Estimation of BBR shift due to Stark effect for the Microwave $^{113}$Cd$^+$ Ion Clock

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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 reported as $15199862855.0192(10)$ Hz [Opt. Lett. 40, 4249 (2015)]. Fractional systematic due to the black-body radiation (BBR) shift ($\beta$) arising from the Stark effect in the above clock transition was used as $-1.1 \times 10^{-16}$ from our unpublished preliminary estimation. We present here a precise value as $\beta = -1.815(77) \times 10^{-16}$ by carrying out rigorous calculations of third-order polarizabilities of the hyperfine levels associated with the clock transition. This is determined by evaluating matrix elements of the magnetic dipole hyperfine interaction Hamiltonian, electric dipole operator and energies between many low-lying states of $^{113}$Cd$^+$. We employ all-order relativistic many-body theories in the frameworks of Fock-space coupled-cluster and relativistic multi-configuration Dirac-Fock methods.

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The today’s definition of unit of time in the International System of Units (SI) is based on the microwave transition frequency of the ground state hyperfine splitting of $^{133}$Cs [1]. However, singly charged ions have now paved the way to carry out many precise experiments with the advent of new technologies for cooling and trapping a singly charged ion. In fact single trapped ions $^{171}$Yb$^+$ [2] and Al$^+$ [3] provide now clock frequencies with fractional uncertainties below $10^{-17}$. The advantage of considering an ion incur to its nature for being controlled easily by the electromagnetic radiation. Thus, it can be isolated from the external perturbations better than a neutral atom. As a matter of fact, several singly charged ions such as Hg$^+$, Ca$^+$, Sr$^+$, Yb$^+$ among others are under consideration in the laboratory for atomic clocks (e.g. see [4]). However it is aimed at to construct optical frequency clocks using these ions. Both microwave and optical frequency based clocks have advantages in their own perspectives [5]. Since frequencies in both the categories differ by several orders in magnitude, their applications could be totally diverse in nature. It means development of both are indispensable. Also, it is convenient to build up microwave-frequencies using compact electronic devices than the optical frequencies that are required for the deep-space science and commercial purposes [6, 7]. In fact, trapping of the Cd$^+$ ion in a semi-conductor chip has already been demonstrated [8]. Also, cooling and crystallization of $^{113}$Cd$^+$ has been performed successfully [9] and a proof-of-principle to realize a transportable clock using this ion has been discussed [10]. Such technologies are useful for better quantum computers [11, 12]. Micro-chip clocks are also of immense interest for various reasons. Micro-chip clocks using neutral atoms are based on the coherent-population trapping of atoms that avoids use of microwave cavity to probe the atomic resonance [13]. As a result, this provides a very compact clock. On the other hand, confinement of more number of neutral atoms can cause large collisional shifts in the clock frequency. This can be minimized by using singly charged ions trapped in a micro-chip.

A number of ions are under consideration for microwave clocks such as $^{199}$Hg$^+$, $^{137}$Ba$^+$, $^{171}$Yb$^+$, $^{113}$Cd$^+$, $^9$Be$^+$ etc. [14]. Among these ions, high precision measurement of frequency of the ground state hyperfine splitting in the $^{113}$Cd$^+$ ion is under progress [15]. The advantage of this ion, except in $^{199}$Hg$^+$ [10], for microwave clock is its ground state hyperfine splitting is relatively larger; about 15.2 GHz. Moreover, it requires only one laser for cooling, pumping and detection purposes, which is a big advantage from the experimental set-up point of view. Clock frequency of the $|F = 0, M_F = 0\rangle \rightarrow |F' = 1, M_F' = 0\rangle$ transition in the ground state $5s\ 2S_{1/2}$ of $^{113}$Cd$^+$ has already been achieved as $\nu_0 = 15199862855.0192(10)$ Hz with a fractional precision of $6.6 \times 10^{-14}$ [17, 18]. The major uncertainties in the systematics of these measurements come from the Zeeman shift, but uncertainty due to the black-body radiation (BBR) shift due to stray electric fields also contribute significantly. It is feasible to minimize uncertainties due to the Zeeman shifts in few years by improving magnetic shielding and other instrumental errors by optimizing controlling sequences and suppress-

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ing laser technical noise [17]. In case these uncertainties reach below 10^{-16} level, it would be necessary at that point to reduce uncertainty due to the BBR shift observed at the room temperature. Thus, it is imperative to estimate this quantity more precisely for the Cd^+ ion. Measuring BBR shift in an atomic system at the level of 10^{-16} precision level is strenuous. Previously, a number of theoretical calculations have been performed on the BBR shifts for many of the atomic clock candidates with ultra-high precision [4,10,22]. However, the BBR shift due to the Stark effect in the Cd^+ clock transition has not been estimated so far. The fractional BBR shift used in the reported clock frequency by Miao et al [17] was based on our unpublished work. We had given them a ball-park figure of this quantity from our preliminary estimation. Therefore, knowledge of a more reliable value of BBR shift in this clock transition is of immense interest.

