Relativistic coupled-cluster calculation of hyperfine-structure constants of $^{229}Th^{3+}$ and evaluation of the electromagnetic nuclear moments of ^{229}Th

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^{229}Th is a promising candidate for developing nuclear optical clocks and searching for new physics beyond the standard model. For this purpose, it is important to have accurate knowledge of the nuclear properties of ^{229}Th. In this work, we calculate hyperfine-structure (HFS) constants for the lowest four states of $^{229}Th^{3+}$ using the relativistic coupled-cluster method based on the Gaussian basis set. The no-pair Dirac-Coulomb-Breit Hamiltonian with the lowest-order quantum electrodynamics (QED) correction is the starting point, and all linear and nonlinear terms of single and double excitations are included in the coupled-cluster calculation. Combining the measured HFS constants [Campbell *et al.*, Phys. Rev. Lett. **106**, 223001 (2011)] and the present atomic calculations, we extract the magnetic dipole moment, $\mu = 0.359(9)$, and the electric quadrupole moment, $Q = 2.95(7)$, of the ^{229}Th nucleus. Our magnetic dipole moment is perfectly consistent with the recommended value from the all-order calculation by Safronova *et al.* [Phys. Rev. A **88**, 060501(R) (2013)], but our electric quadrupole moment is smaller than their recommended value by about 5%. A detailed analysis indicates that the nonlinear terms of single and double excitations, not included in the all-order calculation, are crucial to produce a precise Q value for ^{229}Th. In addition, we also report the magnetic octupole hyperfine-structure constants and some important nondiagonal hyperfine transition matrix elements, which are required for further extraction of the magnetic octupole moment Ω of ^{229}Th nucleus.

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I. INTRODUCTION

^{229}Th possesses an extremely low first excited isomeric state of only several eV [1,2], which opens the possibility to construct a high-precision nuclear optical clock [3–5] and provides strongly enhanced sensitivity for searching for new physics beyond the standard model [6,7]. To achieve these attractive objectives, accurate knowledge of the nuclear and electronic properties of ^{229}Th, such as the nuclear moments, plays a fundamental role. The accurate nuclear moment values not only can help us to grasp the hyperfine structures (HFSs) of ^{229}Th atoms and related ions but also provide a benchmark tool to improve nuclear model theory, thereby helping us to reliably predict the properties of its isomers such as the isomer transition rate and the nuclear moments [8]. The nuclear quadrupole moment of ^{229}Th can also be used to assess the sensitivity of the isomeric transition to the possible variation of the fine-structure constant α and other fundamental constants [7,9,10].

There have been some reported works on the magnetic dipole and electric quadrupole moment, μ and Q, of the ^{229}Th nucleus [8,10–15]. These results are summarized in Table I, and one can find obvious discrepancies between the predicted values from the nuclear theory [8,11] and the deduced values from the atomic structure calculation combined with experimental measurements [10,12,13,15]. For μ, the previous nuclear theory predictions [8,11] are significantly greater than the experimentally deduced values [12,15], but for Q, the nuclear theoretical prediction [8] is lower than the experimentally deduced values [10,12,13,15]. Among these results, the values extracted by Safronova *et al.* [15] using all-order calculations based on $^{229}Th^{3+}$ combined with precise hyperfine spectral measurement [14] are considered the most reliable [16]. In their calculations, all possible single and double excitations are iterated to all orders of perturbation theory, and part of the triple excitations is included perturbatively; thus, it is termed the SDpT method. However, only the linear coupled-cluster terms of single and double excitations are included in the SDpT method, and we notice that the correlation effects represented by the nonlinear terms play a crucial role in the precise prediction for the HFSs of Fr or Fr-like monovalent systems [17,18]. Thus, it is necessary and important to accurately assess the contribution of nonlinear terms in the HFS calculations of Fr-like $^{229}Th^{3+}$.

Theoretical investigation of the HFSs of $^{229}Th^{3+}$ is also of much interest in some other aspects. It has been reported as the most promising system for the realization of a single-ion nuclear clock based on a virtual clock transition composed by a pair of stretched hyperfine states of both nuclear ground and isomeric manifolds [4]. Knowledge of the relevant hyperfine-

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TABLE I. The magnetic dipole moment μ (in units of μ_N) and electric quadrupole moment Q (e b) of ^{229}Th reported in previous studies. "Theoretical prediction" results are obtained from calculations based on various nuclear theoretical models. "Experimentally deduced" values are found from laser spectroscopy measurements in combination with atomic calculations. Q of the penultimate column was derived by Campbell *et al.* [14], combining their measurements and the calculations by Berengut *et al.* [10]. μ and Q of the last column were derived by Safronova *et al.* [15], combining their calculations and the measurements by Campbell *et al.* [14].

