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Roles of electron correlation effects for the accurate determination of g_j factors of low-lying states of ^{113}Cd$^+$ and their applications to atomic clocks

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We investigate roles of electron correlation effects in the determination of g_j factors of the $ns\,^2S_{1/2}$ (n=5,6,7), $np\,^2P_{1/2,3/2}$ (n=5,6), $5d\,^2D_{3/2,5/2}$, and $4f\,^2F_{5/2,7/2}$ states of the singly ionized cadmium (Cd$^+$) ion. Single and double excited configurations along with important valence triple excited configurations through relativistic coupled-cluster (RCC) theory are taken into account for incorporating electron correlation effects in our calculations. We find significant contributions from the triples to the lower S and P states for attaining high accuracy results. The contributions of Breit interaction and lower-order quantum electrodynamics effects, such as vacuum polarization and self-energy corrections, are also estimated using the RCC theory and are quoted explicitly. In addition, we present energies of the aforementioned states from our calculations and compare them with the experimental results to validate g_j values. Using the g_j factor of the ground state, systematical shift due to the Zeeman effect in the microwave clock frequency of the $|5s\,^2S_{1/2}, F = 0, m_F = 0\rangle \leftrightarrow |5s\,^2S_{1/2}, F = 1, m_F = 0\rangle$ transition in the ^{113}Cd$^+$ ion has been estimated.

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I. INTRODUCTION

The use of high-precision atomic clocks for both scientific and commercial applications is widely accepted in many areas of physics. Today optical atomic clocks offer the most precise frequencies to recalibrate units of time (e.g., seconds). Microwave atomic clocks are extremely robust in numerous scientific and industrial fields including satellite navigation systems, network synchronization, timekeeping applications, and defense systems [1] owing to their several-order-lower frequencies compared with optical clock frequencies. Mostly microwave clocks are based on the neutral atoms, but making these clocks using singly charged ions has many advantages. They can be more compact in size and consume low power, which are the imperative criteria for making a portable atomic clock. Compared with the other developed trapped-ion microwave clocks, e.g., ^{199}Hg$^+$ [2,3], microwave clocks using ^{113}Cd$^+$ have the unique feature that their cooling and pumping lines have a frequency difference of only 800 MHz. Therefore, their cooling, pumping, and detecting processes can be carried out by the same laser. This is advantageous for making miniaturized atomic clocks for aerospace applications [5]. Since 2012, there has been much progress in the making of high-performance miniaturized cadmium ion atomic clocks [4–7]. A frequency uncertainty and stability for the ground-state hyperfine splitting of 6.6×10^{-14} and $6.1 \times 10^{-13}/\sqrt{\tau}$, respectively, where τ is the average time, were achieved in 2015 [4]. Sympathetic cooling of Cd$^+$ ions was accomplished in the mean time, which lowers the second-order Doppler shift and dead-time drastically [8]. In order to improve uncertainty of the clock frequency to below 10^{-16} or make clocks comparable with the currently available ^{133}Cs fountain clocks, one of the important tasks is to estimate the second-order Zeeman shift accurately.

In the microwave atomic clocks a small external magnetic field is applied to break the degeneracy of the ground-state hyperfine levels. The fluctuation arising from the background magnetic field can be suppressed down to 10^{-9} T or even lower by using multilayer magnetic shields. When the stability of the background magnetic field is well controlled, it becomes important to calibrate the applied magnetic field very strictly. This can affect precise estimate of the Zeeman shift, and hence accurate determination of the clock transition. For this purpose precise knowledge of the g_j factor of the ground state of the Cd$^+$ ion is strongly desired. There has also been immense interest in understanding roles of various physical effects for the accurate determination of the g_j factors of atomic states. Most of the g_j factor studies are concentrated on the highly charged ions (HCIs) with few electrons in which relativistic effects play crucial roles for their accurate determination. This demands rigorous treatments of quantum electrodynamics (QED) to higher orders and nuclear recoil (NRec) effects. For example, agreements between the theoretical and experimental values of the g_j factors in the H-like

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C^{5+}, O^{7+}, and Si^{13+} ions [9–12], and in the Li-like Si^{11+} and Ca^{17+} [13–15] HCIs at the eight or even lower decimal places, serve as the most stringent test of the bound-state QED theory. Such studies yield unprecedented values of the ratio between the mass of an electron and the mass of a proton, and the fine-structure constant [16]. Contrasting to the great success in achieving high-precision values of the g_j factors in few-body systems, accurate determination of these factors in many-electron systems is challenging owing to strong electron correlation effects associated with this property. In the neutral atoms or singly charged ions, these interactions contribute predominantly to the g_j factors over the QED interactions [17–20]. In this context, the relativistic coupled-cluster (RCC) theory, which is currently known as one of the leading quantum many-body methods and has been referred to as the gold standard for treating electron correlations, is apt to determine atomic properties including g_j factors accurately. This theory was employed to study the g_j factors of the ground states of Li, Be^+, and Ba^+ by Lindroth and Ynnerman [21], but they determined only the corrections to the g_j factors (Δg_j) due to electron correlation effects with respect to the bare Dirac values. Recently, the roles of electron correlation effects in the net g_j factors of ground and few excited states of Ca^+ were demonstrated by employing RCC theory [22].