The clock transition in the ground state of $^{113}$Cd has null differential second-order dipole polarizabilities owing to the same scalar polarizabilities of the hyperfine levels. However, the hyperfine interaction induced third-order dipole polarizabilities can offer finite contributions to the BBR shifts in the above clock transition. In this Rapid Communication, we estimate the fractional uncertainty due to the BBR shift of the $^{113}$Cd^+ clock transition by evaluating third-order dipole polarizabilities of the associated hyperfine levels. For this purpose, we employ a relativistic coupled-cluster (RCC) method in the Fock-space framework by considering Dirac-Coulomb-Breit Hamiltonian along with lower-order corrections due to quantum electrodynamics effects, as in our previous work [22], and relativistic multi-configuration Dirac-Fock methods (MCFD) method using the GRASP2K package [24] to evaluate the required matrix elements of the electric dipole (E1) and magnetic dipole (M1) hyperfine interaction operators.

The light shift due to the third-order Stark effect in the hyperfine level $|F,m_F\rangle$, for $F = I + J$ with the nuclear spin $I$ and total electron momentum $J$ and $m_F$ is the projection of $F$ on the quantization axis, of a $S$-state by a laser field with strength $\mathcal{E}$ can be given by

$$\delta E_F^{(2)}(\omega) = \frac{\mathcal{E}^2}{2} F_{m_F}^{(3)} \cdot (1)$$

| TABLE I: Important reduced E1 matrix elements (in a.u.) between many low-lying states of Cd^+ from the CCSD method. $n$ corresponds to the principal quantum number of the states. |
|---|---|---|---|---|---|---|---|---|---|
| Transition | $n = 5$ | $n = 6$ | $n = 7$ | $n = 8$ | $n = 9$ | $n = 10$ | $n = 11$ | $n = 12$ |
| $np^2 P_{1/2} - 5s^2 S_{1/2}$ | -1.97 | 0.08 | -0.08 | 0.07 | -0.05 | 0.04 | -0.02 | -0.01 |
| $np^2 P_{1/2} - 5s^2 S_{1/2}$ | 2.79 | -0.03 | 0.08 | 0.07 | 0.06 | -0.05 | -0.03 | -0.02 |
| $np^2 P_{1/2} - 6s^2 S_{1/2}$ | 1.65 | -5.11 | -0.13 | -0.006 | 0.02 | -0.02 | 0.02 | 0.01 |
| $np^2 P_{3/2} - 6s^2 S_{1/2}$ | -2.52 | -7.15 | 0.35 | 0.08 | 0.02 | -0.005 | 0.001 | 0.002 |
| $np^2 P_{1/2} - 7s^2 S_{1/2}$ | -0.48 | 3.83 | -9.07 | 0.40 | -0.08 | 0.02 | 0.03 | 0.007 |
| $np^2 P_{3/2} - 7s^2 S_{1/2}$ | 0.69 | 5.77 | 12.66 | 0.82 | 0.25 | -0.11 | -0.05 | -0.02 |
| $np^2 P_{1/2} - 8s^2 S_{1/2}$ | 0.26 | -0.96 | -6.72 | -14.13 | 0.74 | -0.19 | 0.05 | -0.001 |
| $np^2 P_{3/2} - 8s^2 S_{1/2}$ | -0.38 | -1.37 | 10.08 | -19.67 | -1.42 | 0.46 | 0.17 | 0.05 |
| $np^2 P_{1/2} - 9s^2 S_{1/2}$ | -0.18 | 0.51 | 1.59 | -10.27 | -20.63 | 1.17 | -0.31 | -0.06 |
| $np^2 P_{3/2} - 9s^2 S_{1/2}$ | 0.25 | 0.71 | -2.26 | -15.37 | 28.71 | -2.17 | -0.66 | -0.19 |
| $np^2 P_{1/2} - 10s^2 S_{1/2}$ | 0.13 | -0.32 | -0.80 | 2.36 | -13.95 | -29.82 | 1.29 | 0.26 |
| $np^2 P_{3/2} - 10s^2 S_{1/2}$ | -0.18 | -0.45 | 1.12 | 3.36 | 20.87 | 41.61 | 2.42 | 0.57 |
| $np^2 P_{1/2} - 11s^2 S_{1/2}$ | 0.09 | -0.23 | -0.50 | 1.18 | -3.38 | 16.01 | 44.06 | -0.06 |
| $np^2 P_{3/2} - 11s^2 S_{1/2}$ | -0.13 | -0.32 | 0.70 | 1.66 | 4.85 | -23.93 | 61.84 | 0.37 |
| $np^2 P_{1/2} - 12s^2 S_{1/2}$ | 0.09 | -0.22 | -0.44 | 0.91 | -2.08 | 5.07 | -14.94 | 65.89 |
| $np^2 P_{3/2} - 12s^2 S_{1/2}$ | -0.13 | 0.30 | 0.61 | 1.28 | 2.97 | -7.39 | -22.16 | 90.10 |

