PHYSICAL REVIEW A **88**, 052518 (2013)

Finite-field calculation of the polarizabilities and hyperpolarizabilities of Al^+

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(Received 25 September 2013; published 25 November 2013)

In this study, accurate static dipole polarizability and hyperpolarizability are calculated for Al^+ ground state $3s^2\,{}^1S_0$ and excited state $3s3p\,{}^3P_J$ with $J = 0,1,2$. The finite-field computations use energies obtained with the relativistic configuration interaction approach and the relativistic coupled-cluster approach. Excellent agreement with previously recommended values is found for the dipole polarizability of Al^+ ground state $3s^2\ {}^1S_0$ and excited state $3s3p\,{}^3P_0$ as well as the hyperpolarizability of the ground state $3s^2\ {}^1S_0$. The recommended values of the dipole polarizability of the Al^+ $3s3p\ {}^3P_1$ and ${}^3P_2$ and the hyperpolarizability of Al^+ $3s3p\,{}^3P_0$, ${}^3P_1$, and ${}^3P_2$ are also given. The impacts of the relativity and spin-orbit coupling are elucidated by analyzing the angular momentum dependence of the dipole polarizability and the hyperpolarizability, and comparing the fully and scalar relativistic calculated data. It is shown that the impact of the relativity and spin-orbit coupling are small for the dipole polarizability but become significant for the hyperpolarizability. Finally, the blackbody radiation shifts contributed by the dipole polarizability and hyperpolarizability, respectively, are evaluated for transitions of Al^+ $3s^2\ {}^1S_0$ to $3s3p\,{}^3P_J$ with $J = 0,1,2$.

DOI: 10.1103/PhysRevA.88.052518 PACS number(s): 31.15.ap, 31.15.aj, 32.10.Dk

I. INTRODUCTION

The polarizabilities and hyperpolarizabilities are very useful quantities in many areas of atomic and molecular physics. The recent advance in development of the atomic optical clock has elevated great interest in the atomic polarizabilities and hyperpolarizabilities. The dipole polarizability determines the first-order response of the trapped atom or ion under the external perturbation, such as the electric field generated by the electrodes of an ion trap or the probe optical field, which brings the energy shifts that are main contributions to the frequency uncertainty budget of the atomic optical clock [1–4]. The higher-order response of atoms or ions to the applied electric field also contributes to the energy shift of the optical frequency standards, being small but not necessarily negligible [5,6]. Increasing order gives more accurate estimates of the polarization energy shift and the associate uncertainty. There already are plenty of articles about the dipole polarizabilities of atoms and ions, most of which are about the ground state or monovalent system [7–14]. The angular moment resolved dipole polarizability of the divalence systems and the hyperpolarizability remain very scarce for the majority of atoms or ions.

One important application of the highly accurate data of polarizabilities is to estimate the energy shifts in an optical clock. As one of the highly accurate atomic clocks to date [15], the Al^+ optical clock, based on $3s^2\,{}^1S_0 \rightarrow 3s3p\,{}^3P_0$ transition, has attracted great interest in the study of the polarizability properties of Al^+ [16–18]. The coupling between the angular and spin momenta determines the multiple structure of the Al^+ $3s3p$ state, where in addition to ${}^3P_0$, there are two other energetically higher lying states, ${}^3P_1$ and ${}^3P_2$. The polarizabilities of the P state are dependent on the different J components; for example, Fleig has studied the group-13 atoms, which has shown that the $J = 1/2$ state differs from that of the $J = 3/2$ as it directly depends on the spatial distribution of the electron density and also the mixing of spin and spatial degrees of freedom [8].

The relation between the polarizabilities corresponding to different J components can be determined through basic vector algebra [3,12,19]. For the heavy elements, the spin splitting becomes very large and therefore the difference contributed by the spatial distribution of the electron density will become more pronounced. Such influence comes from the scalar relativity, the spin-orbit coupling, and their combination, causing the possible deviation from the relationship derived by the basic vector algebra. Furthermore, the dipole polarizability and the hyperpolarizability are probably of different sensibility to the relativity. Therefore, it is important to resolve the polarizabilities for all J components and their magnetic M_J components directly, where M_J is the projection onto the field axis, in order to understand the impacts of the relativity and the spin-orbit coupling on polarizabilities.

In the investigation of the dipole polarizability and hyperpolarizability, the finite-field (FF) method can provide reliable data if the field-dependent energies are calculated with high precision [20,21]. Recently, the FF method has been implemented in the relativistic configuration interaction (CI) and the coupled-cluster (CC) methods based on the four-component Dirac-Hatree-Fock calculation [7,8,11,17]. The fully relativistic calculation allows us to resolve electron states by total angular moment J, thus J-dependent properties can be obtained directly.

In the previous calculations, because the ${}^3P_0$ component is directly involved in the optional clock transition, most calculations are concentrated on this state; for example, Mitroy *et al.* and Kallay *et al.* have provided the dipole polarizability data of Al^+ $3s3p\,{}^3P_0$, while the components with $J = 1$ and 2 remain unavailable [16,17]. Safronova *et al.* have provided the dipole polarizability data of $nsnp\,{}^3P_0$ of B^+, Al^+, In^+, Tl^+, and Sr [18,22,23]. Cheng and Mitroy have done calculations on B^+ and Ga^+ [24,25]. The polarizability data for the other

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P_J states is scarce for long time. Cheng *et al.* have calculated the dipole polarizability of the $nsnp\ {}^3P_1$ state of Be, Mg, Ca, and Sr atoms [26].

