Comparative studies of dipole polarizabilities in Sr$^+$, Ba$^+$ and Ra$^+$ and their applications to optical clocks

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Static dipole polarizabilities are calculated in the ground and metastable states of Sr$^+$, Ba$^+$ and Ra$^+$ using the relativistic coupled-cluster method. Trends of the electron correlation effects are investigated in these atomic ions. We also estimate the Stark and black-body radiation shifts from these results for these systems for the transitions proposed for the optical frequency standards and compare them with available experimental data.

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I. INTRODUCTION

There have been a number of significant proposals for new optical clocks that are more accurate than the current standard; the Cs clock $^{1,2,3}$. Singly charged ions are some of the prominent candidates in this category due to the remarkable advances in modern ion trapping and laser cooling techniques $^{1,2,3,4}$. S-D transitions in Sr$^+$ $^{5,6}$, Yb$^+$ $^{6}$, Hg$^+$ $^{7}$, Ba$^+$ $^{8,9}$ and Ra$^+$ $^{10}$ can serve as clock transitions. It is necessary to estimate the shifts of the energy levels for these cases due to stray electromagnetic fields in order to determine the accuracies of these potential optical clocks. A knowledge of hyperfine structure constants, electric quadrupole moments, gyromagnetic constants and polarizabilities are essential quantities that can be used to estimate various possible shifts $^{11}$. In our previous studies, we have already calculated hyperfine structure constants and electric quadrupole moments for the above ions $^{12,13}$. It is possible to find the gyromagnetic constants approximately using analytical approaches for different states $^{11}$. There have been extensive studies of the hyperfine structure constants of the low-lying states in the above ions using the relativistic coupled-cluster (RCC) method $^{10,12,14,15}$. A few calculations of polarizabilities in these ions using the sum-over-states approach have also been reported recently $^{14,16}$.

Both Ba$^+$ and Ra$^+$ have also been proposed as suitable candidates for atomic parity violation (APV) experiments $^{17,18}$. Determination of polarizabilities depends on the electric dipole (E1) matrix elements and excitation energies. On the other hand, the determination of APV amplitudes also depends on E1 matrix elements and excitation energies. Therefore, studies of correlation effects in these properties involving quantities in these systems are also useful for the APV studies. In contrast to hyperfine structure constants where the explicit behavior of electron correlation has been studied elaborately, the same cannot be done for polarizabilities using the sum-over-states approach. Also, the sum-over-states approach considers only a limited number of states, mainly from the single excited states and misses out contributions from continuum, double excited states, normalization of the wave functions etc.

In this work, we have employed an ab initio method in the RCC framework to calculate dipole polarizabilities of Sr$^+$, Ba$^+$ and Ra$^+$. The roles of different types of electron correlation effects in determining these quantities are studied and comparisons between these results are given explicitly. Contributions arising from different types of excited states and normalization of the wave functions through the RCC method have also been evaluated. Using these results, we then estimate the Stark and black-body radiation shifts in these systems which will be useful for the proposed optical clock experiments in the ions mentioned above.

II. THEORY

The polarizability of a given state $|J_nM_n\rangle$ can be expressed by

$$\alpha_0' = 2 \sum_{m \neq n} C_i(J_n) \frac{|\langle J_n || D || J_m \rangle|^2}{E_n - E_m}$$

$$= 2 \sum_{m \neq n} C_i(J_n) (-1)^J_n-J_m \frac{|\langle J_n || D || J_m \rangle | \langle J_m || D || J_n \rangle |}{E_n - E_m}$$

where the subscript 0 represents for the static values and angular momentum coefficients ($C_i(J_n)$) for the scalar (with superscript 1) and tensor (with superscript 2) dipole polarizabilities are given as

$$C_1(J_n) = \frac{1}{3(2J_n + 1)}$$  \hspace{1cm} (2.2)
where appears as a first order correction to the atomic states.

respectively. Es are the energies of the corresponding atomic states.

By defining a modified wave function due to the dipole operator, D, we can rewrite the above expression as

\[ \alpha^j_0(J_n) = \langle J_n | \tilde{D} | J_n^{(1)} \rangle + \langle J_n^{(1)} | \tilde{D} | J_n \rangle, \tag{2.4} \]

where

\[ |J_n^{(1)}\rangle = \sum_{m \neq n} \frac{|J_m\rangle \langle J_m||D||J_n\rangle}{E_n - E_m}. \tag{2.5} \]

appears as a first order correction to the \( |J_n\rangle \) state due to the dipole operator \( D \). In the above expression, we also define an effective dipole operator as

\[ \tilde{D}_i = C_i(J_n)(-1)^{J_n - J_m} D, \tag{2.6} \]

whose matrix element between the original and perturbed wave functions will give the dipole polarizabilities. Here the intermediate states, \( |J_m\rangle \), have parities opposite to that of \( |J_n\rangle \) and they have to satisfy the usual triangular condition for the vector operator \( D \).

To avoid the sum-over-states approach in the determination of the polarizabilities, we avoid the explicit form of \( |J_n^{(1)}\rangle \) that is given by Eq. 2.5. Instead, we obtain \( |J_n^{(1)}\rangle \) by solving the following equation

\[ (H - E_n)|J_n^{(1)}\rangle = -D|J_n\rangle, \tag{2.7} \]

that is similar to the first order perturbative equation. Here \( H \) is the atomic Hamiltonian which in the present work is considered in the Dirac-Coulomb approximation

\[ H = \sum_i \left[ c \alpha \cdot p_i + (\beta - 1) c^2 + V_{\text{nuc}}(r_i) \right] + \sum_{i>j} \frac{1}{r_{ij}}, \tag{2.8} \]

where \( c \) is the velocity of light, \( \alpha \) and \( \beta \) are the Dirac matrices and \( V_{\text{nuc}}(r) \) is the nuclear potential.