In this paper, we have applied the RCC theory to calculate the g_j factors of the ground state $5s\,^2S_{1/2}$ and some of the low-lying $ns\,^2S_{1/2}$ (n=6,7), $np\,^2P_{1/2,3/2}$ (n=5,6), $5d\,^2D_{3/2,5/2}$, and $4f\,^2F_{5/2,7/2}$ excited states of Cd^+. We have also determined electron affinities (EAs) of the valence electrons of the above states with the $[4d^{10}]$ closed-shell configuration by considering singles and doubles excitations approximation in the RCC theory (RCCSD method) and compared them with the available experimental results to validate our calculations. We have incorporated contributions from the important valence triples excitations in a perturbative approach in the RCCSD method (RCCSDpT method) only in the g_j factor evaluation expression as described in [22]. Further, systematic shift due to the Zeeman effect in the microwave clock frequency of the $^{113}Cd^+$ ion has been estimated by using the calculated g_j factor of its ground state. We give all the quantities in atomic units (a.u.) unless otherwise specified explicitly.

II. THEORY

In the presence of an external homogeneous magnetic field $\vec{\mathbf{B}}$, the interaction Hamiltonian of electrons in an atomic system in a.u. is given by [21,23]

$$H_{\rm mag} = -c\sum_i \vec{\alpha}_i \cdot \vec{\mathbf{A}}_i = \frac{c}{2}\sum_i \vec{\alpha}_i \cdot (\vec{\mathbf{r}}_i \times \vec{\mathbf{B}}), \tag{1}$$

where c is the speed of light, $\vec{\alpha}$ is the Dirac operator, and $\vec{\mathbf{A}}$ is the vector field seen by the electron located at $\vec{\mathbf{r}}$ due to the applied magnetic field. We can rewrite the above expression as

$$\begin{aligned} H_{\rm mag} &= \frac{c}{2}\sum_i (\vec{\alpha}_i \times \vec{\mathbf{r}}_i)\cdot \vec{\mathbf{B}} \\ &= -i\frac{c}{\sqrt{2}}\sum_i r_i\{\vec{\alpha}_i \otimes \vec{\mathbf{C}}^{(1)}\}^{(1)} \cdot \vec{\mathbf{B}} = \tilde{\mathcal{M}} \cdot \vec{\mathbf{B}} \end{aligned} \tag{2}$$

where $\vec{\mathbf{C}}^{(1)}$ is the Racah coefficient of rank 1 and magnetic moment operator given by

$$\vec{\mathcal{M}} = \sum_{i,q=-1,0,1} \vec{\mu}_q^{(1)}(r_i) = -i\frac{c}{\sqrt{2}}\sum_i r_i\{\vec{\alpha}_i \otimes \vec{\mathbf{C}}^{(1)}\}^{(1)}. \tag{3}$$

Using this operator, the Dirac contribution to the Landé g_j factor of a bound-state electron in an atomic system is given by

$$g_j^D = \frac{1}{\mu_B}\frac{\tilde{\mathcal{M}}}{\vec{\mathbf{J}}} \tag{4}$$

with total angular momentum of the state $\mathbf{J}$ and the Bohr magneton $\mu_B = 1/2$ in a.u.. Using the reduced matrix element, it can be expressed as

$$g_j^D = \frac{1}{2\mu_B}\frac{\langle J||\vec{\mathcal{M}}||J\rangle}{\sqrt{J(J+1)(2J+1)}}. \tag{5}$$

For the calculation of this factor, the single-particle reduced matrix element of $\mu_q^{(1)}$ is given by

$$\begin{aligned} \langle \kappa_f||\mu^{(1)}||\kappa_i\rangle &= -(\kappa_f+\kappa_i)\langle -\kappa_f||\mathbf{C}^{(1)}||\kappa_i\rangle \\ &\quad \times \int_0^\infty dr\, r\,(P_f Q_i + Q_f P_i), \end{aligned} \tag{6}$$

where $P(r)$ and $Q(r)$ are the large and small components of the radial parts of the single-particle Dirac orbitals, respectively, and κ is the relativistic angular momentum quantum number. The reduced matrix element of the Racah $\vec{\mathbf{C}}^{(1)}$ operator is calculated as

$$\begin{aligned} \langle \kappa_f\,||\,\mathbf{C}^{(k)}\,||\,\kappa_i\rangle &= (-1)^{j_f+1/2}\sqrt{(2j_f+1)(2j_i+1)} \\ &\quad \times \begin{pmatrix} j_f & k & j_i \\ 1/2 & 0 & -1/2 \end{pmatrix} \Pi\left(l_{\kappa_f}, k, l_{\kappa_i}\right), \end{aligned} \tag{7}$$

with

$$\Pi\left(l_{\kappa_f}, k, l_{\kappa_i}\right) = \begin{cases} 1 & \text{for } l_{\kappa_f}+k+l_{\kappa_i} = \text{even} \\ 0 & \text{otherwise}, \end{cases} \tag{8}$$

for the corresponding orbital momentum l_κ of the orbital with relativistic quantum number κ.

For evaluating g_j^D using Eq. (5), it is necessary to calculate wave functions of the states in an atomic system considering relativistic effects. It is also known that the Dirac value of the Landé g factor of a free electron (g_f^D) has significant corrections from the QED theory. The net value with the QED effects is approximately given by [24]

$$\begin{aligned} g_f &\simeq g_f^D \times \left[1 + \frac{1}{2}\frac{\alpha_e}{\pi} - 0.328\left(\frac{\alpha_e}{\pi}\right)^2 + \cdots\right] \\ &\approx 1.001160 \times g_f^D, \end{aligned} \tag{9}$$

where α_e is the fine-structure constant. To account for this correction along with g_j^D (denoted by Δg_j^Q) for the net result as $g_j = g_j^D + \Delta g_j^Q$, we consider the additional interaction Hamiltonian with the magnetic field as [25]