| TABLE II: Values of the E1 matrix elements (in a.u.) for some of the transitions associated with the states having $4d^55s^2 2D_{3/2}$ and $4d^55s^2 2D_{5/2}$ configurations in Cd^+ from the MCFD method of GRASP2K package [24]. |
|---|---|
| Transition | Value |
| $4d^55s^2 2D_{3/2} - 5p^2 P_{1/2}$ | 0.24 |
| $4d^55s^2 2D_{3/2} - 5p^2 P_{3/2}$ | 0.21 |
| $4d^55s^2 2D_{3/2} - 6p^2 P_{1/2}$ | 0.25 |
| $4d^55s^2 2D_{3/2} - 6p^2 P_{3/2}$ | 0.07 |
| $5s^2 S_{1/2} - 4d^55s(3D)5p^2 P_{1/2}$ | 0.28 |
| $5s^2 S_{1/2} - 4d^55s(3D)5p^2 P_{3/2}$ | 0.22 |
| $5s^2 S_{1/2} - 4d^55s(3D)5p^2 F_{3/2}$ | 0.03 |
| $5s^2 S_{1/2} - 4d^55s(3D)5p^2 D_{3/2}$ | 0.23 |
| $5s^2 S_{1/2} - 4d^55s(3D)5p^2 D_{5/2}$ | 0.80 |
| $5s^2 S_{1/2} - 4d^55s(3D)5p^2 D_{5/2}$ | -1.05 |
| $5s^2 S_{1/2} - 4d^55s(3D)5p^2 D_{5/2}$ | 0.16 |
| $5s^2 S_{1/2} - 4d^55s(3D)5p^2 P_{3/2}$ | -1.23 |
| $5s^2 S_{1/2} - 4d^55s(3D)5p^2 P_{1/2}$ | 0.67 |
Here, the third-order scalar polarizability \( \alpha_F^{(3)} \) can be conveniently expressed as:

\[
\alpha_F^{(3)}(\omega) = \frac{2}{3} \sqrt{(I + 1)(2I + 1)} \left\{ \begin{array}{ccc} J & I & F \\ J & I & J \\ I & J & 1 \end{array} \right\} \times \frac{\mu_I}{I} \frac{(-1)^{F + I + J} [2T(\omega) + C(\omega) + R(\omega)]}{},
\]

where \( \mu_I \) is the nuclear magnetic moment in unit of Bohr magnetron \( \mu_N \). We use here \( \mu_I / I = -1.24464 \mu_I \) with \( I = 1/2 \) for \( ^{113}\text{Cd}^{+} \). Other factors are given by

\[
T(\omega) = \frac{1}{2(2J + 1)} \sum_{J',J''} \delta_{J,J''} (-1)^{J + J'} \langle \gamma J || D || \gamma' J' \rangle \langle \gamma' J' || D || \gamma'' J'' \rangle \langle \gamma'' J'' || T_{hf} || \gamma J \rangle
\]

\[
C(\omega) = \frac{1}{2} \sum_{J',J''} (-1)^{J'' - J'} \left\{ \begin{array}{ccc} J & J & J' \\ J' & J & J'' \end{array} \right\} \times \left[ \frac{1}{(E_{\gamma J} - E_{\gamma' J' + \omega})} + \frac{1}{(E_{\gamma J} - E_{\gamma'' J'' - \omega})} \right],
\]

\[
R(\omega) = \frac{1}{2(2J + 1)} \langle \gamma J || T_{hf} || \gamma J \rangle \sum_{J'} \langle \gamma J || D || \gamma' J' \rangle^2 \times \left[ \frac{1}{(E_{\gamma J} - E_{\gamma' J' + \omega})^2} + \frac{1}{(E_{\gamma J} - E_{\gamma' J' - \omega})^2} \right]
\]

where \( E \) with subscript \( \gamma J \) represent for the energies of the state with angular momentum \( J \) and additional quantum numbers \( \gamma \), and \( T_{hf}(r) = -\sqrt{2} (\alpha \cdot C^{(1)}(\vec{r})) / (\alpha^2) \) is the electronic component of the M1 hyperfine interaction operator with the Dirac operator \( \alpha \), Racah operator \( C^{(1)} \) and speed of light \( c \), for which the M1 hyperfine structure constant is defined as

\[
A_{hf} = \frac{\mu_I}{I} \frac{\langle \gamma J || T_{hf} || J \rangle}{\sqrt{J(J + 1)(2J + 1)}}.
\]

The BBR shift due to the Stark shift in the \( |F,m_F\rangle \) level can be estimated by [20]

\[
\delta E_{F}^{BBR} \simeq -\frac{1}{2} (831.9 \text{ V/m})^2 \left( \frac{T(K)}{300} \right)^4 \alpha_F^{(3)},
\]

where \( T(K) \) is the laboratory temperature in kelvin (K) with respect to the room temperature 300K and \( \alpha_F^{(3)} \) is in atomic unit (a.u.). Hence, the fractional differential BBR shift for the clock transition can be given by

\[
\beta_{F'}^{BBR} = \frac{1}{\nu_0} (\delta E_{F}^{BBR} - \delta E_{F'}^{BBR}) \\
\simeq -\frac{(831.9 \text{ V/m})^2}{2\nu_0} \left( \frac{T(K)}{300} \right)^4 \left[ \alpha_F^{(3)} - \alpha_{F'}^{(3)} \right].
\]

Evaluation of \( T, C \) and \( R \) require many more matrix elements between different possible intermediate states of both the even and odd parities. They mainly involve E1 matrix elements between the \( ns^2 \text{S}_1/2 \) and \( mp^2 \text{P}_{1/2,3/2} \) states with \( n \) and \( m \) representing the principal quantum numbers of different atomic states. It can also involve E1 matrix elements between the ground state and possible states with the \( 4d^9 \text{ 5s}^2 \) configurations. Moreover, it also requires E1 matrix elements involving the \( 4d^9 \text{ 5s}^2 \) states with the \( mp^2 \text{P}_{1/2,3/2} \) states and states with the \( 4d^9 \text{ 5s}^5 \) configurations. Similarly, both the diagonal and off-diagonal matrix elements between states of the
TABLE IV: Breakdown of contributions from various intermediate states \( J' \) and \( J'' \) to \( T(0) \), \( C(0) \) and \( R(0) \) (in \( 10^{-8} \) a.u.) as defined in Eqs. (3)-(5). Contributions from “Tail”, core-core, core-valence, valence-core and core contributions to these quantities are quoted explicitly from the DHF method. Estimated uncertainties due to the matrix elements obtained from the CCSD and MCDF methods, and contributions from the DHF method are also given.

