Accurate determination of quadrupole polarizabilities of the excited states of alkali-metal atoms

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The scalar and tensor components of the electric quadrupole (E2) polarizabilities of the first two excited states of all the alkali-metal atoms are determined. To validate the calculations, we have evaluated the ground state E2 polarizabilities of these atoms and compared them with the literature values. We could not find the ground state E2 polarizability value for Fr in the literature to compare with our result. The dominant parts of these quantities are estimated by combining the precisely calculated E2 transition matrix elements of many low-lying transitions with the experimental energies, while the other contributions are estimated using lower-order methods. Our estimated values for the ground states of the above atoms are in good agreement with the literature values suggesting that our estimated E2 polarizabilities for the excited states of the alkali atoms, which were not known earlier except for the Li atom, are also quite accurate. These reported E2 polarizabilities could be useful in guiding many precision measurements in the alkali atoms.

I. INTRODUCTION

Studies of electric polarizabilities of atoms, molecules and clusters are highly demanding for both the experimental and theoretical perspectives [1, 2]. High precision values of polarizabilities of these systems are very useful in several branches of science [3–5]. Some of the examples of prominent applications of electric polarizabilities in atomic systems, which are of present interest, include the optical atomic clock measurements [6], discrete symmetry violations [7], condensates of dilute atomic gases [8], etc. [9, 10]. Atoms are spherically symmetric, but upon the influence of stray electric fields result in multi-order shifts in energy levels [11]. The interaction between any system and an electric field is predominately treated in the framework of electric dipole (E1) approximation [11]. However, higher-order contributions from the interaction of quadrupole operator with external electric field gradient may become significant for some of the applications that aim to achieve ultra-precision measurements [12–17]. The first-order shift due to electric quadrupole (E2) interaction renders E2 moment that is generally zero for atomic states with angular momentum $J < 3/2$; otherwise they can also offer non-vanishing contributions [18]. The second-order shift gives finite E2 polarizability and plays a dominant part after E1 polarizabilities and E2 moments [19]. Particularly, E2 polarizabilities arising due to contribution from the forbidden transitions, might play a significant role in deducing one of the dominant environment induced blackbody radiation (BBR) shifts in order to reach the required accuracy level below $10^{-19}$ in the atomic clocks [20–22].

Alkali metal atoms are desired for many experimental studies as they form well controlled and character-ized systems. Owing to their easily laser accessible level structures, they are used for vital applications such as atomic clocks [23, 24], scattering phenomena [25], quantum computation [26], quantum sensing [27], cold collision [28], long-range interactions [29], etc. Among alkali atoms, the Rb and Cs atoms have been considered as the best candidates for microwave clocks [30, 31], whereas the Fr atom has attracted a lot of attention as a candidate for studying fundamental symmetry tests [32–35]. Since there is a similarity between the energy level spacing between Rb and Fr, Fr can also be laser cooled and trapped using available lasers [36]. This is what, besides being the heaviest alkali atom, makes it favorite for probing new physics beyond the Standard Model of elementary particles [37].

Precise determination of E2 polarizabilities for alkali atoms have been given a very little attention, especially for the excited states. Compared to the E1 polarizabilities, it is strenuous to measure the E2 polarizabilities in atomic systems due to their extremely weak contributions to the energy level shifts caused by the spatial gradient of electric fields. This is why accurate theoretical calculations of these quantities are very crucial. While a number of theoretical studies exist for the ground state E2 polarizabilities of the alkali atoms [20, 38–43] (except for Fr), very limited studies have been conducted for the excited states [44]. Since the D1 and D2 lines of the alkali atoms directly participate in the laser cooling process of alkali atoms, accurate knowledge of the E2 polarizabilities for the first two excited states of alkali atoms are quite useful. Furthermore, accurate knowledge of quadrupole polarizabilities are essential for estimating dispersion potentials among atomic systems [45, 46]. The importance of polarizabilities of excited states of atoms was demonstrated by Zhu et al. in the studies of long-range interactions of the alkali-metal atoms in their ground and excited states with helium atom for astrophysical applications [47]. Their reliable values are also crucial in order to describe the the van der Waal
atom-surface potentials [46, 48, 49]. Accurate values of quadrupole polarizabilities are required to construct the scattering potentials in the ultracold physics and determining scattering cross-sections of electrons or positrons from an atomic system [50, 51]. Precise calculations of polarizabilities of heavier atomic systems depend upon the potential of the many-body method used to account for the relativistic and electron correlation effects [52–55].

Previously, the static E2 polarizabilities for the ground states of the alkali atoms have been calculated using simple analytic wave functions by Patil et al. [38] and semi-empirical calculations by Jiang et al. [39]. Combining the relativistic many-body perturbation theory (RMBPT) and random phase approximations (RPA), the ground state E2 polarizabilities of the alkali-metals have been evaluated by Porseev and Derevianko [20]. Safronova et al. have calculated high-precision spectroscopic properties including E2 polarizabilities of the ground states of Li, K, Rb and Cs using linearized coupled-cluster method [40–43]. The static E2 polarizabilities of the ground state and a few low-lying excited states of Li have been evaluated by Wansbeeck et al. by adopting relativistic coupled-cluster method in fully ab initio procedure [44].