In the present work, we investigate Al$^+$ in order to give the J-resolved dipole polarizability and hyperpolarizability by using the FF method. The field-dependent energies are obtained by using the relativistic CI calculation and the relativistic CC calculation. In addition to the dipole polarizability of $3s^{2}\,{}^1S_0$ and $3s3p\,{}^3P_0$ and the hyperpolarizability of $3s^2\,{}^1S_0$, which is in excellent consistence with the previously recommended values [16–18,27], we also give the recommended values of the dipole polarizability of $3s3p\,{}^3P_1$ and ${}^3P_2$ and the hyperpolarizability of $3s3p\,{}^3P_J$ with $J = 0,1,2$. The differences in the dipole polarizability and hyperpolarizability for the different components of the $3s3p\,{}^3P$ state are studied, including the directional dependence by resolving the property in the azimuth projection M_J substrates of the J state, i.e., the anisotropy component. The impact of the relativistic effect on the dipole polarizability and the hyperpolarizability are elucidated by analogizing the J dependence of such properties. The sole effect of the spin-orbit coupling on the polarizability and anisotropy components is determined by comparing the spin-dependent and the spin-free CI calculated data. Finally, the blackbody radiation shifts by contributions from the dipole polarizability and hyperpolarizability are evaluated, respectively, for the transitions of Al$^+$ $3s^{2}\,{}^1S_0$ to $3s3p\,{}^3P_J$ with $J = 0,1,2$.

II. COMPUTATIONAL METHOD

The change in energy of an atom or ion upon introduction of a static, homogeneous, axially symmetric field F_z is given by

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

where $\bar{\alpha}$ is the dipole polarizability and $\bar{\gamma}$ is the hyperpolarizability. We apply the field in the z direction, which allows us to retain a rotational axis, and therefore our symmetry choice is the double group C_{2v}^* in the Dirac-Hartree-Fock calculation and C_2^* in the relativistic CI and the relativistic CC calculations. The $\bar{\alpha}$ and $\bar{\gamma}$ are obtained by fitting $\Delta E_q(F_z)$ versus F_z with a fourth-order polynomial relationship. The field-dependent energies are calculated in an electric field range $F_z = [0,0.0045]$ a.u. with a 0.0005 a.u. interval. Arbitrarily, more than four sample points are taken for fitting in order to check and remove the dependence of the studied properties on sampling. The reliable finite-field procedure depends on precise energies, where we converge the energies to 10^{-10} hartree.

The field-dependent energy is calculated on the different levels of theory, i.e., the spin-free CI calculation (implemented by the LUCITA module in DIRAC package [28]), the spin-dependent CI calculation (implemented by the KRCI module of the DIRAC package), and the spin-dependent CC calculation (implemented by the MRCC suite [29]). The Dyall's Hamiltonian [30] is used in spin-free calculation and the spin-dependent calculations are based on the Dirac-Coulomb Hamiltonian. In contrast to the spin-free calculation, all J components of the ${}^3P(3s3p)$ state are obtained as unique eigensolutions in the spin-dependent calculation. The degeneracy ($2L + 1$ levels) in the spin-free case, wherein L is the orbital angular momentum quantum number, and the ($2J + 1$ levels) degeneracy in the spin-dependent cases are broken to be different M_L and M_J components upon the external perturbation, where M_L and M_J are the projections of L and J onto the field axis in the z direction. Therefore, the polarizabilities of ${}^3P$ are obtained for each M_L and M_J component. For the spin-dependent case, the dipolarizability for a specific state $|JM_J\rangle$ can be defined as [3,12,19,31]

$$\langle JM_J|\alpha_{zz}|JM_J\rangle = \alpha_J(M_J) = \bar{\alpha}^J + \alpha_a^J \frac{3M_J^2 - J(J+1)}{J(2J-1)}, \tag{2}$$

where the scalar $\bar{\alpha}^J$ and the tensor polarizability and α_a^J are formulated by

$$\begin{aligned} \bar{\alpha}^J &= \frac{1}{2J+1}\sum_{M_J}\alpha_{zz}(J,M_J), \\ \alpha_a^J &= \frac{5}{(J+1)(2J+1)(2J+3)} \\ &\quad \times \sum_{M_J}[3M_J^2 - J(J+1)]\alpha_{zz}(J,M_J). \end{aligned} \tag{3}$$

In the spin-free case, the scalar and tensor polarizabilities $\bar{\alpha}^L$ and α_a^L are also given by Eqs. (2) and (3) with J and M_J replaced by L and M_L. The relation between the polarizabilities for different M_J components can be given more explicitly as follows, for J or $L = 1$:

$$\begin{aligned} M_{L,J} = 0:&\ \ \alpha(0) = \bar{\alpha} - 2\alpha_a, \\ M_{L,J} = \pm 1:&\ \ \alpha(1) = \bar{\alpha} + \alpha_a, \end{aligned} \tag{4}$$

and for J or $L = 2$,

$$\begin{aligned} M_{L,J} = 0:&\ \ \alpha(0) = \bar{\alpha} - \alpha_a, \\ M_{L,J} = \pm 1:&\ \ \alpha(1) = \bar{\alpha} - \tfrac{1}{2}\alpha_a, \\ M_{L,J} = \pm 2:&\ \ \alpha(2) = \bar{\alpha} + \alpha_a. \end{aligned} \tag{5}$$