$$\Delta H_{\rm mag} \approx 0.001160\,\mu_B\beta\,\vec{\Sigma}\cdot\vec{\mathbf{B}} = 0.001160\,\Delta\tilde{\mathcal{M}}\cdot\vec{\mathbf{B}}, \tag{10}$$

where β is the Dirac matrix, $\vec{\Sigma}$ is the four-component spinor, and $\Delta\vec{\mathcal{M}} = \sum_{i,q=-1,0,1} \Delta\vec{\mu}_q^{(1)}(r_i) = \sum_i \beta_i \vec{\Sigma}_i$. Using this Hamiltonian, we determine Δg_j^Q as [26]

$$\Delta g_j^Q = 0.001160 \, \frac{\langle J || \Delta\vec{\mathcal{M}} || J \rangle}{\sqrt{J(J+1)(2J+1)}}, \tag{11}$$

for which the single-particle matrix element is given by

$$\langle \kappa_f || \Delta\mu^{(1)} || \kappa_i \rangle = (\kappa_f + \kappa_i - 1)\langle -\kappa_f || \mathbf{C}^{(1)} || \kappa_i \rangle \times \int_0^\infty dr (P_f P_i + Q_f Q_i). \tag{12}$$

Contribution due to the NRec effect to the bound state g_j factors in Cd$^+$ can be estimated using the formula [27]

$$\Delta g_j^{\text{NRec}} = \frac{(\alpha_e Z)^2}{n^2} \frac{1}{M_{\text{nuc}}}, \tag{13}$$

where M_{nuc} is the mass of the atomic nucleus, Z is the atomic number, and n is the principal quantum number of the interested states. This is found to be of the order of $\approx 10^{-7}$, which is neglected because such uncertainty is much lower than the intended precision that can be achieved in the present paper.

III. METHOD OF CALCULATIONS

We consider the Dirac-Coulomb (DC) Hamiltonian to calculate the wave functions of the atomic states, which, in a.u., is given by

$$H^{\text{DC}} = \sum_i [c\alpha_i \cdot \mathbf{p}_i + (\beta_i - 1)c^2 + V_{\text{nuc}}(r_i)] + \sum_{i,j>i} \frac{1}{r_{ij}}, \tag{14}$$

where $\mathbf{p}_i$ is the momentum operator, $V_{nuc}(r)$ denotes the nuclear potential, and $\frac{1}{r_{ij}}$ represents the Coulomb potential between the electrons located at the i and j positions. The Breit interaction contribution is estimated by incorporating the interaction potential

$$V^B(r_ij) = -\frac{[\alpha_i \cdot \alpha_j + (\alpha_i \cdot \hat{\mathbf{r}}_{\mathbf{ij}})(\alpha_j \cdot \hat{\mathbf{r}}_{\mathbf{ij}})]}{2r_{ij}}, \tag{15}$$

where $\hat{\mathbf{r}}_{\mathbf{ij}}$ is the unit vector along $\mathbf{r}_{ij}$. Similarly, we also include effective potentials for vacuum polarization and self-energy interactions as discussed in our previous work [28] to account for QED interactions in the determination of the atomic wave functions.

The investigated states of the Cd$^+$ ion can be expressed in the RCC theory as [29,30]

$$|\Psi_v\rangle = e^T\{1 + S_v\}|\Phi_v\rangle, \tag{16}$$

where $|\Phi_v\rangle = a_v^\dagger|\Phi_0\rangle$ is the reference state with valence orbital v for the Dirac-Hartree-Fock (DHF) wave function of the $[4s^2 4p^6 4d^{10}]$ closed-shell configuration. The RCC excitation operators T and S_v are responsible for exciting electrons from the $|\Phi_0\rangle$ and $|\Phi_v\rangle$ reference states, respectively. The amplitudes of these RCC operators are evaluated by solving the following equations:

$$\langle \Phi_0^* | \overline{H}_N | \Phi_0 \rangle = 0 \tag{17}$$

and

$$\langle \Phi_v^* | (\overline{H}_N - \Delta E_v) S_v | \Phi_v \rangle = -\langle \Phi_v^* | \overline{H}_N | \Phi_v \rangle, \tag{18}$$

where $|\Phi_0^*\rangle$ and $|\Phi_v^*\rangle$ are the singly and doubly excited-state configuration with respect to $|\Phi_0\rangle$ and $|\Phi_v\rangle$, respectively. The notation $\overline{H}_N$ is defined as $\overline{H}_N = (He^T)_l$ where subscript N means the normal order form of the operator and l means that all the terms are linked. The quantity ΔE_v corresponds to the EA of the state with the valence electron v. We evaluate ΔE_v by

$$\Delta E_v = \langle \Phi_v | \overline{H}_N \{1 + S_v\} | \Phi_v \rangle - \langle \Phi_0 | \overline{H}_N | \Phi_0 \rangle. \tag{19}$$

In the RCCSD method, the singles and doubles excitations are denoted by

$$T = T_1 + T_2 \quad \text{and} \quad S_v = S_{1v} + S_{2v}. \tag{20}$$

After obtaining amplitudes of the RCC operators, the expectation value of an operator O is evaluated as

$$\frac{\langle \Psi_v | O | \Psi_v \rangle}{\langle \Psi_v | \Psi_v \rangle} = \frac{\langle \Phi_v | \{1 + S_v^\dagger\} e^{T^\dagger} O e^T \{1 + S_v\} | \Phi_v \rangle}{\langle \Phi_v | \{1 + S_v^\dagger\} e^{T^\dagger} e^T \{1 + S_v\} | \Phi_v \rangle}. \tag{21}$$