In the present work, we conduct extensive calculations of many E2 matrix elements of the transitions of alkali-metal atoms using the relativistic all-order (AO) method that predominantly contribute to the determination of E2 polarizabilities. We provide both the scalar and tensor components of the E2 polarizabilities of the excited np1/2 states, with the ground state principal quantum number n, along with the scalar E2 polarizabilities of the ground states ns1/2 and excited state np1/2, of the considered atoms. The accuracy of these quantities are estimated by comparing the E2 matrix elements and polarizability values of the ground states from the previous works. The bifurcation of the paper is as follows: Sec. II includes a brief theory on E2 polarizability. Sec. III consists of methods of evaluation of wave functions and E2 matrix elements in the framework of relativistic all-order approach. The E2 polarizability results along with their uncertainties have been given and discussed in Sec. IV. Finally, we have concluded our work in Sec. V.

II. THEORY

When an atom is placed in a static electric field, it experiences shifts in the energy levels which can be conveniently expressed in terms of electric multipole effects. In particular, the perturbation interaction Hamiltonian, $H_{int}^q = Q \cdot \vec{\nabla}\varepsilon$ with quadrupole operator $Q = \sum q_i$, due to interaction of quadrupole effect with the gradient of an electric field ($\vec{\nabla}\varepsilon$) gives second-order energy shift in the energy level of an atom in state $|\Psi_n\rangle$, is given by

$$\Delta E_n^{(2)} = \sum_{k \neq n} \frac{\langle q*_nk|Q|q_k\rangle}{\delta E_{nk}}.$$

where $(q)_n^k = \langle \Psi_n|H_{int}^q|\Psi_k\rangle$ with $k$ denoting the index for the intermediate states that are permitted by the quadrupole selection rules and $\delta E_{nk} = E_n - E_k$ with $E_{i=n,k}$’s are the energies of the corresponding states. The quadrupole moments of the np1/2 states, which can be used to estimate the first-order effects, in the considered systems have been determined accurately earlier [56]. For the computational simplicity, $\Delta E_n^{(2)}$ for linearly polarized light with polarization vector along the quantization axis can be expressed as [57]

$$\Delta E_n^{(2)} = -\frac{1}{8} \alpha_n^q (\nabla \varepsilon)^2$$

with

$$\alpha_n^q = \left[ \alpha_n^{q(0)} - \alpha_n^{q(2)} \frac{3M_n^2 - J_n(J_n + 1)}{J_n(2J_n - 1)} - 3\alpha_n^{q(4)}(5M_n^2 - J_n^2 - 2J_n) \right. \times \left. \frac{(5M_n^2 + 1 - J_n^2) - 10M_n^2(4M_n^2 - 1)}{J_n(J_n - 1)(2J_n - 1)(2J_n - 3)} \right].$$

where $M_{J_n}$ is the magnetic quantum number. Here $\alpha_n^q$ is the total quadrupole polarizability, which is given in terms of $M_{J_n}$ independent quantities as $\alpha_n^{q(0)}$, $\alpha_n^{q(2)}$, and $\alpha_n^{q(4)}$ - referred to as the scalar, tensor of rank 2 and tensor of rank 4 components, respectively [19, 58]. It clearly shows that for $J_n = 1/2$, contributions from both $\alpha_n^{q(2)}$ and $\alpha_n^{q(4)}$ to $\alpha_n^q$ vanish; otherwise they will contribute. Similarly, $\alpha_n^{q(4)}$ is non-zero when $J_n > 3/2$. Since we consider states with $J_n = 1/2$ and $J_n = 3/2$ in the present work, contributions from $\alpha_n^{q(4)}$ become irrelevant. Expressions for the $M_{J_n}$ independent $\alpha_n^{q(0)}$ and $\alpha_n^{q(2)}$ are given by [19]

$$\alpha_n^{q(0)} = -2 \sum_{k \neq n} W_n^{q(0)} \left[ \frac{\langle |\psi_{n}\rangle |Q|\psi_{k}\rangle^2}{\delta E_{nk}} \right]$$

and

$$\alpha_n^{q(2)} = -2 \sum_{k \neq n} W_n^{q(2)} \left[ \frac{\langle |\psi_{n}\rangle |Q|\psi_{k}\rangle^2}{\delta E_{nk}} \right],$$

where the factors $W_n^{q(0)}$ and $W_n^{q(2)}$ are given by

$$W_n^{q(0)} = \frac{1}{5(2J_n + 1)}$$

and

$$W_n^{q(2)} = \sqrt{\frac{10J_n(2J_n - 1)}{7(2J_n + 1)(2J_n + 3)}} \times (-1)^{J_n + J_k + 1} \left\{ \begin{array}{ccc} J_n & 2 & J_k \\ 2 & J_k & 2 \end{array} \right\}$$

with $\left\{ \begin{array}{ccc} J_n & 2 & J_k \\ 2 & J_k & 2 \end{array} \right\}$ as the Wigner angular momentum coupling 6-j symbol.
III. METHOD OF EVALUATION

The procedure to determine wave functions of the ground and intermediate states of alkali atoms using relativistic AO method are already presented in Ref. [59]. In brief, using Dirac-Fock (DF) method, the electronic configuration of alkali atoms are divided into a closed-core and valence orbital in order to obtain the mean-field wave function of the respective closed-shell (\( |0_\text{c}\rangle \)). Further, the mean-field wave functions of the atomic states are obtained by appending the respective valence orbital \( v \) as

\[
|\phi_v\rangle = a^+_v |0_\text{c}\rangle.
\]

To obtain the DF orbitals, we use a set of 50 B-splines of order \( k = 11 \) for each angular momentum. The basis set orbitals are constrained to a large spherical cavity of a radius \( R = 220 \) a.u.