In the LS coupling approximation one finds [3,12,19]

$$\bar{\alpha}^J = \bar{\alpha}^L, \tag{6}$$

$$\begin{aligned} \alpha_a^J &= \alpha_a^L(-1)^{S+L+J+2}(2J+1)\begin{Bmatrix} S & L & J \\ 2 & J & L \end{Bmatrix} \\ &\quad \times \begin{pmatrix} J & 2 & J \\ -J & 0 & J \end{pmatrix}\begin{pmatrix} L & 2 & L \\ -L & 0 & L \end{pmatrix}. \end{aligned} \tag{7}$$

Equations (6) and (7) show the relations between the polarizabilities in the J and L representations of an energy level. For the Al$^+$ $3s3p\,{}^3P$ state, $L = 1$, $S = 1$, Eq. (7) can be rewritten as [3,19]

$$\alpha_a^J({}^3P_1) = -\alpha_a^J({}^3P_2)/2 = -\alpha_a^L/2. \tag{8}$$

The definitions of the scalar and tensor hyperpolarizability are the same as Eqs. (2)–(8) with α replaced by γ. For the ${}^1S_0$ and ${}^3P_0$ states the dipole polarizability and hyperpolarizability have only one component, whereas we remain using $\bar{\alpha}$ and $\bar{\gamma}$ in order to avoid verbose constructions.

The value of the studied properties is convergent with the basis sets of the progressively larger sizes in the CI and CC calculations. We choose the hierarchy of the uncontracted aug-cc-pCVXZ basis set with $X = 2$, 3, 4, and 5ζ [32], where two diffusion functions are added to each shell of the $X = 2$, 3, and 4 basis sets, and $2s3p1d1g$ are added to the $X = 5\zeta$ basis set.

TABLE I. Dipole polarizability α_{zz} (a.u.) of Al^+.

Level of excitation	$^1S_0$	$^3P_0$	$^3P_1$				$^3P_2$				
			$M_J = 0$	$M_J = 1$	$\bar{\alpha}^J$	α_a^J	$M_J = 0$	$M_J = 1$	$M_J = 2$	$\bar{\alpha}^J$	α_a^J
(a) Spin-dependent CI											
Basis: $2\zeta(16s,12p,5d)$											
S10(2in4)SD(<100 a.u.)	23.565	24.381	24.829	24.217	24.421	−0.204	24.126	24.314	24.878	24.502	0.376
S10(2in4)SDT(<1 a.u.)SD(<100 a.u.)	23.611	24.370	24.816	24.207	24.410	−0.203	24.117	24.304	24.865	24.491	0.374
Basis: $3\zeta(20s,14p,7d,5f)$											
S10(2in4)SD(<100 a.u.)	23.707	24.505	25.047	24.294	24.545	−0.251	24.155	24.390	25.097	24.626	0.471
S10(2in4)SD(<10 a.u.)	23.862	24.765	25.267	24.576	24.806	−0.230	24.459	24.673	25.317	24.888	0.429
S10(2in4)SDT(<1 a.u.)SD(<10 a.u.)	23.900	24.763	25.263	24.575	24.804	−0.229	24.459	24.672	25.313	24.886	0.427
Basis: $4\zeta(22s17p9d7f5g)$											
S10(2in4)SD(<100 a.u.)	23.784	24.231	24.891	23.967	24.275	−0.30	23.781	24.073	24.946	24.364	0.582
Basis: $5\zeta(23s16p10d8f5g3h)$											
S10(2in4)SD(<100 a.u.),P_{CISD}	23.742	24.177	24.835	23.906	24.216	−0.309	23.700	24.000	24.883	24.293	0.590
Error in P_{CISD}	±0.084	±0.108	±0.112	±0.122	±0.118	±0.018	±0.162	±0.146	±0.126	±0.141	±0.016
ΔP_T	0.038	−0.002	−0.004	−0.001	−0.002	0.001	0.000	−0.001	−0.004	−0.002	0.002
Error in ΔP_T	±0.076	±0.004	±0.008	±0.002	±0.004	±0.002	±0.000	±0.002	±0.008	±0.004	±0.004
$P = P_{\mathrm{CISD}} + \Delta P_T$											
Composite	23.780	24.175	24.831	23.905	24.214	−0.308	23.700	23.999	24.879	24.291	0.588
Error	±0.150	±0.112	±0.120	±0.124	±0.122	±0.020	±0.162	±0.148	±0.134	±0.145	±0.020
Uncertainty (%)	0.63	0.46	0.48	0.52	0.50	6.49	0.68	0.61	0.54	0.60	3.40
(b) Spin-dependent CC											
CCSD (<10000 a.u.)-2ζ	24.007	24.818		24.666			24.589	24.765	25.293	24.941	0.352
CCSDT (<1000 a.u.)-2ζ	23.876	24.768		24.633			24.572	24.732	25.200	24.887	0.313
CCSD (<10000 a.u.)-3ζ	24.164	24.977		24.770			24.637	24.869	25.565	25.101	0.464
CCSD (<10000 a.u.)-4ζ,P_{CCSD}	24.238	24.656		24.632			24.182	24.478	25.367	24.774	0.593
Error in P_{CCSD}	±0.148	±0.642		±0.276			±0.910	±0.782	±0.396	±0.653	±0.257
$\Delta P_{5\zeta}$[a]	−0.042	−0.054		−0.067			−0.081	−0.073	−0.063	−0.071	0.010
ΔP_T	−0.131	−0.050		−0.033			−0.017	−0.033	−0.093	−0.054	−0.039
Error in ΔP_T	±0.262	±0.100		±0.060			±0.034	±0.066	±0.186	±0.108	±0.078
$\mathrm{P} = P_{\mathrm{CCSD}} + \Delta P_T$											
Composite	24.065	24.552		24.532			24.084	24.372	25.211	24.650	0.564
Error	±0.410	±0.742		±0.342			±0.944	±0.848	±0.582	±0.760	±0.178
Uncertainty (%)	1.70	3.01		1.39			3.92	3.47	2.31	3.08	31.56
(c) Spin-free CI											
	^1S		^3P								
			$M_L = 0$		$M_L = 1$		$\bar{\alpha}^L$		α_a^L		
S10(2in4)SDT(all orbits)-3ζ	23.742		23.614		25.053		24.573		0.480		
S10(2in4)SDT(all orbits)-4ζ	23.816±0.074		23.092±0.52		24.880±0.170		24.280±0.293		0.600±0.293		
Ref. [16]	24.140	24.622									
Ref. [17]	24.137	24.614									
Ref. [18]	24.048	24.543									