For an atomic system with zero nuclear spin, the Stark shift to the second order in the presence of an electric field (quadratic Stark shift) for \( |J_n, M_n\rangle \) state is given by [19]

\[ \Delta W_E(J_n, M_n; E) = -\frac{1}{2} \alpha^J_0(J_n) E^2 - \frac{1}{4} \alpha_0^2(J_n) \left[ \frac{3M_n^2 - J_n(J_n + 1)}{J_n(2J_n - 1)} \right] (3E_z^2 - E^2), \tag{2.9} \]

where \( E \) and \( E_z \) are the magnitudes of the externally applied electric field in any arbitrary and z directions, respectively.

For atomic systems with non-zero nuclear spin \( (I) \), the expression for hyperfine states are given by [19]

\[ \Delta W_E(F_n, M_{F_n}; E) = -\frac{1}{2} \alpha^J_0(F_n) E^2 - \frac{1}{4} \alpha_0^2(F_n) \left[ \frac{3M_{F_n}^2 - F_n(F_n + 1)}{F_n(2F_n - 1)} \right] (3E_z^2 - E^2), \tag{2.10} \]

where \( F_n = I + J_n \) and \( M_{F_n} \) are the total spin due to nuclear spin \( F \) and atomic state spin \( J_n \) and its azimuthal component, respectively. Since it is easier for us to deal with \( J_n \) of the electronic states, therefore we express all the above quantities in terms of electronic coordinate. By using the following relations [11]

\[ \alpha_0^J(F_n) = \alpha_0^J(J_n), \tag{2.11} \]

and

\[ \alpha_0^2(F_n) = (\alpha^{I+J_n+F_n}_0(J_n) \left[ \frac{F_n(2F_n - 1)(2F_n + 1)}{(2F_n + 3)(F_n + 1)} \right] \left[ \frac{(2J_n + 1)(J_n + 1)(2J_n + 3)}{J_n(2J_n - 1)} \right] \left\{ \frac{F_n I}{J_n} \left\{ \frac{J_n}{2} \right\} \right\}, \tag{2.12} \]

between the dipole polarizabilities of the electronic and hyperfine states, we obtain

\[ \Delta W_E(F_n, M_{F_n}; E) = -\frac{1}{2} \alpha^J_0(J_n) E^2 - \frac{1}{4} (\alpha^{I+J_n+F_n}_0(J_n) \left[ \frac{3M_{F_n}^2 - F_n(F_n + 1)}{F_n(2F_n - 1)} \right] \left[ \frac{F_n(2F_n - 1)(2F_n + 1)(2J_n + 1)(J_n + 1)(2J_n + 3)}{(2F_n + 3)(F_n + 1)J_n(2J_n - 1)} \right] \left\{ \frac{F_n I}{J_n} \left\{ \frac{J_n}{2} \right\} \right\} (3E_z^2 - E^2). \tag{2.13} \]

Again, the blackbody-radiation (BBR) shift of a given state \( |J_n, M_n\rangle \) in the adiabatic expansion due to the ap-
plied isotropic electric field radiated at temperature T (in Kelvin (K)) can be assumed as [20]
\[ \Delta_{BBR} = -\frac{1}{2}(831.9 V/m)^2 \left( \frac{T(K)}{300} \right)^4 \alpha^4(J_n). \] (2.14)

III. METHOD OF CALCULATIONS

The RCC method, which is equivalent to all order perturbation theory, has been recently used to obtain precise results and account for the correlation effects accurately in single valence systems [10, 12, 13, 14, 15]. In the RCC framework, the wave function of a single valence atom can be expressed as
\[ |\Psi_n^{(0)}\rangle = e^T(1 + S_n)|\Phi_n\rangle, \] (3.1)
where \( |\Phi_n\rangle \) is the reference state constructed from the Dirac-Fock wave function \( |\Phi_0\rangle \) of the closed-shell configuration by appending the corresponding valence electron as \( |\Phi_n\rangle = a_n^\dagger |\Phi_0\rangle \) with \( a_n^\dagger \) representing addition of a valence electron \( n \). Here \( T \) and \( S_n \) are the RCC excitation operators which excite electrons from \( |\Phi_0\rangle \) and \( |\Phi_n\rangle \), respectively. The amplitudes of these excitation are obtained by the following equations
\[ \langle \Phi^L_n | \{ H_N e^T \} | \Phi_0 \rangle = 0 \] (3.2)
\[ \langle \Phi^L_n | \{ H_N e^T \} S_n | \Phi_n \rangle = -\langle \Phi^L_n | \{ H_N e^T \} | \Phi_n \rangle \]
+ \( \langle \Phi^L_n | S_n | \Phi_n \rangle \Delta_{E_n} \), (3.3)

with the superscript \( L(=1,2) \) representing the single and double excited states from the corresponding reference states and the wide-hat symbol over \( H_N e^T \) represent the linked terms of normal order atomic Hamiltonian \( H_N \) and RCC operator \( T \). For the single and double excitations approximation (CCSD method), the corresponding RCC operators are denoted by
\[ T = T_1 + T_2 \] (3.4)
and
\[ S_n = S_{1n} + S_{2n} \] (3.5)
for the closed-shell and single valence configurations, respectively. Again, \( \Delta_{E_n} \) in the above expressions is the corresponding valence electron affinity (negative of the ionization potential (IP)) energy which is evaluated by
\[ \Delta_{E_n} = \langle \Phi_n | \{ H_N e^T \} (1 + S_n) | \Phi_n \rangle. \] (3.6)