	Theoretical prediction		Experimentally deduced			
	Ref. [8]	Ref. [11]	Ref. [12]	Ref. [13]	Ref. [14]	Ref. [15]
μ	0.530–0.655	0.54	0.46(4)			0.360(7)
Q	2.80		4.3(9)	3.15(3)	3.11(16)	3.11(6)

interaction matrix elements is helpful to extract the nuclear excitation energy [19]. Moreover, $^{229}Th^{3+}$ is also a possible system for atomic parity-nonconserving experiments [20], and its magnetic dipole HFS constant would be a reliable probe for the estimate of the theoretical accuracy of the related weak matrix elements.

In the present work, we calculate the HFS constants of the low-lying states of $^{229}Th^{3+}$ using the relativistic coupled-cluster method based on the Gaussian basis set. The correlation effects are investigated by the *ab initio* methods at different levels, including the Dirac-Fock approximation, low-order many-body perturbation theory, and the linearized and fully single- and double-excitation relativistic coupled-cluster method. The magnetic dipole and electric quadrupole moment, μ and Q, of the ^{229}Th nucleus are extracted by combining the present recommended theoretical results with the available experimental values. The hyperfine-interaction matrix elements required to extract the magnetic octupole moment are also presented. In Sec. II, we provide a brief overview of the coupled-cluster method and the hyperfine-structure theory. Numerical results and discussion are presented in Sec. III. Finally, a summary is given in Sec. IV.

II. THEORETICAL METHOD

A. A brief description of the relativistic coupled-cluster approach

For Th^{3+}, a monovalent atomic system, the exact wave function with a valence orbital υ can be formally expressed in the form

$$|\Psi_\upsilon\rangle = e^S|\Phi_\upsilon\rangle, \tag{1}$$

where $|\Phi_\upsilon\rangle$ is the zeroth-order wave function obtained by the Dirac-Fock calculation and the exponential cluster operator, $e^S = 1 + S + \frac{1}{2!}S^2 + \cdots$, represents the expansion of wave operators in the framework of the coupled-cluster theory. According to the number of particles n to be excited from the reference configuration, the cluster operator S can be partitioned into

$$S = S_1 + S_2 + \cdots + S_n. \tag{2}$$

In practice, the contributions from the triple and higher excitations are always expected to be relatively small, and the computations are extremely time-consuming. Thus, only the single (S_1) and double (S_2) excitations are considered in the present coupled-cluster calculation (CCSD), and Eq. (1) can be written as

$$|\Psi_\upsilon\rangle_{\rm CCSD} = \left\{1 + S_1 + S_2 + \tfrac{1}{2!}\left(S_1^2 + S_2^2 + S_1S_2\right) + \tfrac{1}{3!}\left(S_1^3 + 3S_1^2S_2\right) + \tfrac{1}{24}S_1^4\right\}|\Phi_\upsilon\rangle. \tag{3}$$

Equation (3) is a nearly complete expression of the wave function within the single- and double-excitation approximation (SD), where the first three terms are linear terms and provide the majority of the contribution. A more convenient and simplified treatment is to retain only the linear terms, which are referred to as the linearized coupled-cluster (LCCSD) wave function,

$$|\Psi_\upsilon\rangle_{\rm LCCSD} = (1 + S_1 + S_2)|\Phi_\upsilon\rangle. \tag{4}$$

However, for some strongly correlated systems, the contribution from nonlinear terms may be important and may need to be evaluated carefully, especially in the high-precision calculations of some special properties.

The transition matrix elements of an operator $\hat{O}$ from state $|\Psi_w\rangle$ to $|\Psi_\upsilon\rangle$ can be evaluated according to

$$\bar{O} = \frac{\langle\Psi_w|\hat{O}|\Psi_\upsilon\rangle}{\langle\Psi_w \mid \Psi_\upsilon\rangle} = \frac{\langle\Phi_w|e^{S\dagger}\hat{O}e^S|\Phi_\upsilon\rangle}{\langle\Phi_w|e^{S\dagger}e^S|\Phi_\upsilon\rangle}, \tag{5}$$

where $e^{S\dagger}$ stands for the complex conjugate of e^S. Expanding the wave function Ψ using Eq. (3) or Eq. (4), one would obtain the transition matrix element within the CCSD or LCCSD approximation, respectively. The specific calculation steps are described in detail in previous works [18,21].

