Long-range interactions between the alkali-metal atoms and alkaline earth ions

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(Dated: Received date; Accepted date)

Accurate knowledge of interaction potentials among the alkali atoms and alkaline earth ions is very useful in the studies of cold atom physics. Here we carry out theoretical studies of the long-range interactions among the Li, Na, K, and Rb alkali atoms with the Ca\textsuperscript{+}, Ba\textsuperscript{+}, Sr\textsuperscript{+}, and Ra\textsuperscript{+} alkaline earth ions systematically which are largely motivated by their importance in a number of applications. These interactions are expressed as a power series in the inverse of the internuclear separation $R$. Both the dispersion and induction components of these interactions are determined accurately from the algebraic coefficients corresponding to each power combination in the series. Ultimately, these coefficients are expressed in terms of the electric multipole polarizabilities of the above mentioned systems which are calculated using the matrix elements obtained from a relativistic coupled-cluster method and core contributions to these quantities from the random phase approximation. We also compare our estimated polarizabilities with the other available theoretical and experimental results to verify accuracies in our calculations. In addition, we also evaluate the lifetimes of the first two low-lying states of the ions using the above matrix elements. Graphical representation of the interaction potentials versus $R$ are given among all the considered atoms and ions.

PACS numbers: 05.45.Ac,34.20.Cf,34.50.Cx

I. INTRODUCTION

Advancements in the simultaneous trapping and cooling of both ions and atoms in a hybrid trap\textsuperscript{1,2} has in resulted significant upsurge in the precise description of the atom-ion interactions. This new development of using hybrid traps in which neutral atoms and ions are confined together lead to search for many exotic phenomenon in the quantum information science and condensed matter related fields\textsuperscript{3}. Interaction between these systems can be described as the special case of the van der Waal long range forces caused due to the fluctuating dipole moments of the systems\textsuperscript{4}. These interactions can enable many chemical reactions like charge-exchange and molecule formations at the single particle level, hence better understanding of these interactions is very useful in a number of studies such as explaining the underlying reasons for various quantum phase transitions\textsuperscript{5}, establishing sustained atom-ion sympathetic cooling mechanism\textsuperscript{7,8}, designing ultracold superchemistry\textsuperscript{9}, studying the physics of impurities in the Bose gases\textsuperscript{10,11}, interpreting cold atom collision processes\textsuperscript{8} etc.

Co-trapping of atoms and ions have several applications. Observations of the scattering between the atoms and the ions at low energy scale have been reported by a number of groups\textsuperscript{12,14}. Early studies on the properties of the mixed atom-ion systems were reported by Côté and his coworkers in order to investigate the ultracold atom-ion collision dynamics, charge transportation processes, and to realize possible formation of the combined stable system\textsuperscript{15}. Recently, Härter et.al. observed that the elastic scattering cross section of an atom-ion system depends on the collisional energy in the semi classical regime and favors scattering at small angles\textsuperscript{16}. Furthermore, the results of an atom-ion scattering event has been utilized to develop a novel and effective method to compensate excessive ion micro-motion in a trap\textsuperscript{16}. Although there have been attempts to study the atom-ion interactions in the past, the reported results were not very accurate. Due to the experimental advancements in the atom-ion trapping experiments, it is now the time to provide more accurate description of these potentials to infer important signatures of new physics. Owing to the simplified and well understood structures of the alkali atoms and alkaline-earth ions, they seem to be the natural choices and of immense interest for the experimental investigations\textsuperscript{17} for which we intend to carry out accurate theoretical studies of the long-range atom-ion interactions among these systems. In this work, we particularly undertake the Li, Na, K and Rb alkali atoms and the Ca\textsuperscript{+}, Sr\textsuperscript{+}, Ba\textsuperscript{+} and Ra\textsuperscript{+} alkaline earth ions to estimate their long range interactions.

Determination of the van der Waal coefficients of the atom-ion interactions require evaluation of the dynamic dipole and quadrupole polarizabilities at imaginary frequencies\textsuperscript{18}. We evaluate these polarizabilities by using dominant contributing matrix elements and experimental energies in a sum-over-states approach. These transition matrix elements are extracted either from the measurements of the lifetimes and the static dipole polarizabilities of the atomic states or using a relativistic coupled-cluster (RCC) method. Other contributions such as from...
the core and core-valence correlations, which cannot be estimated using the sum-over-states approach, are estimated using other suitable many-body methods. Unless stated otherwise, we use atomic unit (au) throughout this paper.

II. ATOMIC CORE AND CORE-VALENCE CORRELATIONS

The long range potential \( V(R) \) between an electrically charged ion and a neutral atom in their ground states, with \( R \) as the internuclear distance, is divided in terms of the induced and dispersive interactions among the multipole moments as \[26, 27\]

\[
V(R) = V_{ind}(R) + V_{dis}(R),
\]

where \( V_{ind}(R) \) and \( V_{dis}(R) \) are known as the induced and dispersion potentials, respectively. It can be noted that a small contribution coming from the exchange potential \[27\] has been neglected in the above expression. The induced potential due to polarization from the attractive interaction of the permanent multipole of the ion with the induced multipole of the atom due to the ion and is expressed in terms of the induction coefficients \( C_{2n} \) as \[27, 22\]

\[
V_{ind}(R) = -Q^2 \sum_{n=1}^{\infty} C_{2n}/R^{2n},
\]