[a] $\Delta P_{5\zeta}$ is the correction to the basis set enlarging from $X = 4\zeta$ to 5ζ obtained from CISD calculation.

The details of the basis sets are given in Tables I and II. The CI calculations are implemented in the general active space [33] and the details of the CI treatment are illustrated in Tables I and II, where "S10" means the single excitation is allowed from ten core electrons ($1s^2 2s^2 2p^6$), and "(2in4)SD" means the reference states are generated by two valence electrons distributing all possible ways in $3s3p$ orbits, allowing the single and double (SD) excitations to the virtual orbits with energy less than a given cutoff (for example, <100 a.u.).

The triple excitation into part of the virtual orbits (less than 1 a.u.) is considered for the small basis sets $X = 2\zeta$ and 3ζ within spin-dependent CI calculations in order to extract the correction of the triple excitation to polarizibilities. The higher level of electron correlation is considered within the spin-free CI calculation, which includes the single (S) excitation in the core shell, and the single, double, and triple (SDT) excitations from core and valence shells into all virtual orbits. In the spin-dependent CC calculations, the electron correlation of single and double (SD) excitations into virtual orbits with a cutoff 10 000 a.u. is considered within the basis set of $X = 2$, 3, and 4ζ. The triple excitation is considered for the small basis set $X = 2\zeta$ in order to extract the correction of the polarizabilities due to the triple excitation.

In order to present the accurate data of $\bar{\alpha}$ and $\bar{\gamma}$, we adopt the same composite scheme as suggested in Ref. [17], which is evaluated by

$$P = P_{\mathrm{SD}} + \Delta P_{\mathrm{T}}, \tag{9}$$

where P means the studied properties, $\Delta P_{\mathrm{T}} = P_{\mathrm{SDT}} - P_{\mathrm{SD}}$, and P_{SD} and P_{SDT} are the CI or CC calculated values with SD

TABLE II. Hyperpolarizability γ_{zz} (10^3 a.u.) of Al^+.

Level of excitation	$^1S_0$	$^3P_0$	$^3P_1$				$^3P_2$				
			$M_J = 0$	$M_J = 1$	$\bar{\gamma}^J$	γ_a^J	$M_J = 0$	$M_J = 1$	$M_J = 2$	$\bar{\gamma}^J$	γ_a^J
(a) Spin-dependent CI											
Basis: $2\zeta(16s,12p,5d)$											
S10(2in4)SD(<100 a.u.)	2.411	6.591	0.589	9.874	6.779	3.095	6.544	3.252	0.570	2.838	−2.473
S10(2in4)SDT(<1 a.u.)SD(<100 a.u.)	2.463	6.591	0.599	9.932	6.821	3.111	6.615	3.284	0.583	2.870	−2.495
Basis: $3\zeta(20s,14p,7d,5f)$											
S10(2in4)SD(<100 a.u.)	2.651	12.186	3.871	16.845	12.520	4.325	11.303	6.657	3.897	6.482	−2.905
S10(2in4)SD(<10 a.u.)	2.729	11.907	3.990	16.287	12.188	4.099	12.183	7.817	4.032	7.176	−3.410
S10(2in4)SDT(<1 a.u.)SD(<10 a.u.)	2.849	11.904	4.007	16.284	12.192	4.092	12.259	7.912	4.029	7.228	−3.461
Basis: $4\zeta(22s17p9d7f5g)$											
S10(2in4)SD(<100 a.u.)	2.290	12.779	3.548	18.074	13.232	4.842	9.825	4.551	3.586	5.219	−2.058
Basis: $5\zeta(23s16p10d8f5g3h)$											
S10(2in4)SD(<100 a.u.),P_{CISD}	2.505	13.537	3.314	19.173	13.887	5.286	8.610	3.074	3.536	4.366	−1.318
Error in P_{CISD}	±0.428	±1.516	±0.468	±2.200	±1.622	±0.578	±2.430	±2.954	±0.100	±1.706	±1.481
ΔP_T	0.120	−0.003	0.016	−0.003	0.004	−0.006	0.077	0.095	−0.003	0.052	0.047
Error in ΔP_T	±0.24	±0.006	±0.032	±0.006	±0.0008	±0.012	±0.154	±0.19	±0.006	±0.104	±0.095
$P = P_{\text{CISD}} + \Delta P_T$											
Composite	2.625	13.534	3.330	19.171	13.891	5.280	8.687	3.169	3.533	4.418	−1.365
Error	±0.648	±1.522	±0.50	±2.206	±1.63	±0.59	±2.584	±3.144	±0.106	±1.81	±1.576
Uncertainty (%)	25.45	11.24	15.01	11.5	11.73	11.17	29.75	99.21	3.00	40.96	115
(b) Spin-dependent CC											
CCSD(<10000 a.u.)-2ξ	2.513	6.105		9.802			7.141	3.967	0.637	3.270	−2.810
CCSDT(<1000 a.u.)-2ξ	2.523	6.473		9.245			7.330	3.636	0.743	3.218	−2.709
CCSD(<10000 a.u.)-3ξ	2.881	12.146		17.129			11.653	7.057	3.803	6.675	−3.173
CCSD(<10000 a.u.)-4ξ,P_{CCSD}	2.538	13.728		20.682			9.930	3.683	3.404	4.821	−1.944
Error in P_{CCSD}	±0.686	±3.165		±7.106			±3.447	[a]	±0.799	±3.707	
ΔP_T	0.010	0.735		−0.557			0.189	−0.330	0.107	−0.052	0.101
Error in ΔP_T	±0.020	±1.470		±1.147			±0.378	±0.660	±0.214	±0.104	±0.202
$P = P_{CCSD} + \Delta P_T$											
Composite	2.548	14.463		20.126			10.119	3.353	3.511	4.769	−1.843
Error	±0.786	±4.463		±8.253			±3.825		±1.013	±3.811	
Uncertainty (%)	27.70	32.04		41.01			37.80		28.85	79.91	