B. The hyperfine-structure theory

The hyperfine-interaction (HFI) Hamiltonian for a relativistic electron can be expressed as [22]

$$H_{\rm HFI} = \sum_k T_k^e \cdot T_k^n, \tag{6}$$

where T_k^e and T_k^n are the spherical tensor operators with rank k ($k > 0$) in the electronic and nuclear coordinates, respectively. A matrix element of the HFI between the basis of the hyperfine states $|\alpha I, \gamma J; FM_F\rangle$, which couple a nuclear eigenstate $|\alpha I, M_I\rangle$ and an atomic eigenstate $|\gamma J, M_J\rangle$, is

$$\langle\alpha'I', \gamma'J'; F'M_F'|H_{\rm HFI}|\alpha I, \gamma J; FM_F\rangle = \delta_{F'F}\delta_{M_F'M_F}(-1)^{I+J+F} \times \sum_k \begin{Bmatrix} F & J & I \\ k & I & J' \end{Bmatrix} \langle\gamma'J'\|T_k^e\|\gamma J\rangle\langle\alpha'I'\|T_k^n\|\alpha I\rangle, \tag{7}$$

where F is the total angular momentum with $\mathbf{F} = \mathbf{I} + \mathbf{J}$, I is the nuclear spin, J is the total electronic angular momentum,

TABLE II. The parameters of the Gauss basis set. N is the number of basis sets for each symmetry. N_c and N_v represent the numbers of core orbitals and virtual orbitals, respectively.

	s	p	d	f	g	h	i	k
$\alpha \times 10^3$	3.3	3.0	4.6	13.5	12	22	23	24
β	1.95	1.95	1.695	1.681	1.95	2.05	2.15	2.25
N	40	38	35	32	25	20	15	10
N_c	6	5	3	1	0	0	0	0
N_v	22	22	26	24	19	16	15	10

and α and γ encapsulate the remaining nuclear and electronic quantum numbers, respectively. Then the first-order correction $E^{(1)}_{F,J}$ of the hyperfine interaction to the energy is defined as

$$E^{(1)}_F = (-1)^{I+J+F} \sum_k \begin{Bmatrix} F & J & I \\ k & I & J \end{Bmatrix} \langle \gamma J \| T^e_k \| \gamma J \rangle \langle \alpha I \| T^n_k \| \alpha I \rangle. \tag{8}$$

Restricted to $k \leqslant 3$, $E^{(1)}_F$ can be parameterized in terms of the HFS constants A, B, and C. These HFS constants are expressed as follows:

$$A = \mu_N \frac{\mu_I}{I} \frac{\langle \gamma J \| T^e_1 \| \gamma J \rangle}{\sqrt{J(J+1)(2J+1)}}, \tag{9}$$

$$B = 2Q \left[\frac{2J(2J-1)}{(2J+1)(2J+2)(2J+3)} \right]^{1/2} \langle \gamma J \| T^e_2 \| \gamma J \rangle, \tag{10}$$

and

$$C = \Omega_I \left[\frac{J(2J-1)(J-1)}{(J+1)(J+2)(2J+1)(2J+3)} \right]^{1/2} \langle \gamma J \| T^e_3 \| \gamma J \rangle, \tag{11}$$

where A, B, and C are the magnetic dipole ($M1$), electric quadrupole ($E2$), and magnetic octupole ($M3$) hyperfine-structure constants, respectively. μ_N is the nuclear Bohr magneton, and the diagonal nuclear reduced matrix elements $\langle \alpha I \| T^n_k \| \alpha I \rangle$ in Eq. (8) are contained in the nuclear moments, μ_I ($k = 1$), Q ($k = 2$), and Ω_I ($k = 3$), respectively.

The contributions from second-order hyperfine interactions are generally on the same order as the magnetic octupole contribution; thus, we also take into account these terms here. In addition, because the first excited nuclear state of ^{229}Th has an anomalously small excitation energy, there should also be a small, but observable, contribution in the second-order correction that corresponds to the hyperfine mixing between the electronic states of the ground nuclear states and the electronic states of the isomer nuclear states [19]. Then the second-order correction $E^{(2)}_F$ of the hyperfine interaction to the energy in ^{229}Th is defined as

$$E^{(2)}_F = \sum\nolimits' \frac{1}{E_{\alpha I,\gamma J} - E_{\alpha' I',\gamma' J'}} \sum_{k_1,k_2} \begin{Bmatrix} I & J & F \\ J' & I & k_1 \end{Bmatrix} \begin{Bmatrix} I & J & F \\ J' & I & k_2 \end{Bmatrix} \langle \alpha I \| T^n_{k_1} \| \alpha' I' \rangle \langle \alpha' I' \| T^n_{k_2} \| \alpha I \rangle \langle \gamma J \| T^e_{k_1} \| \gamma' J' \rangle \langle \gamma' J' \| T^e_{k_2} \| \gamma J \rangle. \tag{12}$$

The summation involves all possible excited nuclear states and electronic states, and $E_{\alpha I,\gamma J}$ includes both nuclear and electronic energies. $\langle \alpha I \| T^n_k \| \alpha' I' \rangle$ and $\langle \gamma J \| T^e_k \| \gamma' J' \rangle$ correspond to the reduced matrix elements of the nuclear part and electronic parts, respectively. The off-diagonal reduced matrix elements of the nuclear part can be found in Ref. [19]. In the present work, we focus on the $M1$ and $E2$ off-diagonal reduced matrix elements from the fine-structure splitting (electronic part) because their contributions dominate owing to small energy denominators.

