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Polarizabilities of low-lying states of silver

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Assembly of ultracold polar molecules containing silver (Ag) from laser-cooled atoms requires knowledge of the dynamic polarizabilities of Ag at convenient laser wavelengths. We present calculations and analysis of the energies and electric-dipole dc and ac polarizabilities of the low-lying states of neutral Ag. Calculations of the properties of the $4d^{10}x$ states, where $x = 5s,\ 6s,\ 7s,\ 5p,\ 6p,\ 7p,\ 5d,\ 6d$, and $4f$, are performed using the linearized coupled cluster single-double method. The properties of the $4d^9 5s^2\ {}^2D_{5/2,3/2}$ states are obtained within the framework of configuration interaction with 11 and 17 electrons in the valence field. We analyze the different contributions to the polarizabilities and estimate the uncertainties of our predictions.

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I. INTRODUCTION

The transition-metal silver atom has recently begun to attract increased attention from theorists and experimentalists. The prospect of using the electric quadrupole $4d^{10}5s\ {}^2S_{1/2} - 4d^9 5s^2\ {}^2D_{5/2}$ transition as a transition in the optical lattice clock was studied in Ref. [1]. This very narrow transition was observed in Ref. [2] and the hyperfine transition frequencies in the 107 and 109 isotopes of Ag were measured using two-photon laser spectroscopy.

One of the interesting features of silver is its ability to form ultracold, highly polar diatomic molecules containing the silver atom (in its ground state) interacting with a noble gas [3–5], an alkali-metal, or an alkaline-earth-metal atom [6].

Ag-alkaline-earth-metal molecules were predicted to have exceptionally large dipole moments that exceeded those typically observed in alkali-metal dimers [6], motivating the use of Ag-based molecules for quantum simulations, ultracold chemistry, and fundamental physics. The possible sensitivity of the diatomic molecule AgPb to the electron electric dipole moment was suggested in a recent work [7]. The RaAg molecule was proposed to probe new physics beyond the standard model and search for the electron's electric dipole moment and scalar-pseudoscalar interaction [5]. Experimental efforts toward next-generation EDM searches with molecules containing Ag are underway [8].

To address questions in condensed-matter physics and quantum dynamics by achieving full quantum control over all degrees of freedom in a molecular gas, the potassium-silver molecule (KAg) was proposed for a study by the University of Chicago group [9]. Compared to other ultracold molecules, the electric dipolar interaction of KAg is expected to be an order of magnitude stronger [6], facilitating engineering and detecting many-body effects arising from interactions [9].

However, proposed experiments require the assembly of ultracold polar molecules containing silver from laser-cooled atoms, which requires knowledge of the dynamic polarizabilities of Ag at convenient laser wavelengths. To support the experimental efforts, we calculated the dc and ac polarizabilities at the 532 nm and 1064 nm wavelengths, convenient for laser trapping, for the relevant states of Ag and evaluated their uncertainties.

A specific feature of the Ag atom is the presence of low-lying states with the unfilled $4d$ shell, $4d^9 5s^2\ {}^2D_{3/2,5/2}$, along with the states belonging to the $4d^{10}x$ configuration (where $x \equiv 5, 6s; 5, 6p, 5d$, etc.), complicating the accurate prediction of the atomic properties of Ag.

To calculate the properties of the $4d^{10}x$ states, we consider Ag as an atomic system with a single valence electron above the core $[1s^2, 2s^2, \ldots, 4d^{10}]$. We need to accurately take into account the correlations between the valence and core electrons. We perform computations using the all-order linearized coupled cluster single-double (LCCSD) method. To evaluate the uncertainty, we also carry out the computations using many-body perturbation theory (MBPT) over the residual Coulomb interaction.

For calculating the properties of the $4d^9 5s^2\ {}^2D_{3/2,5/2}$ states, a single-electron approach is not applicable. In this case, we consider Ag as an atom with many valence electrons and apply the configuration-interaction (CI) method. 11- and 17-electron ($17e$) CI calculations are carried out, assuming that (i) $4d$ and (ii) $4d$ and $4p$ electrons are in the valence field. In the following, we describe the computations and discuss the results.