| \( J'' \) | \( T(0) \) value | \( C(0) \) value | \( R(0) \) value |
|---|---|---|---|
| \( 6s^2S_{1/2} \) | 13350.910 | 5\(^2\)P\(_{1/2} \) | 21.122 |
| \( 7s^2S_{1/2} \) | 2319.697 | 5\(^2\)P\(_{1/2} \) | −853.041 |
| \( 8s^2S_{1/2} \) | 784.107 | 6\(^2\)P\(_{1/2} \) | 0.027 |
| \( 9s^2S_{1/2} \) | 374.568 | 6\(^2\)P\(_{3/2} \) | 0.006 |
| \( 10s^2S_{1/2} \) | 220.400 | 7\(^2\)P\(_{1/2} \) | 0.021 |
| \( 11s^2S_{1/2} \) | 92.335 | 7\(^2\)P\(_{3/2} \) | −0.016 |
| \( 12s^2S_{1/2} \) | 109.521 | 8 − 12p\(^2\)P\(_{1/2,3/2} \) | −1.216 |
| [4d\(^5\)5s\(^2\) \( 2D_{3/2} \)] states | 48.97 | [4d\(^5\)5s\(^5\)p] states | −546.265 |
| Uncertainty | ±1087.159 | Uncertainty | ±244.49 |
| Tail | 142.741 | Tail | −10.640 |
| Core-valence | 24.937 | Core-valence | 0.417 |
| Valence-core | −226.153 | Valence-core | 0.417 |
| Core-core | 21.122 | Core-core | −0.188 |
| Final | 17263(1129) | Final | −686(245) |

The \( T_{hf} \) operator will be required. Contributions to the sum of \( \langle J'|O_1||J''\rangle\langle J''||O_2||J'\rangle\langle J'||O_3||J \rangle \), for \( O_1, O_2 \) and \( O_3 \) being either \( D \) or \( T_{hf} \) operators, from all possible excited states and core orbitals are evaluated in several steps. The \( T \) and \( C \) values are evaluated by dividing into valence, core-core, core-valence, and valence-core contributions when both \( J' \) and \( J'' \) belong to virtual states, when both \( J' \) and \( J'' \) belong to core orbitals, when \( J' \) is from virtual and \( J'' \) is from core, and when \( J' \) is from core and \( J'' \) is from virtual, respectively. Similarly, the sum of square of the matrix element \( \langle J'|D||J''\rangle \) for the evaluation of \( R \) are estimated by dividing contributions as valence, core-valence and core contributions following the procedures described in Refs. [22-27]. As can be seen from Eqs. (3)-(5), the low-lying excited states will contribute most to \( T, C \) and \( R \) while the core, core-valence and valence-core contributions will be relatively small. Thus, we evaluate these contributions by the Dirac-Hartee-Fock (DHF) method. For evaluating the valence correlations, we have calculated up to 12p\(^2\)P\(_{1/2,3/2} \) states, that correspond to excitation energies about 131300 cm\(^{-1} \) from the ground state. All the above excited states, except those having configurations 4d\(^5\)5s\(^5\)p and 4d\(^9\)5s\(^2\), are calculated using the RCC method, described in our earlier works [22-28], with the singles and doubles excitation approximation (CCSD method). To determine matrix elements associated with the states with 4d\(^5\)5s\(^5\)p and 4d\(^9\)5s\(^2\) configurations, we apply the MCDF method using the GRASP2K package [24]. Contributions above than 12p\(^2\)P\(_{1/2,3/2} \) states are estimated by the DHF method and refer to as “Tail” contributions.

We have compared calculated energies with the National Institute of Science and Technology database (NIST) [29] for the states determined by the RCC and MCDF methods, which are given in the Supplemental material. The CCSD values are found to be within 1% accuracy and the MCDF results for the states with 4d\(^5\)5s\(^5\)p and 4d\(^9\)5s\(^2\) configurations are found to be about 4% compared to the NIST data. We also give the E1 matrix elements among various low-lying states in Table I from the RCC and MCDF methods. Experimental values for the E1 matrix elements of the 5s\(^2\)S\(_{1/2} \), 5p\(^2\)P\(_{1/2} \) and 5p\(^2\)P\(_{3/2} \) transitions are obtained from the precise lifetime measurements of the 5p\(^2\)P\(_{1/2} \) and 5p\(^2\)P\(_{3/2} \) states as 1.913(3) a.u. and 2.717(5) a.u., respectively, [30]. Our values are in reasonably agreement with these results. Some of the important E1 matrix elements obtained by the MCDF method are given in Table II for the \( 5s^2S_{1/2} \), 5p\(^2\)P\(_{1/2} \) and 5p\(^2\)P\(_{3/2} \) transitions are inferred from experiments as 0.487(17) a.u. and 0.295(37) a.u., respectively, [31]. They are almost twice than the calculated values. The remaining E1 matrix elements from the MCDF method can be found from the Supplemental material.