The single-particle reduced matrix elements of the operators T^e_1, T^e_2, and T^e_3 are given by

$$\langle \kappa_i \| T^e_1 \| \kappa_j \rangle = -\langle -\kappa_i \| C^{(1)} \| \kappa_j \rangle (\kappa_i + \kappa_j) \int_0^\infty dr \frac{P_i(r)Q_j(r) + P_j(r)Q_i(r)}{r^2} \times F(r), \tag{13}$$

$$\langle \kappa_i \| T^e_2 \| \kappa_j \rangle = -\langle \kappa_i \| C^{(2)} \| \kappa_j \rangle \int_0^\infty dr \frac{P_i(r)P_j(r) + Q_j(r)Q_i(r)}{r^3}, \tag{14}$$

and

$$\langle \kappa_i \| T^e_3 \| \kappa_j \rangle = -\frac{1}{3} \langle -\kappa_i \| C^{(3)} \| \kappa_j \rangle (\kappa_i + \kappa_j) \int_0^\infty dr \frac{P_i(r)Q_j(r) + P_j(r)Q_i(r)}{r^4}, \tag{15}$$

where the relativistic angular momentum quantum number $\kappa = \ell(\ell+1) - j(j+1) - 1/4$ and P and Q are the large and small radial components of the Dirac wave function, respectively.

In the present work, we employed a finite basis set composed of even-tempered Gaussian-type functions expressed as $G_i = \mathcal{N}_i r^{\ell+1} e^{-\alpha_i r^2}$ to expand the Dirac radial wave function P and Q as in Refs. [18,21,23], where $\mathcal{N}_i$ is the normalization factor and $\alpha_i = \alpha\beta^{i-1}$, where the two independent parameters α and β are optimized separately for each orbital symmetry. Table II lists the Gauss basis parameters. N is the number of basis sets for each symmetry. N_c and N_v represent the numbers of core and virtual orbitals, respectively.

In our calculations, the no-pair Dirac Hamiltonian is set as the starting point. Breit interaction and the lower-order quantum electrodynamics (QED) radiative potential proposed by Flambaum and Ginges [24] are considered on the same footing as Coulomb interaction. The Fermi nuclear distribution was employed to describe the Coulomb potential between electrons and the nucleus. All the core orbitals and virtual orbitals with energies smaller than 10 000 a.u. are included in the correlation calculations.

TABLE III. Zeroth-order DF Coulomb correction $E^{(0)}$, second-order MBPT correction $E^{(2)}$, the linearized part of the single- (S_1) and double- (S_2) excitation correction $E^{(S_1+S_2)}$, the nonlinear coupled-cluster term corrections $E^{(\mathrm{NL})}$, the corrections of Breit, and QED effects on the energies for Th^{3+} (in cm^{-1}). $E_{\mathrm{MBPT(2)}} = E^{(0)} + \mathrm{Breit} + E^{(2)}$, $E_{\mathrm{LCCSD}} = E^{(0)} + \mathrm{Breit} + E^{(S_1+S_2)}$, $E_{\mathrm{CCSD}} = E_{\mathrm{LCCSD}} + E^{(\mathrm{NL})}$, and $E_{\mathrm{Final}} = E_{\mathrm{CCSD}} +$ QED represent the results obtained within second-order MBPT, LCCSD, CCSD, and CCSD results with QED correction approximations, respectively. The experiment energies E_{Expt}, with the uncertainty in parentheses, are also listed for comparison.

Level	$E^{(0)}$	Breit	$E^{(2)}$	$E^{(S_1+S_2)}$	$E^{(\mathrm{NL})}$	QED	$E_{\mathrm{MBPT(2)}}$	E_{LCCSD}	E_{CCSD}	E_{Final}	E_{Expt} [25,26]
$5f_{5/2}$	−206 612	−737	−31 348	−25 459	754	−204	−238 697	−232 808	−232 054	−232 258	−231 065(200)
$5f_{7/2}$	−203 185	−869	−29 828	−24 413	754	−198	−233 882	−228 467	−227 714	−227 911	−226 740
$6d_{3/2}$	−211 800	−48	−12 980	−11 154	441	−89	−224 828	−223 002	−222 562	−222 650	−221 872
$6d_{5/2}$	−207 687	−129	−12 314	−10 923	422	−68	−219 055	−217 663	−217 241	−217 308	−216 579
$7s_{1/2}$	−200 273	−90	−10 931	−9173	378	−182	−211 294	−209 536	−209 157	−208 975	−207 934
$7p_{1/2}$	−165 094	−167	−7587	−6746	365	−3	−172 848	−172 007	−171 643	−171 645	−170 826
$7p_{3/2}$	−153 571	−57	−6042	−5450	319	−7	−159 670	−159 079	−158 760	−158 753	−158 009