II. SINGLE-ELECTRON APPROACH

We consider Ag as a univalent atom with a core $[1s^2, 2s^2, \ldots, 4d^{10}]$ and a valence electron above it. The initial Dirac-Hartree-Fock (DHF) self-consistency procedure included the Breit interaction and was performed for the core electrons. Then, the 5–$7s$, 5–$7p$, $5d$, and $4f$ orbitals were constructed in the frozen core potential. The remaining virtual orbitals were formed using a recurrent procedure described in Refs. [10,11] on a nonlinear grid with 500 points. The last point of the radial grid is at 60 a.u.

The lowest virtual orbitals can be constructed from the DHF orbitals. The large component of the radial Dirac bispinor, $f_{n'l'j'}$, is obtained from a function f_{nlj} constructed previously by multiplying it by $r^{l'-l}\sin(kr)$. Here, l' and l

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TABLE I. Energies of the low-lying states, calculated in the DHF (labeled as "DHF"), MBPT (labeled as "MBPT"), and all-order (labeled as "All") approximations are presented. For the ground state, we present its removal energy (in cm^{-1}) which can be compared to the ionization potential, IP(Ag$^+$) [14]. For the excited states, the excitation energies (in cm^{-1}) are displayed. The experimental values from the NIST database [14] are given in the column labeled "Expt." The difference between the experiment and theory is presented in the last three columns.

	DHF	MBPT	All	Expt. [14]	Expt. HFD	Expt. MBPT	Expt. All
$5s\ ^2S_{1/2}$	50337	61991	61295	61106	18%	−1%	−0.3%
$6s\ ^2S_{1/2}$	33228	43490	42885	42556	22%	−2%	−0.8%
$5d\ ^2D_{3/2}$	38354	49664	48946	48744	21%	−2%	−0.4%
$5d\ ^2D_{5/2}$	38369	49685	48965	48764	21%	−2%	−0.4%
$7s\ ^2S_{1/2}$	41684	52848	52126	51887	20%	−2%	−0.5%
$6d\ ^2D_{3/2}$	43778	55261	54566	54203	19%	−2%	−0.7%
$6d\ ^2D_{5/2}$	43788	55273	54578	54214	19%	−2%	−0.7%
$5p\ ^2P_{1/2}$	23628	30550	29809	29552	20%	−3%	−0.9%
$5p\ ^2P_{3/2}$	24202	31512	30728	30473	21%	−3%	−0.8%
$6p\ ^2P_{1/2}$	38557	49281	48594	48297	20%	−2%	−0.6%
$6p\ ^2P_{3/2}$	38722	49496	48802	48501	20%	−2%	−0.6%
$7p\ ^2P_{1/2}$	43830	55187	54488	54041	19%	−2%	−0.8%
$7p\ ^2P_{3/2}$	43887	55289	54593	54121	19%	−2%	−0.9%
$4f\ ^2F_{5/2}$	44000	55433	54737	54205	19%	−2%	−1.0%
$4f\ ^2F_{7/2}$	44088	55489	54793	54205	19%	−2%	−1.1%

are the orbital quantum numbers of the new and old orbitals ($l' \geqslant l$) and the coefficient k is determined by the properties of the radial grid. The small component $g_{n'l'j'}$ is found from the kinetic balance condition:

$$g_{n'l'j'} = \frac{\boldsymbol{\sigma}\mathbf{p}}{2mc} f_{n'l'j'},$$

where $\boldsymbol{\sigma}$ are the Pauli matrices, $\mathbf{p}$ and m are the electron momentum and mass, and c is the speed of light. The newly constructed functions are then orthonormalized to the functions of the same symmetry. The basis set included a total of six partial waves ($l_{\max} = 5$) and orbitals with a principal quantum number n up to 35.

In our approach, the wave functions and energy levels of the valence electrons were found by solving the relativistic equation [12],

$$H(E_n)|n\rangle = E_n|n\rangle, \tag{1}$$

where the effective Hamiltonian is defined as

$$H(E) = H_{\rm FC} + \Sigma(E). \tag{2}$$

Here $H_{\rm FC}$ is the Hamiltonian in the frozen-core approximation and the energy-dependent operator $\Sigma(E)$, accounting for the virtual excitations of the core electrons, was constructed in two ways: using (i) the second-order MBPT over the residual Coulomb interaction [12] and (ii) the linearized coupled cluster single-double (all-order) method [13]. In the following, we refer to these approaches as MBPT and all-order methods. The difference between the results obtained by these two methods allows us to estimate the uncertainty of our calculation.