Similarly, the reduced matrix elements of \( T_{hf} \) obtained in the RCC and MCDF methods for some of the important contributing states are listed in Table III. The rest of the matrix elements for other excited states that are calculated by us are given in the Supplemental material. Using the relation given by Eq. (6), we have also extracted out the reduced expectation values for the 5s\(^2\)S\(_{1/2} \), 5p\(^2\)P\(_{1/2} \) and 4d\(^5\)5s\(^2\) \( 2D_{3/2} \) states as 227.66(1) \( \times 10^{-8} \) a.u. [17].
18.94 \times 10^{-8} \text{ a.u.} \text{ } ^{32} \text{ and } 75.10(3) \times 10^{-8} \text{ a.u.} \text{ } ^{33}, \text{ respectively, from the precise measurements of } A_{hf}. \text{ Comparison of these values with our calculations show good agreement between them.}

Using all the reduced matrix elements discussed above, we determine the static values of } T, C \text{ and } R \text{ for the ground state of } ^{113}\text{Cd}^{+} \text{ and give them in Table } A \text{ after summing contributions from various intermediate states. To reduce uncertainties in these calculations, we use the experimental energies and replace the calculated reduced matrix elements by the precisely known experimental values wherever possible. It to be noted that knowledge of the contributions to } C(0) \text{ cannot be determined. In this case, we use the magnitudes from the measurements and signs from the MCDF results. We also give contributions explicitly from the core-core, core-valence, valence-core and core-core contributions to these quantities in the same table. As can be seen from the table, the } 6s^{2}S_{1/2} \text{ and } 7s^{2}S_{1/2} \text{ states contribute extremely large to } T(0). \text{ Other } S\text{-states also contribute significantly here. Tail, core-valence and valence-core contributions to } T(0) \text{ are also non-negligible, but core-core contribution is found to be small. The net contributions from the states with } 4d^{3}5s^{2} \text{ configuration are also found to be relatively small. The dominant uncertainty contributions come from the matrix elements involving the calculated } S\text{-states. On other hand, most of the contributions to } C(0) \text{ comes from the } 5P\text{-states. The net contributions from the states with } 4d^{3}5s5p \text{ configurations are also found to be quite significant. For the } R(0) \text{ value, the most dominant contributions come from the } 5P\text{-states followed by the states with } 4d^{3}5s5p \text{ configuration. The core contribution is also found to be quite large. We estimate uncertainties to the above quantities by assigning an overall } \pm 3\% \text{ errors to the CCSD results and } \pm 20\% \text{ errors to the MCDF results. Uncertainties due to the other contributions given from the DHF method are estimated to be about } 10\%.}

Accounting for all these values along with the uncertainties, we find the differential BBR shift coefficient \( \beta_{BBR}^{FF} = -1.815(77) \times 10^{-16} \) for the \( |5s^{2}S_{1/2}, F = 0, m_F = 0 \rangle \leftrightarrow |5s^{2}S_{1/2}, F' = 1, m_{F'} = 0 \rangle \) clock transition in the \(^{113}\text{Cd}^{+}\) ion in contrast to \(-1.1 \times 10^{-16} \) that was used in Ref. \[17\]. Uncertainty to this value can be further reduced by improving precision of the matrix elements obtained by the MCDF method.

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Supplemental Material

Many excited states of Cd+ ion along with its ground state can be conveniently calculated by treating configurations of these states as a common core \[4d^{10}\] with different valence orbitals. In the relativistic coupled-cluster theory (RCC) ansatz, we express wave functions of states with a closed-core and a valence orbital \(v\) as \([1, 2]\)

\[
|\Psi_v\rangle = e^T \{1 + S_v\} |\Phi_v\rangle,
\]

where \(|\Phi_v\rangle\) is the reference state and \(T\) and \(S_v\) are the excitation operators involving core and core-valence electrons, respectively, that produce different determinants from \(|\Phi_v\rangle\). Again, we define \(|\Phi_v\rangle = a_v^\dag |\Phi_0\rangle\), where \(|\Phi_0\rangle\) is a mean-field wave function of the closed-core \(4d^{10}\). We apply the Dirac-Hartree-Fock (DHF) method by considering the Dirac-Coulomb-Breit Hamiltonian (DCB) along with lower-order corrections due to quantum electrodynamics (QED) effects to obtain the mean-field wave function as described in Refs. \([3, 4]\). We consider all the core electrons active and approximate the method by considering the Dirac-Coulomb-Breit Hamiltonians, respectively, that produce different determinants, which are \(e^T\{1 + S_v\}\), \(e^T\{1 + S_v\}\), and \(e^T\{1 + S_v\}\), respectively, that produce different determinants from \(|\Phi_v\rangle\). Again, we define \(|\Phi_v\rangle = a_v^\dag |\Phi_0\rangle\), where \(|\Phi_0\rangle\) is a mean-field wave function of the closed-core \(4d^{10}\). We apply the Dirac-Hartree-Fock (DHF) method by considering the Dirac-Coulomb-Breit Hamiltonian (DCB) along with lower-order corrections due to quantum electrodynamics (QED) effects to obtain the mean-field wave function as described in Refs. \([3, 4]\). We consider all the core electrons active and approximate the RCC method only to the single-electron and double excitations (CCSD method). Amplitudes of the RCC excitation operators are evaluated using the equations

\[
\langle \Phi_0^\dagger | \mathcal{T}_N | \Phi_0 \rangle = 0
\]

and

\[
\langle \Phi_v^\dagger | (\mathcal{T}_N - \Delta E_v) S_v | \Phi_v \rangle = -\langle \Phi_v^\dagger | \mathcal{T}_N | \Phi_v \rangle,
\]

where \(|\Phi_0^\dagger\rangle\) and \(|\Phi_v^\dagger\rangle\) are the excited state configurations with respect to the DHF states \(|\Phi_0\rangle\) and \(|\Phi_v\rangle\) respectively and \(\mathcal{T}_N = (H^2 e^T)\), with subscript \(l\) represents for the linked terms only. The attachment energy \(\Delta E_v\) of the electron in the valence orbital \(v\) is evaluated by

\[
\Delta E_v = \langle \Phi_v | \mathcal{T}_N | 1 + S_v \rangle | \Phi_v \rangle.
\]

