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Ab initio relativistic many-body calculation of hyperfine splittings of ^{113}Cd$^+$

Gopal Dixit,[1] H. S. Nataraj,[2] B. K. Sahoo,[3] R. K. Chaudhuri,[2] and Sonjoy Majumder[4]
[1]*Department of Physics, Indian Institute of Technology-Madras, Chennai 600 036, India*
[2]*Indian Institute of Astrophysics, Bangalore 34, India*
[3]*Max Planck Institute for the Physics of Complex Systems, D-01187 Dresden, Germany*
[4]*Department of Physics, Indian Institute of Technology, Kharagpur 721302, India*

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This work presents accurate *ab initio* determination of the hyperfine splitting for the ground state and a few low-lying excited states of ^{113}Cd$^+$, an important candidate for the frequency standard in the microwave region, using the coupled-cluster theory in the relativistic framework. The hyperfine energy splittings, which are estimated here theoretically in the literature, are in good agreement with the recent experimental results. We have also carried out the lifetime calculations of the $5\,^2P_{1/2}$ and $5\,^2P_{3/2}$ states, which are in good agreement with the available experimental results. The role of different electron correlation effects in the determination of these quantities are discussed and their contributions are presented.

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The current frequency standard is based on the ground state hyperfine transition in ^{133}Cs which is in the microwave regime and has an uncertainty of one part in 10^{15} [1]. The trapped and laser-cooled ions are excellent candidates for many high precision measurements [2,3]. Due to the decoupling of the internal states caused by the perturbations arising from the collisions and Doppler shifts, the trapped and laser-cooled ions have been regarded as isolated quantum systems [4]. Therefore, precise measurements of transition frequencies of several species of trapped ions have been performed for the purpose of developing the better frequency standard in microwave and optical frequency regions [4,5]. Singly ionized cadmium (Cd$^+$) is a potential candidate for the applications in quantum-information processing where the microwave transition between the hyperfine states of the ground state is used for both the repumping process and manipulation of quantum states of the trapped ions [4]. Recently, ^{113}Cd$^+$ has been proposed for the design of a space qualified atomic clock [6]. In this respect, a series of measurements for the ground state hyperfine splitting of ^{113}Cd$^+$ has been performed [4–6]. In recent experiments, the control of quantum states of ^{113}Cd$^+$ with high degree has become possible [7], because it has a simple energy-level structure and accessible wavelengths for different excited energy levels. This can also be regarded as a step towards the development of a new frequency standard in the microwave regime [4]. In this work, we have used the coupled-cluster theory with single, double, and partial triple excitations [CCSD(T)] in the relativistic framework to calculate the hyperfine energy splitting of the ground state and a few low-lying excited states of ^{113}Cd$^+$. This is a relativistic *ab initio* many-body study of the hyperfine splitting of ^{113}Cd$^+$.

The hyperfine interaction in an atom is generated due to the interaction of different electromagnetic multipole moments of the nucleus and electrons of an atom. The corresponding Hamiltonian is given by [8]

$$H_{\rm hfs} = \sum_k \mathbf{M}^{(k)} \cdot \mathbf{T}^{(k)}, \tag{1}$$

where $\mathbf{M}^{(k)}$ and $\mathbf{T}^{(k)}$ are the spherical tensor operators of rank k of the nucleus and the electronic system, respectively. Since nuclear spin of ^{113}Cd$^+$ is $\frac{1}{2}$, the hyperfine splitting due to electric quadrupole moment will be zero. Magnetic hyperfine interaction, which is the only important hyperfine interaction in this system, for a relativistic electron with nuclear magnetic moment μ_I is given by [9]

$$H_{\rm hfs} = \sum_i ec\boldsymbol{\alpha}_{\mathbf{i}} \frac{\boldsymbol{\mu}_{\mathbf{I}} \times \mathbf{r}_{\mathbf{i}}}{r_i^3}, \tag{2}$$

where $\boldsymbol{\alpha}_{\mathbf{i}}$ are the Dirac matrices for the ith electron.