We adopt an iterative procedure to include contributions from the nonterminative terms from the above expressions. Here, O stands for both the $\mathcal{M}$ and $\Delta\mathcal{M}$ operators for the evaluations of the g_j^D and Δg_j^Q contributions, respectively. In our previous work, we had observed that triples excitations play important roles in the determination of the g_j factors [22]. Inclusion of these excitations requires huge computational resources, which we are lacking at present. Therefore, we take into account these contributions in the RCCSDpT method only by defining excitation operators in the perturbative approach as

$$T_3^{\text{pert}} = \frac{1}{6} \sum_{abc,pqr} \frac{(H_N T_2)_{abc}^{pqr}}{\epsilon_a + \epsilon_b + \epsilon_c - \epsilon_p - \epsilon_q - \epsilon_r} \tag{22}$$

and

$$S_{3v}^{\text{pert}} = \frac{1}{4} \sum_{ab,pqr} \frac{(H_N T_2 + H_N S_{2v})_{abv}^{pqr}}{\Delta E_v + \epsilon_a + \epsilon_b - \epsilon_p - \epsilon_q - \epsilon_r}, \tag{23}$$

where $\{a, b, c\}$ and $\{p, q, r\}$ represent the occupied and virtual orbitals, respectively, and ϵs are their single-particle orbital energies. Contributions from these operators to the g_j factors are then given in terms of $T_2^\dagger O T_3^{\text{pert}}$, $S_{2v}^\dagger O T_3^{\text{pert}}$, $S_{2v}^\dagger O S_{3v}^{\text{pert}}$, $T_2^\dagger O S_{3v}^{\text{pert}}$, $S_{1v}^\dagger T_2^\dagger O S_{3v}^{\text{pert}}$, $T_3^{\text{pert}\dagger} O T_3^{\text{pert}}$, and $S_{3v}^{\text{pert}\dagger} O S_{3v}^{\text{pert}}$ along with their possible complex conjugate (c.c.) terms as part of Eq. (21) in the RCCSD expression.

IV. RESULTS AND DISCUSSION

To verify accuracies of the wave functions of the atomic states, the g_j factors of which are investigated here, we have evaluated EAs and compared them with their available experimental values. In Table I, we give EAs of 11 low-lying states of Cd$^+$ from the DHF, second-order relativistic many-body perturbation theory [RMBPT(2)] and RCCSD methods. As can be seen, the DHF method gives lower values while the RMBPT(2) method gives larger values compared to the results

TABLE I. Electron affinities (EAs) of the 5–7$s\,^2S_{1/2}$, 5 and 6$p\,^2P_{1/2,3/2}$, 5$d\,^2D_{3/2,5/2}$, and 4$f\,^2F_{5/2,7/2}$ states (in cm^{-1}) of ^{113}Cd$^+$ from DHF, second-order relativistic many-body perturbation theory [RMBPT(2)], and RCCSD methods are given. Corrections from the Breit (ΔBreit) and low-order QED (ΔQED) interactions are quoted separately. The final results obtained by the RCCSD values adding ΔBreit and ΔQED are compared with the experimental values listed in the NIST database [31]. Uncertainties in our final results are estimated using triple excitations in the perturbative approach. Differences between our results from the NIST data are mentioned as Δ in percentage.

State	DHF	RMBPT(2)	RCCSD	ΔBreit	ΔQED	Final	NIST	Δ
$5s\,^2S_{1/2}$	−124567.93	−138618.14	−136012.37	84.10	60.14	−135868(587)	−136374.34	0.4
$5p\,^2P_{1/2}$	−84902.34	−93102.78	−91847.93	83.31	7.58	−91757(306)	−92238.40	0.5
$5p\,^2P_{3/2}$	−82870.41	−90363.14	−89347.42	50.24	−0.64	−89298(295)	−89755.93	0.5
$6s\,^2S_{1/2}$	−51061.62	−53896.08	−53315.36	18.02	12.42	−53285(147)	−53383.93	0.2
$5d\,^2D_{3/2}$	−45146.73	−46880.67	−46602.79	3.85	0.38	−46599(94)	−46685.35	0.2
$5d\,^2D_{5/2}$	−45009.55	−46667.87	−46445.57	−0.60	0.01	−46446(90)	−46530.84	0.2
$6p\,^2P_{1/2}$	−39865.05	−41935.34	−41536.83	22.69	1.98	−41512(78)	−41664.22	0.4
$6p\,^2P_{3/2}$	−39241.67	−41181.53	−40844.47	13.81	−0.25	−40831(75)	−40990.98	0.4
$7s\,^2S_{1/2}$	−28191.88	−29280.12	−29045.33	7.11	4.87	−29033(58)	−29073.79	0.1
$4f\,^2F_{5/2}$	−27539.36	−27884.18	−27880.85	0.13	0.11	−27881(22)	−27955.19	0.3
$4f\,^2F_{7/2}$	−27542.58	−27886.78	−27884.13	0.23	0.11	−27884(22)	−27942.22	0.2

from the RCCSD method. The RCCSD results are in close agreement with the experimental results. Corrections from the Breit and QED interactions are quoted explicitly from the RCCSD method, and those corrections are found to be comparatively small. Uncertainties in our final results are given by estimating contributions from the valence triple excitations in the perturbative approach, which are reasonably large. This shows that the triple excitations are important to improve accuracies of our calculations. Our results are compared with the experimental values listed in the National Institute of Science and Technology (NIST) database [31]. Differences between our final results from these experimental values are given as Δ in percentage in the same table. This shows that our calculations agree with the experimental values at the sub-1 percentage level in all the states. These uncertainties can be reduced further by incorporating full triple excitations in our RCC method. Nonetheless, this analysis shows that we shall be able to obtain g_j factors with similar accuracies for the considered states as for the case of energies.

