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Ground-state g_j factors of the Cd$^+$, Yb$^+$, and Hg$^+$ ions

Y. M. Yu,[1,4,*] B. K. Sahoo,[2,†] and B. B. Suo[3,‡]
[1]*Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China*
[2]*Atomic, Molecular, and Optical Physics Division, Physical Research Laboratory, Navrangpura, Ahmedabad 380009, India*
[3]*Institute of Modern Physics, Northwest University, Xi'an, Shanxi 710069, China*
[4]*University of Chinese Academy of Sciences, 100049 Beijing, China*

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Accurate calculations of g_j factors of the ground state of the Cd$^+$, Yb$^+$, and Hg$^+$ ions are presented by employing the normal order unrelaxed Λ-approach relativistic coupled-cluster (Λ-RCC) theory. Contributions from the quantum electrodynamics (QED) are estimated from the free electron QED contributions and the roles of electron correlation effects are analyzed with different cutoff of occupied and virtual active orbitals in the Λ-RCC method. Our final g_j factors come out to be 2.002291(4), 2.002798(113), and 2.003128(41) for the Cd$^+$, Yb$^+$, and Hg$^+$ ions, respectively. Our result for Hg$^+$ agrees up to the fourth decimal places with its experimental value 2.0031745(74) indicating that our calculations of the other ions are of similar accuracies. The understanding of roles of electron correlation effects from this study will be useful in improving accuracies of the g_j factors in the considered ions further by adding more physical effects in the future and performing calculations with similar accuracies in other heavier atomic systems. The reported g_j factors can also be used to scrutinize the background noise related to the stray magnetic fields in the laser-cooled microwave ion clocks using the above ions.

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I. INTRODUCTION

The laser-cooled Cd$^+$, Yb$^+$, and Hg$^+$ singly charged ions confined in a linear Paul trap are considered as good candidates for microwave atomic clocks [1–9]. Due to their robustness in offering long-term stability, they can be potential clocks for the applications in the deep space flights. This is because these ions have comparatively large ground-state hyperfine splitting that is one of the primary requirements for a microwave clock. To use them for practical purposes, it is imperative that all possible systematics in these clock frequency measurements should be minimized [10]. The systematic uncertainty of the Hg$^+$ ion clock is currently about 3.4 parts in 10^{15} [11], which is almost close to the uncertainty of the Cs beam fountain clock (2 parts in 10^{15}) [12]. It is anticipated that the uncertainties of the above microwave ion clocks can surpass over the Cs clocks in the near future. It is, however, challenging to measure all the possible systematics in these ions precisely. Owing to their relatively simple electronic structures, it is possible to calculate some of the important spectroscopic properties of these ions accurately and a few selective major systematics can be estimated by using them. The above ions are also believed to be better candidates for testing new physics such as variation of fundamental constants and for quantum information experiments [13–15]. Therefore, it is necessary to carry out theoretical studies in these ions.

The presence of magnetic field in the clock experiments introduces Zeeman shifts in the clock candidates. To estimate systematics due to the external magnetic fields or to calibrate their strengths precisely in the trap of the ion microwave wave clocks, accurate knowledge of the ground-state Lande g_j factors of these clock candidates is required. There has also been a lot of interest to understand the roles of electron correlation effects for the accurate determination of g_j factors of atomic states. In a few-body systems, calculations of g_j factors serve as the benchmark test of quantum electrodynamics (QED) corrections to reproduce the experimental values [16–18]. In the heavier systems, precise determination of g_j factors depends equally on the accurate treatment of electron correlation effects and QED effects [19–22]. On the other hand, the relativistic coupled-cluster (RCC) theory is currently known to be one of the leading quantum many-body methods for treating electron correlations in the evaluation of atomic properties. The electron correlations in the determination of g_j factors of the ground states of Li, Be$^+$, and Ba$^+$ were investigated by Lindroth and Ynnerman [23] by employing the RCC theory. In their work, they estimated the correlations to the g_j factors over the Dirac values. Later, the roles of electron correlation effects to the net g_j factors of the ground and a few excited states of Ca$^+$ and Cd$^+$ were also investigated by employing the RCC theory [24,25]. In these RCC calculations, however, an expression was used that had two nonterminating series that were forcefully truncated at some level.