In the first-order perturbation theory, the hyperfine energy splittings ($E_{\rm hfs}$) between two consecutive hyperfine states is the expectation value of the above interaction Hamiltonian. Details of the expression are given by Cheng and Childs [8]. The energy splitting due to magnetic dipole hyperfine transition is defined as

$$E_{\rm hfs}^{M1} = AK/2, \tag{3}$$

where $K=2\langle I\cdot J\rangle = F(F+1)-I(I+1)-J(J+1)$ with I and J are the total angular momentum of the nucleus and the electronic state, respectively. Here F is the total angular momentum of an atom (nucleus+electrons). The hyperfine constant A corresponding to the magnetic dipole hyperfine interaction is expressed in terms of the electron wave functions as

$$A = \frac{1}{IJ}\langle F\|H_{\rm hfs}\|F\rangle = \mu_N g_I \frac{\langle J\|\mathbf{T}^{(1)}\|J\rangle}{\sqrt{J(J+1)(2J+1)}}, \tag{4}$$

where μ_N is the Bohr magneton and $g_I=\mu_I/I$. The $\mathbf{T}^{(1)}$ operator is defined as

$$\mathbf{T}^{(1)} = \sum_i -ie\sqrt{8\pi/3}\,r_i^{-2}\alpha_i \cdot \mathbf{Y}_1^{(0)}(\hat{r_i}) \tag{5}$$

with $\mathbf{Y}_1^{(0)}$ as the vector spherical harmonic.

The Fock-space multireference coupled-cluster (FSMRCC) theory for the one electron attachment process used here has been described elsewhere [10–13]. We provide here a brief review of this method. The theory for a single valence

TABLE I. Radiative lifetime (ns) for different low-lying states in ^{113}Cd$^+$.

State	Experiment	Other theories	This work
$5\ ^2P_{1/2}$	3.2(2) [17], 3.05(13) [18], 3.11(4) [19], 3.5(2) [19], 4.8(1.0) [20], 3.14(0.011) [21]	2.92 [17], 2.99 [17], 2.74 [18], 3.11 [22]	3.093
$5\ ^2P_{3/2}$	2.5(3) [17], 2.70(25) [18], 2.77(7) [19], 3.5(2) [19], 3.4(7) [20], 2.647(0.01) [21], 3.0(2) [23]	2.50 [17], 2.3 [18], 2.77 [22]	2.602

system is based on the concept of a common vacuum for both the closed shell N and open shell $N\pm1$ electron systems, which allows us to formulate a direct method for energy differences. Also, the holes and particles are defined with respect to the common vacuum for both the electron systems. Model space of a (n,m) Fock space contains determinants with n holes and m particles which are distributed within a set of what are termed *active* orbitals. For example, in this present article, we are dealing with (0,1) Fock space which is a complete model space (CMS) by construction and is given by

$$|\Psi_\mu^{(0,1)}\rangle = \sum_i \mathrm{C}_{i\mu}|\Phi_i^{(0,1)}\rangle, \tag{6}$$

where $\mathrm{C}_{i\mu}$'s are the coefficients of $\Psi_\mu^{(0,1)}$ and $\Phi_i^{(0,1)}$'s are the model space configurations. The dynamical electron correlation effects are introduced through the *valence-universal* wave operator Ω [10,11]

$$\Omega = \{\exp(\widetilde{S})\}, \tag{7}$$

where

$$\widetilde{S} = \sum_{k=0}^{m}\sum_{l=0}^{n} S^{(k,l)} = S^{(0,0)} + S^{(0,1)} + S^{(1,0)} + \cdots. \tag{8}$$