After the investigation of roles of the electron correlation effects in the EAs, we present the calculations of g_j factors of the above-mentioned states of ^{113}Cd$^+$. We give the g_j^D values in Table II from the DHF and RCCSD methods along with the corrections from the terms involving perturbative triple operators of the RCCSDpT method. The estimated Δg_j^Q corrections to the g_j^D values are also quoted from the DHF and RCCSD methods in the same table. They seem to be the decisive contributions to obtain the final results. Correlation contributions to the g_j^D values due to the perturbative triple excitations, and contributions from the Breit and QED interactions, are shown explicitly. The final g_j values, $g_j = g_j^D + \Delta g_j^Q$, of the respective states are obtained by adding all these corrections. In our calculations we find the perturbatively triple excitation terms have sizable contributions to the

TABLE II. The g_j factors of the 5–7$s\,^2S_{1/2}$, 5 and 6$p\,^2P_{1/2,3/2}$, 5$d\,^2D_{3/2,5/2}$, and 4$f\,^2F_{5/2,7/2}$ states. The Dirac contributions to the g_j factor denoted by g_j^D from the DHF and RCCSD methods along with corrections due to the perturbatively triple excitation terms and the Breit and QED electronic interactions are given. Contributions to Δg_j^Q from the DHF and RCCSD method are quoted correspondingly. The final values, $g_j^D + \Delta g_j^Q$ by adding corrections to g_j^D, are taken from the RCCSD method. The uncertainties are mentioned in the parentheses by estimating as half of the contributions due to the perturbatively triple excitation terms.

	Contributions to g_j^D		Corrections to g_j^D			Contributions to Δg_j^Q		
State	DHF	RCCSD	Triples	Breit	QED	DHF	RCCSD	Final
$5s\,^2S_{1/2}$	1.999876	2.001624	−0.001064	−0.000020	−0.0000050	0.002320	0.002324	2.00286(53)
$5p\,^2P_{1/2}$	0.666604	0.666568	0.001662	0.000013	0.0000007	−0.000773	−0.000773	0.66747(83)
$5p\,^2P_{3/2}$	1.333283	1.333522	0.000860	−0.000003	−0.0000006	0.000773	0.000773	1.33515(43)
$6s\,^2S_{1/2}$	1.999967	2.000202	−0.000253	−0.000003	−0.0000007	0.002320	0.002321	2.00227(13)
$6p\,^2P_{1/2}$	0.666647	0.666657	0.000407	0.000004	0.0000003	−0.000773	−0.000773	0.66630(20)
$6p\,^2P_{3/2}$	1.333315	1.333396	0.000189	−0.000001	−0.0000003	0.000773	0.000773	1.33436(1)
$7s\,^2S_{1/2}$	1.999984	2.000070	−0.000099	−0.000001	−0.0000003	0.002320	0.002320	2.00229(5)
$5d\,^2D_{3/2}$	0.799982	0.800013	0.000645	0.000002	−0.0000001	−0.000464	−0.000464	0.80020(32)
$5d\,^2D_{5/2}$	1.199982	1.200094	0.000375	−0.000002	−0.0000014	0.000464	0.000464	1.20093(19)
$4f\,^2F_{5/2}$	0.857136	0.857140	−0.000027	0.000000	0.0000001	−0.000331	−0.000331	0.85678(1)
$4f\,^2F_{7/2}$	1.142850	1.142855	−0.0000427	0.000000	−0.0000001	0.000331	0.000331	1.14314(2)

TABLE III. The contributions to g_j^D obtained in the perturbative triples using the RCCSDpT method.

States	$T_2^\dagger OS_{3v}^{\text{pert}}$	$S_{1v}^\dagger T_2^\dagger OS_{3v}^{\text{pert}}$	$T_3^{\text{pert}\dagger} OT_3^{\text{pert}}$	$S_{3v}^{\text{pert}\dagger} OS_{3v}^{\text{pert}}$
$5s\,^2S_{1/2}$	−0.001070	−0.000037	0.000154	−0.000111
$5p\,^2P_{1/2}$	0.000830	0.000050	0.000033	0.000749
$5p\,^2P_{3/2}$	0.000137	0.000011	0.000073	0.000639
$6s\,^2S_{1/2}$	−0.000286	−0.000030	0.000026	0.000037
$6p\,^2P_{1/2}$	0.000173	−0.000018	0.000008	0.000244
$6p\,^2P_{3/2}$	−0.000001	−0.000014	0.000018	0.000186
$7s\,^2S_{1/2}$	−0.000107	−0.000011	0.000010	0.000009
$5d\,^2D_{3/2}$	0.000025	≈0.0	0.000027	0.000586
$5d\,^2D_{3/2}$	−0.000056	≈0.0	0.000041	0.000389
$4f\,^2F_{5/2}$	−0.000027	≈0.0	≈0.0	≈0.0
$4f\,^2F_{7/2}$	−0.000043	≈0.0	≈0.0	≈0.0

g_j factors. This suggests a full account of triple and other higher level excitations would improve the results further. Nonetheless, we anticipate additional contributions from these higher level excitations will be within the half of the estimated contributions due to the perturbative triple excitations. On this basis we assign uncertainties as 50% of the perturbative excitation contributions to the final values of the g_j factors. There are no experimental values of the g_j factors of the considered states in Cd$^+$ available to compare with our calculations.