In Eq. (3.2), we have considered only the single and double excitations, however we have incorporated contributions from important triple excitations (CCSD(T) method) perturbatively in Eq. (3.3) by defining
\[ S_{3n}^{pert} = H_N T_2 + H_N S_{2n}, \] (3.7)
where the superscript \( pert \) denotes for the perturbation, and evaluating their contributions to \( \Delta_{E_n} \) from these operators by
\[ \Delta_{E_n}^{trip} = T_2 S_{3n}^{pert}. \] (3.8)

After obtaining the amplitudes for \( T \), the core excitation operator, we solve Eqs. (3.3) and (3.6) simultaneously to obtain the amplitudes for the \( S_n \) operators.

We extend the RCC ansatz for the perturbed atomic state in the presence of the electric dipole operator \( D \) by writing the total atomic wave function as
\[ |\tilde{\Psi}_n\rangle = e^{T+\Omega(1+S_n+\Lambda_n)}|\Phi_n\rangle, \] (3.9)
where \( \Omega \) and \( \Lambda_n \) are the first order corrections to the RCC operators \( T \) and \( S_n \), respectively. Since Eq. (2.7) is first order in the operator \( D \), the above expression will reduce to
\[ |\tilde{\Psi}_n\rangle = e^{T(1+S_n+\Omega(1+S_n)+\Lambda_n)}|\Phi_n\rangle. \] (3.10)

Now, separating the above wave function as \( |\Psi_n^{(0)}\rangle \) and \( |\Psi_n^{(1)}\rangle \), we get
\[ |\Psi_n^{(1)}\rangle = e^{T\{\Omega(1+S_n)+\Lambda_n\}}|\Phi_n\rangle. \] (3.11)

Following Eq. (2.7), we solve again the amplitudes for the modified operators as
\[ \langle \Phi^L_n | \{ H_N e^T \} \Omega | \Phi_0 \rangle = -\langle \Phi^L_n | \{ D e^T \} | \Phi_0 \rangle \] (3.12)
\[ \langle \Phi^L_n | \{ H_N e^T \} \Lambda_n | \Phi_n \rangle = -\langle \Phi^L_n | \{ D e^T \Omega(1+S_n) + D e^T \} (1+S_n) | \Phi_n \rangle + \langle \Phi^L_n | \Lambda_n | \Phi_n \rangle \Delta_{E_n}, \] (3.13)

where \( D e^T \) represents the connecting terms between \( D \) and \( T \) operators. Again in our CCSD approximation, we have
\[ \Omega = \Omega_1 + \Omega_2 \] (3.14)
and
\[ \Lambda_n = \Lambda_{1n} + \Lambda_{2n}. \] (3.15)

Therefore, the RCC expression for the dipole polarizability is given by
## TABLE I: Comparison of dipole polarizabilities between different works in Sr\(^+\), Ba\(^+\) and Ra\(^+\).

| System | \(\alpha_{1/2}^0\) | \((n-1)d_{3/2}^0\) | \((n-1)d_{5/2}^0\) | Methods | References |
|--------|-----------------|-----------------|-----------------|---------|------------|
| Sr\(^+(n = 5)\) | | | | DF | This work |
| 127.62 | 145.86 | −91.81 | 136.84 | −116.02 | CCSD(T) | This work |
| 88.29(1.0) | 61.43(52) | −35.42(25) | 62.87(75) | −48.83(30) | DF | This work |
| 132.15 | HF | non-rel. MBPT(2) | 22 | |
| 86.21 | 101.58 | non-rel. CCSD | 22 | |
| 97.91 | 121.33 | DK DF | 22 | |
| 79.89 | 94.31 | DK rel. MBPT(2) | 22 | |
| 91.10 | 124.26(1.0) | 48(12) | | DF | This work |
| 91.3(9) | 90.07 | 62.0(5) | −47.7(3) | Non-rel.+sum-over | 16 |
| 89.88 | 93.3 | Non-rel.+sum-over | 24 | |
| 84.6(3.6) | 91.47 | Non-rel.+sum-over | 5 | |
| 86(11) | Experiment + non-rel. | 26 | |
| Ba\(^+(n = 6)\) | | | | DF | This work |
| 184.49 | 90.07 | −45.07 | 87.66 | −58.02 | CCSD(T) | This work |
| 213.47 | 124.26(1.0) | 48.81(46) | −24.62(28) | 50.67(58) | −30.85(31) | CCSD(T) | This work |
| 110.60 | 148.24 | 146.88 | DK DF | 22 | |
| 177.64 | 94.64 | DK rel. MBPT(2) | 22 | |
| 129.92 | 123.07 | DK rel. CCSD | 22 | |
| 124.15 | 124.7 | Non-rel.+sum-over | 5 | |
| 126.2 | 123.88(5) | Experiment | 27 | |
| 125.5(10) | Experiment | 28 | |
| Ra\(^+(n = 7)\) | | | | DF | This work |
| 164.66 | 183.07 | −114.70 | 143.77 | −98.64 | CCSD(T) | This work |
| 104.54(1.5) | 83.71(77) | −50.23(43) | 82.38(70) | −52.60(45) | CCSD(T) | This work |
| 257.00 | 123.25 | 186.23 | DK DF | 22 | |
| 172.00 | 145.47 | 79.80 | DK rel. MBPT(2) | 22 | |
| 110.48 | 105.37 | DK rel. CCSD | 22 | |
| 106.12 | 106.5 | DK rel. CCSD(T) | 22 | |
| 106.22 | LCCSD(T)+sum-over | 10 | |
| 106.22 | LCCSD(T)+sum-over | 32 | |
| Abbreviations: HF → Hartree-Fock.  
non-rel. → non-relativistic.  
DK rel. → scalar relativistic Douglas-Kroll method.  
MBPT(2) → second order perturbation theory.  
sum-over → sum-over intermediate states. |
\[ \alpha^i_0 = \frac{\langle \psi^{(0)}_n | \tilde{D}_i | \psi^{(1)}_n \rangle + \langle \psi^{(1)}_n | \tilde{D}_i | \psi^{(0)}_n \rangle}{\langle \psi^{(0)}_n | \psi^{(0)}_n \rangle} \]