A. Energy levels

We started by calculating the low-lying energy levels. The results are presented in Table I. The lowest-order DHF contribution to the energies is labeled "DHF." The results obtained in the framework of the MBPT and all-order methods are given in the rows labeled "MBPT" and "All," respectively. For the ground state, we present its removal energy, which can be compared to the ionization potential IP(Ag$^+$) [14]. For the excited states, the excitation energies are displayed. The experimental values from the NIST database [14] are given in the column labeled "Expt." The difference between the experimental and theoretical "DHF," "MBPT," and "All" values is presented in the last three columns. As follows from the table, the difference between the experimental energies and those obtained in the framework of the all-order method is overall better than 1%. The remaining difference can be attributed to a contribution of triple excitations, quantum electrodynamical corrections, and corrections from the higher partial waves.

B. Polarizabilities

We find the static and dynamic electric dipole ($E1$) polarizabilities for the lowest-lying even- and odd-parity states of Ag at the specific wavelengths 532 nm and 1064 nm. The expression for the dynamic $E1$ polarizability at the frequency ω of the state $|0\rangle \equiv |JM\rangle$ (where J is the total angular momentum and M its projection) can be written (in a.u.) as

$$\alpha(\omega) = \sum_n \langle 0|d_z|n\rangle\, \langle n|d_z|0\rangle \times \left[\frac{1}{E_n - E_0 + \omega} + \frac{1}{E_n - E_0 - \omega}\right], \tag{3}$$

where $\mathbf{d}$ is an electric dipole moment operator and E_0 and E_n are the energies of the initial and intermediate states, respectively.

Instead of direct summation over intermediate states, we use the Sternheimer [15] or Dalgarno-Lewis [16] method based on solving an inhomogeneous equation. Assuming that our basis set is numerically complete and the closure relation

$\sum_n |n\rangle\langle n| = 1$ is satisfied, we have, using Eq. (1),

$$|\Phi_\pm\rangle \equiv \sum_n \frac{1}{E_n - E_0 \pm \omega} |n\rangle\langle n|d_z|0\rangle$$
$$= \frac{1}{H - E_0 \pm \omega} d_z|0\rangle. \tag{4}$$

Now, having found $|\Phi_\pm\rangle$ from the inhomogeneous differential equations,

$$(H - E_0 \pm \omega)\, |\Phi_\pm\rangle = d_z\, |0\rangle, \tag{5}$$

we arrive at the simple expression for the polarizability:

$$\alpha(\omega) = \langle 0|d_z|\Phi_+\rangle + \langle 0|d_z|\Phi_-\rangle. \tag{6}$$

We note that this approach allows us to implicitly sum over *all* intermediate states, including the continuum.

Disregarding the vector polarizability, we can present the expression for $\alpha(\omega)$ as the sum of the scalar and tensor parts,

$$\alpha = \alpha_0 + \alpha_2 \frac{3M^2 - J(J+1)}{J(2J-1)}. \tag{7}$$

The explicit expressions for α_0 and α_2 are given elsewhere (see, e.g., Ref. [17]).

We consider Ag as an atom with one valence electron above the closed core. Both the valence and core electrons can be excited and contribute to the polarizability. Accordingly, the polarizability can be divided into two parts,

$$\alpha \equiv \alpha_v + \alpha_c,$$

where α_v and α_c are the valence and core contributions.

Both the valence and core parts contribute to the scalar polarizability, α_0. Only the valence part gives the contribution to the tensor polarizability α_2.

To find α_v we apply the method of solving the inhomogeneous equation, described above. The core contribution is noticeably smaller than α_v and we calculate it in the single-electron approximation using a sum-over-state approach. The single-electron matrix elements (MEs) of the electric dipole operator include the random-phase approximation (RPA) corrections. Note that, in calculating α_c, a core electron can be excited to the occupied valence state. The Pauli principle forbids this. We take this into account by subtracting this contribution from α_c.