where \( Q \) is the charge of the ion and negative sign indicates that the force is attractive in nature. In the present article, we have truncated the series at powers of \( R^{-6} \) and contributions from the higher order coefficients associated with \( R^{-8} \) and \( R^{-10} \) terms are suppressed here. In the above equation, the term \( R^{-2} \) which corresponds to the charge-dipole interaction vanishes for the interaction of an ion with a neutral atom. The second term inside the summation, corresponding to \( n = 2 \), is a spherically symmetric term arising due to the ion-induced dipole potential and is given as \( C_4/R^4 \) with \( C_4 = \alpha_1/2 \) for the static dipole polarizability \( \alpha_1 \) of the atom. This term originates due to the electric field created by the ion which induces an electric dipole moment in the neutral atom. This part of the potential is independent of the electronic state of the ion, but varies with the electronic state of the atom due to the dependencies on their \( \alpha_{1s} \). Once the \( C_4 \) coefficients are known, one can also calculate the characteristic length scale \( \langle R^2 \rangle \), the effective range of the polarization potential, by equating the potential to the kinetic energy as \( E^* = \sqrt{2\mu C_4} \).\[3, 28\]. The characteristic energy scale is further expressed in terms of \( R^* \) as \( E^* = 1/2\mu R^2 \). Here \( \mu = (m_{ion})(m_{at})/(m_{ion} + m_{at}) \) is the reduced mass of the system for the mass of the ion \( m_{ion} \) and mass of the atom \( m_{at} \). The next term with powers of \( R^{-6} \) in the general expression (Eq. 2) appears due to the instantaneous fluctuating dipole moments between the atoms and can be expressed as \( C_6 \) with \( C_6 = \alpha_2/2 \) for the quadrupole polarizability \( \alpha_2 \) of the atom.

For the atom and ion being in their respective ground states, the expression for the dispersion interaction potential is given by \[15, 20\]

\[
V_{dis}(R) = \frac{c_6}{R^6} - \frac{c_8}{R^8} + \frac{c_{10}}{R^{10}} \ldots \tag{3}
\]

The coefficients \( c_6, c_8, c_{10}, \ldots \) etc. emerge from the instantaneous dipole-dipole, dipole-quadrupole, dipole-octupole, quadrupole-quadrupole, etc. interactions and are known as the dispersion coefficients. In the long-ranged potential, first term dominates over the other terms and the higher order terms are sufficiently weak to be neglected. In Eq. (3), the dispersion coefficient \( c_{6AB} \) between an atom \( A \) and an ion \( B \) can be estimated using the expression given as \[30\]

\[
c_{6AB} = \frac{3}{\pi} \int_0^\infty d\omega \alpha_A^A(\omega) \alpha_B^B(\omega). \tag{4}
\]

Here \( \alpha_A^A(\omega) \) and \( \alpha_B^B(\omega) \) are the atomic and ionic polarizabilities respectively. Since it is cumbersome to determine these dynamic polarizabilities for a sufficiently large number of frequencies, therefore instead of using the exact \textit{ab initio} methods alternative approaches have been adopted to calculate the \( c_{6AB} \) coefficients in the literature. Among these the Slater-Kirkwood formula \[31\] is one of the popular methods \[32\] in which the dispersion coefficients for atom-ion system are approximated by

\[
c_{6AB} = \frac{3}{2} \frac{\alpha_A^A \alpha_B^B}{(\alpha_A^A/N_A)^{1/2} + (\alpha_B^B/N_B)^{1/2}}, \tag{5}
\]

where \( N_A \) and \( N_B \) are the effective number of electrons and determined using the following empirical formula which assumes that the dominant contributions arise from the loosely bound electrons present in the outer shell of the systems

\[
(N_A)^{1/2} = \frac{4}{3} c_{6AA}/(\alpha_A^A)^{3/2}, \tag{6}
\]

with the van der Waals coefficient \( c_{6AA} \) of the homonuclear dimer and static polarizability \( \alpha_A^A \) of the atom \( A \). This approximation may work reasonably if the dynamic polarizabilities are very large for lower frequencies, falling swiftly towards the asymptotic region of the frequencies and when the trends of the dynamic polarizabilities are almost same in both the coupled atomic systems. Substituting the above relation, we get

\[
c_{6AB} = \frac{2 c_{6AA} c_{6BB}}{\alpha_A^A c_{6AB} + \alpha_A^B c_{6BB} + c_{6AB}^2 \Delta E_A^A \Delta E_B^B}. \tag{7}
\]

Another approximation to calculate the dispersion coefficients among the hetero-nuclear alkali dimers has been considered by Derevianko \textit{et al.} \[33\] as

\[
c_{6AB} = \frac{1}{2} \sqrt{c_{6AA} c_{6BB} \Delta E_A^A \Delta E_B^B}. \tag{8}
\]
In this approach, it is assumed that the most contribution to $c_0$ coefficient comes from a principal transition in each system whose transition energies are denoted by $\Delta E^A$ and $\Delta E^B$. Nevertheless, both the above approximations are only valid for the qualitative description of the atom-ion interaction potentials, but it is imperative to use more accurate values of the dynamic multipole polarizabilities for the precise description of the atom-ion interaction potentials. In our earlier works, we had determined dynamic dipole polarizabilities of the alkali atoms for a sufficiently large number of imaginary frequencies very precisely [34, 35]. In the present work, we determine further these quantities for the alkaline earth ions and quadrupole polarizabilities of the alkali ions in order to determine the above discussed van der Waals coefficients accurately. We compare these coefficients with the values obtained using the Slater-Kirkwood formula [31] given by Eq. (11) and with the approximation used by Derevianko and coworkers [32] in the previous studies. Moreover, we also determine the lifetimes of the first excited np states of the alkaline earth ions and compare them with the available experimental and other precise calculations in order to test the accuracies of the dipole matrix elements of the transitions that are predominantly contributing in the determination of the dipole polarizabilities of the considered ions.