The contributions to g_j^D of the perturbatively triple excitations terms originate mainly from the $T_2^\dagger OS_{3v}^{\text{pert}}$, $S_{1v}^\dagger T_2^\dagger OS_{3v}^{\text{pert}}$, $T_3^{\text{pert}\dagger} OT_3^{\text{pert}}$, and $S_3^{\text{pert}\dagger} OS_{3v}^{\text{pert}}$ terms, which are given explicitly in Table III. Computing these terms is very time consuming. As can be seen, these triple contributions are as large as the correlation contributions due to the RCCSD method. Contributions from $T_2^\dagger OS_{3v}^{\text{pert}}$ are found to be relatively larger compared to the other terms followed by $T_3^{\text{pert}\dagger} OT_3^{\text{pert}}$, $S_{1v}^\dagger T_2^\dagger OS_{3v}^{\text{pert}}$, and $S_3^{\text{pert}\dagger} OS_{3v}^{\text{pert}}$ and there are strong cancellations among the contributions from the above terms. The computation of $S_3^{\text{pert}\dagger} OT_3^{\text{pert}}$ is extremely costly, and hence it is neglected in the g_j^D calculation of $4f$ states. As shown in Sec. III the contributions of the triple excitation terms for the $4f$ states are far less than the other states. In Fig. 1, we plot magnitudes of these contributions from the individual terms explicitly in order to highlight their roles. It can be seen from these figures that the triples excitations have substantially large contributions for the ground state and $n = 5$ excited states and smaller contributions for higher-lying excited states.

Another motivation of the present paper is to estimate the typical order of systematic effect due to the applied magnetic field to the microwave clock frequency of the ground-state hyperfine structure splitting in ^{113}Cd$^+$. The present level of accuracy of this clock is ≈10^{-14} [4] and our desired precision level is 10^{-16}. In ^{113}Cd$^+$, the $^2S_{1/2}\,(F = 0, m_F = 0) \rightarrow (F = 1, m_F = 0)$ transition is considered for making the clock, with $F = I \pm J$ for the nuclear spin I and electron angular momentum J and with its projection m_F. Under the low magnetic field, the energies $W(F, m_F, B)$ (given in SI unit) of different hyperfine-Zeeman sublevels $|(J, m_J)F, m_F\rangle$ for a given magnetic-field strength B can be approximately estimated as [32–34]

$$W(0,0,B) \simeq W(0,0,0) - \frac{3hA_{\text{hf}}}{4} - \frac{[g_j - g_I]^2 \mu_B^2 B^2}{4hA_{\text{hf}}}, \quad (24)$$

$$W(1,0,B) \simeq W(1,0,0) + \frac{hA_{\text{hf}}}{4} + \frac{[g_j - g_I]^2 \mu_B^2 B^2}{4hA_{\text{hf}}}, \quad (25)$$

and

$$W(1,\pm 1,B) \simeq W(1,\pm 1,0) + \frac{hA_{\text{hf}}}{4} \pm \frac{[g_j + g_I]\mu_B B}{2} \quad (26)$$

where g_j and g_I are the electronic and nuclear g factors, μ_B is the Bohr magneton, and A_{hf} is the magnetic dipole hyperfine-structure constant. Using Eqs. (24) and (25), the energy difference between the clock states of the ground state in ^{113}Cd$^+$ is given by

$$W(0,0,B) - W(1,0,B) \simeq -hA_{\text{hf}} - \frac{[g_j - g_I]^2 \mu_B^2 B^2}{2hA_{\text{hf}}}. \quad (27)$$

As can be seen, the energy shift depends on the stray magnetic field, where the second term in Eq. (27) is referred to as the second-order Zeeman shift. Thus, the change in frequency due

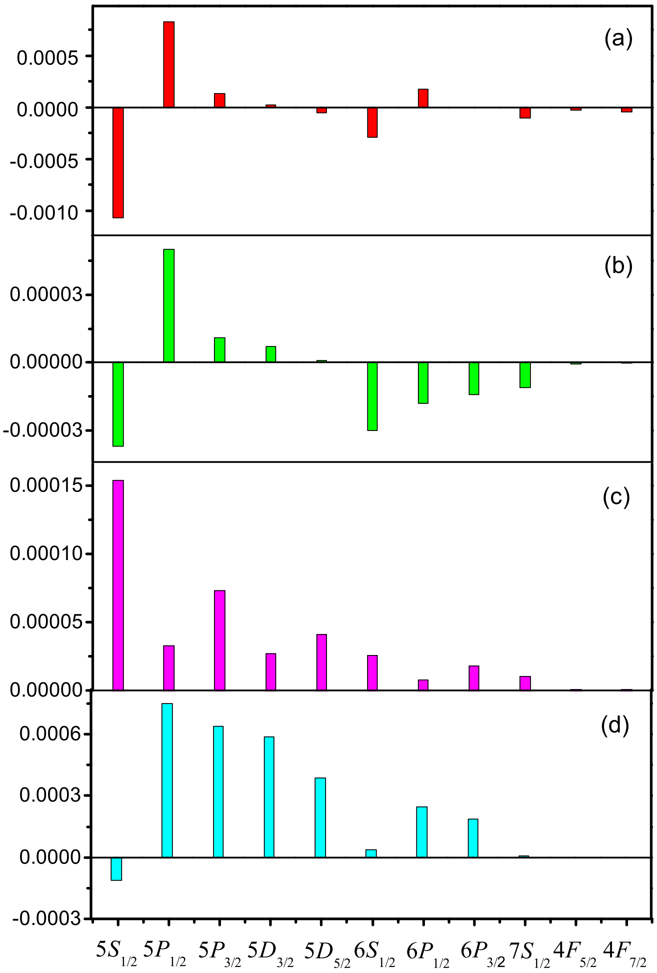

FIG. 1. The values of the triple contributions of (a) $T_2^\dagger OS_{3v}^{\text{pert}}$, (b) $S_{1v}^\dagger T_2^\dagger OS_{3v}^{\text{pert}}$, (c) $T_3^{\text{pert}\dagger} OT_3^{\text{pert}}$, and (d) $S_3^{\text{pert}\dagger} OS_{3v}^{\text{pert}}$ for different valence states.