where we define \( \tilde{D}_i = (e^{T_i} \tilde{D}_i e^T_i) \) and \( \mathcal{N}_0 = e^{T_0} e^T \). The non-truncative series for \( \tilde{D}_i \) and \( \mathcal{N}_0 \) are expanded using the Wick’s generalized theorem and truncated the series when the leading order non-accounted terms are below fifth order of Coulomb interaction. These operators are then contracted with the \( \Omega \) to get fully contracted terms that give rise core electron contributions. The core-valence and valence correlation contributions are obtained from the open contraction between the operators with \( \Omega \) and \( \Omega \{1+S_n\} + \Lambda_n \) operators, respectively.

Corrections due to the normalization of the wave functions are accounted by evaluating

\[ \text{Norm} = \left[ \langle \psi^{(0)}_n | \tilde{D}_i | \psi^{(1)}_n \rangle + \langle \psi^{(1)}_n | \tilde{D}_i | \psi^{(0)}_n \rangle \right] \left\{ \frac{1}{1+N_n} - 1 \right\}, \]  

(3.17)

where \( N_n = \langle \Phi_n | \{1+S_n\} \mathcal{N}_0 (1+S_n) | \Phi_n \rangle \).

IV. RESULTS AND DISCUSSIONS

A. General discussions

![FIG. 1: Break-down of RCC terms into lower-order perturbative diagrams.](image)

The orbitals used in the present work are generated on a radial grid given by

\[ r_i = r_0 \left[ e^{h(i-1)} - 1 \right], \]  

(4.1)

where \( i \) represents a grid point. The total number of grid points in our calculations is 750, the step size \( h \) is taken as 0.03 in the present case and \( r_0 \) is taken as \( 2 \times 10^{-6} \) atomic units. To construct the basis functions, we use Gaussian type orbitals (GTOs) defined as

\[ F_{\text{GTO}}(r_i) = n_{\alpha i} e^{-\alpha_i r_i^2}. \]  

(4.2)

Here \( n_{\alpha i} \) is the radial quantum number of the orbitals and \( \alpha_i \) is a parameter whose value is chosen to obtain orbitals with proper behavior inside and outside the nucleus of an atomic system. Further, the \( \alpha_i \)s satisfy the even tempering condition

\[ \alpha_i = \alpha_0 \beta^{i-1}. \]  

(4.3)

We have chosen same \( \alpha_0 = 0.00525 \) and \( \beta = 2.73 \) values to construct the basis functions in Sr\(^+\), Ba\(^+\) and Ra\(^+\), so that effects due to the different sizes of the systems can be compared. Finite size of the nucleus in these systems are accounted by assuming a two-parameter Fermi-nuclear-charge distribution for evaluating the electron density over nucleus as given by

\[ \rho(r_i) = \frac{\rho_0}{1 + e^{(r_i-c)/a}}, \]  

(4.4)

where \( c \) and \( a \) are the half-radius and skin thickness of the nucleus. These parameters are chosen as

\[ a = 2.3/4(ln3) \]  

(4.5)

and

\[ c = \sqrt{\frac{5}{3}} \overline{r_m^2} - \frac{7}{3} a^2 \pi^2, \]  

(4.6)

where \( \overline{r_m^2} \) is the root mean square radius of the corresponding nuclei which is determined as discussed in [21].

In Table II we present our DF and CCSD(T) results along with other available calculations and experimental results for the dipole polarizabilities of the ground and metastable states of Sr\(^+\), Ba\(^+\) and Ra\(^+\). The differences between the DF and CCSD(T) results indicate the magnitudes of the electron correlation effects in the determination of the dipole polarizabilities in these systems.
TABLE II: Contributions from the DF and various CCSD(T) terms to the dipole polarizability calculations in Sr$^+$. The subscripts $c$, $n$ and $v$ of the RCC terms correspond to the core, valence and virtual correlation contributions. $D_c$ and $D_n$ give the DF results from the core and valence orbitals.