In this work, we intend to determine the ground-state g_j factors of the Cd$^+$, Hg$^+$, and Yb$^+$ ions, which can be applied for precise estimate of Zeeman shifts in the microwave clocks using these ions. Apart from Hg$^+$ [26], no experimental value

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[*] ymyu@aphy.iphy.ac.cn

[†] bijaya@prl.res.in

[‡] bsuo@nwu.edu.cn

of this quantity is available in other two ions. We include electron correlation effects by constructing single, double and triple excitations in the RCC theory framework. Moreover, we adopt the Λ-approach formalism in the RCC theory (Λ-RCC theory) [27–31] to evaluate the g_j factor to avoid appearance of nonterminating series in the expressions in contrast to the previous calculations [23–25].

II. THEORY AND METHOD OF CALCULATIONS

In the presence of an external homogeneous magnetic field $\vec{\mathbf{B}}$, the interaction Hamiltonian of electrons in an atomic system in atomic units (a.u.) is given by [23]

$$H_{\rm mag} = \mu_B \sum_i [\vec{\boldsymbol{\alpha}}_i \times \vec{\mathbf{r}}_i] \cdot \vec{\mathbf{B}}, \tag{1}$$

where μ_B is the Bohr magneton and α is the Dirac operator. The first-order Zeeman shift $\Delta E^{(1)}_{\rm Zeem}$ of the atomic state with the angular momentum j and projection Ω_j is directly related to the g_j factor as (assuming nuclear spin as zero for simplicity)

$$\Delta E^{(1)}_{\rm Zeem} = g_j \Omega_j \mu_B |\vec{\mathbf{B}}|. \tag{2}$$

This follows that the Dirac contribution to the Lande g_j factor of a bound-state electron in an atomic system with wave function $|\Psi\rangle$ can be evaluated as an expectation value of an operator

$$g_j^D = \frac{1}{\Omega_j}\left\langle \sum_i (\vec{\boldsymbol{\alpha}}_i \times \vec{\mathbf{r}}_i)_z \right\rangle_\Psi. \tag{3}$$

It is also known in the free electron case that QED corrections contribute significantly to the g_j factor. To account for the dominant contribution from the QED effects, we estimate its correction separately as [32,33]

$$\Delta g_j^Q = \frac{g_e - 2}{2\Omega_j}\left\langle \sum_i (\beta \Sigma_z)_i \right\rangle_\Psi, \tag{4}$$

where β is the Dirac matrix, Σ is the 4×4 spin matrix, and $g_e = 2.0023193$ is the free-electron Lande g factor. Therefore, the net value to the bound electron Lande g_j factor is given by

$$g_j = g_j^D + \Delta g_j^Q. \tag{5}$$

To determine the expectation values of the above quantities, we calculate the wave function of atomic states using the RCC theory by expressing as

$$|\Psi\rangle = e^{\hat T}|\Phi\rangle, \tag{6}$$

where $|\Phi\rangle$ is the reference determinant, which is obtained by the Dirac-Hartree-Fock (DHF) method, and $\hat T$ is the hole-particle excitation operators. For an N-electron system, we can express

$$\hat T = \sum_{k=1}^{N} \hat T_k, \tag{7}$$

where the operator $\hat T_k$ generates k-fold hole-particle excitations as

$$\hat T_k = \sum_{\substack{a_1 < a_2 \cdots < a_k \\ p_1 < p_2 \cdots < p_k}} t^{a_1 a_2 \cdots a_k}_{p_1 p_2 \cdots p_k} a_1^\dagger p_1 a_2^\dagger p_2 \cdots a_k^\dagger p_k, \tag{8}$$

where the indices p_i and a_i with $i = 1, 2, 3, \ldots,$ refer to the second quantization operators for the occupied and virtual orbitals, respectively.