III. RESULTS AND DISCUSSION

A. Energies

We carried out a series of calculations for the energies of some important low-lying states of $^{229}Th^{3+}$ at different correlation levels, including Dirac-Fock (DF), second-order many-body perturbation theory [MBPT(2)], LCCSD, and full CCSD calculations. We also classified the contributions from different terms, including the zeroth-order DF Coulomb correction $E^{(0)}$, the Breit corrections, the second-order MBPT correction $E^{(2)}$, the linearized part of the single- (S_1) and double- (S_2) excitation correction $E^{(S_1+S_2)}$, the nonlinear coupled-cluster term correction $E^{(\mathrm{NL})}$, and the QED correction. All these results are listed in Table III and compared with experimental values [25,26] labeled E_{Expt}. $E_{\mathrm{MBPT(2)}} = E^{(0)} + \mathrm{Breit} + E^{(2)}$, $E_{\mathrm{LCCSD}} = E^{(0)} + \mathrm{Breit} + E^{(S_1+S_2)}$, $E_{\mathrm{CCSD}} = E_{\mathrm{LCCSD}} + E^{(\mathrm{NL})}$, and $E_{\mathrm{Final}} = E_{\mathrm{CCSD}} +$ QED represent the results obtained within second-order MBPT, LCCSD, CCSD, and CCSD results with QED correction approximations, respectively.

From Table III, the importance of including the correlation effect can be found. Take the incorrect determination of the ground state in the DF calculation as an example: the spectral measurements confirm that the ground state of Th^{3+} is the $5f_{5/2}$ state, while the ground state generated from the DF calculation is the $6d_{3/2}$ state. The MBPT(2) results obviously overestimated the correlation effect and predicted much lower energies for all the states tabulated. The contribution from the QED correction is about 0.1% for $5f$ and $7s$ states, while it is negligible for other states. The CCSD results show better agreement with experiments since the contribution from the nonlinear single- and double-excitation terms, which is about 0.3% for $5f$ and 0.2% for other states, has been included. Finally, for the two $5f$ states, the differences between E_{Final} and the experimental values are about 0.5%. The main reason for this discrepancy is the omission of the higher-order correlation effects, such as the triple and higher excitation terms.

Table IV presents a detailed comparison of our LCCSD, CCSD, and CCSD+QED transition energies with other *ab initio* results. It can be observed that in terms of transition energy, our CCSD results are consistent with the results obtained by relativistic intermediate Hamiltonian Fock-space coupled-cluster methods (FSCCSDs) [27], and both are much closer to the experimental value than the results obtained by the all-order calculations including partial extra third-order terms [28]. The contributions from different corrections are given in the all-order calculations [28], allowing us to explore the origin of the difference from our results. It can be found that the DF Coulomb energies $E^{(0)}$ obtained in Ref. [28] and our calculations agree well with each other, while the absolute values of the Breit correction to energies in Ref. [28] are significantly greater than our estimation. In addition, we also calculated the energy under the condition of $\ell_{\max} = 6$, and we found that our MBPT(2) and LCCSD results are completely consistent with their corresponding results. Making a comparison with the current calculation results for $\ell_{\max} = 7$, we observe that for the energies of the $5f$ states, the contributions of the partial wave $\ell = 7$ are about $-520\ cm^{-1}$. This suggests that the contribution of higher-order fractional waves to en-

TABLE IV. Comparison of our calculated E_{LCCSD}, E_{CCSD}, and E_{Final} transition energies with other available theoretical and experimental data (in cm^{-1}), with the difference between theoretical and experimental data labeled by △. The first row lists the absolute energy of the ground state, and the other rows list the excitation energies of other states with respect to the ground state.