| Terms               | $5s^2 2S_{1/2}$ | $4d^2 2D_{3/2}$ | $4d^2 2D_{5/2}$ |
|---------------------|-----------------|-----------------|-----------------|
| $\bar{D}_c$         | 6.15            | 6.15            | 6.15            |
| $\bar{D}_n$         | 121.47          | 139.71          | 130.69          |
| $\bar{D}_c \Omega + cc$ | 4.98            | 4.98            | 4.98            |
| $\bar{D}_c \Lambda_{1n} + cc$ | 93.78          | 67.05           | 68.14           |
| $\bar{D}_n \Lambda_{2n} + cc$ | -2.87          | -2.54           | -2.43           |
| $S_{1n} \bar{D}_n \Lambda_{1n} + cc$ | -3.74          | -6.06           | -6.10           |
| $S_{2n} \bar{D}_n \Lambda_{2n} + cc$ | -3.03          | -1.47           | -1.39           |
| $S_{1n} \bar{D}_n \Lambda_{1n} + cc$ | -0.04          | 0.06            | 0.05            |
| $S_{2n} \bar{D}_n \Lambda_{2n} + cc$ | 0.13           | -0.05           | -0.06           |
| Others              | 0.13            | 0.22            | -0.14           |
| Norm                | -1.15           | -0.96           | -0.97           |

using the CCSD(T) method. They are 45%, 48% and 58% for the ground states of Sr$^+$, Ba$^+$ and Ra$^+$, respectively. They increase with the size of the system. However, the correlation effects in the $d_{3/2}$ metastable states are 137%, 85% and 119% for the scalar polarizabilities and 159%, 83% and 128% for the tensor polarizabilities in Sr$^+$, Ba$^+$ and Ra$^+$, respectively. This shows that the correlation effects reduce in these states from Sr$^+$ to Ba$^+$, but the presence of the core $f$-orbitals increases the correlation effects in Ra$^+$. The correlation effects in the $d_{3/2}$ metastable states are 117%, 73% and 75% for the scalar polarizabilities and 138%, 88% and 87% for the tensor polarizabilities in Sr$^+$, Ba$^+$ and Ra$^+$, respectively. This implies that the correlations in the $d$-metastable states do not depend upon the size but the internal structure of the systems. Our previous studies on the hyperfine structure constants in these systems[10,12,13,14,15] had shown peculiar behavior of the core-polarization effects. These effects were comparatively smaller in the $d_{3/2}$ metastable states. In contrast, the correlation effects are larger in the $d_{3/2}$ metastable states compared to the $d_{5/2}$ metastable states and the ground states in the dipole polarizabilities calculations.

The upper limits to the error bars in these quantities were determined by taking the differences of the results obtained using CCSD(T) and CCSD methods and the inaccuracies due to the self-consistent results obtained at the DF levels by varying the number of GTOs considered in the calculations. These results are quoted inside the parentheses in Table II.

We explicitly present the diagrams in Fig. 1 corresponding to various RCC terms that are significant in determining the dipole polarizabilities. As seen from the figure, Fig. 1(a) which arises from the fully contracted terms of $\bar{D}_\Omega$ corresponds to the core-correlation contributions. Its lower order terms corresponds mainly to the diagrams coming from the random-phase approximation (RPA). There are also core-correlation contributions arising from $\bar{D}_{\Lambda}$, but they are relatively small and are not shown in Fig. 1. The core-valence correlation contributions are determined by open diagrams from $\bar{D}_\Omega$ as shown in Fig. 1(b). The most important correlation contributions arise through the valence correlation effects and they are shown in Fig. 1(c) and 1(d). Important pair-correlation and core-polarization effects are accounted through $\bar{D}_\Lambda$, however core-polarization effects arising from the perturbed doubly excited states are accounted through $\bar{D}_\Lambda_{1n}$. The DF contributions involving the core, core-valence and virtual orbitals are the lowest order diagrams to the fully contracted $\bar{D}_\Omega$, open $\bar{D}_\Omega$ and $\bar{D}_\Lambda_{1n}$ RCC terms, respectively. Based on the above mentioned correlation diagrams, we analyze their roles in different systems considered below.

**B. Sr$^+$**

There are no experimental results of the dipole polarizabilities available for the ground and metastable excited states in Sr$^+$. However, a number of calculations have been carried out using different methods and we have compared their results with the present work in Table II. Lim and Schwerdtfeger[22] have done comparative studies between the non-relativistic and scalar relativistic Douglas-Kroll calculations using four different mani-
TABLE III: Contributions from the DF and various CCSD(T) terms to the dipole polarizability calculations in Ba\(^+\). The subscripts c, n and v of the RCC terms correspond to the core, valence and virtual correlation contributions. \(\Delta_c\) and \(\Delta_n\) give the DF results from the core and valence orbitals.

| Terms                           | \(6s^2_{1/2}\) \(\alpha_0^{\perp}\) | \(5d^2_{3/2}\) \(\alpha_0^{\perp}\) | \(5d^2_{3/2}\) \(\alpha_0^{\parallel}\) | \(5d^2_{5/2}\) \(\alpha_0^{\parallel}\) |
|---------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|
| \(\Delta_c\)                   | 11.73                            | 11.73                            | −0.46                            | 11.73                            |
| \(\Delta_n\)                   | 172.76                           | 78.33                            | −44.61                           | 75.93                            |
| \(\Delta_c \Omega + cc\)       | 9.35                             | 9.35                             | −0.56                            | 9.35                             |
| \(\Delta_n \Lambda_{1n} + cc\) | 0.23                             | 0.33                             | −0.64                            | 0.82                             |
| \(\Delta_c \Lambda_{2n} + cc\) | 133.01                           | 49.20                            | −25.61                           | 50.17                            |
| \(S_{2n} \Delta_{1n} + cc\)    | −4.93                            | −3.23                            | −1.36                            | −3.05                            |
| \(S_{2n} \Delta_{2n} + cc\)    | −6.58                            | −4.45                            | 2.39                             | −4.42                            |
| \(S_{2n} \Delta_{2n} + cc\)    | −5.18                            | −1.98                            | 0.84                             | −1.83                            |
| \(S_{2n} \Delta_{2n} + cc\)    | −0.06                            | 0.05                             | 0.03                             | 0.03                             |
| Others                          | 0.27                             | −0.10                            | 0.05                             | −0.09                            |
| Norm                            | −2.06                            | −0.81                            | 0.49                             | −0.80                            |