From the Schrödinger equation $\hat H|\Psi\rangle = E\Psi\rangle$ with atomic Hamiltonian $\hat H$ and energy eigenvalue E, we get

$$\hat H e^T|\Phi\rangle = E e^T|\Phi\rangle \Rightarrow e^{-T}\hat H e^T|\Phi\rangle = E|\Phi\rangle. \tag{9}$$

Now projecting bras of $|\Phi\rangle$ and $|\Phi^{a_1 a_2 \cdots a_k}_{p_1 p_2 \cdots p_k}\rangle = a_1^\dagger p_1 a_2^\dagger p_2 \cdots a_k^\dagger p_k |\Phi\rangle$ from the left, we get the energy and amplitudes of the T_k operators as

$$\langle \Phi | e^{-\hat T} \hat H e^{\hat T} |\Phi\rangle = E \tag{10}$$

and

$$\left\langle \Phi^{a_1 a_2 \cdots a_k}_{p_1 p_2 \cdots p_k} \right| e^{-\hat T} \hat H e^{\hat T} |\Phi\rangle = 0, \ \ (k = 1, \ldots, N), \tag{11}$$

respectively. We use the Dirac-Coulomb Hamiltonian along with the Gaunt term of the Breit interaction in our calculations, which is given by

$$\begin{aligned}\hat H =& \sum_i [c(\vec{\boldsymbol{\alpha}} \cdot \vec{\mathbf{p}})_i + (\beta - 1)_i m_0 c^2 + V_{iA}] \\ &+ \sum_{i<j}\left[\frac{1}{r_{ij}} - \frac{1}{2}\frac{\vec{\boldsymbol{\alpha}}_i \cdot \vec{\boldsymbol{\alpha}}_j}{r_{ij}}\right],\end{aligned} \tag{12}$$

where i, j denote electrons, r_{ij} is the distance between i and j electrons, $m_0 c^2$ is the rest mass energy of an electron with speed of light c, and V_{iA} is the nuclear potential with atomic mass number A.

As can be followed from Eqs. (3) and (4), it is necessary to evaluate the expectation value expression accurately to determine g_j factors precisely. In the traditional RCC approach, the expectation value of an operator $\hat O$ can be obtained as [31]

$$\langle \hat O \rangle_\Psi = \frac{\langle\Psi|\hat O|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{\langle\Phi|e^{\hat T^\dagger}\hat O e^{\hat T}|\Phi\rangle}{\langle\Phi|e^{\hat T^\dagger}e^{\hat T}|\Phi\rangle} = \langle\Phi|e^{\hat T^\dagger}\hat O e^{\hat T}|\Phi\rangle_C, \tag{13}$$

where subscript C implies connected terms in the expression only. Keeping only the connected terms help in reducing number of terms in the computation, otherwise it would have been challenging to deal with the disconnected terms. As can be noticed it has a nonterminative series, so forcefully truncating the the expression may introduce unknown uncertainty to the calculation. Moreover, the above expression does not satisfy the Hellmann-Feynman theorem of evaluating properties. To avoid this, the expectation value can be evaluated by introducing the biorthonormal bra state to the corresponding ket state through the Λ deexcitation operator in the Λ-RCC theory framework [27–31] as described briefly below.

In the Λ-RCC theory framework, the bra-state wave function is expressed as [31,34]

$$\langle \tilde\Psi | = \langle \Phi | (1 + \tilde\Lambda) e^{-\hat T}, \tag{14}$$

where $\tilde{\Lambda}$ is the de-excitation operator like $\hat{T}^\dagger$ and is given by

$$\tilde{\Lambda} = \sum_{k=1}^{N} \tilde{\Lambda}_k, \tag{15}$$

where

$$\tilde{\Lambda}_k = \sum_{\substack{a_1<a_2\cdots<a_k \\ p_1<p_2\cdots<p_k}} \lambda_{a_1a_2\cdots a_k}^{p_1p_2\cdots p_k} a_1 p_1^\dagger a_2 p_2^\dagger \cdots a_k p_k^\dagger, \tag{16}$$

with $\lambda_{a_1a_1\cdots a_k}^{p_1p_2\cdots p_k}$ are the de-excitation RCC amplitudes. It can be noticed that

$$\langle\tilde{\Psi}|\Psi\rangle = \langle\Phi|(1+\tilde{\Lambda})e^{-\hat{T}}e^{\hat{T}}|\Phi\rangle = 1. \tag{17}$$

The amplitudes of the Λ_k-operators are obtained by solving

$$\langle\Phi|(1+\tilde{\Lambda})(e^{-\hat{T}}\hat{H}e^{\hat{T}} - E)\big|\Psi_{p_1p_2\cdots p_k}^{a_1a_2\cdots a_k}\big\rangle = 0. \tag{18}$$