To evaluate the E2 matrix elements for the main part, we determine E2 matrix elements up to \( l_{\text{max}} \) many E2 matrix elements up to \( l \), where the sum is restricted by the number of core orbitals \( N_\text{c} \) to exclude their contributions. We calculate many E2 matrix elements up to \( k \leq I \) states that contribute significantly to the above quantity using our relativistic AO method and use experimental values from the National Institute of Science and Technology (NIST) database [61]. These contributions are referred as main part and are denoted by \( a_{n,v}^{(t=0,2)} \) in the present work.

To evaluate the E2 matrix elements for the main part, atomic wave functions \( |\psi_v\rangle \), with \( v \) denoting different valence orbitals, are expressed in the singles and doubles approximated (SD) all-order method as [62]

\[
|\psi_v\rangle_{SD} = \left[ 1 + \sum_{ma} \rho_{ma} a^+_m a_a + \frac{1}{2} \sum_{mab} \rho_{mab} a^+_m a^+_a a_b a_a + \sum_{n \neq v} \rho_{nv} a^+_n a_v + \sum_{mlva} \rho_{mlva} a^+_m a^+_l a_v a_a \right] |\phi_v\rangle,
\]

where \( a^+ \) and \( a \) represent second quantization creation and annihilation operators, respectively, whereas excitation coefficients are denoted by \( \rho \). The subscripts \( m, l, r \) and \( a, b, c \) refer to the virtual and core orbitals, respectively. \( \rho_{ma} \) and \( \rho_{mv} \) are the single whereas \( \rho_{mab} \) and \( \rho_{mlva} \) are the double excitation coefficients. In addition to this, we also evaluated wave functions that includes the missing third-order terms, by adding the two triple-excitation coefficients - \( \rho_{mtrabc}^{\text{pert}} \) and \( \rho_{mtrabc}^{\text{pert}} \) perturbatively in the SD wave function solving equation (SDpT) by defining as follows [62]

\[
|\psi_v\rangle_{SDpT} = |\psi_v\rangle_{SD} + \left[ \frac{1}{18} \sum_{mtrabc} \rho_{mtrabc}^{\text{pert}} a^+_m a^+_l a^+_a a_c a_a + \frac{1}{6} \sum_{mtrabc} \rho_{mtrabc}^{\text{pert}} a^+_m a^+_l a^+_a a_c a_a \right] |\phi_v\rangle.
\]

After obtaining wave functions of the considered states of alkali-metal atoms, we determine E2 matrix elements using the following expression [63]

\[
Q_{vk} = \frac{\langle \psi_v | Q | \psi_k \rangle}{\sqrt{\langle \psi_v | \psi_v \rangle \langle \psi_k | \psi_k \rangle}}.
\]

In order to estimate contributions due to the neglected physical effects, we scale the wave functions (through the amplitudes of the excitation coefficients) to match the calculated energies with their experimental values [64]; i.e.

\[
\rho'_{mv} = \rho_{mv} \frac{\delta E_{\text{exp}}^{q(t=0,2)}}{\delta E_{\text{theory}}},
\]

where \( \delta E_{\text{exp}}^{q(t=0,2)} \) are the energy differences between the experimental and DF values, and \( \delta E_{\text{theory}}^{q(t=0,2)} \) are the energy differences between the experimental results and our final calculations. Then, the E2 matrix elements are reevaluated with the modified excitation amplitudes. By analysing the differences between the \( ab \text{ initio} \) values and the scaled values of the E2 matrix elements, we quote the uncertainties to the E2 matrix elements.

Contributions from the remaining excited states including continuum for valence polarizability are estimated separately using the DF method which are referred as tail part of the valence contribution \( \alpha_{n,v}^{(q(t=0,2) T)} \) and are evaluated using the relation

\[
\alpha_{n,v}^{(q(t=0,2) T)} = -2 \sum_{k>N_\text{c},k \neq n} W_n^{q(t=0,2)} \sum_{k>N_\text{c}} \left[ \frac{|\langle \psi_n | Q | \phi_k \rangle|^2}{\delta E_{nk}} \right],
\]
with $\delta \epsilon_{nk} = \epsilon_n - \epsilon_k$ for the DF energies $\epsilon_n$ and the sum $k \neq I$ corresponding to the excited states whose matrix elements are not accounted earlier. The valence-core contributions ($\alpha_{n,vc}^{q(t=0)}$) are estimated using the DF method. To estimate the core contribution ($\alpha_{n,c}^{q(t=0)}$), however, we have used the following formula \[ \alpha_{n,c}^{q(t=0)} = \langle \phi_n | Q | \psi_n^{(1)} \rangle \] (16)

where $| \psi_n^{(1)} \rangle = \sum_{k \neq n} c_k | \phi_k \rangle$ is the first-order perturbed wave function due to application of $Q$ operator on ground state $| \psi_n \rangle$ with $c_k$ is a coefficient containing all-order core-polarization effects due to the residual Coulomb interactions. We have obtained $| \psi_n^{(1)} \rangle$ in the random phase approximation (RPA) as described in [66].