body methods. They demonstrate the importance of the relativistic methods to calculate dipole polarizabilities. Jiang et al. \[16\] have used E1 matrix elements obtained using the linearized RCC method with the singles, doubles and partial triple excitations (LCCSD(T)) to evaluate the valence correlation contributions for a few intermediate states. The core-correlations are accounted through the RPA method and contributions from higher states were estimated using the DF method. Mitroy et al. \[23\] have used a non-relativistic method using the sum-over-states approach to determine polarizabilities of the ground and d-state. As seen in Table I, the dipole polarizabilities of the 4d\(_{1/2}\) and 4d\(_{5/2}\) states are not the same and they cannot be evaluated separately using a non-relativistic method. However, our ground state polarizability for Sr\(^+\) agrees with their result. Similar approaches were also employed by Barklem and O'Mara \[24\]. Patil and Tang \[25\] have employed a summation and integration approach to determine the ground state polarizability. Recently, Nunkaew et al. \[26\] have estimated E1 matrix elements using the non-relativistic theory and microwave resonance measurements in Sr and have extracted dipole polarizability of the ground state of Sr\(^+\), although small in magnitude. Jiang et al. \[16\] have neglected this contribution in their calculations. We have also given DF results from the core (\(\Delta_c\)) and virtual (\(\Delta_v\)) orbitals separately in the same table. Our DF result and that reported by Lim and Schwerdtfeger \[22\] differ. Comparing our DF results given in Table I and Table III it seems that Lim and Schwerdtfeger have not included core correlation contributions at the DF level. Again, the lowest order contributions to \(\Delta_c\) and \(\Delta_v\Lambda_{1n}\) terms correspond to \(\Delta_c\) and \(\Delta_v\), respectively. The differences between the lowest order and all order results seem to be significant in this system. The largest contributions to the final results come from \(\Delta_v\Lambda_{1n}\) as it contains DF results due to virtual orbitals in it. Contributions from \(\Delta_v\Lambda_{2n}\) correspond to doubly excited perturbed states and they are also large in both the ground and metastable states. Therefore, the exclusion of these contributions in the sum-over-state approach may not be appropriate. Again, normalization corrections (\(\text{Norm}\)) are also non-negligible.

C. Ba\(^+\)

Two experimental results with small uncertainties \[27,28\] are available for the ground state dipole polarizability in Ba\(^+\). There have also been studies of this quantity by Lim and Schwerdtfeger \[22\], Iskrenova-Tchoukova and Safonova \[29\] have employed E1 matrix elements from the LCCSD(T) method in the sum-over-states approach using a few states for the valence correlation effects and estimating the core-correlation and core-valence correlation contributions from lower order pertur-
bation theory to determine this quantity. Other available calculations \cite{23, 30} are based on non-relativistic methods. Again, there are no other results available for the metastable d-states in Ba\(^+\) to compare with our results. However, we have also carried-out a sum-over-states calculation using the E1 matrix elements from the CCSD(T) method \cite{31} that agrees with our \textit{ab initio} results.

We present contributions from individual RCC terms to the dipole polarizabilities calculations on Ba\(^+\) in Table III. The trends of these correlation effects seem to be the same as in Sr\(^+\). However, the core correlation effects in this system seem to be almost twice than in the case of Sr\(^+\). The core-valence correlations coming through the open \(D_c \Omega\) diagrams are also larger than Sr\(^+\). Contributions from the doubly excited perturbed states and corrections due to the normalization of the wave functions also seem to be significant.

| Terms         | \(7s\) \(^2S_{1/2}\) \(\alpha_0\) | \(6d\) \(^2D_{3/2}\) \(\alpha_0\) | \(6d\) \(^2D_{3/2}\) \(\alpha_0\) | \(6d\) \(^2D_{5/2}\) \(\alpha_0\) | \(6d\) \(^2D_{5/2}\) \(\alpha_0\) |
|---------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| \(D_c\)       | 15.56                           | 15.56                           | –0.56                           | 15.56                           | –0.56                           |
| \(D_0\)       | 149.10                          | 167.51                          | –114.14                         | 128.21                          | –98.07                          |
| \(D_c \Omega + cc\) | 11.66                           | 11.66                           | –0.71                           | 11.66                           | –0.71                           |
| \(D_c \Lambda_{1n} + cc\) | 107.74                          | 91.30                           | –54.32                          | 85.59                           | –62.17                          |
| \(D_c \Lambda_{2n} + cc\) | –4.15                           | –5.92                           | –2.84                           | –4.85                           | 3.68                            |
| \(S_{1n} D_c \Lambda_{1n} + cc\) | –5.17                           | –7.62                           | 4.51                            | –6.65                           | 5.13                            |
| \(S_{2n} D_c \Lambda_{1n} + cc\) | –4.93                           | –4.64                           | 2.68                            | –3.44                           | 1.76                            |
| \(S_{1n} D_c \Lambda_{2n} + cc\) | –0.02                           | 0.05                            | 0.05                            | 0.02                            | –0.01                           |
| \(S_{2n} D_c \Lambda_{2n} + cc\) | 0.25                            | –0.18                           | 0.07                            | –0.15                           | 0.10                            |
| Others        | 0.29                            | 0.61                            | –0.34                           | 0.64                            | –0.43                           |
| Norm          | –1.73                           | –1.76                           | 1.21                            | –1.47                           | 1.08                            |