Level	E_{LCCSD}	△	E_{CCSD}	△	E_{Final}	△	E_{FSCCSD} [27]	△	$E_{\mathrm{all-order}}$ [28]	△	E_{Expt} [25,26]
$5f_{5/2}$	−232 808	−1743	−232 054	−989	−232 258	−1193	−231 957	−892	−230 304	761	−231 065
$5f_{7/2}$	4341	16	4340	15	4346	21	4320	−5	4136	−189	4325
$6d_{3/2}$	9806	613	9492	299	9608	415	9416	223	8304	−889	9193
$6d_{5/2}$	15 145	659	14 812	326	14 949	463	14 738	252	13 377	−1109	14 486
$7s_{1/2}$	23 272	141	22 896	−235	23 282	151	22 833	−308	22 229	−902	23 131
$7p_{1/2}$	60 800	561	60 411	172	60 612	373	60 346	109	59 213	−1026	60 239
$7p_{3/2}$	73 729	673	73 293	237	73 504	448	73 206	150	71 932	−1124	73 056

TABLE V. Determination of the ^{229}Th nuclear magnetic dipole moment using measured A (MHz) from Ref. [14] and the calculated A/μ from the present work. The present A/μ column contains *ab initio* results at different correlation levels (in MHz/μ_N). The results deduced from the SDpT calculation and other methods are also listed here for comparison.

		Present A/μ				Other A/μ	μ			
Level	A_{Expt}	DF	MBPT(3)	LCCSD	CCSD	SDpT [15]	LCCSD	CCSD	SDpT [15]	Others
$5f_{5/2}$	82.2(6)	203.73	250.52	232.28	230.53	229.2	0.354(3)	0.357(3)	0.359	
$5f_{7/2}$	31.4(7)	105.79	81.49	87.14	87.12	86.1	0.360(8)	0.360(8)	0.365	
$6d_{3/2}$	155.3(12)	331.75	455.21	442.71	431.85	431.5	0.351(3)	0.360(3)	0.360	
$6d_{5/2}$	−12.6(7)	121.73	−34.43	−35.39	−23.31	−36.7	0.356(20)	0.541(30)	0.343	
Final							0.355(9)	0.359(9)	0.360(7)	0.530–0.655 [8] 0.54 [11] 0.46(4) [12]

ergy is important, and the same conclusion also can be drawn from the work of Ref. [28].

B. Magnetic dipole moment

A/μ for the first four states of $^{229}Th^{3+}$ are calculated at different correlation levels, including DF, third-order many-body perturbation theory [MBPT(3)], LCCSD, and CCSD. The magnetic dipole moments μ are then extracted by combining our theoretical results with the experimental HFS constants [14]. The results are listed in Table V and are compared with other available calculated values [8,11,12,15]. Uncertainties are given in parentheses.

As seen from Table V, the MBPT(3) calculations significantly overestimated the correlation effect compared with our CCSD results, which is consistent with the case for energies. For the $5f$ states, the LCCSD results are very close to the CCSD results, where the contribution of the nonlinear terms to A/μ is about 1%, while it is about 2.5% for the $6d_{3/2}$ state. The main source of theoretical uncertainty is the electron correlation. States with smaller correlation effects tend to be more conducive to accurate calculation. The correlation effects (CCSD − DF)/CCSD × 100% and the nonlinear effects (CCSD − LCCSD)/CCSD × 100% accounted for in A/μ of the above states are no more than 25% and 3%, respectively, with the only exception being 565% and −35% for $6d_{5/2}$, respectively. Therefore, even if these calculations are carried out under the same theoretical framework, it is not guaranteed that the results for different states can achieve the same precision because different states are different in sensitivity to various correlation effects. In this case, averaging the theoretical calculation results of several states can effectively reduce the uncertainty caused by different sensitivities of different states to the correlation effect. Here we abandon the $6d_{5/2}$ state which is strongly dependent on the correlation effect and take the average value of the other three states to obtain the final μ value, i.e., 0.359(9), where the uncertainty in parentheses is entirely from the measurement.

Our CCSD value of 0.359(9) matches well the all-order SDpT result of 0.360(7) but is much lower than all other reported results [8,11,12]. For example, our results are about 50%–80% lower than the previous nuclear theory predictions and about 30% lower than the experimentally deduced values from Fourier spectroscopy in 1974 [12]. It must be pointed out that the results obtained by combining spectroscopy measurements with atomic structure calculations are more reliable than the predictions directly using nuclear model theory. Furthermore, current laser spectroscopy measurement techniques and the theoretical calculation method for the atomic structure have improved a lot over time, which is also one of the important reasons why we think the current results as well as Safronova *et al.*'s results are more reliable than the 1974 results [12]. Recall that the all-order SDpT calculation corresponds to a full consideration of linear single- and double-excitation terms and further inclusion of some triple excitations perturbatively, while our CCSD calculation includes all the linear and nonlinear single- and double-excitation terms. Thus, it is reasonable to extract the contribution of the triple-excitation terms from the comparison between SDpT results and our LCCSD results. The comparison of our CCSD result and the SDpT result indicates that the contributions of the partial triple excitations and the nonlinear term on A/μ to the first three states are really small. Another interesting feature we observed is that A/μ of the $6d_{5/2}$ state obtained using the SDpT method is −36.7, which is almost the same as our LCCSD value of −35.4. This is independent validation for both the SDpT results and our LCCSD results, and this also suggests strong dependence of A/μ of $6d_{5/2}$ on the nonlinear single- and double-excitation terms.