### III. EVALUATION OF MULTIPOLAR POLARIZABILITIES

The dynamic dipole (E1) and quadrupole (E2) polarizabilities of the atomic systems with an imaginary frequency $\omega$ are given by

$$\alpha_k(\omega) = - \sum_{I \neq n} \frac{(E_n - E_I)(\langle \Psi_n|O_k|\Psi_I\rangle)^2}{(E_n - E_I)^2 + \omega^2},$$

(9)

where $n$ is the principal quantum number of the ground state of the respective system, $I$ represents all possible allowed intermediate states, $k = 1$ and $O_1 \equiv D = |e|r$ for the dipole polarizability ($\alpha_1$) and $k = 2$ and $O_2 \equiv Q = \frac{|e^2|}{2}(3z^2 - r^2)$ for the quadrupole polarizability ($\alpha_2$). For the ab initio evaluation of these quantities, one can express them as

$$\alpha_k(\omega) = \langle \Psi_n|O_k|\Psi_n^-\rangle + \langle \Psi_n^+|O_k|\Psi_n\rangle$$

(10)

with $|\Psi_n\rangle = \sum_{I \neq n} |\Psi_I\rangle (\langle \Psi_n|O_k|\Psi_I\rangle/E_n - E_I + \omega)$, which can be treated analogous to the first order wave function with respect to the ground state wave function $|\Psi_n\rangle$ due to the operator $D$. However, it is complicated to obtain these wave functions using sophisticated many-body methods like RCC owing to the presence of the imaginary factor in the denominator. Alternatively, we try to determine the ground and singly excited state wave functions of these systems using the following procedure. Indeed these states can be treated as a closed-shell configuration with a respective valence electron in the outermost orbital. We, therefore,
calculate the Dirac-Fock (DF) wave function (|Φ₀⟩) for the closed-shell configuration first and then define the DF wave function of the ground or singly excited states of the considered systems by appending the valence orbital (v) to the DF wave function of the closed-shell as |Ψ_v⟩ = a_v|Φ₀⟩. The exact atomic wave functions of these states can now be evaluated by considering the correlations among the electrons within |Φ₀⟩ which is referred as core correlation, correlations seen by the valence and core electrons of |Φ_v⟩ termed as valence correlation and the correlations between the core electrons with the valence electron v named as the core-valence contributions. Using the wave operator formalism, we can write these wave functions accounting the above correlations independently as

|Ψ_v⟩ = a′_vΩ_c|Φ₀⟩ + Ω_cv|Ψ_v⟩ + Ω_v|Φ_v⟩, \quad (11)

where Ω_c, Ω_cv and Ω_v are known as the wave operators for the core, core-valence and valence correlations, respectively.

With the above prescription, the square of the matrix element of \(O_k\) from Eq. \(9\) can be expressed as

\[
\langle \Psi_v | O_k | \Psi_I \rangle^2 = \langle \Psi_v | O_k | \Psi_I \rangle \langle \Psi_I | O_k | \Psi_v \rangle = \langle \Phi_0 | \Omega_c^\dagger \Omega_v^\dagger O_k \Omega_c O_v | \Phi_0 \rangle + \sum_{l \neq n} \frac{\langle l | O_k | n \rangle \langle n | O_k | l \rangle \langle \Psi_l | e^{T} \Omega_v^\dagger \Omega_c^\dagger O_k \Omega_c O_v | \Psi_l \rangle}{(E_n - E_l)^2 + \omega^2},
\]

where we have used the generalized Wick’s theorem to assemble different terms and assumed all the operators are in normal ordered form so that only the connected terms survive. For the brevity, we categorize the first term as core (c), the next two terms as valence (v) and the last term as core-valence (cv) contributions, for which we can now write the total polarizability as

\[
\alpha_k = \alpha_k^{c} + \alpha_k^{v} + \alpha_k^{cv}, \quad (13)
\]

for the notations \(\alpha_k^{c}\), \(\alpha_k^{v}\) and \(\alpha_k^{cv}\) corresponding to the above mentioned three correlation contributions, respectively.

