is performed using the 3ζ basis set at (core8)SD(2in4)SD < 2 level, which yields $\alpha=179.5$ and 394.5 for the $5s^2\,^1S_0$ and $5s5p\,^3P^o_0$ states, $\bar{\alpha}^J=409.7$ and $\alpha^J_a=23$ for the $5s5p\,^3P^o_1$ state, and $\bar{\alpha}^J=455.2$ and $\alpha^J_a=-51.8$ for the $5s5p\,^3P^o_2$ state.
[b]Here given are the scalar and tensor (in parentheses) polarizabilities for $5s5p\,^3P^o_1$.

using the CI + all-order method [11], the calculation of Mitroy and Zhang using the CICP method [17], and the calculation of Porsev *et al.* using CI + all-order method [20]. Noteworthy to mention are the CI + all-order results of Safronova *et al.* that give $\alpha^J=194.4$ and 441.9 for $5s^2\,^1S_0$ and $5s5p\,^3P^o_0$, respectively. For such two states, we obtain $\alpha^J=199.7$ and 444.1 in the relativistic CC calculation, which are slightly larger than the values of Safronova *et al.* Such discrepancies indicate that the magnitudes of ΔP_T and ΔP_{core} are underestimated in our calculations. Porsev *et al.* obtained $\alpha^J=498.8$ for the $5s5p\,^3P^o_1$ state with $M_J=1$ state by using the CI + MBPT method, which is close to our calculated result $\alpha^J=480.9$. The scalar and tensor polarizabilities of $5s5p\,^3P^o_1$ have also been given as $\bar{\alpha}^J=497.0$ and $\alpha^J_a=27.7$ by Mitroy and Zhang [17] and $\bar{\alpha}^J=459.2$ and $\alpha^J_a=26.0$ by Porsev *et al.* [20]. The experimental value of α^J_a for $5s5p\,^3P^o_1$ is 24.5 [36]. By using the relativistic CI method we obtain $\bar{\alpha}^J=409.7$ and $\alpha^J_a=23.0$ for Sr $5s5p\,^3P^o_1$, which is closed to Porsev's values within a 11% error. There is no reported data available for the dipole polarizability of the Sr $5s5p\,^3P^o_2$ state. We recommend $\bar{\alpha}^J=491.1$ and $\alpha^J_a=-54.5$ for the $5s5p\,^3P^o_2$ state of Sr in Table IV. The data of the dipole hyperpolarizabilities of Sr are very scarce. In Table V we recommend $\gamma^J=691\,957$ and $3\,228\,219$ for the $5s^2\,^1S_0$ and $5s5p\,^3P^o_0$ states of Sr by using the relativistic CC calculation.

The results of α^L for the $5s^2\,^1S$ and $5s5p\,^3P^o$ states of Sr calculated by using the scalar relativistic CI method are given in Table VI. Being similar to the situation in the relativistic CC calculation shown in Table IV, the α^L value of the $5s^2\,^1S$ state converges very rapidly with the increasing size of the basis set, and the corresponding ΔP_Q and ΔP_{core} corrections are also small; on the other hand, the convergence of the α^L values of the $5s5p\,^3P^o$ states with the increasingly large basis sets is slow. The induced error in P_{SD} is rather large. The magnitudes of the ΔP_T and ΔP_{core} corrections of the α^L values of the $5s5p\,^3P^o$ state are also large. But their opposite signs lead to a certain cancellation in the uncertainty of the P_{final} values of α^L. Analyzing the relativistic CC and scalar relativistic CI results of Sr shown in Tables IV and VI, we can find that the calculated values of α of the $5s5p\,^3P^o$ states of Sr are dependent on the basis set strongly. A further expansion of the basis set will improve the accuracy of α. Besides, we can find that ΔP_{core} has reached convergence upon inclusion of the $3d$, $4s$, and $4p$ shells into the electron correlations. This indicates that the required correlated outer-core shells should at least contain the $3d$, $4s$, and $4p$ shells in order to achieve the accurate α values.

The relativistic effect in the four-component relativistic formalism can be understood as a combination of the spin-orbit coupling effect and contraction or decontraction of the radial electron density, i.e., the scalar relativistic effect. Among the $5s5p\,^3P^o_J$ states, the $^3P^o_0$ state is of a spherically symmetric electronic density and therefore has only the scalar dipole polarizabilities. In this situation, the difference of the J-resolved polarizabilities, α^J and γ^J, of the $^3P^o_0$ state and the

TABLE V. Values of the dipole hyperpolarizabilities γ^J of the $5s^2\,^1S_0$ and $5s5p\,^3P_0^o$ states of Sr obtained by the relativistic CC calculations.