After obtaining amplitudes for the $\hat{T}_k$ and $\hat{\Lambda}_k$ operators, the expectation value of an operator $\hat{O}$ can be evaluated as [31,34]

$$\begin{aligned}\langle\hat{O}\rangle_\Psi \equiv \frac{\langle\tilde{\Psi}|\hat{O}|\Psi\rangle}{\langle\tilde{\Psi}|\Psi\rangle} &= \langle\Phi|(1+\tilde{\Lambda})e^{-\hat{T}}\hat{O}e^{\hat{T}}|\Phi\rangle \\ &= \langle\Phi|(1+\tilde{\Lambda})\big(\hat{O}e^{\hat{T}}\big)_C|\Phi\rangle.\end{aligned} \tag{19}$$

As can be seen, this expression of evaluating expectation value contains only finite number of terms. In addition, it also satisfies the Hellmann-Feynman theorem [34]. To carry out these calculations, we obtained the one-body and two-body integrals using the four-component relativistic Kramers-paired molecular Dirac orbitals through the DIRAC program package [35]. Then, the RCC calculations are performed by using the MRCC package [36] that is interfaced with the DIRAC program [37].

To obtain the single-particle orbitals in the DHF method, we used the Dyall's uncontracted correlation consistent double-, triple-, quadruple-ζ functions [38,39] constructed as linear combinations of Gaussian type orbitals. These basis functions are referred to as $X\zeta$ with $X = 2$, 3, and 4 for the double-, triple-, and quadruple-ζ functions, respectively. It can be noted that if the kinetic balance condition [40] between the large and small components of the DHF orbitals are maintained, both the occupied and virtual orbitals are generated simultaneously by solving the Roothan equation self-consistently [41].

III. RESULTS AND DISCUSSION

The roles of electron correlation effects in the determination of g_j factors of atomic states are peculiar in nature [42]. Contributions from the higher-level excitations are nonnegligible to this property. Therefore, it is very challenging to produce their accurate values; particularly in the considered heavy atomic systems. To be able to account for dominant electron correlation effects and estimate the neglected contributions reliably, we adopted different steps. First, we approximate the RCC theory at the singles and doubles excitations level (RCCSD method) and used the $X = 4$ basis set, that has a reasonably large basis size, to obtain the main results and given as $\mathrm{P}|_{(4\zeta)}$. Here, we froze some of the inner core and high-lying virtual orbitals to perform the calculations with the available computational resources. Nonetheless, we also estimated contributions from the frozen orbitals, which are added as corrections and used as a part of the uncertainty estimations. For this purpose, we carried out calculations including more core electrons using a smaller size basis set in the RCCSD method, such as $X = 3$ for Cd^+ and Hg^+ (contribution is given as $\mathrm{P}|_{(3\zeta)}$), whereas for Yb^+ we took $X = 2$ (contribution is given as $\mathrm{P}|_{(2\zeta)}$). Calculations are also repeated using such a basis function, but considering the number of core orbitals that were included in the $\mathrm{P}|_{(4\zeta)}$ calculations and the differences in the respective ion were quoted as $\Delta\mathrm{P}_{\mathrm{core}}$. The reason for which we considered $X = 2$ size basis in Yb^+ is that it required us to allow correlations among more number of electrons, especially from the $4f$ orbitals, in this ion to achieve convergence in the calculations.

Similarly, we analyzed contributions from high-lying virtuals by performing calculations by cutting active virtuals energy levels at 10, 50, and 100 atomic units (a.u.) with the $X = 3$ basis functions in Cd^+ and Hg^+, but with $X = 2$ in Yb^+. Differences in the results estimated in such analyses are considered as the extrapolated contributions from the neglected virtuals and given as $\Delta\mathrm{P}_{\mathrm{virt}}$. Again, we performed calculations using the smaller size basis function after considering same number of occupied and virtual orbitals as were taken in the $\mathrm{P}|_{(4\zeta)}$ in the calculations, which indicates about possible corrections due to use of the finite-size basis functions. So these differences in the results from both the sets of calculations are given as $\Delta\mathrm{P}_{\mathrm{basis}}$. We also performed calculations considering triple excitations along with the singles and doubles excitations (RCCSDT method) using the aforementioned smaller size basis functions, and the differential g_j values from the same basis functions arising through the RCCSD and RCCSDT methods are quoted as $\Delta\mathrm{P}_{\mathrm{T}}$.