It is possible to evaluate dominant contributions to \(\alpha_k^{v}\) by calculating many low-lying singly excited states |Ψ_I⟩ of the considered systems by expressing them as

\[
\alpha_k^{v}(\omega) = \frac{2}{(2k + 1)(2J_n + 1)} \sum_{l \neq n} \frac{\langle l | O_k | n \rangle \langle n | O_k | l \rangle \langle \Psi_l | e^{T} \Omega_v^\dagger \Omega_c^\dagger O_k \Omega_c O_v | \Psi_l \rangle}{(E_n - E_l)^2 + \omega^2}, \quad (14)
\]

where \(\langle \Psi_n | O_k | \Psi_I \rangle\) is the reduced matrix element of \(O_k\) and the symbol (') in the summation implies that only the excited states are included in the sum. In order to determine the E1 and E2 matrix elements between the ground state wave function |Ψ_n⟩ and the excited state wave function |Ψ_I⟩, we express them in a general form as \(|Ψ_v⟩\) with a common core and for a valence orbital v representing either n or I, which in the Fock-space RCC formalism is defined as

\[
|Ψ_v⟩ = e^{T} \{1 + S_v\}|Φ_v⟩. \quad (15)
\]

Here the operator \(T\) and \(S_v\) excite core electrons and the valence electron along with the core electrons due to the electron correlations. We consider all possible single and double excitations with the important valence triple excitations in our calculations (referred as CCSD(T) method
in the literature) within a sufficiently large configuration space. From the practical limitation, we calculate as many as $|\Psi_f\rangle$ states possible for the estimation of their contributions to $\alpha^k_\gamma$ and refer as main contribution ($\alpha^{nm}_\gamma$). Contributions from the higher excited states, which are relatively small, are estimated using the following equation at the DF approximation

$$\alpha^{ret}_k(\omega) = \langle \Psi_n | O_k | \Psi_n^{(1)} \rangle,$$  \hspace{1cm} (16)

where $|\Psi_n^{(1)}\rangle$ is obtained by solving the following inhomogeneous equation for the effective Hamiltonian $H_{eff} = (H - E_n)O_k$ as

$$[(H - E_n)^2 + \omega^2] |\Psi_n^{(1)}\rangle = -H_{eff} |\Psi_n\rangle$$  \hspace{1cm} (17)

given as tail contribution ($\alpha^{ret}_k$).

We also obtain the $\alpha^{ct}_k$ contributions using the same procedure as has been described by the above equation. Nonetheless, the $\alpha^{ct}_k$ contributions may not be smaller to be estimated using the DF method for which we employ the random phase approximation (RPA) to solve for the core configuration (denoted by subscript 0) with the similar logic as Eq. (17) by defining

$$|\Psi_0^{(1)}\rangle = \sum_{\beta} \sum_{p,a} \Omega_{a \rightarrow p}^{(\beta)} |\Phi_0\rangle$$

$$= \sum_{\beta=1}^{\infty} \sum_{pq,ab} \left\{ \frac{(pb)_{1\rightarrow 12} |aq\rangle - (pb)_{1\rightarrow 12} |qa\rangle}{(\epsilon_p - \epsilon_a)^2 + \omega^2} \right\} \Omega_{b \rightarrow q}^{(\beta-1,1)}$$

$$+ \frac{\Omega_{b \rightarrow q}^{(\beta-1,1)}[(pq)_{1\rightarrow 12} |ab\rangle - (pq)_{1\rightarrow 12} |ba\rangle]}{(\epsilon_p - \epsilon_a)^2 + \omega^2} \times (\epsilon_p - \epsilon_a) |\Phi_0\rangle,$$  \hspace{1cm} (18)

where $\Omega_{a \rightarrow p}^{(\beta)}$ is the wave operator that excites an occupied orbital a of $|\Phi_0\rangle$ to a virtual orbital p which alternatively refers to a singly excited state with respect to $|\Phi_0\rangle$ with $\Omega_{a \rightarrow p}^{(0)} = \frac{(p(\epsilon_\alpha - \epsilon_\alpha)O_k |a\rangle}{(\epsilon_p - \epsilon_a)^2 + \omega^2}$ for the single particle orbitals energies $\epsilon_\alpha$ and the superscripts $\beta$ and 1 representing the number of the Coulomb ($\frac{1}{r_{12}}$) and $O_k$ operators, respectively.

### IV. RESULTS AND DISCUSSION

#### A. Calculation of lifetimes of the $np$ states

As a test of accuracy of our calculated principal matrix elements which are going to contribute predominantly to the $\alpha_1$ results of the alkaline earth ions, we estimate the lifetimes ($\tau$s) of the $np$ states using these matrix elements with $n$ being the principal quantum number of the ground states of the respective ions and compare them with the experimental and other high precision calculations. These values are given in Table III and are estimated considering only the dominant E1 transition probabilities $(A)$, which are evaluated (in s$^{-1}$) using the formula

$$A_{ij}^{E1} = \frac{2.02613 \times 10^{15} |\langle i | D | j \rangle|^2}{\lambda^3 (2j_1 + 1)},$$  \hspace{1cm} (19)

where $\lambda$ is the wavelength of the transition in Å and $|\langle i | D | j \rangle|^2$ is the reduced E1 matrix elements in au. Since our aim is to know the accuracies of the E1 matrix elements alone, we use the experimental $\lambda$ values in these calculations. As can be seen from the table, the experimental results have large error bars however our calculated values are compared with another high precision calculations $^{19}$ in Ca$^+$. The lifetimes of the 5$p_{1/2,3/2}$ states of Sr$^+$ and the 6$p_{1/2,3/2}$ states of Ba$^+$ are observed by Gallagher $^{22}$ using the Hanle-effect method with the optical excitations from the ground states. These values are 7.35(0.3) ns and 6.53(0.2) ns for the 5$p_{1/2}$ and 5$p_{3/2}$ states of Sr$^+$, respectively, which are later improved by Pinnington et. al. $^{23}$. Our results are close to these values and the used E1 matrix elements can be used further to estimate $\alpha_1$ of Sr$^+$ within a reasonably accuracy. Similarly, the experimental lifetimes of the 6$p_{1/2,3/2}$ states of Ba$^+$ are reported as $\tau(6p_{1/2}) = 7.74(0.4) ns$ and $\tau(6p_{3/2}) = 6.27(0.25) ns$ $^{22}$ and other theoretical values are given as $\tau(6p_{1/2}) = 7.83 ns$ and $\tau(6p_{3/2}) = 6.27 ns$ $^{24}$ which are in good agreement with our results suggesting that when the corresponding E1 matrix elements are used, we will be able to achieve high accuracy $\alpha_1$ value.