After obtaining amplitudes of the RCC operators using the above described equations, the E1 matrix elements and the matrix elements of the \(\mathcal{T}_{hf}\) operator between the states \(|\Psi_i\rangle\) and \(|\Psi_f\rangle\) are evaluated using the expression

\[
\langle \Psi_f | O | \Psi_i \rangle = \frac{\Phi_f^\dagger \hat{O}_{fi} | \Phi_i \rangle}{\sqrt{\langle \Phi_f ^\dagger | \{1 + \hat{N}_{hf}\} | \Phi_f \rangle \langle \Phi_i ^\dagger | \{1 + \hat{N}_{i}\} | \Phi_i \rangle}},
\]

where \(\hat{O}_{fi} = \{1 + S_f^\dagger\} e^T O e^T \{1 + S_i\}\) and \(\hat{N}_{k=hf,i} = \{1 + S_f^\dagger\} e^T e^T \{1 + S_i\}\), assuming either \(O \equiv D\) or \(O \equiv \mathcal{T}_{hf}\). The expectation values are evaluated by assuming \(|\Psi_i\rangle = |\Psi_f\rangle = |\Psi_v\rangle\). As can be seen, the above expression involves two non-terminating series in the numerator and denominator, which are \(e^T O e^T\) and \(e^T e^T\) respectively. We adopt iterative procedures to account for contributions from these non-terminating series as have been described in our earlier works \([2, 3, 4]\).

The above RCC method formulated in the Fock space formalism is not suitable to obtain the low-lying states with the \(4d^8\) 5s5p and \(4d^0\) 5s2 configurations of Cd+ from a common reference state along with the other excited states. Since matrix elements involving these states are less significant to the properties of our interest, we calculate atomic state functions (ASFs) of these states by employing relativistic multi-configuration Dirac-Hartree-Fock (MCDF) method that is available in the GRASP2K package \([5]\). In this MCDF method, we again consider only the singles and doubles excitations to construct configuration state functions (CSFs). We have also taken into account the Breit and QED interactions that are available in this package. Due to availability of limited computational resources with us, we only include upper core orbitals in the active space of the MCDF method that are summarized in Table I.

In Table III, we present excitation energies of the excited states of Cd+ from both the CCSD and MCDF methods. These values are also compared with the data listed in the National Institute of Science and Technology database \([6]\). Small differences between the CCSD results and NIST data suggest that our calculations are within 1% accuracy. Energies obtained by the MCDF method have relatively large errors. Nonetheless, we use the experimental energies to reduce uncertainties in the evaluation of the polarizabilities.

Similarly, a list of important diagonal and off-diagonal matrix elements of \(\mathcal{T}_{hf}\) obtained by the CCSD and MCDF methods are given in atomic unit (a.u.) in Table III. Some of the diagonal elements extracted from the measured magnetic dipole hyperfine structure constants are also quoted in the same table. It shows very good agreement between the measured and calculated values, especially from the CCSD method. In our polarizability calculations, we replace calculated values with the available experimental results to reduce the uncertainties. Since the higher excited states than the \(4d^8\) 5s2 2D5/2 state that are obtained by the MCDF method do not contribute significantly to the polarizabilities, accuracies of the polarizabilities obtained by using these matrix elements are estimated to be within the intended level.

The E1 matrix elements obtained from the CCSD and MCDF methods are quoted in Table IV. Experimental values of the E1 matrix elements of few low-lying transitions are also quoted by extracting them out from the precise lifetime measurements of the atomic states in Cd+. As can be seen values obtained by the CCSD method are more reliable. The E1 matrix elements of the \(4d^8\) 5s2 2D5/2 - 4d10 5s8 2P1/2 and \(4d^0\) 5s2 2D5/2 - 4d10 5s8 2P3/2 transitions obtained by the MCDF method are found to be almost half of the experimental values. In this case, we use the experimental values in our polarizability calculations but signs of these values are decided from the MCDF results. Again, contributions from the remaining E1 matrix elements of the MCDF method are accounted for assuming 20% uncertainties in these values.
TABLE I: A brief summary of active CSFs considered in our calculations using the MCDF method. As seen orbitals from the inner core [3d^{10}] are not included in the MCDF procedure due to limitations in the computational resources. Different possible multi-reference (MR) space for constructing atomic state functions (ASFs) and higher orbitals up to which active space is constructed for the MCDF method are mentioned. Total number of CSFs generated in these process are quoted as $N_{CSFs}$.