C. Electric quadrupole moments

Like for the case of the magnetic dipole moment, we also determine the ^{229}Th nuclear electric quadrupole moment Q using measured B (in megahertz) from Ref. [14] and our calculated B/Q. The results are listed in Table VI and are compared with SDpT results [15]. From Table VI, one can see that the correlation effects in the MBPT(3) calculation are significantly different from the LCCSD and full CCSD results. Except for the $6d_{3/2}$ state, the contributions from the third-order MBPT correction to the zeroth-order DF values are negative, while the corrections of the linear terms (LCCSD − DF) and nonlinear coupled-cluster terms (CCSD − LCCSD) are positive for these four states. The total correlation effects of the $5f_{5/2,7/2}$ states are very strong, about 30% of the total CCSD results, while the correlation effects of the $6d_{3/2,5/2}$ states are relatively small. In addition, it can be found that the higher the angular momentum is, the greater the total correlation effect is. Furthermore, the contribution

TABLE VI. Determination of the ^{229}Th nuclear electric quadrupole moment using measured B (MHz) from Ref. [14] and the calculated B/Q from the present work. The present B/Q column contains *ab initio* results at different correlation levels (in MHz/e b). The results deduced from SDpT calculation are also listed.

		Present B/Q				Other B/Q	Q		
Level	B_{Expt}	DF	MBPT(3)	LCCSD	CCSD	SDpT [15]	LCCSD	CCSD	SDpT [15]
$5f_{5/2}$	2269(6)	537	436	743	783	725	3.06(1)	2.90(1)	3.13
$5f_{7/2}$	2550(12)	575	388	829	879	809	3.07(2)	2.90(2)	3.15
$6d_{3/2}$	2265(9)	609	717	746	758	738	3.04(1)	3.00(1)	3.07
$6d_{5/2}$	2694(7)	648	474	883	897	873	3.05(1)	3.00(1)	3.09
Final							3.05(3)	2.95(7)	3.11(6)

of the nonlinear terms accounts for approximately a quarter of the total correlation effect in the $5f$ states but less than a tenth in the $6d$ states. Both the total correlation effects and the nonlinear term corrections are significantly larger than those in A/μ for each state, which is the opposite of Ra^+ [18]. Such strong and unusual correlation effects indicate that it is more difficult to accurately calculate B/Q of the ground state of $^{229}Th^{3+}$. Here we take the average value of all four states as the final Q value, i.e., 2.95(7), where the uncertainty in parentheses is also entirely from the measurement.

It is found that the Q value from the SDpT calculation is significantly greater than the present final CCSD value. As we have stated, the contribution of the triple-excitation terms can be extracted from the comparison between the SDpT results and our LCCSD results, and the difference between the LCCSD and CCSD results is due to the nonlinear terms. Taking the present LCCSD result [3.05(3)] as a reference, the SDpT result [3.11(6)] and the CCSD result [2.95(7)] are on both sides of it. This indicates that the contribution of the partial triple-excitation terms is positive, about 2%, while the contribution of the SD nonlinear terms is negative, about 3%. This trend will lead to a cancellation. Therefore, in order to extract Q accurately, it is important not only to evaluate the contribution of nonlinear terms accurately but also to consider the contribution of triple-excitation terms completely. Furthermore, comprehensive observations show that the contribution of the nonlinear term to A/μ is positive, while the contribution to B/Q is negative. The relative ratio of the correlation represented by nonlinear terms (CCSD − LCCSD)/(CCSD − DF) in B/Q is much large than in A/μ, which is different from those of Fr and Ra^+.

D. Magnetic octupole hyperfine interaction

Recently, the rapid development of spectroscopy technology made the extraction of some high-order nuclear moments possible. For example, the nuclear magnetic octupole moments Ω of ^{133}Cs [29], $^{137}Ba^+$ [30], and ^{171}Yb [31,32] have been successfully determined. $^{229}Th^{3+}$ is also a good candidate for studies of nuclear structure beyond the first two electromagnetic moments since its ground state, $5f_{5/2}$, has a large angular momentum and thus a large coupling to Ω. Safronova *et al.* suggested that this coupling effect may induce a hyperfine interval at the level of a few hertz [15]. To extract Ω, an accurate calculation of the relevant octupole hyperfine-interaction matrix elements, including the diagonal and important nondiagonal matrix elements of low-lying states in $^{229}Th^{3+}$, is necessary. Once the accurate HFS constant C is measured, these matrix elements can be used to determine the magnetic octupole moment immediately. In addition, the present octupole matrix elements are expected to possess a higher level of accuracy than those from the previous calculations using the third-order perturbation method mentioned in Refs. [19,33]. Then the excitation energy of the ^{229}Th nucleus may be determined more accurately to a certain extent using the method reported by Beloy [19].