(c) Spin-free CI

	^1S	^3P			
		$M_L = 0$	$M_L = 1$	$\bar{\gamma}^L$	γ_a^L
S10(2in4)SDT(all orbits)-3ζ	2.760	19.697	3.905	9.169	−5.264
S10(2in4)SDT(all orbits)-4ζ	2.457±0.606	19.152±0.544	3.594±0.311	8.780±0.777	−5.186±0.293
Ref. [27]	2.368				

[a] Here, we fail to estimate the error of P_{CCSD} because of the anomalous value for $^3P_2$, $M_J = 2$ at the basis set of $X = 3\xi$.

and SDT excitation, respectively. Within the spin-dependent CI calculation the values of P_{SD} and ΔP_{T} are taken from the $X = 5\zeta$ and $X = 3\zeta$ basis sets, respectively. Within the spin-dependent CC calculation the values of P_{SD} and ΔP_{T} are taken from the $X = 4\zeta$ and $X = 2\zeta$ basis sets, respectively. The error of P_{SD} is computed by $2(P_{\text{SD}}|_{5\zeta} - P_{\text{SD}}|_{4\zeta})$ in the spin-dependent CI calculation and $2(P_{\text{SD}}|_{4\zeta} - P_{\text{SD}}|_{3\zeta})$ in the spin-dependent CC calculation. The error of ΔP_{T} is roughly estimated with twice itself in both spin-dependent CI and CC calculations. The composite value is determined by Eq. (3) with its error being the sum of errors of P_{SD} and ΔP_{T}. The uncertainty of the composite data is assessed by the error divided by the composite data.

III. RESULTS AND DISCUSSION

Consider the dipole polarizability first. Table I summarizes the dipole polarizabilities of the Al^+ ground state $3s^2\ ^1S_0$ and three lower-lying excited states $3s3p\,^3P_0$, $^3P_1$, and $^3P_2$, as obtained by the different levels of electron correlation calculations. The spin-dependent CI and CC calculations give the J-resolved polarizability data for each M_J component; then the scalar and tensor polarizabilities $\bar{\alpha}^J$ and α_a^J are obtained in terms of Eq. (3). The spin-free CI calculation gives the scalar relativistic data of $\bar{\alpha}$ for Al^+ $3s^{2}\,^1S_0$ and $3s3p\,^3P$ states and α_a for the Al^+ $3s3p\,^3P$ state.

For the Al^+ $3s^{2}\,^1S_0$ and $3s3p\,^3P_0$ states, there are already accurate dipole polarizability data available. Mitroy and co-workers have given the first reliable data, $\bar{\alpha} = 24.140$ a.u. for $3s^{2}\,^1S_0$ and 24.622 a.u. for $3s3p\,^3P_0$ [16]. Based on the large basis set up to $X = 5\zeta$ and the high-leveled treatment of the electron correlation up to quadruple excitation within the coupled-cluster calculations, Kalläy and co-workers have recommended $\bar{\alpha} = 24.137$ a.u. for $3s^{2}\,^1S_0$ and $\bar{\alpha} = 24.614$ a.u. for $3s3p\,^3P_0$ [17]. Within another calculation that the electron correlation is handled elaborately within the CI plus CC procedures, Safronova and co-workers have recommended $\bar{\alpha} = 24.048$ a.u. for $3s^{2}\,{}^1S_0$ and $\bar{\alpha} = 24.543$ a.u. for Al^+ $3s3p\,{}^3P_0$ [18]. These previously recommended data [16–18] provide a good benchmark criterion for comparison to prove the accuracy of our calculated results.

The quality of the spin-dependent CI results is demonstrated in direct comparison with the spin-dependent CC results. We find an overall trend that the spin-dependent CI values are lower than their corresponding spin-dependent CC values at the same level of the basis set. With the basis set expanding to 5ζ, the spin-dependent CI calculation arrives at the composite value $\bar{\alpha} = 23.780$ a.u. for $3s^{2}\,{}^1S_0$ and $\bar{\alpha} = 24.175$ a.u. for $3s3p\,{}^3P_0$. These results are within 2% error, as compared with the previously recommended data [16–18].