To determine uncertainties of the polarizabilities, we calculated them in three ways. The first two are the MBPT and all-order methods, where we include only RPA corrections to the electric dipole operator. The third and most complete calculation additionally includes the smaller corrections to the operator **d** beyond RPA, such as the core-Brueckner, structural radiation, and normalization corrections (see Refs. [12,18] for details). We designate this approximation as all-order + AC, where the abbreviation “AC” means all corrections.

The results obtained in these approximations for the scalar parts of the polarizabilities are presented in Table II. In most cases, there are several low-lying intermediate states [see Eq. (3)] that give a dominant contribution to the polarizability. The final values for such polarizabilities are obtained by replacing theoretical energies with experimental ones in the dominant contributions. The only exclusions are the dynamic polarizabilities of the $6p\ ^2P_{1/2,3/2}$ states, for which the contribution of high-lying states is substantial. For these polarizabilities, we did not make such a replacement.

TABLE II. dc and ac ($\lambda = 532$ and 1064 nm) scalar polarizabilities α_0 (in a.u.) of the low-lying states, calculated in the MBPT, all-order (labeled as “All”), and all-order+AC (labeled as “All+AC”) approximations, are presented. The final (recommended) values are given in the column labeled “Final.” The uncertainties are given in parentheses.

		MBPT	All	All+AC	Final
$5s\ ^2S_{1/2}$	Static	48.3	50.2	49.1	49.5(1.2)
	532 nm	70.9	75.8	74.0	75.3(3.3)
	1064 nm	52.3	54.6	53.4	53.8(1.4)
$6s\ ^2S_{1/2}$	Static	1768	1822	1816	1805(47)
	532 nm	−111	−105	−106	−108(5)
	1064 nm	−1579	−1525	−1514	−1533(64)
$5d\ ^2D_{3/2}$	Static	−17540	−19628	−19556	−13600(2000)
	532 nm	−1210	−1124	−1109	−935(100)
	1064 nm	−921	−926	−921	−795(65)
$5d\ ^2D_{5/2}$	Static	−30472	−35312	−35186	−21100(4700)
	532 nm	583	673	662	770(80)
	1064 nm	−1001	−1006	−1002	−853(75)
$5p\ ^2P_{1/2}$	Static	142	141	139	139(3)
	532 nm	2310	2163	2132	1840(180)
	1064 nm	219	214	212	213(7)
$5p\ ^2P_{3/2}$	Static	167	165	163	103(18)
	532 nm	−1257	−1412	−1392	−1540(135)
	1064 nm	292	280	277	279(16)
$6p\ ^2P_{1/2}$	Static	28025	30262	30158	24035(2130)
	532 nm	−765	−743	−742	−740(25)
	1064 nm	−127	−101	−100	−100
$6p\ ^2P_{3/2}$	Static	56178	64363	64141	40400(8000)
	532 nm	−463	−464	−464	−465
	1064 nm	39	48	50	50

To assign uncertainties to the polarizabilities, we need to take into account the uncertainties of the valence and core parts, α_v and α_c.

The former were determined for most polarizabilities based on the difference between the MBPT and all-order + AC results. In two cases, the uncertainties were determined differently. As seen from Table II, the scalar polarizabilities of the $5d\ ^2D_{3/2,5/2}$ states calculated at $\lambda = 1064$ nm are very insensitive to the high-order corrections to the wave functions and corrections to the electric dipole operator. However, comparing the final and all-order + AC results, we see that they are sensitive to the replacement of the theoretical energies with the experimental ones. In these particular cases, the uncertainty was determined as half of the difference between the final and all-order + AC values.

Another source of uncertainty is the core polarizability. They were calculated in the single-electron approximation. This method is not very accurate and we assume that the uncertainty of α_c is about 10%. The core part of the polarizability is rather insensitive to the frequency and is virtually the same for the static and dynamic polarizabilities. We find it to be $\alpha_c = 8.8(0.9)$ a.u. for the even and $6p\ ^2P_J$ states. For the $5p\ ^2P_J$ states, $\alpha_c = 8.4(0.9)$ a.u.

TABLE III. dc and ac tensor polarizabilities α_2 (in a.u.) of the low-lying states, calculated in the MBPT, all-order (labeled "All"), and all-order+AC (labeled "All+AC") approximations, are presented. The final (recommended) values are given in the column labeled "Final." The uncertainties are given in parentheses.