to the second-order Zeeman shift is expressed as

$$\Delta\nu^{(2)}_{\text{Zeem}}(B) = -\frac{[g_j - g_I]^2\mu_B^2 B^2}{2h^2 A_{\text{hf}}}. \tag{28}$$

As can be seen, uncertainty in this quantity depends on the uncertainties in both the g_j factor and the applied magnetic field B. In our experiment, the magnetic field is generated by a pair of Helmholtz coils and the current controls the strength of the magnetic field. Thus, it is not straightforward for us to measure the applied magnetic-field strength very accurately. Under such circumstances, the value of B needs to be calibrated.

Assuming the B value is known precisely, the fractional frequency uncertainty in $\Delta\nu^{(2)}_{\text{Zeem}}(B)$ can be obtained by

$$\begin{aligned}\delta\big[\Delta\nu^{(2)}_{\text{Zeem}}(B)\big] &= \frac{\partial\big[\Delta\nu^{(2)}_{\text{Zeem}}(B)\big]}{\partial g_j A_{\text{hf}}}\delta g_j\\ &= (g_j - g_I)\frac{\mu_B^2 B^2}{h^2 A_{\text{hf}}^2}\delta g_j\\ &\approx 1.70\times10^{-14}\delta g_j,\end{aligned} \tag{29}$$

where δg_j is the estimated uncertainty of g_j. The above value is estimated by considering $B = 10^{-7}$ T for our typical condition of the experiment, $A_{\text{hf}} \simeq -15.2$ GHz [4], and $g_I = 0.6223009(9)\times10^{-3}$ [35]. By substituting our determined values $g_j = 2.00286$ and $\delta g_j = \pm0.00053$, we find that uncertainty in the second-order Zeeman shift will not affect the clock frequency at the 10^{-16} precision level if the applied magnetic field is lower than the above assumed value. It is also imperative to estimate the maximum level of fluctuation in order to sustain the aforementioned precision level of the clock frequency. For this purpose, we use two magnetic-field sensitive transitions; i.e., ν_+ and ν_- correspond to the transitions from $(F, m_F) = (0, 0)$ to $(F, m_F) = (1, 1)$ and from $(F, m_F) = (0, 0)$ to $(F, m_F) = (1, -1)$, respectively. Using Eqs. (24) and (26), their energy differences at the first-order level of B can be given by

$$W(0,0,B) - W(1,1,B) \simeq -hA_{\text{hf}} - \frac{[g_j + g_I]\mu_B B}{2} \tag{30}$$

and

$$W(0,0,B) - W(1,-1,B) \simeq -hA_{\text{hf}} + \frac{[g_j + g_I]\mu_B B}{2}. \tag{31}$$

This yields the frequency difference as

$$\delta\nu_{\mp} \equiv \nu_- - \nu_+ \simeq \frac{[g_j + g_I]\mu_B B}{h}. \tag{32}$$

Using this expression, the magnetic-field strength B can be determined as

$$B \simeq \frac{h\delta\nu_{\mp}}{[g_j + g_I]\mu_B}. \tag{33}$$

This leads to uncertainty in the calibration of magnetic field with respect to the g_j factor as

$$\delta B = \frac{\partial B}{\partial g_j}\delta g_j \simeq -\frac{h\delta\nu_{\mp}}{(g_j + g_I)^2\mu_B}\delta g_j \approx -5.0\times10^{-8}\delta g_j \text{ T}. \tag{34}$$

Here, we have used $\delta\nu_{\mp} \simeq 2.8$ kHz for $B = 10^{-7}$ T [4] along with values for other variables as defined above. According to this, the calibration of the B value will be affected by the uncertainty in the value of g_j. Using our estimated g_j value, we anticipate the uncertainty in B would be less than 10^{-10} T. This is sufficiently low to maintain the uncertainty in the fractional second-order Zeeman shift with respect to the clock frequency lower than 10^{-17} for the assumed magnetic field. This is good enough for ensuring the 10^{-16} precision level measurement of clock frequency.

V. CONCLUSION

The g_j factors of the ground $5s\,^2S_{1/2}$ state, and the excited $6-7s\,^2S_{1/2}$, 5 and $6p\,^2P_{1/2,3/2}$, $5d\,^2D_{3/2,5/2}$, and $4f\,^2F_{5/2,7/2}$ states, of ^{113}Cd$^+$ are calculated by using the relativistic coupled-cluster theory. We have also evaluated energies of these states and compared them with their experimental results to verify reliability of our calculations. We observed triples effects are significant for high-precision calculation of the g_j factors of the aforementioned states, especially for the low-lying states, in Cd$^+$. Using the precisely determined g_j factor of the ground state, we have analyzed typical order of systematic shift due to the second-order Zeeman effect in the clock frequency of the $|5s^2S_{1/2}, F = 0, m_F = 0\rangle \leftrightarrow |5s^2S_{1/2}, F = 1, m_F = 0\rangle$ transition in the ^{113}Cd$^+$ ion and found it will be within the desired fractional uncertainty 10^{-16} level.