Table VII lists the electronic octupole hyperfine-interaction matrix elements from DF, LCCSD, and CCSD calculations, including diagonal C/Ω [in kHz/(μ_N × b)] and nondiagonal matrix elements (in megahertz) of low-lying states. The uncertainty of these octupole parameters mainly comes from the unconsidered high-order correlation effects beyond CCSD, which are generally not greater than the contribution of the SD nonlinear terms (i.e., CCSD-LCCSD). Therefore, we take the CCSD results as the recommended values listed in the "Final" column and the corresponding absolute value of the difference between the CCSD and LCCSD results as the uncertainty enclosed in parentheses. It can be observed from Table VII that for the $5f_{5/2,7/2}$ and $6d_{5/2}$ states, the correlation effects are significant compared with the relatively small matrix elements, which would lead to large uncertainties in the calculations. For the $6d_{3/2}$ state, the conclusion is the opposite. It is worth noting that the contributions of the nonlinear term on C/Ω to the $5f$ and $6d$ states are very large, which is

TABLE VII. C/Ω [kHz/(μ_N × b)] and off-diagonal matrix elements (in MHz) from DF, LCCSD, and CCSD calculations. The CCSD results are taken as the recommended values listed in the "Final" column, and the corresponding absolute value of the difference between CCSD and LCCSD results are given as the uncertainty enclosed in parentheses.

Level	DF	LCCSD	CCSD	Final
$5f_{5/2}$	0.68	−0.60	−0.38	−0.38(22)
$5f_{7/2}$	0.31	1.83	1.12	1.12(71)
$6d_{3/2}$	6.77	7.91	7.88	7.88(3)
$6d_{5/2}$	1.84	0.21	0.05	0.05(16)
Off-diagonal matrix elements				
$\langle 5f_{5/2}\|\|T_1^e\|\|5f_{7/2}\rangle$	329	1121	1189	1189(68)
$\langle 5f_{5/2}\|\|T_2^e\|\|5f_{7/2}\rangle$	423	605	637	637(32)
$\langle 6d_{3/2}\|\|T_1^e\|\|6d_{5/2}\rangle$	355	4180	3962	3962(218)
$\langle 6d_{3/2}\|\|T_2^e\|\|6d_{5/2}\rangle$	695	815	830	830(15)

somewhat different from A/μ. This may be because the value of C/Ω is too small to be accurate enough. The larger the HFS constant C is, the more conducive to accurate calculation and measurement it is. Therefore, the results for the $6d_{3/2}$ state are more suitable for roughly predicting the magnitude of the HFS constant C. These matrix elements are of great significance for extracting Ω of the ^{229}Th nucleus.

IV. CONCLUSION

In summary, we carried out a comprehensive study of the energies and HFS constants for several low-lying states in $^{229}Th^{3+}$ using a relativistic CCSD method based on a large Gaussian basis set. To clarify the role of different correlation corrections, we also provided some intermediate results, including the results from DF, MBPT, and LCCSD calculations. The Breit and QED corrections to the energies were also investigated. Our calculations indicated that more higher-order corrections not included in our calculations are important to further reduce the difference between the theoretical prediction and experimental measurement. The magnetic dipole moment μ and the electric quadrupole moment Q of ^{229}Th were obtained by combining our atomic calculation with the measured HFS A and B values. Our recommended μ value of 0.359(9) is in excellent agreement with the SDpT result of 0.360(7). The present electric quadrupole moment, $Q = 2.95(7)$, is smaller than the recommended value of Ref. [15], $Q = 3.11(6)$, by about 5%, possibly owing to the fact that the electron correlations represented by the nonlinear terms, omitted in the SDpT calculations, contribute significantly to the electric quadrupole moment and reduce the values. Further analysis showed that the third-order many-body perturbation theory is not a very effective tool to generate sufficiently accurate nuclear moments μ and Q of ^{229}Th. It always strongly overestimates the magnitude and sometimes gives an incorrect sign of the correlation effect. Additionally, we also presented the magnetic octupole HFS constants C/Ω and some important nondiagonal hyperfine transition matrix elements, which are required for further extracting the magnetic octupole moment Ω of the ^{229}Th nucleus. Our calculations also showed that $6d_{3/2}$ is a suitable state to carry out precise measurements of the hyperfine splittings from which Ω of ^{229}Th can be inferred.

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