IV. RESULTS AND DISCUSSION

A. Quadrupole polarizability of ground state

We present the static values of $\alpha_n^{q(0)}$ of the ground states of alkali-metal atoms and compare them with other available data in Table I. The scaled SD values of matrix elements for the main part of the polarizability have been taken as final values as recommended in previous studies [41, 64, 69]. The breakdown of total polarizability into the main, tail, core and valence-core polarizabilities are presented. The valence-core contributions for Li, Na and K are zero due to non-availability of $D$ orbitals in the core of these atoms whereas very insignificant contributions have been encountered for Rb, Cs and Fr. To provide estimates for error bars in the net value of each contribution of polarizability, we have incorporated the uncertainties for main, tail and core using different procedures. The uncertainty in the main part of valence polarizability is solely attributed to the uncertainty in matrix elements of the dominant transitions. The percentage uncertainty in tail part has been estimated by calculating the percentage deviation between the polarizability contribution of highest lying transition of main part calculated by DF and SD method. Recent experimental measurement on quadrupole core polarizability by Berl et al. [70] are found to be in good agreement with the core polarizability calculated using RPA for Rb. However, the RPA value for Rb gives maximum of 8% uncertainty when compared with the experimental value. Therefore, we have assigned 8% uncertainty to the core polarizability for all the atoms. The net uncertainty in the total value of polarizability has been accomodated by adding individual uncertainties in quadrature.

As Table I suggests, the main part of valence polarizability is responsible for over 90% of the total polarizability value for every considered atom. We ascribe 3%, 5%, 65%, 65%, 5% and 15% uncertainty to the tail part for Li, Na, K, Rb, Cs and Fr, respectively. Our values for the static quadrupole polarizability of Li, Na and K are found to be 1424(35), 1880(5) and 4934(107) a.u., respectively. Our results values match very well with other theoretical values calculated using semi-empirical [39], RMBPT [13] and CCSD [67] methods. For K, the quadrupole polarizability value recommended by Safronova et al. is 5018 using the SD values with 70 splines [41]. To authenticate our precisely calculated E2 matrix elements of the dominant transitions, we compare our E2 matrix element for Rb, Cs and Fr with the values that are available in the literature. Our E2 matrix elements , 32.88(74) and 40.29(90) a.u., from the $5S_{1/2} \rightarrow 4D_{3/2}$ and $5S_{1/2} \rightarrow 4D_{5/2}$ transitions, respectively of Rb are in excellent agreement with our values, 33.62(1.77) and 41.56(2.07) a.u. as reported in a recent study [69]. Furthermore, Gossel et al. reported the matrix element of 33.42 a.u. for the $5S_{1/2} \rightarrow 4D_{3/2}$ transition calculated using the relativistic Hartree-Fock approximation in a $V^{-1}$ potential [71] which lies within the uncertainty limit of our value. Theoretical E2 values of the corresponding matrix elements for Cs, 33.61(28) and 41.46(24) a.u., for the $6S_{1/2} \rightarrow 5D_{3/2}$ and $6S_{1/2} \rightarrow 5D_{5/2}$ transitions, respectively are in excellent agreement with our values, 33.62(1.77) and 41.56(2.07) a.u. as reported in a recent study [69]. These values for the $6S_{1/2} \rightarrow 5D_{3/2}$ transition computed using the highly accurate methods deviate from the experimental value which has been measured by the method of two-photon ionization of the ground 6S state, using the 5D as an intermediate state [72] by 2% only. On comparing the E2 matrix elements of most dominant transitions of Fr i.e., $7P_{3/2} \rightarrow 6D_{3/2}$ and $7P_{1/2} \rightarrow 6D_{5/2}$, our values, 33.40(1.33) and 41.54(1.47) a.u. are again in reasonable agreement with the values, 33.43(19) and 41.58(18) a.u., recommended by Safronova et al. [69]. Our final quadrupole polarizability values of 6440(246) and 10606(736) a.u. of Rb and Cs, respectively advocate the results evaluated by Safronova et al. [42, 43] and are comparable to the values calculated using RMBPT [13] and semi-empirical [39] approaches. Combining all the individual contributions for Fr, the ground state quadrupole polarizability value comes out to be $8756(560)$ a.u. The trend of rising quadrupole polarizability down the group I breaks at Cs as Fr offers lower value of the ground state quadrupole polarizability than Cs. Quantitatively, both the matrix elements and energies of the transitions play principal roles in the determination of this lower value of polarizability. The smaller values of the E2 matrix elements and large values of the energy differences among the primary transitions of Fr are responsible for such smaller value as compared to its preceding alkali atom. The quadrupole polarizability for Fr has not been explored to date by any other group. Nevertheless, the accuracy in the ground state quadrupole polarizability values of all other alkali-metal atoms makes the resulted polarizability value for Fr as much authentic as for other considered alkali-metal atoms.
TABLE I: Contributions to the ground state quadrupole polarizabilities (in a.u.) of the Li, Na, K, Rb, Cs and Fr atoms. Uncertainties to the estimates values are quoted in the parentheses. Final results are compared with the previously available values.