| ASFs                          | MR space                              | Active space                              | $N_{CSFs}$ |
|-------------------------------|----------------------------------------|--------------------------------------------|------------|
| $4d^{10}5s,4d^{9}5s^2,4d^{10}6s$ | $\{4s^2\}S\{4p^8\}\{4d^{10}5s\}SD$ $\{4s^2\}S\{4p^8\}\{4d^{10}6s\}SD$ $\{4s^2\}S\{4p^8\}\{4d^{9}5s^2\}SD$ $\{4s^2\}\{4p^6\}S\{4d^{10}5s\}SD$ $\{4s^2\}\{4p^6\}S\{4d^{10}6s\}SD$ $\{4s^2\}\{4p^6\}S\{4d^{9}5s^2\}SD$ | $\{8s,6p,6d,5f\}$ | 59636 |
| $4d^{10}5p,4d^{9}5s5p,4d^{10}6p$ | $\{4s^2\}S\{4p^8\}\{4d^{10}5p\}SD$ $\{4s^2\}S\{4p^8\}\{4d^{10}6p\}SD$ $\{4s^2\}\{4p^6\}S\{4d^{10}5p\}SD$ $\{4s^2\}\{4p^6\}S\{4d^{10}6p\}SD$ $\{4s^2\}\{4p^6\}S\{4d^{9}5s5p\}SD$ | $\{7s,8p,6d,5f\}$ | 480071 |

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TABLE II: Excitation energies (in cm$^{-1}$) of many low-lying states of Cd$^+$ from the CCSD and MCDF methods. Calculated values are compared against the data listed in the NIST database [7]. Comparison among the calculations with the NIST data suggests CCSD values are less than 1% accurate while MCDF results have relatively large uncertainties.

| Level | CCSD      | MCDF      | NIST     |
|-------|-----------|-----------|----------|
| 5p $^2P_{1/2}$ | 44145.46  | 43005     | 44136.08 |
| 5p $^2P_{3/2}$ | 46648.51  | 45165     | 46618.55 |
| 6s $^2S_{1/2}$ | 82721.43  | 79291     | 82900.66 |
| 6p $^2P_{1/2}$ | 94488.98  | 90686     | 94710.41 |
| 6p $^2P_{3/2}$ | 95181.70  | 91331     | 95383.63 |
| 7s $^2S_{1/2}$ | 107002.20 | 107300.88 |          |
| 7p $^2P_{1/2}$ | 111960.45 | 112361.06 |          |
| 7p $^2P_{3/2}$ | 112261.59 | 112490.39 |          |
| 8s $^2S_{1/2}$ | 117760.13 | 118040.65 |          |
| 8p $^2P_{1/2}$ | 120302.71 | 120618.46 |          |
| 8p $^2P_{3/2}$ | 120461.36 | 120711.18 |          |
| 9s $^2S_{1/2}$ | 127031.96 | 127152.89 |          |
| 9p $^2P_{1/2}$ | 127862.19 | 127996.73 |          |
| 9p $^2P_{3/2}$ | 127916.41 | 128076.30 |          |
| 10s $^2S_{1/2}$ | 129423.70 | 129343.05 |          |
| 10p $^2P_{1/2}$ | 129830.45 | 129956.30 |          |
| 10p $^2P_{3/2}$ | 129855.73 | 130216.60 |          |
| 11s $^2S_{1/2}$ | 131192.37 | 130835.86 |          |
| 11p $^2P_{1/2}$ | 131333.96 | 131261.10 |          |
| 11p $^2P_{3/2}$ | 131341.95 | 131374.70 |          |
| 12s $^2S_{1/2}$ | 132821.90 | 132767.89 |          |
| 12p $^2P_{1/2}$ | 13341.95  | 13341.95  |          |
| 12p $^2P_{3/2}$ | 13341.95  | 13341.95  |          |

4d$^5$s$^2$ $^2D_{5/2}$  69035  69258.51
4d$^5$s$^2$ $^2D_{3/2}$  74680  74893.66
4d$^5$5s$^2$($^3D$)5p $^4P_{1/2}$  104981  104440.86
4d$^5$5s$^2$($^3D$)5p $^4P_{3/2}$  107886  112196.5
4d$^5$5s$^2$($^3D$)5p $^4P_{5/2}$  108486  112785.19
4d$^5$5s$^2$($^3D$)5p $^4D_{3/2}$  116263  116225.71
4d$^5$5s$^2$($^3D$)5p $^4D_{5/2}$  115311  117988.79
4d$^5$5s$^2$($^3D$)5p $^2P_{3/2}$  113909  119056.11
4d$^5$5s$^2$($^3D$)5p $^2P_{1/2}$  115086  119293.99
4d$^5$5s$^2$($^3D$)5p $^2D_{3/2}$  112390  120135.22
4d$^5$5s$^2$($^3D$)5p $^2D_{5/2}$  129150  129344.86
### TABLE III: Diagonal and off-diagonal reduced matrix elements of the magnetic hyperfine operator \( \mathcal{H}_f \) (in \( 10^{-8} \) a.u.) from the CCSD and MCDF methods. Some of the diagonal elements are also compared with the available experimental results.