		MBPT	All	All+AC	Final
$5d\ ^2D_{3/2}$	Static	8140	8499	8468	7650(330)
	532 nm	1290	1230	1213	1073(77)
	1064 nm	203	205	205	175(15)
$5d\ ^2D_{5/2}$	Static	31755	36584	36457	22420(4700)
	532 nm	−709	−800	−788	−885(80)
	1064 nm	341	343	342	291(26)
$5p\ ^2P_{3/2}$	Static	−58	−55	−55	−43(5)
	532 nm	164	191	188	204(15)
	1064 nm	−174	−139	−137	−140(13)
$6p\ ^2P_{3/2}$	Static	−5725	−6396	−6396	−4420(650)
	532 nm	39	38	38	38
	1064 nm	−106	−112	−111	−111

For the dc and ac polarizabilities of the ground state, the uncertainties of α_v and α_c are comparable. Our final value for the static scalar polarizability of the ground state $\alpha_0(5s\ ^2S_{1/2}) = 49.5(1.2)$ a.u. is in good agreement with the recommended value 55(8) a.u. [19] obtained by compiling theoretical and experimental results. For all other states, the uncertainty of α_v gives a dominant contribution to the uncertainty budget.

Calculating the static scalar and tensor polarizabilities of the $4d^{10}5p\ ^2P_{3/2}$ state takes some care. The even state $4d^95s^2\ ^2D_{5/2}$ is separated from $4d^{10}5p\ ^2P_{3/2}$ by the small energy interval of 230 cm^{-1} and can contribute to the polarizability of $^2P_{3/2}$. The properties of states with the unfilled $4d$ shell cannot be studied in the framework of a single-electron approach. To do that, we apply the CI method. We will discuss in detail the calculation performed within the framework of the CI method in Sec. III. Here we mention only the main results. Using the CI method, we obtain $|\langle 4d^95s^2\ ^2D_{5/2}||d||5p\ ^2P_{3/2}\rangle| = 0.61(9)$ a.u. and the transition rate $W(^2P_{3/2} \rightarrow {}^2D_{5/2}) \approx 2.3$ s that can be compared with the experimental value 1.6(6) s [20]. The experimental result is not very precise and does not allow us to accurately determine the theoretical uncertainty. Based on the difference of 30% between our result and the experimental central value, we estimate the uncertainty of ME at the level of 15%.

Using this ME and experimental energy levels, we can easily calculate the contribution of the $4d^95s^2\ ^2D_{5/2}$ state to the static scalar and tensor polarizabilities of the $5p\ ^2P_{3/2}$ state to be −60(18) a.u. and 12(4) a.u., respectively. These contributions were taken into account in the final values of α_0 and α_2 presented in Tables II and III. We note that, for all other dc and ac polarizabilities of odd states, the contribution of $4d^95s^2\ ^2D_{3/2,5/2}$ is small and is within the assigned uncertainties.

For $\alpha_0(6p\ ^2P_{1/2})$ at $\lambda = 1064$ nm and $\alpha_0(6p\ ^2P_{3/2})$ at $\lambda = 532$ and 1064 nm, the uncertainties are not assigned. This is due to large contributions from high-lying states that are difficult to control and large cancellations between different contributions. For example, when the two MEs in Eq. (6) are close to each other in absolute value but are of opposite sign, they substantially cancel each other out, significantly worsening the accuracy of the final value.

In Table III, we present the tensor polarizabilities for states with total angular momentum $J > 1/2$. The final values of the tensor polarizabilities and their uncertainties were determined in the same way as was done for the scalar polarizabilities. Since there is no core contribution to tensor polarizability, the valence part determines its value and uncertainty. The designations used in the table are the same as in Table II.

III. CONFIGURATION-INTERACTION METHOD

As seen in the NIST database [14], there are two low-lying states with the unfilled $4d$ shell ($4d^95s^2\ ^2D_{3/2,5/2}$) whose properties are of interest to experimentalists. These properties cannot be studied in the framework of a single-electron method, so the configuration-interaction method is used instead. Here, we utilize the pCI software package for computations [21]. We note that the method, including CI, can be applied not only in atomic physics, but also in quantum chemistry. Multireference single and double configuration-interaction (MRSDCI) methods [22,23] have been well established and widely applied.