|   | Li   | Na   | K    | Rb   | Cs   | Fr   |
|---|------|------|------|------|------|------|
| \( q^{(0)} \) | 1310 | 1773 | 4866 | 6209 | 9670 | 7009 |
| \( \alpha_{n,v(M)}^{(0)} \) | 114(3) | 104(8) | 98(64) | 224(145) | 644(32) | 478(72) |
| \( \alpha_{n,v(T)}^{(0)} \) | 0.112(5) | 1.5(2) | 16(1) | 35(2) | 86(7) | 125(10) |
| \( \alpha_{n,c}^{(0)} \) | 0 | 0 | 0 | \( \sim 0 \) | \( \sim 0 \) | \( \sim 0 \) |
| Total(\( \alpha_{n}^{(0)} \)) | 1424(35) | 1880(5) | 4934(107) | 6440(246) | 10606(736) | 8756(560) |
| Others | 1424 [13] | 1885 [13] | 5000 [13] | 6520 [13] | 10470 [13] | 10390 [39] |
|        | 1421 [67] | 1906 [67] | 4933 [67] | 6525 [42] | 10390 [39] | 10521 [43] |
|        | 1424 [39] | 1878 [39] | 5000 [39] | 6479 [39] | 10521 [43] | 5018 [41] |

B. Quadrupole polarizabilities of excited states

The calculated values of static quadrupole polarizabilities of the first two excited states, \( nP_{1/2} \) and \( nP_{3/2} \), of alkali-metal atoms are presented in Tables II and III. Same procedures have been followed for the calculations of these quantities, i.e. main, tail, valence-core and core contributions as discussed in Sec. IV A. The \( nP_{3/2} \) state quadrupole polarizabilities have contributions from the scalar as well as tensor components. The main contributions rising from the most dominant E2 matrix elements are quoted explicitly here, while the rest are given separately as ‘Remaining’ in the above tables. The difference between the tail and ‘Remaining’ contributions is that the tail contributions are coming from the high-lying states including continuum and estimated using the DF method, while the ‘Remaining’ contributions are arising from the low-lying bound states and estimated more accurately by combining the E2 matrix element from the scaled SD methods and the experimental energies. We could not find any other values in the literature for the \( nP_{3/2} \) state of Li as discussed below.

1. Li

Table II consists of static quadrupole polarizability values for both the \( 2P_{1/2} \) and \( 2P_{3/2} \) states of Li along with the main, tail, and core contributions. For Li, we used energies for the \((6-8)F_{5/2,7/2}\) states from the SD method as the NIST energies are not available. For the main part, other than the listed transitions, \( 2P_{1/2} \rightarrow (4-7)P_{3/2}, (6-8)F_{5/2} \) transitions have been included, the contribution of these transitions are given in Remaining part of \( \alpha_{n,v(M)}^{(t)} \). As shown in Table II, the individual contributions from the dominant transitions considered for the \( 2P_{1/2} \) state of Li clearly suggest that the largest contribution towards the total polarizability value is coming from the \( 2P_{1/2} \rightarrow 2P_{3/2} \) transition by the reason of large matrix element as well as a very small difference between the experimental excitations energies (0.34 cm\(^{-1}\)) of the corresponding states. This small difference in the energy can be attributed to very small fine splitting of the \( 2P \) state coming into effect due to spin-orbit coupling. Another effective contribution towards the main part of total polarizability of the \( 2P_{1/2} \) state has been provided by the \( 2P_{1/2} \rightarrow 4F_{5/2} \) transition. For the \( 2P_{1/2} \) state, the tail part offers a very little contribution (<1%) whereas the core polarizability is 0.11 a.u.. A7% uncertainty has been considered in the tail part. Total polarizability value of the \( 2P_{1/2} \) state of Li is found to be 757.31(15) \times 10^5 \text{ a.u.} We found another work reported by Wansbeeck et al. for the calculation of quadrupole polarizability of the \( 2P_{1/2} \) excited state of Li atom using \textit{ab initio} CCSD(T) method [44, 68]. As can be noticed from the Table II, there is a large deviation in the results between this work and the value reported in Ref. [44, 68]. From the contributions explicitly quoted in Table II, it is obvious that such a huge deviation would have been caused due to estimate of different contribution from its fine-structure partner \( 2P_{3/2} \) excited state as the magnitudes of other contributions are relatively small. A furthermore analysis suggests that the fine-structure splitting of the \( 2P \) state is extremely small and it is a challenge to estimate this splitting as precisely as the experimental value using a numerical calculation without considering contributions from the higher-order relativistic effects. This is the only reason why we observe a huge difference between the \textit{ab initio} calculation of Ref. [44, 68] and the present work, where we have considered the experimental energies in the sum-over-states approach to determine the quadrupole polarizabilities. From this view point, the result reported in this work is more reliable. For the \( P_{3/2} \) state, we have estimated contributions from a large number of dominant transitions i.e., \( 2F_{3/2} \rightarrow (2-7)P_{1/2}, (3-8)P_{3/2}, (4-8)F_{5/2,7/2} \) out of which 4 dominant transitions are listed in the ta-
TABLE II: The scalar and tensor components of the quadrupole polarizabilities (in a.u.) of the first two excited states of the Li, Na and K atoms. Different contributions along with the corresponding uncertainties to these quantities are listed explicitly. The numbers in square brackets represent powers of 10. Our results are compared with the values reported earlier for Li.