Level of excitation	$^1S_0$	$^3P_0^o$
Basis:$2\zeta\,(23s,17p,12d,3f)$		
(core8)SD	484 500	7 050 552
(core8)SDT	510 144	6 905 904
ΔP_T	25 644	−144 648
Error in ΔP_T	±128 22	±72 324
Basis:$3\zeta\,(31s,22p,15d,7f,3g)$		
(core8)SD	680 965	3 568 344
(core18)SD	672 720	3 452 688
(core26)SD	674 592	3 289 040
ΔP_{core}	−6373	−279 304
Error in ΔP_{core}	±1872	±163 648
Basis:$4\zeta\,(35s,27p,17d,9f,7g,3h)$		
(core8)SD, P_{SD}	672 686	3 652 171
Error in P_{SD}	±8279	±83 827
$P_{\text{final}} = P_{SD} + \Delta P_{\text{core}} + \Delta P_T$		
Final data, P_{final}	691 957	3 228 219
Uncertainty (%)	2.22	6.12

M_L-averaged polarizabilities, $\bar\alpha^L$ and $\bar\gamma^L$, for the $^3P^o$ state can be understood as the sole effect of the spin-orbit coupling on the polarizabilities, as has been studied for the group-13 atoms [24] and Al$^+$ [28]. The fractional difference is defined as

$$\frac{\bar Q^L(^3P^o) - Q^J\left(^3P_0^o\right)}{Q^J\left(^3P_0^o\right)}. \tag{8}$$

Using our relativistic CC and scalar relativistic CI results given in Tables I, II, and III, the fractional difference of formula (8) is evaluated to be about 8% in α and 22% in γ for the $5s5p\,^3P^o$ states of In$^+$, indicating an evident spin-orbit effect in α and γ. The fractional difference of formula (8) is evaluated to be 2% in α for Sr using the our relativistic CC and scalar relativistic

CI results shown in Tables IV and VI, which is smaller than that of In$^+$. This implies that the effect of the spin-orbit coupling on α for Sr is weaker than that for In$^+$.

B. Quadrupole moment and polarizability

Table VII summarizes our results of the quadrupole moment θ and the quadrupole polarizabilities α_2 of the $5s^2\,^1S_0$ and $5s5p\,^3P_{0,1,2}^o$ states of In$^+$ and Sr. Here, given for the $5s5p\,^3P_{1,2}^o$ states, are the scalar quadrupole polarizabilities. The L-resolved values are obtained by the (core10)SD(2in4)SDTQ (In$^+$) and (core8)SD(2in4)SDTQ (Sr) calculations by using the scalar relativistic CI method, and the J-resolved values are obtained by the (core10)SD (In$^+$) and (core8)SD

TABLE VI. Values of the dipole polarizabilities α^L of the $5s^2\,^1S$ and $5s5p\,^3P^o$ states of Sr obtained by the scalar relativistic CI calculations.

Level of excitation	$^1S_0$	$^3P^o$			
		$\|M_L\| = 0$	$\|M_L\| = 1$	$\bar\alpha^L$	α_a^L
Basis:$2\zeta\,(23s,17p,12d,3f)$					
(core8)SD(2in4)SDT	199.5	443.7	312.6	356.3	−43.7
(core18)SD(2in4)SDT	198.2	427.5	302.3	344.0	−41.8
(core26)SD(2in4)SDT	197.8	427.6	302.3	344.1	−41.7
(core8)SDT(2in4)SDTQ	198.7	457.2	325.2	369.3	−44.0
ΔP_Q	−0.7	13.5	12.6	12.9	−0.3
Error in ΔP_Q	±0.4	±6.8	±6.3	±6.5	±0.2
ΔP_{core}	−1.6	−16.2	−10.3	−12.3	2.0
Error in ΔP_{core}	±0.35	±0.01	±0.05	±0.04	±0.04
Basis:$3\zeta\,(31s,22p,15d,7f,3g)$					
(core8)SD(2in4)SDT	198.4	528.4	381.9	430.7	−48.8
Basis:$4\zeta\,(35s,27p,17d,9f,7g,3h)$					
(core8)SD(2in4)SDT, P_{SD}	197.1	547.7	396.7	447.0	−50.3
Error in P_{SD}	±0.7	±9.6	±7.4	±8.1	±0.7
$P_{\text{final}} = P_{SDT} + \Delta P_{\text{core}} + \Delta P_Q$					
Final data, P_{final}	194.7	544.9	398.9	447.6	−48.7
Uncertainty(%)	1.3	1.8	2.5	2.1	3.5

TABLE VII. L- and J-resolved values of the quadrupole moments θ and the quadrupole polarizabilities α_2 of the $5s^2\,^1S$ and $5s5p\,^3P^o$ states of In$^+$ and Sr. For the $5s5p\,^3P^o_{1,2}$ states the scalar quadrupole polarizabilities are given.