### TABLE III: Calculated values of effective $R^*$ range of the atom-ion interaction potentials and energy scale for the given atom-ion system. The results are compared with other theoretical works wherever available.

| $R^*$ (in au) | $E^* \times 10^{11}$ (au) |
|--------------|--------------------------|
| Li-Ca$^+$    | 1336                     | 0.09 |
| Li-Sr$^+$    | 1393                     | 0.11 |
| Li-Ba$^+$    | 1412                     | 0.12 |
| Li-Ra$^+$    | 1423                     | 0.13 |
| Na-Ca$^+$    | 2079                     | 0.57 |
| Na-Sr$^+$    | 2324                     | 0.89 |
| Na-Ba$^+$    | 2412                     | 1.04 |
| Na-Ra$^+$    | 2486                     | 1.17 |

| $R^*$ (in au) | $E^* \times 10^{11}$ (au) |
|--------------|--------------------------|
| K-Ca$^+$     | 3231                     | 1.88 |
| K-Sr$^+$     | 3779                     | 3.52 |
| K-Ba$^+$     | 3999                     | 4.41 |
| K-Ra$^+$     | 4193                     | 5.33 |
| Rb-Ca$^+$    | 3991                     | 3.95 |
| Rb-Sr$^+$    | 5042                     | 10.03 |
| Rb-Ba$^+$    | 5545                     | 14.6 |
| Rb-Ra$^+$    | 6042                     | 20.57 |
in Ba\(^+\). There are no experimental results available for the lifetimes of the \(7p_{1/2,3/2}\) states of Ra\(^+\), however our results are close agreement with another calculations by Pal et al. \[26\]. Therefore, the resulting \(\alpha_1\) values in all the above discussed ions will be reliable and hence we expect to attain accurate values of the dispersion coefficients when \(\alpha_1\) values are used from our calculations.

B. Calculation of \(C_4\) coefficients

In Table [III] we present the static dipole polarizabilities of the alkali atoms that were reported by us in Ref. \[52\] and compare with the earlier theoretical and experimental results. The details of the calculations are presented in Ref. \[52\] and we do not repeat them here again. The reported values of \(\alpha_1\) are slightly different than Ref. \[52\], since the core contributions from the DF method are replaced by the RPA values here. From the comparison between the measured and calculated results, as shown in the table, it is clear that our static polarizabilities are in close agreement with the experimental and theoretical values which gives us confidence in using these values for the calculation of the \(C_4\) coefficients as 82.1, 81.2, 144.9 and 156.0 au in the Li, Na, K, and Rb atoms respectively. Using these \(C_4\) values, we further obtain range of potential \(R^*\) and compare them with the values obtained by Idziaszek \[10\] and Deork \[28\], as shown in Table [III].

Idziaszek and Deork have applied the multichannel quantum defect theory to describe the range of the atom-ion systems. On comparison, we observe that our calculated values of range are close to the values tabulated in these references. From the table, we note that the effective length scale of the atom-ion potential is much more long ranged than the interaction between two neutral atoms. In the same table we also present the characteristic energies for their direct applications in the future experimental studies.

C. Calculation of \(C_6\) coefficients

In order to obtain the \(C_6\) coefficients, we first carry out systematic calculations of the quadrupole polarizabilities of the Li, Na, K, and Rb atoms. As given in Table [III] terms \(\alpha_2^{nc}\) and \(\alpha_2^{ve}\) summarizes the contributions to the quadrupole polarizabilities from the core, valence and valence-core correlation terms. Here the matrix elements of the first five \(ns−n′d_{5/2}\) transitions in each alkali atoms are included into the main term \(\alpha_2^{nm}\) calculations, where \(n\) is the principal quantum number of the ground state of the respective atom. For example in the Na atom, 3s to (3-7)d\(_{5/2}\) transition E2 matrix elements are included in the main polarizability calculations. Moreover, for the Li atom calculation, we have included two more transitions \(2s−8d_{5/2}\) and \(2s−9d_{5/2}\) in the main polarizability calculations. In the above table, we compare our results with the predictions by other studies. For the Li atom, accurate value of the quadrupole polarizability is obtained as 1424 au by Porsey et al. \[43\] using the relativistic many-body calculations. Our result 1426 au is in very good agreement with this value. Theoretical values of the quadrupole polarizability of the Na atom were given by the group of Spelsberg \[14\] and Makarov \[29\] as 1879 and 1902 au respectively and are also in close agreement with our value 1895 au. Group of Makarov had calculated the quadrupole polarizability of Na by using the Möller Plesset second-order perturbation theory with an extended Gaussian basis. From the earlier studies, the results available to compare the polarizability values of the K and Rb atoms are 5000 and 6459 au \[13\] by using a model potential method showing only small variations from our results 4947 and 6491 au respectively. The comparisons, as given in Table [III] reflects that our polarizabilities are reliable enough for the accurate determination of the \(C_6\) results of the alkali atoms. Our numerical calculations for the \(C_6\) coefficients give the values as 713, 947, 2474 and 3245 in au for the Li, Na, K, and Rb atoms respectively.