The electron correlation is more completely considered in the spin-dependent CC calculations, and therefore to prove our accuracy, the most direct comparison is between our CC results and the previously recommended data [16–18]. Our CC calculation is truncated to the $X = 4\zeta$ basis set due to our limited computer power, which may lead to the decrease of accuracy of the CC calculation. However, we find that our CI and CC results change almost the same quantity with increasing basis set, therefore, it is possible to improve our CC results by adding the basis set correction from $X = 4\zeta$ to 5ζ obtained from our CI calculation. Finally, our CC results present $\bar{\alpha} = 24.065$ a.u. for $3s^{2}\,{}^1S_0$ and $\bar{\alpha} = 24.552$ a.u. for $3s3p\,{}^3P_0$. As compared with the previously recommended data [16–18], our CC data is closest to Safronova's data [18] with agreement up to the first decimal place. This means that our CC data have already arrived at sufficient accuracy. However, we have to admit that such truncation of the basis set at $X = 4\zeta$ enlarged the uncertainty margins of our calculated results as compared with the previous benchmark calculations [16–18].

The overall agreement between our calculated results and the previously recommended data [16–18] for the Al^+ $3s^{2}\,{}^1S_0$ and $3s3p\,{}^3P_0$ states gives us confidence in the accuracy of our results for the other two energetically higher-lying excited states, $3s3p\,{}^3P_1$ and ${}^3P_2$, that have no recommended data available yet, to the best of our knowledge. Here, we expect that the results of $3s3p\,{}^3P_1$ and ${}^3P_2$ are of the same precision and reliability because they are obtained together with $3s^{2}\,{}^1S_0$ and $3s3p\,{}^3P_0$ in one calculation with the same energy convergence threshold. The spin-dependent CI calculation arrives at $\bar{\alpha}^J = 24.214$ a.u. for $3s3p\,{}^3P_1$ and $\bar{\alpha}^J = 24.291$ a.u. for $3s3p\,{}^3P_2$. The spin-dependent CC calculation yields $\bar{\alpha}^J = 24.650$ a.u. for $3s3p\,{}^3P_2$ (the $\bar{\alpha}^J$ value for $3s3p\,{}^3P_1$ is not obtained because the $M_J = 0$ component fails to be found). The tensor polarizability $\alpha_a^J = -0.308$ a.u. (spin-dependent CI value) for $3s3p\,{}^3P_1$, and $\alpha_a^J = 0.588$ a.u. (spin-dependent CI value) and 0.564 a.u. (spin-dependent CC value) for $3s3p\,{}^3P_2$. The deviation of $\bar{\alpha}^J$ for the $3s3p\,{}^3P_2$ state between our CI and CC calculations is less than 1.7%, within error margins 1.5% obtained for the ground state $3s^2\ {}^1S_0$ and 1.8% obtained for the lowest-lying excited state $3s3p\,{}^3P_0$. The good agreement in such comparison confirms that our calculations for $3s3p\,{}^3P_1$ and ${}^3P_2$ have delivered a good description of the spin-orbit components.

The relativistic effect in the four-component relativistic calculation can be understood as a combination of the spin-orbit coupling effect and contraction or decontraction of radial electron density, i.e., the so-called scalar relativistic effect. The relativistic effect is discussed through analyzing the J dependence of the scalar and tensor polarizability in this study. In our calculations, the difference $\bar{\alpha}^J({}^3P_0) - \bar{\alpha}^J({}^3P_1)$ is -0.039 a.u. (spin-dependent CI data), which amounts to only 0.16% of $\bar{\alpha}^J({}^3P_0)$. The difference $\bar{\alpha}^J({}^3P_0) - \bar{\alpha}^J({}^3P_2)$ is -0.117 a.u. (spin-dependent CI data) and -0.098 a.u. (spin-dependent CC data), which are 0.47% and 0.40% of $\bar{\alpha}^J({}^3P_0)$, respectively. Such variations of $\bar{\alpha}^J$ for different J components are minor and therefore negligible. The ${}^3P_0$ component is of spherically symmetric electron density, and therefore the difference of $\bar{\alpha}^J({}^3P_0)$ with respect to the scalar polarizability obtained from the spin-free CI calculation, i.e., $\bar{\alpha}^L({}^3P) - \bar{\alpha}^J({}^3P_0)$, can be regarded as the impact of the spin-orbit coupling only on the polarizability [8]. This difference is only 0.105 a.u., indicating a weak spin-orbit coupling effect on the dipole polarizability.

Furthermore, the tensor dipole polarizability represents $\alpha_a^J({}^3P_1) \approx -\alpha_a^J({}^3P_2)/2 \approx -\alpha_a^L/2$, which is in accordance with Eq. (8). The J-resolved $\bar{\alpha}$ and α_a both comply with the basic vector algebra, i.e., Eqs. (6) and (7), implemented under the LS approximation, which reflects a weak impact of the relativity effect on the dipole polarizability of the Al^+ $3s3p\,{}^3P$ state. The J dependence of the dipole polarizability of Al^+ is similar to the Al atom. In Ref. [8], Fleig has found the difference of dipole polarizability between the $J = \frac{1}{2}$ and $J = \frac{3}{2}$ components of the Al atom is small, only 0.002 a.u., and therefore the Al atom is justified to be essentially nonrelativistic.