	State	θ^L	θ^J
In$^+$	$5s5p\,^3P^o$	4.36	4.64
Sr	$5s5p\,^3P^o$	15.56, 15.52 [21]	15.76, 15.6 [22]
		α_2^L	α_2^J
In$^+$	$5s^2\,^1S$	127	129
Sr	$5s^2\,^1S$	4688, 4640 [17]	4608, 4545 [20]
In$^+$	$5s5p\,^3P^o$	145	1425 ($^3P^o_0$)
			1678 ($^3P^o_1$)
			−859.3 ($^3P^o_2$)
Sr	$5s5p\,^3P^o$	6756, 6949 [17]	9.75×10^4 ($^3P^o_0$)
			1.17×10^5 ($^3P^o_1$), 1.05×10^5 [20]
			$−7.39\times10^4$ ($^3P^o_2$)

(Sr) calculations by using the relativistic CC method. The results of θ and $\bar{\alpha}_2$ of the $5s5p\,^3P^o_1$ state is obtained by the relativistic CI calculations that are carried out at the (core10)SD(2in4)SD < 2 (In$^+$) and (core8)SD(2in4)SD < 2 (Sr) levels. All calculations are carried out with the $X = 3$ basis set. For the quadrupole moment of the $5s5p\,^3P^o$ state and the quadrupole polarizabilities of the $5s^2\,^1S_0$ state of In$^+$ and Sr, the relativistic CC and the scalar relativistic CI calculations produce much close results, which indicates the negligible spin-orbit coupling effect. In contrast, for the quadrupole polarizabilities of the $5s5p\,^3P^o$ state, there are great discrepancies between the L- and J-resolved values. The α_2^J values of the $5s5p\,^3P^o_J$ states vary greatly for the different J.

The available literature data are also given in Table VII for comparison. The quadrupole moment of the $5s5p\,^3P^o$ state of Sr has been calculated in earlier works, yielding 15.52 [21] and 15.6 [22]. All these data are in agreement with our data with a 1% error. Mitroy *et al.* have recommended the quadrupole polarizabilities of the $5s^2\,^1S_0$ and $5s5p\,^3P^o$ states of Sr to be 4640 and 6949, respectively, by using the CICP method [17]. Their recommended data are consistent with our L-resolved data obtained by the scalar relativistic CI method. Porsev, *et al.*, have recently calculated the quadrupole polarizabilities of the $5s^2\,^1S_0$ and $5s5p\,^3P^o$ states of Sr by using the CI + all-order method with the random-phase approximation [20]. Their recommended values for the quadrupole polarizabilities of the $5s^2\,^1S_0$ and $5s5p\,^3P^o_1$ states of Sr are 4545 and 1.05×10^5, respectively, consistent with our J-resolved data obtained by the relativistic CC and CI calculations with errors being around 2% and 11%, respectively. From the above comparisons, we can see that our results of θ and α_2 for the $5s^2\,^1S_0$ and $5s5p\,^3P^o_{0,1,2}$ states of In$^+$ and Sr have good accuracy and therefore can be used for estimation of the energy shifts of the related optical transitions.

C. Blackbody-radiation shift

Finally, our results for the dipole polarizabilities, dipole hyperpolarizabilities, and quadrupole polarizabilities are used to estimate the BBR shift in the clock transition frequency of

In$^+$ and Sr. The BBR shift can be written in the form [12,13]

$$\delta E_{\text{BBR}} = -\tfrac{1}{2}\Delta\alpha\langle E_{E1}^2\rangle - \tfrac{1}{24}\Delta\gamma\langle E_{E1}^2\rangle^2 - \tfrac{1}{2}\Delta\alpha_2\langle E_{E2}^2\rangle, \quad (9)$$

where $\langle E_{E1}^2\rangle$ and $\langle E_{E2}^2\rangle$ are the averaged electric fields induced by the electric dipole $E1$ and the electric quadrupole $E2$ and they are, respectively,

$$\langle E_{E1}^2\rangle = \frac{4\pi^3\alpha_{\text{fs}}^3}{15}\left(\frac{k_B T}{E_h}\right)^4 \quad (10)$$

and

$$\langle E_{E2}^2\rangle = \frac{8\pi^5\alpha_{\text{fs}}^5}{189}\left(\frac{k_B T}{E_h}\right)^6. \quad (11)$$