|   | 2P_{1/2} |   | 2P_{3/2} |   |
|---|----------|---|----------|---|
|   |          |   |          |   |
| Contribution | E2 | \(\alpha_n^{(0)}\) | Contribution | E2 | \(\alpha_n^{(0)}\) | \(\alpha_n^{(2)}\) |
| \(\alpha_n^{(t)}\) \(n,v\) (M) | 2P_{1/2} \(-\) 2P_{3/2} | 24.22(2) | 757.26(15)[5] | 2P_{1/2} \(-\) 2P_{3/2} | 24.22(2) | -378.63(75)[5] | 378.63(75)[5] |
| \(\alpha_n^{(t)}\) | 2P_{1/2} \(-\) 3P_{3/2} | 21.14(2) | 122.51(2)[1] | 2P_{1/2} \(-\) 3P_{3/2} | 21.14(2) | 612.6(1)[1] | 0 |
| \(\alpha_n^{(t)}\) | 2P_{1/2} \(-\) 4P_{3/2} | 22.99(3) | 106.8(3)[1] | 2P_{1/2} \(-\) 4P_{3/2} | 12.30(1) | 152.7(2)[0] | 109.1(7)[0] |
| \(\alpha_n^{(t)}\) | 2P_{1/2} \(-\) 5P_{3/2} | 14.45(6) | 37.9(3)[1] | 2P_{1/2} \(-\) 5P_{3/2} | 30.13(2) | 917(1)[0] | -262.0(3)[0] |
| Remaining | 461.3(1)[0] | Remaining | 145.7(1)[1] | -776.8(6)[0] |
| \(\alpha_n^{(t)}\) \(n,v\) (T) | 1.01(7)[3] | \(\alpha_n^{(t)}\) \(n,v\) (T) | 1.00(7)[3] | -1.6(1)[2] |
| \(\alpha_n^{(t)}\) \(n,v\) | 1.10(8)[-1] | \(\alpha_n^{(t)}\) \(n,v\) | 1.10(8)[-1] | 0 |
| \(\alpha_n^{(t)}\) \(n,vc\) | 0 | \(\alpha_n^{(t)}\) \(n,vc\) | 0 | 0 |
| Total(\(\alpha_n^{(0)}\)) | 757.3(15)[5] | Total(\(\alpha_n^{(0)}\)) | -378.59(75)[5] | 378.62(75)[5] |
| Others | 1.434[5] [68] |   |   |   |

Moreover, the contributions of the lower energy value of the \(2P_{1/2}\) state, the same transition provides a positive contribution which is attributed to negative \(W_{n,k}^{(2)}\) coefficient of the tensor component that negates with negative sign in Eq. (5). Moreover, the contributions of \(P_{3/2} \rightarrow P_{3/2}\) transitions for any principal quantum number in the main part of
TABLE III: The scalar and tensor components of the quadrupole polarizabilities (in a.u.) of the $P_{1/2}$ and $P_{3/2}$ states of the Rb, Cs and Fr atoms are given. Individual contributions are listed explicitly. There are no literature values available to compare with our results.

|       | $5P_{1/2}$                  |       | $5P_{3/2}$                  |
|-------|-----------------------------|-------|-----------------------------|
|       | Contribution               | E2    | $\alpha_n^{(0)}$            | $\alpha_n^{(0)}$            | $\alpha_n^{(2)}$            |
|       |                            |       | $\alpha_n^{(0)}$            | $\alpha_n^{(0)}$            | $\alpha_n^{(2)}$            |
| Rb    | $\alpha_n^{(1)}$           | $\alpha_n^{(1)}$ | $\alpha_n^{(1)}$ | $\alpha_n^{(1)}$ | $\alpha_n^{(1)}$ |
|       | $\alpha_n^{(0)}$           | $\alpha_n^{(0)}$ | $\alpha_n^{(0)}$ | $\alpha_n^{(0)}$ | $\alpha_n^{(0)}$ |
|       | $\alpha_n^{(0)}$           | $\alpha_n^{(0)}$ | $\alpha_n^{(0)}$ | $\alpha_n^{(0)}$ | $\alpha_n^{(0)}$ |
|       | Remaining                   | $\alpha_n^{(1)}$ | $\alpha_n^{(1)}$ | $\alpha_n^{(1)}$ | $\alpha_n^{(1)}$ |
|       | $\alpha_n^{(0)}$           | $\alpha_n^{(0)}$ | $\alpha_n^{(0)}$ | $\alpha_n^{(0)}$ | $\alpha_n^{(0)}$ |
|       | $\alpha_n^{(0)}$           | $\alpha_n^{(0)}$ | $\alpha_n^{(0)}$ | $\alpha_n^{(0)}$ | $\alpha_n^{(0)}$ |
| Cs    | $\alpha_n^{(2)}$           | $\alpha_n^{(2)}$ | $\alpha_n^{(2)}$ | $\alpha_n^{(2)}$ | $\alpha_n^{(2)}$ |
| Fr    | $\alpha_n^{(3)}$           | $\alpha_n^{(3)}$ | $\alpha_n^{(3)}$ | $\alpha_n^{(3)}$ | $\alpha_n^{(3)}$ |