We constructed the basis set differently from the single-electron approach. The initial self-consistent DHF procedure was performed for the $4d^95s^2$ configuration. Then, all electrons were frozen and an electron was moved from the $5s$ to $5p$ shell, to construct the $5p_{1/2,3/2}$ orbitals for the $4d^95s5p$ configuration. Other DHF orbitals were constructed for the $4d^{10}x$ configurations, where $x \equiv 4f, 5d, 6s, 6p, 7s, 7p$. The remaining virtual orbitals were formed using the same recurrent procedure as was described in Sec. II. In total, the basis set included five partial waves ($l_{\max} = 4$) and orbitals with the principal quantum number n up to 25.

A. Energies

We carried out CI calculations with 11 and 17 electrons in the valence field. In the first case, we include the $4d$ electrons in the valence field, doing the calculation within the framework of the 11-electron (11e) CI. In the second case, we include the $4d$ and $4p$ electrons in the valence field, performing the 17e CI calculation. For the 11e CI, the set of configurations was constructed by including single and double excitations from the main configurations, $4d^{10}(5s, 6s, 7s)$ and $4d^9(5s^2, 5p^2)$ for the even-parity states and $4d^{10}(5p, 6p, 7p)$ and $4d^9(5s5p, 5s6p)$ for the odd-parity states, to the shells up to $12s$, $12p$, $12d$, $12f$ (we designate it as [$12spdf$]). For the 17e CI, the main configurations remained the same, but single and double excitations were also allowed from the $4p$ shell.

Since our goal is to calculate the polarizabilities of the $4d^95s^2\ ^2D_{5/2,3/2}$ states, our main focus is the odd-parity states that can contribute a lot to these polarizabilities. From general considerations, we can expect a large contribution from the states belonging to the configuration $4d^95s5p$ because there is a single-electron electric-dipole $5p - 5s$ transition between these configurations. Furthermore, strong electric-dipole transitions can be expected from $^2D_{5/2,3/2}$ to odd states with the same total spin $S = 1/2$. As seen in the NIST database [14],

TABLE IV. Energies (in cm^{-1}) of the even- and odd-parity levels calculated in the framework of the $11e$ and $17e$ CI methods with excitations to $[12spdf]$ and the $11e$ CI method with excitations to $[20s19pdfg]$ are presented. The excitation energies are counted from the $4d^95s^2\ ^2D_{5/2}$ state. The experimental values from the NIST database [14] are given in the last column.

	$[12spdf]$		$[20s19pdfg]$	
	$11e$ CI	$17e$ CI	$11e$ CI	Experiment
$4d^95s^2\ ^2D_{5/2}$	0	0	0	0
$4d^95s^2\ ^2D_{3/2}$	4325	4450	4368	4472
$4d^{10}5p\ ^2P_{3/2}$	394	2520	−754	230
$4d^95s5p\ ^2P_{3/2}$	42067	42664	44680	41942
$4d^95s5p\ ^2F_{7/2}$	42393	42937	44900	42092
$4d^95s5p\ ^2D_{5/2}$	43950	44566	46156	43285
$4d^95s5p\ ^2P_{1/2}$	46260	47008	48976	46162
$4d^95s5p\ ^2F_{5/2}$	46838	47517	49345	46568
$4d^95s5p\ ^2D_{3/2}$	48293	49038	50527	47700

TABLE V. Static and dynamic scalar (α_0) and tensor (α_2) polarizabilities (in a.u.) of the $4d^95s^2\ ^2D_{5/2,3/2}$ states, calculated in the framework of the CI method, are presented. The final (recommended) values are given in the column labeled "Final."

			$[12spdf]$		$[20s19pdfg]$	
State	Polariz.		$11e$ CI	$17e$ CI	$11e$ CI	Final
$^2D_{5/2}$	α_0	Static	93	95	84	95
		532 nm	65	65	58	65
		1064 nm	56	56	49	56
	α_2	Static	−40	−41	−34	−41
		532 nm	−0.8	−2.1	−0.7	−2
		1064 nm	−1.0	−0.6	−1.0	−1
$^2D_{3/2}$	α_0	Static	53	53	46	53
		532 nm	62	65	59	65
		1064 nm	57	56	50	56
	α_2	Static	0.6	1.5	2.0	1.5
		532 nm	−0.07	−0.9	10	−1
		1064 nm	−1.2	−0.8	6	−1

there are such odd states, but they lie very high (above the ionization limit), making their accurate calculation particularly difficult.