At this juncture, it is convenient to single out the core-cluster amplitudes $S^{(0,0)}$ and call them T, where the rest of the cluster amplitudes will, hereafter, be called S. Since Ω is in normal order form, we can rewrite Eq. (7) as

$$\Omega = \exp(T)\{\exp(S)\}. \tag{9}$$

In this work, the cluster operators T and S are truncated to include only single (T_1,S_1) and double (T_2,S_2) excitations. The wave function of the system with single valence orbital v is given by

$$|\Psi_v\rangle = \Omega_v|\Phi_{\mathrm{DF}}\rangle = e^{T_1+T_2}\{1 + S_{1v} + S_{2v}\}|\Phi_{\mathrm{DF}}\rangle. \tag{10}$$

Triple excitations are included in open shell CC amplitudes which correspond to the correlation to the valence orbitals, by an approximation that is similar in the spirit of the CCSD(T) method [14]. The approximate valence triple excitation amplitudes are given by

$$S_{abv}^{(0,1)^{pqr}} = \frac{\{\overbrace{VT_2}\}_{abv}^{pqr} + \{\overbrace{VS_2^{(0,1)}}\}_{abv}^{pqr}}{\varepsilon_a + \varepsilon_b + \varepsilon_v - \varepsilon_p - \varepsilon_q - \varepsilon_r}, \tag{11}$$

where $S_{abv}^{(0,1)^{pqr}}$ are the amplitudes corresponding to the simultaneous excitations of orbitals a, b, v to p, q, r, respectively, where V is the two electron Coulomb integral and ε's are the orbital energies.

The transition matrix element due to any operator O can be expressed, in the CC method, as

$$O_{fi} = \frac{\langle\Psi_f|O|\Psi_i\rangle}{\sqrt{\langle\Psi_f|\Psi_f\rangle\langle\Psi_i|\Psi_i\rangle}} = \frac{\langle\Phi_f|\{1 + S_f^\dagger\}e^{T^\dagger}Oe^{T}\{1 + S_i\}|\Phi_i\rangle}{\sqrt{N_fN_i}}, \tag{12}$$

where f and i represent final and initial states, respectively. For the expectation values, we use $f=i$.

The contribution from the normalization factor is given by

$$(\mathrm{Norm}) = \langle\Psi_f|O|\Psi_i\rangle\left\{\frac{1}{\sqrt{N_fN_i}} - 1\right\}, \tag{13}$$

with $N_v=\langle\Phi_v|e^{T^\dagger}e^{T}+\{S_v^\dagger e^{T^\dagger}e^{T}S_v\}|\Phi_v\rangle$ for the valence electron v.

We calculate the DF wave functions $|\Phi_{\mathrm{DF}}\rangle$ using the Gaussian-type orbitals (GTO) as given in [15] using basis functions of the form

$$F_{i,k}^{L/S}(r) = C_N^{L/S}r^{k}e^{-\alpha_i r^2}, \tag{14}$$

with $k=0,1,2,3,\ldots$ for $s,p,d,f,\ldots$ orbital symmetries, respectively [16]. The radial functions F^L and F^S represent the basis functions and correspond to large and small components of the Dirac orbitals. $C_N^{L/S}$ are the normalization constants which depend on the exponents. The universal even tempering condition has been applied to the exponents, i.e., for each symmetry exponents are assigned as

$$\alpha_i = \alpha_0\beta^{i-1}, \quad i = 1,2,\ldots,M, \tag{15}$$

where M is the number of basis functions for the specific symmetry. In this calculation, we have used $\alpha_0=0.005\,25$ and $\beta=2.73$. The number of basis functions used in the present calculation are 32, 30, 25, 20, and 20 for $l=0$, 1, 2, 3, and 4 symmetries, respectively. Negligible contribution to the DF orbital wave functions has been estimated for the larger basis, both in terms of type of symmetries and number of primitive functions of each symmetry.

The number of DF orbitals for different symmetries used in the CC calculations are based on convergent criteria of core correlation energy for which it satisfies numerical completeness. We consider only 13, 12, 12, 9, and 7 numbers of active orbitals including all the core electrons in the CCSD(T) calculations for $l=0,1,2,3,4$ symmetries, respectively. Other inactive orbitals are neglected in the CC calcu-

TABLE II. Hyperfine energy splitting of different low-lying states of $^{113}\mathrm{Cd}^{+}$.