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[1] S. Weyers, V. Gerginov, M. Kazda, J. Rahm, B. Lipphardt, G. Dobrev, and K. Gobble, Metrologia **55**, 789 (2018).

[2] P. Phoonthong, M. Mizuno, K. Kido, and N. Shiga, Appl. Phys. B **117**, 673 (2014).

[3] E. A. Burt, L. Yi, B. Tucker, R. Hamell, and R. L. Tjoelker, IEEE Trans. Ultrason. Ferroelectr. Freq. Control **63**, 1013 (2016).

[4] K. Miao, J. W. Zhang, X. L. Sun, S. G. Wang, A. M. Zhang, K. Liang, and L. J. Wang, Opt. Lett. **40**, 4249 (2015).

[5] J. W. Zhang, Z. B. Wang, S. G. Wang, K. Miao, B. Wang, and L. J. Wang, Phys. Rev. A **86**, 022523 (2012).

[6] S. G. Wang, J. W. Zhang, K. Miao, Z. B. Wang, and L. J. Wang, Opt. Express **21**, 12434 (2013).

[7] J. W. Zhang, S. G. Wang, K. Miao, Z. B. Wang, and L. J. Wang, Appl. Phys. B **114**, 183 (2014).

[8] Y. N. Zuo, J. Z. Han, J. W. Zhang, and L. J. Wang, Appl. Phys. Lett. **115**, 061103 (2019).

[9] J. Verdú, S. Djekić, S. Stahl, T. Valenzuela, M. Vogel, G. Werth, T. Beier, H.-J. Kluge, and W. Quint, Phys. Rev. Lett. **92**, 093002 (2004).

[10] S. Sturm, A. Wagner, M. Kretzschmar, W. Quint, G. Werth, and K. Blaum, Phys. Rev. A **87**, 030501(R) (2013).

[11] S. Sturm, F. Köhler, J. Zatorski, A. Wagner, Z. Harman, G. Werth, W. Quint, C. H. Keitel, and K. Blaum, Nature (London) **506**, 467 (2014).

[12] F. Köhler, S. Sturm, A. Kracke, G. Werth, W. Quint, and K. Blaum, J. Phys. B **48**, 144032 (2015).

[13] A. Wagner, S. Sturm, F. Köhler, D. A. Glazov, A. V. Volotka, G. Plunien, W. Quint, G. Werth, V. M. Shabaev, and K. Blaum, Phys. Rev. Lett. **110**, 033003 (2013).

[14] A. V. Volotka, D. A. Glazov, V. M. Shabaev, I. I. Tupitsyn, and G. Plunien, Phys. Rev. Lett **112**, 253004 (2014).

[15] F. Köhler, K. Blaum, M. Block, S. Chenmarev, S. Eliseev, D. A. Glazov, M. Goncharov, J. Hou, A. Kracke, D. A. Nesterenko, Y. N. Novikov, W. Quint, E. M. Ramirez, V. M. Shabaev, S. Sturm, A. V. Volotka, and G. Werth, Nat. Commun. **7**, 10246 (2016).

[16] S. Sturm, M. Vogel, F. Köhler-Langes, W. Quint, K. Blaum, and G. Werth, Atoms **5**, 4 (2017).

[17] L. Veseth, Phys. Rev. A **22**, 803 (1980).

[18] L. Veseth, J. Phys. B **16**, 2891 (1983).

[19] V. A. Dzuba, V. V. Flambaum, P. G. Silvestrov, and O. P. Sushkov, Phys. Scr. **31**, 275 (1985).

[20] G. H. Gossel, V. A. Dzuba, and V. V. Flambaum, Phys. Rev. A **88**, 034501 (2013).

[21] E. Lindroth and A. Ynnerman, Phys. Rev. A **47**, 961 (1993).

[22] B. K. Sahoo and P. Kumar, Phys. Rev. A **96**, 012511 (2017).

[23] J. J. Sakurai, *Advanced Quantum Mechanics* (Addison-Wesley, Reading, MA, 1967).

[24] A. Czarnecki, U. D. Jentschura, K. Pachucki, and V. A. Yerokhin, Can. J. Phys. **84**, 453 (2005).

[25] A. J. Akhiezer and V. B. Berestetskii, *Quantum Electrodynamics* (Interscience, New York, 1965), Chap. 8, Sec. 50.2.

[26] K. T. Cheng and W. J. Childs, Phys. Rev. A **31**, 2775 (1985).

[27] V. M. Shabaev, D. A. Glazov, G. Plunien, and A. V. Volotka, J. Phys. Chem. Ref. Data **44**, 031205 (2015).

[28] Y. M. Yu and B. K. Sahoo, Phys. Rev. A **99**, 022513 (2019).

[29] Y. M. Yu and B. K. Sahoo, Phys. Rev. A **96**, 050502(R) (2017).

[30] C. B. Li, Y. M. Yu, and B. K. Sahoo, Phys. Rev. A **97**, 022512 (2018).

[31] http://physics.nist.gov/PhysRefData/ASD/.

[32] G. Breit and I. I. Rabi, Phys. Rev. **38**, 2082 (1931).

[33] J. Vanier and C. Audoin, *The Quantum Physics of Atomic Frequency Standard* (Adam Hilger, Bristol and Philadelphia, 1989), Vol. 1.

[34] Wayne M. Itano, J. Res. Natl. Inst. Stand. Technol. **105**, 829 (2000).

[35] P. W. Spence and M. N. McDermott, Phys. Lett. A **42**, 273 (1972).