In Table IV, we present the energies of the $4d^95s^2\ ^2D_J$ states and the odd states, giving a large contribution to the $4d^95s^2\ ^2D_J$ polarizabilities obtained in the framework of the $11e$ and $17e$ CI methods. To test the sensitivity of these energies to the method of constructing the basis set and size of the CI space, we performed another CI calculation. We used the basis set constructed in V^{N-1} approximation (which we applied in the single-electron approach and described in Sec. II) and allowed single, double, and some triple excitations to $[20s19pdfg]$. In this way, the CI space was substantially extended. These results are labeled "$[20s19pdfg]11e$ CI" in Table IV.

For calculating polarizabilities, we need to have the correct energy difference between the $4d^95s^2\ ^2D_J$ state and an odd-parity state. To follow it, the excitation energies, presented in Table IV, are counted from the $4d^95s^2\ ^2D_{5/2}$ state. Comparing the theoretical and experimental results, we see that the largest difference does not exceed 3% for the high-lying states. Such accuracy is sufficient for our purposes.

B. Polarizabilities

To calculate the polarizabilities of the $4d^95s^2\ ^2D_{5/2,3/2}$ states, we again used the method of solution of the inhomogeneous equation described in Sec. II B. The results of the calculation of the static and dynamic scalar and tensor polarizabilities of the $4d^95s^2\ ^2D_{5/2,3/2}$ states are presented in Table V. The final (recommended) values are given in the column labeled "Final."

As seen in Table V, the values of the scalar polarizabilities α_0 obtained within the framework of $11e$ and $17e$ CI are practically the same. This means that they are insensitive to the addition of the $4p$ electrons to the valence field. Tensor polarizabilities are small in all cases except static $\alpha_2(^2D_{5/2})$. Its relatively large value is determined by the contribution of the intermediate state $4d^{10}5p\ ^2P_{3/2}$ separated from the $^2D_{5/2}$ state by a small energy interval of 230 cm^{-1}. We consider the results obtained within the framework of the $17e$ CI as final.

Our static scalar polarizability $\alpha_0(^2D_{5/2}) = 95$ a.u. differs by two times from the value 47(2) a.u. obtained in Ref. [1]. As mentioned in Ref. [1], the summation over intermediate states in Eq. (3) is strongly dominated by the states of the $4d^95s5p$ configuration. This is true for all the cases considered, except for the static scalar and tensor polarizabilities of the $^2D_{5/2}$ state. Due to the small energy difference between the $^2D_{5/2}$ and $4d^{10}5p\ ^2P_{3/2}$ states, the latter gives a contribution of 40% to $\alpha_0(^2D_{5/2})$. If this contribution was missed in Ref. [1], it could explain this discrepancy.

To correctly account for the contribution of the intermediate state $4d^{10}5p\ ^2P_{3/2}$ in Eq. (3), we used the experimental energy difference $E(4d^{10}5p\ ^2P_{3/2}) - E(^2D_{5/2})$. As seen from Table IV, there is good agreement between the theoretical and experimental energies for the high-lying states of the $4d^95s5p$ configuration. Replacing theoretical energies with experimental ones in contributions of these terms had virtually no effect on the values of polarizabilities.

We present in Table VI the dominant contributions of individual odd-parity states to the scalar static $^2D_{5/2}$ and $^2D_{3/2}$ polarizabilities calculated in the framework of the $17e$ CI method. These contributions are listed separately in the column labeled "α_0," with the corresponding absolute values of the reduced electric-dipole matrix elements given in the column labeled "D" (in a.u.). The experimental [14] transition energies are given in column ΔE (in cm^{-1}). The remaining contributions to the polarizabilities are given in rows labeled "Other."