the tensor polarizability for $P_{3/2}$ states of all the alkali-metal atoms are zero because 6-j symbol in Eq. (7) vanish when triangle conditions are not fulfilled. Owing to negative Wigner coefficient $W_{n,k}^{(2)}$ for the $2P_{3/2} \rightarrow mF_{7/2}$ transitions, where $m > 4$, the contributions of these transitions are negative for main part of the tensor component of the polarizability. This type of behavior is true for all the alkali-metal atoms. Since a lot of dominant transitions have been examined for the main part of tensor component, a very small percentage of the tail part has been encountered giving scalar value of quadrupole polarizability of $-378.59(75) \times 10^5$ a.u. and the tensor polarizability value as $378.62(75) \times 10^5$ a.u.
2. **Na**

Table II provides the individual contributions of the main, tail and core of the total quadrupole polarizability for the 3P1/2 and 3P3/2 states of Na. Using the experimental energies and the precisely calculated E2 matrix elements of all the dominant transitions 3P1/2 → (3 − 8)P3/2, (4 − 8)F5/2, the value of the main part for the 3P1/2 state is amounting about 95% contribution towards the total polarizability value. Such large fraction is solely attributed to the contribution of the first transition of the main polarizability given in the table. The tail and core contribution are quite small with 9% and 8% uncertainties, respectively. With all the contributions of polarizability, the total value of the 3P1/2 state comes out to be 330.7(22) × 10^3. Same can be noticed for scalar and tensor components of the quadrupole polarizability of the 3P3/2 state for which the 3P3/2 → 3P1/2 transition is giving dominant contribution. Other than listed transitions, we included the contributions from 3P3/2 → (4 − 8)P1/2, (5 − 9)P3/2, (5 − 8)F5/2,7/2 in the Remaining part of the main valence contribution. After adding all the individual contributions and uncertainties in the quadrature, the total polarizability values of the scalar and tensor components for 3P3/2 state are −163.84(11) × 10^4 and 164.60(11) × 10^4 a.u., respectively.

3. **K**

We present all the contributions to the quadrupole polarizability for the 4P1/2 and 4P3/2 excited states of K in Table II. Around 98% of the share of total polarizability has been imparted by the main part of the valence polarizability which include contributions from 4P1/2 → (4 − 9)P1/2, (4 − 8)F3/2 transitions. Remainder share is coming from both the tail and core polarizabilities for the 4P1/2 state. The 8% and 18% uncertainty has been given to the core and tail polarizabilities respectively. Net quadrupole polarizability value of 4P1/2 state of K comes out to be 17.05(29) × 10^5 a.u.. For the 4P3/2 state, one can observe that the large matrix elements are rendered by the 4P3/2 → 4F1/2,5P3/2,4F5/2 and 4F7/2 transitions. The largest matrix element given by the 4P3/2 → 4F7/2 transition does not provide immense contribution towards total polarizability due to significant difference in the energy state. Other transitions (4P3/2 → (5 − 9)P1/2, (6 − 10)P3/2, (5 − 8)F5/2,7/2) which account for very less contribution as compared to the dominant ones have been listed as Remaining in the table. From the DF method, tail part has been estimated with 18% uncertainty. Adding all the contributions, the scalar and tensor polarizabilities are −8.24(14) × 10^5 a.u. and 8.38(14) × 10^5 a.u., respectively for 4P3/2 state.

4. **Rb**

The total polarizability values of the 5P1/2 and 5P3/2 excited states for Rb are given in Table III with individual contributions from the main, tail, core and valence-core correlations. For the 5P1/2 state, we carried out precise E2 matrix element calculations of the 5P1/2 → (5 − 10)P3/2, (4 − 5)F5/2,7/2 transitions. The 5P1/2 → 5P3/2 transition is offering an overwhelming contribution of around 96% to the total polarizability for the 5P1/2 state. The tail and core contributions are only 0.4% and 0.006%, respectively, of the total polarizability for the 5P1/2 state with tail uncertainty of 22% whereas valence-core contribution is nearly zero. Thus, a total quadrupole polarizability of 5.40(11) × 10^5 a.u. has been encountered for the 5P1/2 state. For the 5P3/2 state of Rb, similar findings can be observed for both the scalar and tensor components. The 5P3/2 → (5 − 10)P1/2, (6 − 11)P3/2, (4 − 8)F5/2,7/2 transitions have been considered for the main part out of which contributions from the 4 transitions are listed in the above table and the contributions for the remaining have been listed as Remaining. The tail contribution is very small in comparison to the main part. We assign maximum 17% uncertainty to the tail contribution for both the scalar and tensor components. The scalar and tensor quadrupole polarizabilities of the 5P3/2 state are −23.34(56) × 10^4 and 25.18(56) × 10^4 a.u., respectively.