State	Experiment	This work [CCSD(T)]	This work (CCSD)
$5S_{1/2}$	15.2(2 Hz) GHz [4,6]	15.28 GHz	15.26 GHz
$5P_{1/2}$	2.45 GHz [4]	2.43 GHz	2.43 GHz
$5P_{3/2}$	800 MHz [4]	812.04 MHz	813.61 MHz
$6S_{1/2}$		3.23 GHz	3.23 GHz
$6P_{1/2}$		667.81 MHz	671.24 MHz
$6P_{3/2}$		236.24 MHz	237.51 MHz

lations as their energy levels are too large and contribute very little at a cost of large computation. First we calculate T amplitudes using the CC equations of closed-shell systems and then solve for the S amplitudes from the open-shell equations for the considered single valence states of Cd^{+}.

We report the calculated lifetime results of $5P_{1/2,3/2}$ states along with the other calculated and measured results in Table I. As it can be seen from Table I, there are large disagreements among the earlier calculations. The most reliable experimental results are given by Moehring *et al.* [21] to date with a total uncertainty of 0.4%. However, our calculated lifetime for $5P$ fine structure states of $^{113}\mathrm{Cd}^{+}$ is in excellent agreement with the recent measured results [21] and MBPT calculations [22].

Table II presents the computed values of the hyperfine energy splittings for the ground state and a few low-lying excited states of $^{113}\mathrm{Cd}^{+}$. We have used the expression Eq. (3) to compute the highly sensitive property of the electronic wave functions near the nuclear region. To calculate the hyperfine splitting constants corresponding to the magnetic dipole A, we have used $\mu_I=-1.2446$ [24]. It is evident from Table II that our calculated hyperfine energy splittings are in excellent agreement with the measured hyperfine energy splittings wherever available. We have also calculated the hyperfine splitting of a few other excited states for which experimental results are not available in the literature to the best of our knowledge. The comparison between CCSD and CCSD(T) hyperfine energy splittings is also presented in the table. In one way, this is highlighting the convergence of a type of excitations in our CC calculations. The estimated contribution of Breit interactions and nuclear structure hyperfine energy splittings at the DF levels are less than 0.3%, which show their rare importance in our CC calculations.

All the core orbitals are considered as active in our calculations. In Table III, the individual contributions from the one-body and the effective two-body terms to the magnetic dipole hyperfine structure constant A for $^{113}\mathrm{Cd}^{+}$ are listed. The first term (O) is the Dirac-Fock (DF) contribution. From the differences of DF and total CC results, it is evident that the electron correlation effects to the calculated A results vary from 15–45 % among different low-lying states.

It is known that the Bruckner pair-correlation effects are in the form of $\bar{O}S_{1v}$ and its conjugate terms, whereas core-polarization effects are in $\bar{O}S_{2v}$ and its conjugate terms, in their lowest order. The former one represents formally the contribution of an individual electron pair obtained from the Bethe-Goldstone equation [25], and the latter one considers all single excitations from core orbitals [10]. Both these correlations are important for the precise determination of the final results. From Table III, it is clear that the largest contribution of electron correlation effects to the hyperfine structure constants A for the different low-lying states comes from the pair-correlation effects. However, the core-polarization contributions are not the least significant. In Fig. 1, we have plotted the contributions of important correlation effects to the hyperfine constants of the different states with respect to their DF contributions. The core-correlation effects seem to be relatively small compared to the other two effects presented in the above figure. The percentage contribution of the former one is almost the same for all the considered states.

TABLE III. Contributions of different coupled-cluster (CC) terms to the $^{113}\mathrm{Cd}^{+}$ magnetic dipole (A) hyperfine constant. c.c. stands for the complex conjugate part of the corresponding terms.