We note that the contribution of the $4d^{10}5p\ ^2P_{3/2}$ state to the scalar static polarizability of the $^2D_{3/2}$ state is very small, in contrast to $\alpha_0(^2D_{5/2})$. This is because the energy difference $E(4d^{10}5p\ ^2P_{3/2}) - E(^2D_{5/2})$ is 18 times smaller than $E(4d^{10}5p\ ^2P_{3/2}) - E(^2D_{3/2})$, while the reduced matrix element $\langle ^2D_{5/2}||d||^2P_{3/2}\rangle$ is three times larger than $\langle ^2D_{3/2}||d||^2P_{3/2}\rangle$.

TABLE VI. Contributions of individual states to the static scalar polarizabilities $\alpha_0(^2D_{5/2})$ and $\alpha_0(^2D_{3/2})$ (in a.u.) are presented. The dominant contributions to the polarizabilities are listed separately in the column labeled "α_0" with the corresponding absolute values of electric-dipole reduced matrix elements given in the column labeled "D" (in a.u.). The experimental [14] transition energies are given in column ΔE (in cm^{-1}). The remaining contributions to the polarizabilities are given in rows labeled "Other."

State	Contribution	ΔE	D	α_0
$^2D_{5/2}$	$^2D_{5/2} - 4d^{10}5p\ ^2P_{3/2}$	230	0.6	40
	$^2D_{5/2} - 4d^9 5s5p\ ^2P_{3/2}$	41942	4.2	10
	$^2D_{5/2} - 4d^9 5s5p\ ^2F_{7/2}$	42092	6.0	21
	$^2D_{5/2} - 4d^9 5s5p\ ^2D_{5/2}$	43285	4.9	14
	Other			10
	Total			95
$^2D_{3/2}$	$^2D_{3/2} - 4d^9 5s5p\ ^2P_{1/2}$	46162	3.0	8
	$^2D_{3/2} - 4d^9 5s5p\ ^2F_{5/2}$	46568	5.1	22
	$^2D_{3/2} - 4d^9 5s5p\ ^2D_{3/2}$	47700	4.1	14
	Other			7
	Total			53

It is problematic to determine the exact values of the uncertainties of these polarizabilities. We can estimate the quality of the wave functions of the $4d^9 5s^2\ ^2D_{5/2,3/2}$ states by comparing their lifetimes $\tau(^2D_{5/2}) = 0.15$ s and $\tau(^2D_{3/2}) = 68$ µs found in this work with the experimental results, 0.2 s [24] and 40 µs [25], respectively. Taking into account that the uncertainties are not assigned to the experimental values, we can assume that they can be 100% or even more. Based on this, the agreement between the theory and experiment seems reasonable.

A comparison of the results for the polarizabilities obtained in the framework of $11e$ and $17e$ CI is presented in Table V. Here, we see that both the scalar and tensor polarizabilities are rather insensitive to the core-valence correlations. As follows from the comparison of the $11e$ [$12spdf$] and [$20s19spdfg$] CI calculations (see Table VI), the sensitivity of the polarizabilities to the valence-valence correlations is higher. Based on this difference, we estimate the uncertainties of the scalar polarizabilities and the static tensor $^2D_{5/2}$ polarizability at the level of 15–20%. Other tensor polarizabilities are small. This is due to large cancellations between the main contributions. We consider these values to be order-of-magnitude estimates.

IV. CONCLUSIONS

To conclude, we carried out calculations of the energies, $E1$ transition amplitudes, and static and dynamic polarizabilities of the low-lying states, including the states with the unfilled $4d$ shell $4d^9 5s5p\ ^2D_{5/2,3/2}$. To study the properties of the states belonging to the configuration $4d^{10}x$ (where $x \equiv 5, 6s; 5, 6p; 5d$), we used the single-electron approaches combining DHF with MBPT and the all-order method. By comparing the results obtained within the framework of these two methods, we assign uncertainties to the values obtained.

The properties of the $4d^9 5s5p\ ^2D_{5/2,3/2}$ states were studied within the framework of the $11e$ and $17e$ CI methods. We carried out analyses of the different contributions to the dc and ac $^2D_{5/2,3/2}$ polarizabilities and determined the odd-parity states that gave the main contribution. The electric-dipole transition amplitudes from these states to the $^2D_{5/2,3/2}$ states were determined and discussed.

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DATA AVAILABILITY

The data supporting this study's findings are available within the article.

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