After adopting the above procedure for estimating various contributions, the final results ($\mathrm{P}_{\mathrm{Final}}$) to the g_j factors are obtained as

$$\mathrm{P}_{\mathrm{Final}} = \mathrm{P}|_{(4\zeta)} + \Delta\mathrm{P}_{\mathrm{core}} + \Delta\mathrm{P}_{\mathrm{virt}} + \Delta\mathrm{P}_{\mathrm{basis}} + \Delta\mathrm{P}_{\mathrm{T}}. \tag{20}$$

It is also essential to estimate uncertainties to our estimated values for g_j factors to use them in various applications. These uncertainties will arise from the frozen deeper core orbitals, from the frozen virtual orbitals due to use of finite-size basis functions and from the neglected contributions from the higher-level excitations in the RCC theory. We consider $\Delta\mathrm{P}_{\mathrm{core}}$ as the maximum value that will be contributing by the deeper core electrons, while $\Delta\mathrm{P}_{\mathrm{virt}}$ as the maximum contributions coming from the neglected virtual orbitals. Similarly, $\Delta\mathrm{P}_{\mathrm{basis}}$ and $\Delta\mathrm{P}_{\mathrm{T}}$ are assumed to be the maximum contributions arising from the extrapolated basis functions and neglected high-level excitations in the RCC theory. By adding all these contributions in quadrature, we quote the final errors in our calculations.

Having mentioned the general procedures adopted in the evaluation of g_j factors of the ground states of the Cd^+, Yb^+, and Hg^+ ions, we discuss the results of each ion for better understanding of their trends. In Table I, we list the results of the g_j factor for the ground state of Cd^+ from the RCCSD and RCCSDT methods with different size of basis functions. The results after correlating 18 outer lying core electrons from the $4s$, $4p$, and $4d$ orbitals using the RCCSD method

TABLE I. Contributions to the electronic g_j^D factor and Δg_j^Q correction of the ground $5s\,^2S_{1/2}$ state of Cd$^+$ obtained by using the RCC method. Uncertainties to both the quantities are also quoted. The 3ζ and 4ζ basis for Cd$^+$ contain ($28s$, $20p$, $13d$, $5f$, $3g$) and ($33s$, $25p$, $17d$, $7f$, $5g$, $3h$) orbitals, respectively.

Source	g_j^D	Δg_j^Q	g_j
$P\|_{(3\zeta)}$			
(core18)SD $<$ 50 a.u.	1.999974	0.002320	2.002295
(core18)SD $<$ 100 a.u.	1.999975	0.002320	2.002295
(core28)SD $<$ 50 a.u.	1.999977	0.002320	2.002297
(core18)SDT $<$ 50 a.u.	1.999971	0.002320	2.002291
$P\|_{(4\zeta)}$			
(core18)SD $<$ 50 a.u.	1.999973	0.002320	2.002293
$\Delta P_{\rm virt}$	0.000000	0.000000	0.000000
$\Delta P_{\rm core}$	0.000002	0.000000	0.000002
$\Delta P_{\rm basis}$	−0.000001	0.000000	−0.000001
$\Delta P_{\rm T}$	−0.000003	0.000000	−0.000003
$\mathbf{P_{Final}}$	1.999971	0.002320	2.002291
Uncertainty	0.000004	0.000000	0.000004