| Matrix element | CCSD | MCDF | Experiment |
|----------------|------|------|------------|
| \( 5s^2 S_{1/2} - 5s^2 S_{1/2} \) | 228.27 | 221.12 | 227.66(1) [9] |
| \( 6s^2 S_{1/2} - 6s^2 S_{1/2} \) | 47.82 | 39.13 | |
| \( 5s^2 S_{1/2} - 6s^2 S_{1/2} \) | 104.52 | 92.99 | |
| \( 5s^2 S_{1/2} - 7s^2 S_{1/2} \) | -65.56 | | |
| \( 5s^2 S_{1/2} - 8s^2 S_{1/2} \) | 44.98 | | |
| \( 5s^2 S_{1/2} - 9s^2 S_{1/2} \) | -33.88 | | |
| \( 5s^2 S_{1/2} - 10s^2 S_{1/2} \) | 25.94 | | |
| \( 5s^2 S_{1/2} - 11s^2 S_{1/2} \) | 20.44 | | |
| \( 5s^2 S_{1/2} - 12s^2 S_{1/2} \) | 20.95 | | |
| \( 5p^2 P_{3/2} - 5p^2 P_{3/2} \) | 19.66 | 18.58 | 18.94 [10] |
| \( 5p^2 P_{3/2} - 6p^2 P_{1/2} \) | 2.11 | 1.78 | | |
| \( 5p^2 P_{3/2} - 6p^2 P_{3/2} \) | 10.49 | 9.17 | | |
| \( 6p^2 P_{3/2} - 6p^2 P_{1/2} \) | 9.95 | 7.73 | | |
| \( 6p^2 P_{3/2} - 6p^2 P_{3/2} \) | 1.05 | 0.60 | | |
| \( 6p^2 P_{3/2} - 6p^2 P_{3/2} \) | 5.62 | 4.65 | | |
| \( 4d^6 5s^2 D_{3/2} - 4d^6 5s^2 D_{3/2} \) | 99.21 | 75.10(3) [11] | | |
| \( 4d^6 5s^2 D_{3/2} - 5s^2 S_{1/2} \) | -0.03 | | |
TABLE IV: Reduced E1 matrix elements (in a.u.) obtained by the CCSD and MCDF methods. We have also inferred these values from the precisely available lifetime measurements of some of the low-lying excited state to compare with the calculated values. The CCSD results are found to be more accurate than the MCDF values, but the calculated values serve to decide the signs of the matrix elements to use the experimental values in the evaluation of polarizabilities.

| Transition                          | CCSD  | MCDF  | Experiment          |
|-------------------------------------|-------|-------|---------------------|
| $5s \ 2^1S_{1/2} - 5p \ 2^3P_{1/2}$ | −1.97 | −1.98 | 1.913(3) [12]       |
| $5s \ 2^1S_{1/2} - 5p \ 2^3P_{3/2}$ | 2.79  | 2.82  | 2.717(5) [12]       |
| $6s \ 2^1S_{1/2} - 5p \ 2^3P_{3/2}$ | 2.52  | 2.58  |                     |
| $6s \ 2^1S_{1/2} - 5p \ 2^3P_{1/2}$ | 1.65  | 1.70  |                     |
| $6p \ 2^3P_{1/2} - 6s \ 2^3S_{1/2}$ | −5.11 | −5.40 |                     |
| $6p \ 2^3P_{3/2} - 6s \ 2^3S_{1/2}$ | −7.15 | −7.57 |                     |
| $5s \ 2^3S_{1/2} - 6p \ 2^3P_{1/2}$ | 0.08  | 0.07  |                     |
| $6p \ 2^3P_{3/2} - 5s \ 2^3S_{1/2}$ | 0.03  | 0.02  |                     |
| $4d^5s^2 \ 2^3D_{3/2} - 5p \ 2^3P_{1/2}$ | 0.24  |       | 0.487(17) [13]     |
| $4d^5s^2 \ 2^3D_{3/2} - 5p \ 2^3P_{3/2}$ | 0.11  |       | 0.295(37) [13]     |
| $4d^5s^2 \ 2^3D_{3/2} - 6p \ 2^3P_{1/2}$ | 0.25  |       |                     |
| $4d^5s^2 \ 2^3D_{3/2} - 6p \ 2^3P_{3/2}$ | 0.07  |       |                     |
| $5s_{1/2} \ 2^1S_{1/2} - 4d^3s^3(D)5p \ 4^3P_{5/2}$ | 0.28  |       |                     |
| $5s_{1/2} \ 2^1S_{1/2} - 4d^3s^3(D)5p \ 4^1P_{1/2}$ | 0.22  |       |                     |
| $5s_{1/2} \ 2^1S_{1/2} - 4d^3s^3(D)5p \ 4^1P_{3/2}$ | 0.03  |       |                     |
| $5s_{1/2} \ 2^1S_{1/2} - 4d^3s^3(D)5p \ 4^3D_{3/2}$ | 0.23  |       |                     |
| $5s_{1/2} \ 2^1S_{1/2} - 4d^3s^3(D)5p \ 4^1D_{1/2}$ | 0.80  |       |                     |
| $5s_{1/2} \ 2^1S_{1/2} - 4d^3s^3(D)5p \ 4^3P_{1/2}$ | −1.05 |       |                     |
| $5s_{1/2} \ 2^1S_{1/2} - 4d^3s^3(D)5p \ 4^1P_{3/2}$ | 0.68  |       |                     |
| $5s_{1/2} \ 2^1S_{1/2} - 4d^3s^3(D)5p \ 4^3D_{3/2}$ | 0.16  |       |                     |
| $5s_{1/2} \ 2^1S_{1/2} - 4d^3s^3(D)5p \ 4^1P_{3/2}$ | −1.23 |       |                     |
| $5s_{1/2} \ 2^1S_{1/2} - 4d^3s^3(D)5p \ 4^3P_{1/2}$ | 0.67  |       |                     |