CC terms	$5S_{1/2}$ state	$5P_{1/2}$ state	$5P_{3/2}$ state	$6S_{1/2}$ state	$6P_{1/2}$ state	$6P_{3/2}$ state
O	−11 986.36	−1837.36	−284.56	−2753.76	−553.68	−87.78
$\bar{O}$	−11 896.12	−1823.30	−284.76	−2734.74	−550.04	−87.82
$\bar{O}S_{1v}$+c.c.	−2266.42	−476.44	−74.19	−248.89	−75.64	−12.52
$\bar{O}S_{2v}$+c.c.	−1067.66	−107.83	−27.36	−223.06	−38.22	−9.47
$S_{1v}^{\dagger}\bar{O}S_{1v}$	−107.95	−31.23	−4.85	−5.66	−2.65	−0.45
$S_{1v}^{\dagger}\bar{O}S_{2v}$+c.c.	−83.28	−16.14	−3.95	−3.99	−3.16	−0.81
$S_{2v}^{\dagger}\bar{O}S_{2v}$+c.c.	−338.50	−45.99	−21.23	−81.69	−11.16	−9.13
Important effective two-body terms of $\bar{O}$						
$S_{2v}^{\dagger}OT_1$+c.c.	−65.28	−9.57	−1.43	−15.64	−2.83	−0.43
$S_{2v}^{\dagger}OT_2$+c.c.	156.55	23.20	3.25	33.77	5.79	0.80
Norm.	374.86	51.78	8.36	42.14	10.00	1.73
Total	−15 285.99	−2434.01	−406.02	−3237.10	−667.81	−118.12

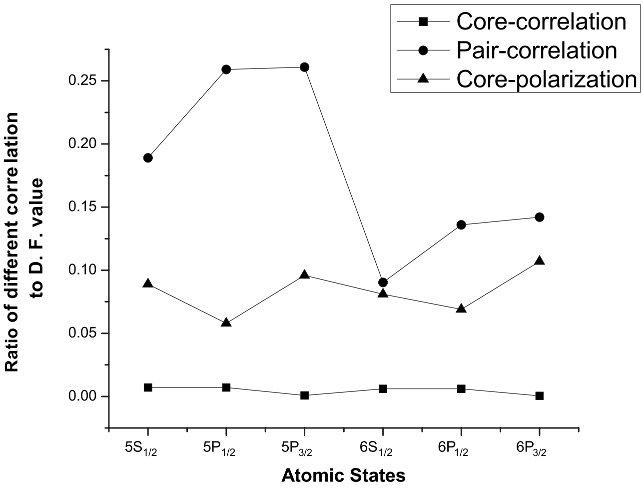

FIG. 1. Ratio of core-correlation, pair-correlation, and core-polarization effects with respect to the DF values.

We see that the ratio of pair-correlation and core-polarization effects is almost one for the $6S_{1/2}$ state; however, it is different for the other states. The pair-correlation effects for the fine structure state of $5P$ are extremely strong (almost 25%) with respect to the DF value, whereas for the other states it is around 10%.

Apart from the above mentioned correlation effects, the prominent contributions are observed from $S_{2v}^{\dagger}\bar{O}S_{2v}$+c.c., which is almost 2% for the S and $P_{1/2}$ states, and more than 5% for $P_{3/2}$ states. Contributions from the effective two-body terms are also significant and comparable with some of the one-body terms like $S_{1v}^{\dagger}\bar{O}S_{2v}$+c.c. for all the states considered in the present work.

In this work, we have determined the hyperfine energy splittings of the ground state and a few low-lying excited states of $^{133}\mathrm{Cd}^{+}$ using the coupled-cluster theory in the relativistic framework. The lifetimes of $5P$ fine structure states of the above system are also presented. Our results are in excellent agreement with the available measurements. This suggests the robustness of the method used and our numerical approach in obtaining the accurate wave functions of the system considered.

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