are given as “(core18)SD.” Initieware carried out using the $X = 3$ basis set. We obtained these results by considering virtual orbitals lying within 50 and 100 a.u., whose contributions are denoted as (core18)SD $<$ 50 a.u. and (core18)SD $<$ 100 a.u., respectively. The difference in the results are given by $\Delta P_{\rm virt}$. Then the calculations are repeated with 28 core electrons after adding low-lying $3d$ orbitals by employing the RCCSD method and the value is quoted as “(core28)SD.” The differential value between the (core18)SD $<$ 50 a.u. and (core28)SD $<$ 50 a.u. results is given as $\Delta P_{\rm core}$. After this, the calculations were repeated using $X = 4$ basis but correlating again the outer 18 electrons. The RCCSD value using the $X = 4$ basis is considered as $P|_{(4\zeta)}$ and the difference in the (core18)SD $<$ 50 a.u. results are quoted as $\Delta P_{\rm basis}$. Further, RCCSDT calculations are carried with $X = 3$ basis after correlating only 18 outer electrons and the change in the results from (core18)SD $<$ 50 a.u. with $X = 3$ is given as $\Delta P_{\rm T}$. It can be seen from all these analyses that $\Delta P_{\rm virt}$ is negligible, and other corrections are quite small. After accounting for all these contributions, we obtain the final g_j factor for Cd$^+$ as 2.002291(4). The uncertainty was estimated by adding all the above corrections quadratically as they are the leading-order contributions to the neglected contributions. This value is consistent with the previous recommendation value, 2.00286(53), within its error range [25] that was determined by employing expectation value method after terminating the infinite series in the property evaluating expression in the brute-force approach. The present calculation, however, has been improved significantly.

TABLE II. Contributions to the electronic g_j^D factor and Δg_j^Q correction of the ground $6s\,^2S_{1/2}$ state of Yb$^+$ obtained by using the RCC method. Uncertainties to both the quantities are also quoted. The 2ζ, 3ζ, and 4ζ basis for Yb$^+$ contain ($21s$, $14p$, $10d$, $3f$), ($30s$, $24p$, $16d$, $11f$, $3g$, $2h$), and ($35s$, $30p$, $19d$, $13f$, $5g$, $4h$, $2i$) orbitals, respectively.

Source	g_j^D	Δg_j^Q	g_j
$P\|_{(2\zeta)}$			
(core22)SD $<$ 10a.u.	2.0004930	0.0023213	2.0028144
(core22)SD $<$ 50a.u.	2.0005016	0.0023213	2.0028230
(core22)SD $<$ 100a.u.	2.0005015	0.0023213	2.0028228
(core32)SD $<$ 50a.u.	2.0005262	0.0023214	2.0028476
(core22)SDT $<$ 10a.u.	2.0003834	0.0023211	2.0027045
$P\|_{(3\zeta)}$			
(core22)SD $<$ 50a.u.	2.0005826	0.0023215	2.0029041
$P\|_{(4\zeta)}$			
(core22)SD $<$ 50a.u.	2.0005721	0.0023215	2.0028936
$\Delta P_{\rm core}$	0.0000247	0.0000000	0.0000247
$\Delta P_{\rm virt}$	−0.0000002	0.0000000	−0.0000002
$\Delta P_{\rm basis}$	−0.0000105	0.0000000	−0.0000105
$\Delta P_{\rm T}$	−0.0001096	−0.0000002	−0.0001098
$\mathbf{P_{Final}}$	2.0004765	0.0023213	2.0027978
Uncertainty	0.0001129	0.0000002	0.0001131

Contributions from various sources to the g_j factor of the ground state of Yb$^+$ are given in Table II. The (core22)SD <10 a.u., (core22)SD $<$ 50 a.u., and (core22)SD $<$ 100 a.u. calculations were carried out with the $X = 2$ basis set by freezing virtual orbitals within 10 a.u., 50 a.u., and 100 a.u., respectively, after correlating electrons from the $5s$, $5p$, and $4f$ core orbitals (with 22 core electrons). The difference in the (core22)SD $<$ 50 a.u. and (core22)SD $<$ 100 a.u. gives the $\Delta P_{\rm virt}$ correction. Then, correlations from the $4d$ electrons (total 32 core electrons) were added and excitations of these electrons to the virtual space within 50 a.u. were allowed. These contributions are given as “(core32)SD $<$ 50 a.u.” in the above table. The differences in the (core22)SD $<$ 50 a.u. and (core32)SD $<$ 50 a.u. results are given as $\Delta P_{\rm core}$ for Yb$^+$. The corresponding RCCSDT calculations with 22 core electrons considering excitations within 50 a.u. virtual space were carried out using $X = 2$ and the contribution is labeled as (core22)SDT $<$ 50 a.u. The difference in the result from (core32)SD $<$ 50 a.u. was quoted as $\Delta P_{\rm T}$ in the above table. The $P|_{(4\zeta)}$ and $\Delta P_{\rm basis}$ contributions were estimated in the similar manner as discussed for Cd$^+$. In Yb$^+$, we find higher-order corrections are larger than Cd$^+$. After considering all the contributions, we obtain g_j factor of Yb$^+$ as 2.002798(113). The uncertainty was determined by adopting the similar procedure as mentioned for Cd$^+$. We did not find any other rigorous evaluation of g_j factor for Yb$^+$ apart from a calculation using the time-dependent Hartree-Fock (TDHF) method [22]. The reported TDHF value is $g_j = 2.003117$ and our result is significantly different than this value. It is known that TDHF captures only the core-polarization effects to all orders. However, a previous study on the g_j factor in Ca$^+$ revealed that pair-correlation effects play important roles in the accurate determination of this quantity. This may be the reason for the large differences in the g_j factors obtained using the RCC and TDHF methods.