D. Ra\(^+\)

There are also no experimental results available for the dipole polarizabilities in Ra\(^+\). In the same work as mentioned above, Lim and Schwerdtfeger \cite{22} have also calculated this quantity in the ground state of Ra\(^+\) using various many-body methods. Safronova et al. \cite{32, 33} have also evaluated this result using the sum-over-states approach. Their valence correlation effects are evaluated using E1 matrix elements for a few important states from the LCCSD(T) method and core-correlation and core-valence correlations are evaluated using lower order many-body methods. In our earlier work \cite{10}, we had also evaluated dipole polarizabilities in the ground and d-metastable states using the sum-over-states approach with the E1 matrix elements from CCSD(T) method and approximated core-correlation and core-valence correlation effects.

In Table IV we present contributions from individual RCC terms to these results. The trend of the correlation effects in the ground state seems similar to those of Sr\(^+\) and Ba\(^+\), but due to the presence of core f-electrons, the behavior of the correlation effects is a little different for the metastable d-states. The size of core-correlation is slightly larger than that of Ba\(^+\), but the difference is not as large as it was between Sr\(^+\) and Ba\(^+\). In contrast to Ba\(^+\) where the \textit{ab initio} and sum-over-states results match, we found discrepancies in this system. The discrepancies are mainly because of the inclusion of the doubly excited states in the present work, but there could be cancellations in Ba\(^+\) due to which the discrepancies are small.

E. Applications to the optical clocks

All the ions considered in this work are important candidates for optical clocks \cite{2, 5, 8, 9, 10}. There has been an absolute frequency measurement of the 5s \(^2S_{1/2} \rightarrow \) 4d \(^2D_{5/2}\) transition in \(^{88}\)Sr\(^+\) by Madej et al. \cite{3}. One of the largest uncertainties due to the applied electric field comes from the quadratic Stark shift. In fact, this shift was earlier over estimated due to the large error bars in the calculated dipole polarizabilities of the 5s \(^2S_{1/2}\) and 4d \(^2D_{5/2}\) states. Madej et al. had used \(\alpha_0^1(5s_{1/2}) = (1.40 \pm 0.06) \times 10^{-39} \text{ C}^2 \text{ s}^2 \text{ kg}^{-1}\) where we obtain this result as \((1.46 \pm 0.02) \times 10^{-39} \text{ C}^2 \text{ s}^2 \text{ kg}^{-1}\). The
the 5s
obtain
Madej et al. as
2
C
0
2
used in [5] as
to encounter the electric quadrupole shift in the 5d
and
(2
C
α
kg
= (γ
quadrupole moments. Our dipole polarizability for the
Zeeman shifts because of finite nuclear magnetic and
tion, one has to again estimate the possible quadratic

is produced at KVI [34] in the accelerator method
results for the dipole polarizabilities of the ground and the metastable d-states in
the considered ions, it is found that these systematic errors are small in Ra
the black-body radiation shift at T = 300K in the 6s
2
S1/2 → 5d
2
D5/2 transition in this system is given as (0.64 ± 0.12) Hz.

Similarly as we had reported earlier [10], both 223Ra
and 225Ra+ have the same advantages like 137Ba+ and
138Ba+, respectively, for considering as optical clock candidates. In fact, all the low-lying energy levels in these ions are in optical region which will be an advantage for the experimentalists to measure the 7s
2
S1/2 → 6d
2
D3/2 or 7s
2
S1/2 → 6d
2
D5/2 or F = 2(7s
1/2) → F = 0(6d3/2) transition frequencies more precisely than other candidates. Recently, 213Ra whose half-life is around 2.75 m was produced at KVI [34] in the accelerator method and its single ion shares the same advantage with 225Ra+ for becoming suitable candidate for the optical clock. Now assuming that due to the suitable choice of hyperfine states in 223Ra+ [10] like the case for 137Ba+, the tensor polarizability contribution to the Stark-shift will be zero and hence using our dipole polarizability results, we obtain the Stark shift rates as (−1.31 ± 0.02) µHz/(V/m)2 and (−1.05 ± 0.02) µHz/(V/m)2 in the 7s
2
S1/2 and 6d
2
D3/2 states, respectively. For other isotopes discussed above, by considering particular M values of the 6d
2
D5/2 state and assuming that the electric field lies in the z-direction, the Stark shifts are evaluated as γ = (−1.56 ± 0.03) µHz/(V/m)2, γ = (−1.16 ± 0.02) µHz/(V/m)2 and γ = (0.29 ± 0.01) µHz/(V/m)2 for M = 0, 1, 2, 3, 4 and M = 5/2, respectively. The result for M = 5/2 has opposite sign than other M values like in 138Ba+. Therefore, the Stark shifts in Ra+ can be estimated accurately using our results for a given applied electric field.