D. Calculations of dispersion coefficients \(c_6^{AB}\)

Table [IV] gives the compiled values of contributions to the total dispersion coefficients \(c_6^{AB}\) between the alkali atoms interacting with the alkaline ions. For the determination of the dispersion coefficients, we perform the RCC calculations to obtain the dipole matrix elements for the evaluation of the required dipole polarizabilities of the Ca\(^+\), Sr\(^+\), Ba\(^+\), and Ra\(^+\) ions. There...
TABLE IV: Individual contributions to $\alpha_1$ of Ca$^+$, Sr$^+$, Ba$^+$ and Ra$^+$ alkaline earth ions from the principal E1 matrix elements and other components. Our results are also compared with other calculations and experimental values.

| Contributions | $E1$ amplitude | $\alpha_1$ | Contributions | $E1$ amplitude | $\alpha_1$ |
|---------------|----------------|-----------|---------------|----------------|-----------|
| $4s_{1/2} \rightarrow 4p_{1/2}$ | 2.91 | 24.64 | $5s_{1/2} \rightarrow 5p_{1/2}$ | 3.12 | 29.82 |
| $4s_{1/2} \rightarrow 5p_{1/2}$ | 0.07 | 0.05 | $5s_{1/2} \rightarrow 6p_{1/2}$ | 0.02 | 0.01 |
| $4s_{1/2} \rightarrow 6p_{1/2}$ | 0.08 | 0.05 | $5s_{1/2} \rightarrow 7p_{1/2}$ | 0.06 | 0.004 |
| $4s_{1/2} \rightarrow 7p_{1/2}$ | 0.06 | 0.004 | $5s_{1/2} \rightarrow 8p_{1/2}$ | 0.05 | 0.003 |
| $4s_{1/2} \rightarrow 8p_{1/2}$ | 0.05 | 0.002 | $5s_{1/2} \rightarrow 9p_{1/2}$ | 4.39 | 57.61 |
| $4s_{1/2} \rightarrow 9p_{1/2}$ | 0.04 | 0.001 | $5s_{1/2} \rightarrow 6p_{3/2}$ | 0.04 | 0.002 |
| $4s_{1/2} \rightarrow 4p_{3/2}$ | 4.12 | 48.86 | $5s_{1/2} \rightarrow 7p_{3/2}$ | 0.05 | 0.003 |
| $4s_{1/2} \rightarrow 6p_{3/2}$ | 0.08 | 0.01 | $5s_{1/2} \rightarrow 8p_{3/2}$ | 0.05 | 0.002 |
| $4s_{1/2} \rightarrow 7p_{3/2}$ | 0.10 | 0.012 | $5s_{1/2} \rightarrow 9p_{3/2}$ | 0.06 | 0.003 |
| $4s_{1/2} \rightarrow 8p_{3/2}$ | 0.08 | 0.01 | $\alpha_c$ | 3.25 | 4.98 |
| $4s_{1/2} \rightarrow 9p_{3/2}$ | 0.07 | 0.004 | $\alpha_{tail}$ | $5.51 \times 10^{-2}$ | $1.96 \times 10^{-2}$ |
| $\alpha_{cc}$ | $-8.85 \times 10^{-2}$ | $\alpha_{cc}$ | -0.19 | $\alpha_{total}(Present)$ | 76.89 | 92.25 |
| $\alpha_{total}(Other)$ | 75.88 [47] | $\alpha_{total}(Other)$ | 91.10 [47] | $\alpha_{total}(Other)$ | 75.49 [26] | 91.39 (47) |
| $\alpha_{total}(Expt.)$ | 75.3(4) [48] | $\alpha_{total}(Expt.)$ | 93.3(9) [49] | $\alpha_{total}(Present)$ | 124.40 | 105.91 |
| $\alpha_{total}(Other)$ | 123.07 [47] | $\alpha_{total}(Other)$ | 105.37 [47] | $\alpha_{total}(Other)$ | 126.2 [50] | 106.5 [48] |
| $\alpha_{total}(Expt.)$ | 123.88(5) [51] | $\alpha_{total}(Expt.)$ | 123.88(5) [51] |

TABLE V: Calculated dispersion coefficients in this work and the estimated effective number of electrons values for the Slater-Kirkwood formula in case of alkali dimers. Results are compared with other available values whose references are given in the square brackets.