We present various contributions to the g_j factor calculation for the ground state of Hg$^+$ in Table III. The (core18)SD $<$ 50 a.u. and (core18)SD $<$ 100 a.u. calculations are carried out using the $X = 3$ basis set, where “(core18)” represents the correlation contributions only from the electrons in the $5s$, $5p$, and $5d$ core orbitals (i.e., total 18 core

TABLE III. Contributions to the electronic g_j^D factor and Δg_j^Q correction of the ground $6s\,^2S_{1/2}$ state of Hg$^+$ obtained by using the RCC method. Uncertainties to both the quantities are also quoted. The 3ζ and 4ζ basis for Hg$^+$ contain ($30s$, $24p$, $15d$, $11f$, $4g$, $1h$) and ($34s$, $30p$, $19d$, $13f$, $7g$, $4h$, $1i$) orbitals, respectively.

Source	g_j^D	Δg_j^Q	g_j
P$\vert_{(3\zeta)}$			
(core18)SD $<$ 50 a.u.	2.000880	0.002322	2.003202
(core18)SD $<$ 100 a.u.	2.000881	0.002322	2.003204
(core32)SD $<$ 50 a.u.	2.000887	0.002322	2.003209
(core18)SDT $<$ 50 a.u.	2.000843	0.002322	2.003165
P$\vert_{(4\zeta)}$			
(core18)SD $<$ 50 a.u.	2.000863	0.002322	2.003185
ΔP$_{\rm virt}$	0.000002	0.000000	0.000002
ΔP$_{\rm core}$	−0.000006	0.000000	−0.000006
ΔP$_{\rm basis}$	−0.000017	0.000000	−0.000017
ΔP$_{\rm T}$	−0.000037	0.000000	−0.000037
P$_{\rm Final}$	2.000806	0.002322	2.003128
Uncertainty	0.000041	0.000000	0.000041

electrons). The difference in the results from the two calculations is given as ΔP$_{\rm virt}$. Then, the RCCSD calculations were carried out by including core electrons from the $4f$ electrons and considering excitations up to 50 a.u. virtual space. This contribution is quoted as "(core32)SD $<$ 50 a.u." in the above table and its difference in the result from (core18)SD $<$ 50 a.u. is given as ΔP$_{\rm core}$. The RCCSDT calculations are carried out by correlating 18 core electrons within 50 a.u. virtual space and its difference from the corresponding calculations using the RCCSD method is given as ΔP$_{\rm T}$. The $P|_{(X=4)}$ and ΔP$_{\rm basis}$ contributions are evaluated using the same procedure as mentioned in the previous two cases. In this ion, we also find the corrections are of similar order like in the Yb$^+$ ion. Adding all the contributions, we obtain the final g_j factor of Hg$^+$ as 2.003128(41) after accounting for the uncertainty in the similar manner to the previously discussed two ions. In contrast to Cd$^+$ and Yb$^+$, there is a precise experimental value of the g_j factor Hg$^+$ that has been reported as 2.0031745(74) [26]. Our result matches within four decimal places with the experimental result. This indicates that accuracies of our calculations of g_j factors in the Cd$^+$ and Yb$^+$ ions are of similar level.