In the above, α_{fs} is the fine structure constant, $k_B T/E_h \approx 10^{-9}$, for the temperature $T = 300$ K, k_B is the Boltzmann constant, E_h is the Hartree energy, and $\Delta\alpha$, $\Delta\alpha_2$, and $\Delta\gamma$, expressed in atomic units, are, respectively, the differences of the dipole polarizability, quadrupole polarizability, and dipole hyperpolarizability between the $5s^2\,^1S_0$ and the $5s5p\,^3P^o_0$ states of In$^+$ and Sr. In Eq. (9) we have neglected the dynamic fractional correction to the total shift [12] and assume that the contribution of the hyperpolarizability to the BBR shift can be approximated by the ac-Stark shift $\langle E_{E1}^2\rangle^2$ for a given electric field. Using our relativistic CC results shown in Tables I, II, and VII for the $5s^2\,^1S_0$ and $5s5p\,^3P^o_0$ states of In$^+$, the BBR shifts due to α, α_2, and γ are determined to be 0.017, 8.33×10^{-10}, and 1.93×10^{-17} Hz, respectively, for the In$^+$ clock transition frequency; and using our relativistic CC results shown in Tables IV, V, and VII for the $5s^2\,^1S_0$ and $5s5p\,^3P^o_0$ states of Sr, the BBR shifts due to α, α_2, and γ are determined to be 2.09, 5.82×10^{-8}, and 1.69×10^{-15} Hz, respectively, for the Sr clock transition frequency.

V. CONCLUSION

In summary, we have calculated the values of α, γ, θ, and α_2 of the $5s^2\,^1S$ and $5s5p\,^3P^o$ states of In$^+$ and Sr by using the finite-field method. A satisfactory accuracy of the polarizabilities is achieved through convergence studies of the basis sets and sufficient inclusion of the electron correlations. In addition to the dipole polarizabilities, the

BBR shifts of the clock transition $5s^2\,^1S_0$-$5s5p\,^3P_0^o$ due to the quadrupole polarizabilities and dipole hyperpolarizabilities are also evaluated, being 8.33×10^{-10} and 1.93×10^{-17} Hz, respectively, for In$^+$ and 5.82×10^{-8} and 1.69×10^{-15} Hz, respectively, for Sr. The BBR shifts due to the quadrupole polarizabilities and dipole hyperpolarizabilities are far less than that due to the dipole polarizabilities; hence, they can be safely omitted for the quoted 10^{-18} uncertainty of the optical frequency standard of In$^+$ and Sr.

The finite-field method can also be applied with similar accuracy to the calculations of the polarizabilities of atomic cores (see the Appendix for α, γ, and α_2 of In^{3+} and Sr^{2+}). It will be useful to employ the finite-field method to perform a fast evaluation of required properties, especially when high-precision experimental studies and sophistical sum-over-state calculations are not available or all available results are not in complete agreement. It is noteworthy to mention that the errors of the finite-field calculations need to be examined carefully and minimized for such applications, which requires a detailed knowledge about the rate of convergence of basis set and electron correlations for a property of interest.

We have investigated the influences of the basis set and the level of electron correlations on the computed properties in the finite-field calculations. For the case of In$^+$, the convergence for α and γ can be reached when the basis set is increased up to $X = 4$ and the correlated outer-core shells includes at least the $4s$, $4p$, and $4d$ shells. In the relativistic CC calculations the dominant correction is from ΔP_T, and thus a more accurate evaluation of the contribution of the triple excitation is needed for higher accuracy. For example, the relativistic CCSDT calculation with the $X = 4$ basis set may give more accurate results, although such a study is prohibited at this moment

TABLE VIII. The dipole polarizability α^J, hyperpolarizability γ^J, and quadrupole polarizability α_2^J for the ground states of In^{3+} and Sr^{2+} obtained by the relativistic CC calculations.