The black-body radiation shift at T = 300K in the 7s
2
S1/2 → 6d
2
D5/2 transition in Ra+ is given as (0.19 ± 0.02) Hz.

From the above Stark shift ratios and BBR shifts in the considered ions, it is found that these systematic errors are small in Ra+ which further supports along with its energy level locations that it will be one of the most suitable candidates for optical clock. In fact, a possible atomic clock with uncertainty in the order of 10−17 seems feasible from these results along with the preliminary analysis of Doppler’s shifts [35] in Ra+.

V. CONCLUSION

We have employed the relativistic coupled-cluster method to determine ab initio results for the dipole polarizabilities of the ground and the metastable d-states in the singly ionized strontium, barium and radium. Electron correlation effects arising through various coupled-cluster terms are given individually and comparative studies are performed for these three ions. Using the results we have obtained, Stark shifts and black-body radiation shifts for these ions are estimated. Using our results, we were able to reduce the errors of the measured scalar and tensor polarizabilities of the 4d
2
D5/2 were used in [3] as α2(4d5/2) = (8 ± 2) × 10−40 C2 s2 kg−1 and α0(4d5/2) = (−7±2) × 10−40 C2 s2 kg−1, respectively. We obtain these results as α0(4d5/2) = (10.37 ± 0.12) × 10−40 C2 s2 kg−1 and α2(4d5/2) = (−8.05 ± 0.05) × 10−40 C2 s2 kg−1. Using Eq. (2.9) and our results, we obtain the shift rate, which is defined as γ = (8(WABS)/9), of the 5s
2
S1/2 state as (1.10 ± 0.01) µHz/(V/m)2 against (1.06 ± 0.04) µHz/(V/m)2 of Madej et al. Similarly, we obtain γ = (−0.78 ± 0.02) µHz/(V/m)2 against results of Madej et al. as γ = (−0.6 ± 0.2) µHz/(V/m)2 in the 4d
2
D5/2 state using only the scalar polarizability. However assuming the direction of the electric field lies in the z-direction, we obtain γ = (−1.27 ± 0.03) µHz/(V/m)2, γ = (−0.91 ± 0.02) µHz/(V/m)2 and γ = (−0.18 ± 0.01) µHz/(V/m)2 for M = 1/2, M = 3/2 and M = 5/2, respectively.

Using Eq. (2.14) and the above results, we also obtain the black-body radiation shift at T = 300K in the 5s
2
S1/2 → 4d
2
D5/2 transition in 88Sr+ as (0.22 ± 0.01) Hz and that is an improvement of 10% over the result of Madej et al. [3].

It appears that both 137Ba+ and 138Ba+ will be suitable candidates for an optical clock [2, 3], but each has some advantages and disadvantages in controlling the systematic errors. For the 6s
2
S1/2 → 5d
2
D5/2 transition in 138Ba+, it would be possible to use techniques similar to the measurement of the frequency in the optical transition in 88Sr+ mentioned earlier. However, one has to encounter the electric quadrupole shift in the 5d
2
D5/2 state for this case. It is possible to overcome this particular shift by considering the possible F = 2(6s1/2) → F = 0(5d3/2) hyperfine transition in 137Ba+. In this transition, one has to again estimate the possible quadratic Zeeman shifts because of finite nuclear magnetic and quadrupole moments. Our dipole polarizability for the 6s
2
S1/2 state is given by (2.05 ± 0.02) × 10−39 C2 s2 kg−1. The scalar and tensor polarizabilities of the 5d
2
D3/2 state are given by (8.05 ± 0.07) × 10−40 C2 s2 kg−1 and (−4.06 ± 0.05) × 10−40 C2 s2 kg−1, respectively. Similarly, the scalar and tensor polarizabilities of the 5d
2
D5/2 state are given by (8.35 ± 0.09) × 10−40 C2 s2 kg−1 and (−5.09 ± 0.05) × 10−40 C2 s2 kg−1, respectively. Due to the choice of the hyperfine transition in 137Ba+, the tensor polarizabilities of these states are zero and hence the polarizabilities of the atomic and hyperfine states are the same. The shift rates are (−1.56 ± 0.03) µHz/(V/m)2 and (−0.61 ± 0.01) µHz/(V/m)2 in the 6s
2
S1/2 and 5d
2
D3/2 states, respectively. For 138Ba+, by considering particular M values of the 5d
2
D3/2 state and assuming that the electric field lies in the z-direction, we can evaluate the Stark shifts. They are γ = (−0.94 ± 0.02) µHz/(V/m)2, γ = (−0.71 ± 0.02) µHz/(V/m)2 and γ = (0.14 ± 0.01) µHz/(V/m)2 for M = 1/2, M = 3/2 and M = 5/2, respectively. As can be noticed, the result for M = 5/2 has opposite sign than other M values. The

V. CONCLUSION

We have employed the relativistic coupled-cluster method to determine ab initio results for the dipole polarizabilities of the ground and the metastable d-states in the singly ionized strontium, barium and radium. Electron correlation effects arising through various coupled-cluster terms are given individually and comparative studies are performed for these three ions. Using the results we have obtained, Stark shifts and black-body radiation shifts for these ions are estimated. Using our results, we were able to reduce the errors of the measured
frequency for the optical clock in $^{88}\text{Sr}^+$. Our calculations of the Stark and black-body radiations shifts in both Ba$^+$ and Ra$^+$ could be used to remove the systematic errors in the proposed optical clock experiments for these ions.

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