|            | $c_6$(Present) | $c_6$ [33] | $N_{eff}$(Present) | $N_{eff}$ [32] | $c_6$(Present) | $N_{eff}$(Present) |
|------------|---------------|-----------|--------------------|----------------|---------------|--------------------|
| Li-Li      | 1390          | 1389      | 0.77               | 0.773          | Ca$^+$-Ca$^+$   | 562                | 1.24               |
| Na-Na      | 1549          | 1556      | 0.99               | -              | Sr$^+$-Sr$^+$   | 831                | 1.52               |
| K-K        | 3895          | 3897      | 1.10               | 1.13           | Ba$^+$-Ba$^+$   | 1436               | 1.89               |
| Rb-Rb      | 4663          | 4691      | 1.19               | 1.20           | Ra$^+$-Ra$^+$   | 1341               | 2.64               |

are several calculations of the ground-state polarizabilities of the alkaline earth ions available using different methods. Similarly, a number of precise measurements of these quantities are also reported in the literature. We have compared these results with the present work in Table IV. As can be seen from the table, Lim et al. [13] listed the static dipole polarizabilities of the considered alkaline earth ions which are in very close agreement with our values. Their values are predicted using the RCC calculations in the finite field gradient technique together
with the optimized Gaussian-type basis set. However, use of a sum over states approach allowed us to use experimental data wherever available, which we believe that can minimize the uncertainties in the results and hence, they are more accurate in our case. Experimental spectral analysis of the dipole polarizability value of the Ca$^+$ ion is observed by Edward [48] and is in very good agreement with our calculated value. As seen from the given table, the calculated values of these quantities by Mitroy et al. [20], which are evaluated by diagonalizing the semi-empirical Hamiltonian in a large dimension single electron basis, are also in agreement with our values. However, we would like to emphasize that our results are more accurate since in our method core correlations are accounted through the all order RPA. The estimate of 93.3 au [53] for the ground state polarizability of Sr$^+$ ion, derived by combining the experimental data given by the group of Barklem [49] with the oscillator strength sums, has a considerable discrepancy with our present results. In contrast, our values match very well with the calculations of Jiang et al. [20] who have used the relativistic all-order method to calculate the polarizabilities of the Sr$^+$ ion. It would be interesting to see the validity of these results when the new measurement of the ground state polarizability for this ion becomes available. The polarizability value of the Ba$^+$ ion was calculated by Miadokova et al. [54] using the relativistic basis set in the Douglas-Kroll no-pair approximation and has a 2% discrepancy from the high precision measurements performed by Snow and Lundeen [51]. This high precision measurement was achieved by a novel technique based on the resonant excitation Stark ionization spectroscopy microwave technique. We also find that our results are in better agreement with the experimental value. There is no experimental result available for the dipole polarizability of Ra$^+$ to compare with our result. However, Safranova et al. [38] have evaluated this result using the relativistic all order method and is in agreement with our result. Having compared all our polarizability results, we are now in the state to justify that since our static polarizability values are very accurate, we anticipate similar accuracies for the calculated dynamic polarizabilities using our method and can be used reliably for the evaluation of the dispersion coefficients.

In Fig. 1 we plot our dynamic polarizabilities obtained for various atoms and ions along the imaginary axis as the functions of the frequencies. Next, we use the dynamic polarizabilities to calculate the dispersion coefficients and effective number of the electrons in case of the alkali atoms and alkaline earth ions, which are presented in Table V. The purpose of calculating and presenting these values is to verify the validity of the results reported using the Slater-Kirkwood formula as given in Eq. (4) and using the approach that was followed by Dereviako et al. [33].

In practice, a number of methods have been employed for the calculations of the dispersion $c^{AB}_6$ coefficients for the hetero-nuclear dimers. Dalgarno et al. [54] had followed a procedure to reduce the two central molecular problem to one central atomic problem at the larger separation distances. Bishop and coworkers [55] computed the $c^{AB}_6$ coefficients by approximating the integral given by Eq. (4) using the Gaussian quadrature technique. In this work, we evaluate the dispersion coefficients $c^{AB}_6$ using three different methods: (i) the exact formula of Eq. (4), (ii) Slater-Kirkwood formula given by Eq. (5), and (iii) using an approximated approach as has been used in Ref. [33] (see Eq. 8) to make a comparative

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### TABLE VI: Comparison of the $c_6$ coefficients for the alkali atoms and alkaline earth ions with various methods.

| Ion   | $|\alpha_v|^2$ | $|\alpha_e|^2$ | $|\alpha_{ve}|^2$ | $\alpha_{c.t.}$ | Total | (S.Kirkwood) | $c_6$(Ref.[33]$^{10}$) |
|-------|----------------|----------------|-----------------|-----------------|-------|--------------|-------------------------|
| Li-Ca$^+$ | 768.4          | 1.0            | 0.0             | 67.35           | 836.7 | 844.0        | 914.9                   |
| Li-Sr$^+$ | 898.1          | 1.5            | 0.0             | 108.4           | 1008.1 | 1025.6       | 1106.3                  |
| Li-Ba$^+$ | 1127.1         | 2.6            | 0.0             | 184.8           | 1314.5 | 1355.3       | 1434.7                  |
| Li-Ra$^+$ | 974.3          | 3.2            | 0.0             | 228.9           | 1206.4 | 1256.2       | 1402.9                  |
| Na-Ca$^+$ | 826.4          | 4.6            | $2.2 \times 10^{-3}$ | 69.7            | 900.8  | 906.5        | 951.7                   |
| Na-Sr$^+$ | 964.6          | 7.4            | $4.3 \times 10^{-3}$ | 113.6           | 1085.7 | 1101.7       | 1152.4                  |
| Na-Ba$^+$ | 1205.7         | 12.4           | $7.4 \times 10^{-3}$ | 195.6           | 1413.5 | 1454.4       | 1500.7                  |
| Na-Ra$^+$ | 1046.5         | 15.1           | $1.3 \times 10^{-2}$ | 244.3           | 1305.8 | 1357.8       | 1462.0                  |
| K-Ca$^+$ | 1231.4         | 19.6           | $1.0 \times 10^{-2}$ | 141.0           | 1392.0 | 1388.9       | 1561.9                  |
| K-Sr$^+$ | 1441.5         | 31.6           | $2.0 \times 10^{-2}$ | 207.1           | 1680.3 | 1687.4       | 1885.7                  |
| K-Ba$^+$ | 1816.2         | 53.0           | $3.6 \times 10^{-2}$ | 328.3           | 2197.5 | 2231.7       | 2435.2                  |
| K-Ra$^+$ | 1563.4         | 66.1           | $6.5 \times 10^{-2}$ | 389.9           | 2019.4 | 2056.8       | 2390.4                  |
| Rb-Ca$^+$ | 1312.9         | 29.6           | $1.8 \times 10^{-2}$ | 184.8           | 1527.9 | 1517.5       | 1715.9                  |
| Rb-Sr$^+$ | 1537.3         | 48.4           | $3.8 \times 10^{-2}$ | 259.5           | 1845.2 | 1843.5       | 2071.0                  |
| Rb-Ba$^+$ | 1938.1         | 81.5           | $6.7 \times 10^{-2}$ | 394.5           | 2414.2 | 2438.4       | 2672.4                  |
| Rb-Ra$^+$ | 1667.2         | 101.6          | 0.1             | 455.5           | 2224.5 | 2246.4       | 2625.0                  |