Consider the hyperpolarizability. Table II presents the results of hyperpolarizability, as computed in the same way as the dipole polarizability. Available hyperpolarizability data are scarce, because such high-order property is hard to obtain due to more critical computational demand than that for dipole polarizabilities. For the ground state $3s^2\ {}^1S_0$, Archibong and Thakkar have obtained $\gamma = 2348$ a.u. (many-body-perturbation theory data). Here, we obtain $\gamma = 2625$ (spin-dependent CI data), 2548 (spin-dependent CC data), and 2457 a.u. (spin-free CI data), which are 4%–10% larger than Archibong and Thakkar's data. This deviation can be attributed to a larger basis set and a more complete treatment of electron correlation than are used in our calculations.

For the Al^+ $3s3p$ excited state, we obtain $\bar{\gamma}^J = 13\,534, 13891$, and 4418 a.u. for ${}^3P_0$, ${}^3P_1$, and ${}^3P_2$ within the spin-dependent CI calculations, and $\bar{\gamma}^J = 14\,463$ and 4769 a.u. for ${}^3P_0$ and ${}^3P_2$ within the spin-dependent CC calculations. (The $\bar{\gamma}^J$ is absent for ${}^3P_1$ because its $J = 0$ component is not found in our spin-dependent CC calculation.) The deviation between the spin-dependent CI and CC results is around 6%–8% [as evaluated by $(\bar{\gamma}^J_{\mathrm{CI}} - \bar{\gamma}^J_{\mathrm{CC}})/\bar{\gamma}^J_{\mathrm{CC}}$], which is within a normal error range considering the hyperpolarizability is very hard to calculate. More comparisons are difficult because there is no data available for the Al^+ $3s3p$ excited state, to the best of our knowledge.

The average of $\bar{\gamma}^J$ of the three J components of the Al^+ $3s3p$ excited state, i.e., $[\bar{\gamma}^J({}^3P_0) + 3\bar{\gamma}^J({}^3P_1) + 5\bar{\gamma}^J({}^3P_2)]/9$, is close to the $\bar{\gamma}^L$, which proves some kind of agreement between $\bar{\gamma}^J$ and $\bar{\gamma}^L$. However, $\bar{\gamma}^J$ represents great variations between different J components, which conflicts with Eq. (6). While the difference $\bar{\gamma}^J({}^3P_0) - \bar{\gamma}^J({}^3P_1)$ is small and therefore negligible, the $\bar{\gamma}^J({}^3P_0) - \bar{\gamma}^J({}^3P_2)$ is remarkably

TABLE III. Differential dipole polarizability $\Delta\bar{\alpha}$, differential hyperpolarizability $\Delta\bar{\gamma}$, and BBR shifts Δv. (BBR shift is evaluated at temperature $T = 300$ K).

Transition	$\Delta\bar{\alpha}$ (a.u.)	$\Delta v_{\Delta\bar{\alpha}}$($10^{-3}$ Hz)	$\Delta\bar{\gamma}$ (10^4 a.u.)	$\Delta v_{\Delta\bar{\gamma}}$ (10^{-17} Hz)[a]	Source
($^1S_0$-$^3P_0$)	0.39 ± 0.038	-3.334 ± 0.324	1.091 ± 0.956	-2.02 ± 1.771	KRCI
	0.487 ± 0.332	-4.163 ± 2.838	1.192 ± 0.324	-2.209 ± 0.600	MRCC
	0.48 ± 0.125	-4.2 ± 3.2			Ref. [16]
	0.477 ± 0.078	-4.1 ± 0.7			Ref. [17]
	0.495	-4.26 ± 0.43			Ref. [18]
($^1S_0$-$^3P_1$)	0.434 ± 0.028	-3.71 ± 0.239	1.127 ± 0.113	-2.924 ± 0.209	KRCI
($^1S_0$-$^3P_2$)	0.508 ± 0.006	-4.342 ± 0.051	0.179 ± 0.127	-0.332 ± 0.235	KRCI
	0.585 ± 0.356	-5.001 ± 3.043	0.221 ± 0.306	-0.410 ± 0.567	MRCC

[a] $\Delta E \sim -\frac{1}{24}\langle E^2_{E1}(\omega)\rangle^2 \Delta\gamma$ is assumed.

large, being as much as 67% of $\bar{\gamma}_0$. The $\bar{\gamma}^J$ results for each component also show more than 50% deviation from the $\bar{\gamma}^L$ results. With respect to the tensor hyperpolarizability, the ratio $\gamma_a^J(^3P_1)$, $\gamma_a^J(^3P_2)$, and $\gamma_a^L(^3P)$ disagree with the relations given by Eqs. (7) and (8). Considering the convergence of the results with the basis set and the electron correlation level, we think that the numerical error is unlikely to cause such big discrepancy.

The setup of Eqs. (6)–(8) is based on the LS coupling. However, the hyperpolarizability, as high order responds, is more sensible to the spin-orbit coupling. The mixing of spin and spatial degrees of freedom leads to deviations from the purely spatial anisotropies. This may cause deviations in the hyperpolarizabilities of light atoms from Eqs. (6)–(8) and dipole polarizabilities of the heavy atoms. The latter has already been found for In and Tl atoms [8]. The discrepancy shown in our data for the Al$^+$ $3s3p$ excited state, as compared with Eqs. (6)–(8), indicates that the hyperpolarizability is still open to question, especially for the excited state. Currently, there are very few hyperpolarizability data for the excited state, even simple atoms, therefore more calculations of high accuracy are needed in the future.