5. **Cs**

The matrix elements and polarizability contributions from the considered transitions of the main part for Cs have been summarized in Table III. The first transition, i.e. 6P1/2 → 6F3/2, of the main part in the given table for the 6P1/2 state is accountable for large value of total polarizability. Other tabulated transitions are also contributing dominantly. Remaining contributions of the main part include contributions from the 6P1/2 → (7 − 11)P3/2, (5 − 8)F5/2,7/2 transitions. The tail and core correlations provide ~ 0.6% and ~ 0.027% contributions of the total polarizability value. 27% uncertainty has been assigned to the tail part. Thus, the total polarizability value of the 6P1/2 state for Cs turns out to be 31.57(92) × 10^4 a.u.. For the scalar component of the 6P3/2 state, the assertive positive contributions in the main part are given by the 6P3/2 → (7 − 11)P1/2, (7 − 12)P3/2, (4 − 8)F5/2,7/2 transitions, core and tail part cancel with some share of the negative contribution given by the most prominent 6P3/2 → 6P1/2 transition, ultimately giving a small value for the main polarizability of −10.64 × 10^5, whereas tensor polarizability is 13.37 × 10^4 a.u.. The assigned tail uncertainty for the 6P3/2 state is 25%. Finally, the total polarizability values for scalar and tensor components of the 6P3/2 state are −10.45(47) × 10^4 and 13.34(46) × 10^4, respectively.
6. Fr

The total polarizability values of the $7P_{3/2}$ and $7P_{3/2}$ states for Fr with the main, tail, core and valence-core contributions is given in Table III. We calculated the E2 matrix elements for the $7P_{1/2} \rightarrow (7−12)P_{3/2}, (4−8)F_{5/2}$ transitions to estimate the quadrupole polarizability of the $7P_{1/2}$ state and the E2 matrix elements for the $7P_{3/2} \rightarrow (7−12)P_{1/2}, (8−13)P_{3/2}(4−8)F_{5/2}, 7/2$ transitions of determining quadrupole polarizability of the $7P_{3/2}$ state. For the $(5−8)F_{5/2,7/2}$ states, we have used our SD excitation energy values as the energies from the NIST database are not available. Our energy values for the $(5−8)F_{5/2,7/2}$ states agree well with values recommended by Tang et al. calculated using relativistic Fock space multi-reference coupled-cluster method [73]. The percentage differences of our energy values with respect to the values evaluated by Tang et al. for the $(5−8)F_{5/2,7/2}$ states ranges from 0.04 to 0.09%. For Fr, the $7P_{1/2} \rightarrow 7P_{3/2}$ and $7P_{1/2} \rightarrow 5F_{5/2}$ transitions play major roles in total polarizability value of the $7P_{1/2}$ state as can be observed from the individual contribution given in Table III. Though matrix elements are large, the effect of polarizability contribution is not prodigious. The reason behind this being the large doublet separation of the $7P$ state. Including the tail and core polarizabilities of $2.20(88) \times 10^3$ a.u. and $125$ a.u. with the corresponding uncertainties of $40$% and $8$%, the total polarizability value for the $7P_{1/2}$ state is $12.43(49) \times 10^3$ a.u.. For the $7P_{3/2}$ state, the $7P_{3/2} \rightarrow 7P_{1/2}, 8P_{3/2}, 5F_{5/2,7/2}$ transitions for scalar component contribute dominantly. It is worth to bring to notice that unlike all other atoms considered in this work, the main part of scalar component for the $7P_{3/2}$ state is giving very small negative contribution. With tail part having $30$% uncertainty and core contribution, the final value for the scalar component for the $7P_{3/2}$ state is $-146.8$ a.u. with a large uncertainty of $2844$ a.u.. For tensor component, the $7P_{3/2} \rightarrow 7P_{1/2}, 8P_{1/2}, 5F_{5/2,7/2}$ transitions contribute dominantly for the main part leading to total polarizability of $3.63(24) \times 10^4$ a.u., respectively after adding all other components. However, the total polarizability value coming from both the scalar and tensor components of the $7P_{3/2}$ state depend upon the magnetic sublevels $M_J$ values.

V. CONCLUSION

We have presented the static quadrupole polarizabilities of the ground state and the first two excited states $nP_{1/2,3/2}$ of the alkali-metal atoms. Uncertainties to these quantities are reduced by using very precise values of electric quadrupole matrix elements of a large number of intermediate states and considering experimental energies. The electric quadrupole matrix elements were evaluated by employing an all-order relativistic many-body method in the singles-doubles scaling procedure that takes experimental correlation effects into account. The calculated quadrupole polarizability values were validated by reproducing the values for the ground states of the above atoms with the literature values. This confirms the credibility of our results for the excited states. To understand their accuracies further, breakdown of contributions towards the net values along with the quadrupole matrix elements and their uncertainties for dominant transitions are also given. The precise values of quadrupole matrix elements given in this work can be used to estimate the dynamic quadrupole polarizabilities of the considered states at real and imaginary frequencies, which are useful for many applications. The reported quadrupole polarizability values can be helpful for estimating systematics associated with the high-precision experiments using alkali-metal atoms.

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