$^{10}$Note: These values do not appear explicitly in the reference, but were deduced using Eq. (8) quoted therein.
FIG. 2: (Color online) Percentage deviations in the $c_{6}^{AB}$ values obtained from this work with the results obtained using the Slater-Kirkwood formula (shown in the red bars) and those obtained using the approximate approach used in Ref. [33] (shown in the green bars).

analysis among the results obtained from all these approaches. In the case of the exact method, we use the Gaussian quadrature method to integrate over the dynamic polarizabilities using the exponential grids. We justify the use of the exponential grids from the fact that maximum contributions to the integrand given in Eq. (4) come from the polarizability values in the vicinity of zero frequency (as shown in Fig. 1) and gradually their contributions falls down. In Table VI, we present details of the calculated values of the dispersion coefficients for the interactions between the alkali atoms and the alkaline ions along with their breakdown from the individual contributions. From the table, it can be inferred that the contribution to the total potential increases as the alkali atoms get bigger in size (i.e. from the Li to Rb sequence), since the polarizability values also increase in the same order. However, we notice that a steady increase in $c_{6}$ values do not occur with respect to the atomic sizes for the ions (i.e. from Ca$^+$ to Ra$^+$). This might seem to be counterintuitive but it is owing to the fact that the polarizability of Ba$^+$ is larger than that for Ra$^+$, as given in Table IV. So it follows a different trend in the $c_{6}^{AB}$ coefficients; decreases in magnitude for the interactions of the alkali atoms with Ra$^+$ and increases with Ba$^+$.

dispersion coefficients for the atom-ion systems obtained using the Slater-Kirkwood formula are listed in column VI of Table VI. In an alternative approach, we also carried out the calculations using the approximated formula given in Eq. (8) and the obtained values are listed in column VII of the same table. Comparison of deviations in percentage from both the approaches are shown in Fig. (2) for all combinations of the alkali atoms-alkaline ions in the form of the histograms. It is apparent from this plot that the Slater-Kirkwood formula shows better agreement with our results as compared to the approximated approach of Derevianko et. al.

In Fig. 3 comparison between the total interaction potential ($V_{total}$) for the undertaken different combinations of Li, Na, K and Rb atoms with Ca$^+$, Sr$^+$, Ba$^+$ and Ra$^+$ ions is shown as function of internuclear distance $R$ by adding both the induction and dispersion parts. Interactions of each alkaline ion (Ca$^+$, Sr$^+$, Ba$^+$, Ra$^+$) is represented in solid red line for the Li, long dashed green line for the Na, short dashed blue line for the K and dotted pink line for the Rb atoms, respectively. It should be noted that our results for these potentials will be valid in the approximation only when the structures of the colliding atom and ion do not undergo internal changes.
V. CONCLUSION

In this work, we have deduced the behavior of the potential curves with respect to the internuclear distances for the alkali atoms correlating with the alkaline-earth ions. The accurate values of the dipole polarizabilities for the alkali atoms and the alkaline earth ions and the quadrupole polarizabilities for the alkali atoms have been investigated using the relativistic coupled-cluster method. Thereafter, evaluation of the dispersion coefficients have been done by integrating the atom-ion dynamic electric polarizabilities product at the imaginary frequencies. The calculated values of the induction coefficients in the form of range of potentials are expected to be very useful to set the actual positions of the bound states and magnetic fields of the Feshbach resonances for these atom-ion correlated systems. The presented data will also be of immense interest for designing better atomic clocks, quantum information processing and quantifying molecular potentials for the ultracold collision studies.

Acknowledgement

The work is supported by CSIR grant no. 03(1268)/13/EMR-II, India and UGC-BSR grant no. F.7-273/2009/BSR. Computations were carried out using 3TFLOPHPC Cluster at Physical Research Laboratory, Ahmedabad. The authors would like to thank R. Côté and S. Banerjee for fruitful discussions.

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