One important application of the scalar polarizabilities is to determine the blackbody radiation (BBR) shift for a transition due to the finite background thermal radiation. For Al$^+$, the BBR shift of the transition $^1S_0$ and $^3P_0$ is of especially important meanings for assessing the systematic error of the clock-frequency measurement. The derivation of the theoretical BBR shift has been presented by Porsev and co-workers [5] and Arora and co-workers [6], which has shown that the dominant term of BBR is determined by the difference in the dipole polarizability as follows:

$$\delta E^{E_1} = -\frac{1}{2}\frac{4\pi^3\alpha^3}{15}(k_B T)^4 \Delta\bar{\alpha}(1+\eta), \tag{10}$$

where E_1 means the first-order channel in electric field, the fine-structure constant $\alpha = 1/137.035\,999\,074(44)$, and $(\frac{k_B T}{E_h}) \approx 10^{-9}$ at room temperature the temperature; $\Delta\bar{\alpha}$ means the difference in $\bar{\alpha}$. The parameter η has been calculated by Mitroy *et al.* [16] and Safronova *et al.* [18], which gives $\eta = 0.000\,22 \sim 0.000\,24$ for Al$^+$. In this paper, we do not calculate this value. Consider that η is very small; we therefore neglect this value in our following estimation of BBR shifts. The above equation can be rewritten as

$$\delta E^{E_1} = -\tfrac{1}{2}\Delta\bar{\alpha}\langle E^2_{E_1}\rangle, \tag{11}$$

where the electric field $\langle E^2_{E_1}\rangle$ is equivalent to F_z^2 shown in Eq. (1). By associating the high-order term in Eq. (1), we suppose that the contribution of the hyperpolarizability to the BBR shift can be written in an approximate way as

$$\delta E^{E_1} = -\tfrac{1}{24}\Delta\bar{\gamma}\langle E^2_{E_1}\rangle^2, \tag{12}$$

where $\Delta\bar{\gamma}$ is the differential hyperpolarizability between two states. Based on the scalar polarizability data shown in Tables I and II, $\Delta\bar{\alpha}$ and $\Delta\bar{\gamma}$ between Al$^+$ $3s^{2\,1}S_0$ and $3s3p\,^3P_J$ with $J = 0,1,2$ and their corresponding BBR shifts can be computed in terms of Eqs. (4)–(6), as given in Table III. Such results show that the BBR shifts caused by the hyperpolarizability are of a factor of 10^{-17}, which is far less than the case of dipole polarizability, and therefore will constitute no impediment to the accuracy of the Al$^+$ optical clock at 10^{-18} and even higher precisions.

IV. SUMMARY

The accurate dipole polarizability and hyperpolarizability have been achieved for Al$^+$ $3s^{2\,1}S_0$ and $3s3p\,^3P_J$ with $J = 0,1,2$ using a relativistic Dirac-Coulomb Hamiltonian within CI and CC theories and a finite-field approach. Our calculations have obtained accurate dipole polarizabilities; more importantly, we present the J dependence and anisotropy of the dipole polarizability and hyperpolarizability. Because of the large computation demands in the finite-field study of the polarizabilities, we do not pursue the highest accuracy; for example, within the spin-dependent CI calculation the single and double electron correlations are limited to virtual orbits less than 100 a.u. and the single, double, and triple electron correlations are limited to virtual orbits less than 1 a.u. Within the spin-dependent CC calculation we truncated the increasing basis set up to $X = 4\zeta$. Such truncations of the electron correlation and the basis set cause the increased uncertainty, as compared with previous benchmark calculations [17,18].

There are more sources of error, such as the correction of quadruples excitation P_Q and the Briet interaction and QEC correction P_{BQ} [17]. In previous benchmark calculations the changes in dipole polarizability due to P_Q and P_{BQ} are found to be less than 0.1% and 1%, respectively. Therefore, the error caused by the absence of P_Q and P_{BQ} should not exceed a factor 1%–2% for our calculated results. The changes of the hyperpolarizability due to P_Q and P_{BQ} should be a small correction in a similar trend shown in the dipole polarizability.

Though imperfect in our calculation, our results have shown excellent agreement with previously recommended data for the dipole polarizability of $3s^{2\,1}S_0$ and $3s3p\,^3P_0$ and the hyperpolarizability of $3s^{2\,1}S_0$ as well as excellent agreement between the spin-dependent CI and CC calculations. It is indicated that the spin-orbit coupling has a negligible contribution for the dipolarizability of Al^+ but becomes significant for the hyperpolarizability. Therefore, the fully relativistic calculation is in great demand for the high-order polarizabilities.

Finally, we evaluated the BBR shift due to dipole polarizability and hyperpolarizability for Al^+ $3s^{2\,1}S_0$ to $3s3p\,^3P_J$ with $J = 0,1,2$. Specifically, the BBR shifts caused by the hyperpolarizability are at the magnitude of 10^{-17} Hz, which is far lower than the precision level of the current Al^+ optical clock and therefore can be safely neglected in uncertainty budget.

ACKNOWLEDGMENTS

The authors thank Dirac experts for helpful discussion through the Dirac mailing list. The authors are grateful to Prof. Zong-Chao Yan and Prof. Jim Mitroy for helpful suggestions. This work is supported by Grants No. 2012CB821305, No. 2010CB922904, No. NSFC 61275129, No. NFSC 21033001, No. NFSC 21203147, and No. CAS KJZD-EW-W02.

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