It should be noted that the many-body corrections to $\delta g_j = g_j^D - g_e$ comes from the residual Coulomb interactions at the first order itself and the contributions from the spin-orbit interactions start appearing at the second order in the perturbation theory. It was shown from the analytical derivation that δg_j scales as $(Z\alpha_e)^4$ in the heavier atomic systems [21,43,44], with the fine-structure constant α_e and atomic number of the system Z. Since we used coupled-cluster theory in the relativistic framework, contributions both the residual Coulomb interactions and the spin-orbit interactions are taken into account to all-orders implicitly. The above scaling law gives estimations of δg_j as 0.36×10^{-4}, 5.85×10^{-4}, and 9.98×10^{-4} in Cd$^+$, Yb$^+$, and Hg$^+$, respectively. Using our Λ-RCC theory, we obtained these values as 0.29×10^{-4}, 4.77×10^{-4}, and 8.06×10^{-4} in Cd$^+$, Yb$^+$, and Hg$^+$, respectively. This shows that our results are consistent with the $(Z\alpha_e)^4$ scaling law.

One of the contributions to the determination of g_j factors that is not mentioned yet is the contribution from the negative energy orbitals. Our estimated uncertainty to the g_j factor of Cd$^+$ from the electron correlation effects has already reached 10^{-6} level, so the roles of the negative energy orbitals to this result needs to be investigated. A recent combined theoretical and experimental study on the g_j factor in boron-like argon ion [45] shows that negative energy orbitals play important roles in achieving good agreement between measurement and calculation. Earlier studies also demonstrated that both relativistic and electron correlation effects behave in a peculiar way in the boron-like ions [46,47]. Since we considered here singly charged ions, we do not expect large contributions from the negative energy orbitals and their contributions could be of the order of 10^{-6} to the g_j factors of the bound electrons [48] in the considered ions. It is important to note that our estimated Δg_j^Q values using the effective Hamiltonian have contributions from these negative orbitals to some extent but their correlation effects with the electrons are only missing. Though we did not state it explicitly, we also included the electron correlation contributions to Δg_j^Q. We found electron correlation effects do not contribute much to these quantities. This was also evident from our previous work [25], where we showed correlation contributions from different RCC terms to both the g_j factor and Δg_j^Q correction explicitly. Similarly, the contribution to g_j from the nuclear recoil effect is inversely proportional to Z in an atomic system. We estimated its value to be below 10^{-7} level in Cd$^+$ [25] and expected it to be of similar order to the other two investigated ions. Therefore, this correction can be safely ignored here due to the intended precision levels of the reported results.

From the above analyses, it can be seen that the calculations of g_j factors in Cd$^+$ and Hg$^+$ are more precise than Yb$^+$. This is owing to different way of electron correlation behaviors in these ions. After the valence orbital, the next outer occupied orbitals belong to the $4f$ subshell in Yb$^+$, while they are the $4d$ and $5d$ subshells in Cd$^+$ and Hg$^+$, respectively. Correlation effects of the electrons from the f orbitals are usually very large compared to the electrons from the d orbitals. In fact, this is why theoretical studies of the quadrupole moment (Θ) of the $4f\,^2F_{7/2}$ state in Yb$^+$ are unable to explain its observed value [49] whereas very good agreement between the theoretical and experimental results for Θ of the $5d\,^2D_{5/2}$ state in Hg$^+$ has been achieved [50].

IV. CONCLUSION

We calculated the values of the g_j factor of the ground states of the Cd$^+$, Hg$^+$, and Yb$^+$ ions by using the relativistic coupled-cluster method by adopting Λ-operator framework. We investigated the influence of electronic correlation effects using the singles and doubles excitation configurations, and then by including triple excitations. Changes in the results with correlations of electrons from different number of occupied orbitals and by varying virtual configuration space are demonstrated in all the three ions. Our final results came out to be 2.002291(4), 2.002798(113), and 2.003128(41) for the Cd^+, Yb^+, and Hg^+ ions, respectively. Our result for Cd^+ is in agreement with the previous calculation [25], but the present calculation provides more precise value. However, we find a significant difference between our result with the previous calculation in Yb^+ [22]. There is only one experimental value available for Hg^+, and our result for this ion is in agreement with the measurement within the quoted error bar [26]. This validates our calculations for the other two investigated ions. These results will be useful for more precise estimation of the Zeeman splitting due to the external magnetic fields for accounting for systematics in the laser cooled Cd^+, Yb^+, and Hg^+ ion microwave clocks.

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