	α^J	γ^J	α_2^J
	In^{3+}		
Basis:$2\xi(23s17p13d4f)$			
(core10)SD	3.186	24.679	
Basis:$3\xi(30s23p17d5f3g)$			
(core10)SD	3.228	28.110	8.52
(core18)SD	3.2882	27.036	
(core28)SD	3.2879	25.413	
(core10)SDT	3.242	28.556	
ΔP_T	0.014	0.446	
Error in ΔP_T	±0.007	±0.223	
ΔP_{core}	0.060	−2.697	
Error in ΔP_{core}	±0.0003	±1.623	
Basis:$4\xi(35s29p20d7f5g3h)$			
(core8)SD, P_{SD}	3.271	28.320	
Error in P_{SD}	±0.022	±0.211	
	$P_{\text{final}} = P_{SD} + \Delta P_{\text{core}} + \Delta P_T$		
Final data, P_{final}	3.345	26.063	
Uncertainity(%)	0.87	6.38	
Coupled HF data [37]	3.22		8.386
	Sr^{2+}		
Basis:$2\xi(23s17p13d4f)$			
(core8)SD	5.810		
Basis:$3\xi(30s23p17d5f3g)$			
(core8)SD	5.831	63.993	17.18
(core18)SD	5.797	60.629	
(core26)SD	5.820	61.439	
(core8)SDT	5.839	64.626	
ΔP_T	0.008	0.633	
Error in ΔP_T	±0.004	±0.317	
ΔP_{core}	−0.011	−2.555	
Error in ΔP_{core}	±0.023	±0.81	
Basis:$4\xi(35s29p20d7f5g3h)$			
(core8)SD < 10, P_{SD}	5.849	64.556	
Error in P_{SD}	±0.009	±0.282	
	$P_{\text{final}} = P_{SD} + \Delta P_{\text{core}} + \Delta P_T$		
Final data, P_{final}	5.846	62.635	
Uncertainty(%)	0.42	1.46	
coupled HF data [37]	5.813		17.15

given the present computing resources. For the case of Sr, the convergence of α and γ are strongly dependent on the quality of the basis set because a neutral atom has more diffused electron density in an external field than a positive charged ion. In this case, the predominant factor will be the expansion and optimization of the basis sets beyond $X = 4$.

Some general trends about the sole effect of the spin-orbit coupling have been found through comparative studies by using the fully and scalar relativistic approaches. The fractional difference between the L- and J-resolved values of α of the $5s5p\,^3P^o$ state is about 8% for In$^+$, but only 2% for Sr, implying that the effect of the spin-orbit coupling on α of In$^+$ is stronger than that for Sr.

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APPENDIX

In Table VIII, we present the α^J and γ^J values for the ground states of In^{3+} and Sr^{2+} by the relativistic CC calculations. The obtained α^J and γ^J values have reached the convergence with the increasing basis sets when $X = 3\zeta$.

The errors in P_{SD} of α^J and γ^J are less than 1%. The ΔP_T corrections to α^J and γ^J are also less than 1%. The largest corrections to α^J and γ^J come from ΔP_{core}. The changes of the α^J and γ^J values between the (core10)SD and (core18)SD calculations for In^{3+} and the (core8)SD and (core18)SD calculations for Sr^{2+} are substantial, whereas the changes induced by inclusion of more core shells are very small, as shown by the (core28)SD calculation for both In^{3+} and Sr^{2+}. This means that the obtained α^J and γ^J values have reached convergence when the $4s$, $4p$, and $4d$ core shells are correlated for In^{3+} and the $3d$, $4s$, and $4p$ core shells are correlated for Sr^{2+}. We also present the α_2^J values for the ground states of In^{3+} and Sr^{2+}, as obtained by the relativistic CC calculations at the (core10)SD (In^{3+}) and (core8)SD (Sr^{2+}) levels. Our α^J and α_2^J data are compared with the previously recommended data by using coupled Hartree-Fock (HF) theory [37], which shows good agreements. The accurate α^J, γ^J, and α_2^J data for the ground states of In^{3+} and Sr^{2+} can provide useful reference data for the CICP for the semiempirical calculation of the atomic structure. On the other hand, our results demonstrate the application of the finite-field calculation for the polarizabilities of the highly charged ions. The highly charged ions have very compact electronic distribution around nucleus generally. In this case, as Table VIII shows, the convergence of the obtained polarizability values with the increasing basis sets is excellent, and the contribution of the triple excitation is also small. The primary factor that influences the accuracy of the obtained polarizability value is to tackle the electron correlation arising from the core shells sufficiently in the finite-field calculations.

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