

# Time-dependent density-functional-theory calculation of the van der Waals coefficient $C_6$ of alkali-metal atoms Li, Na, K; alkali-metal dimers $\text{Li}_2$ , $\text{Na}_2$ , $\text{K}_2$ ; sodium clusters $\text{Na}_n$ ; and fullerene $\text{C}_{60}$

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We have employed time-dependent density-functional theory (TDDFT) to calculate the long-range dipole-dipole dispersion coefficient (van der Waals coefficient)  $C_6$  of alkali-metal atoms Li, Na, K; alkali-metal atom dimers  $\text{Li}_2$ ,  $\text{Na}_2$ ,  $\text{K}_2$ ; sodium clusters containing even number of atoms ranging from 2 to 20 atoms; and fullerene  $\text{C}_{60}$ . The dispersion coefficient is obtained via Casimir-Polder expression which relates it to the frequency dependent linear polarizability at imaginary frequencies. The frequency-dependent polarizabilities are calculated by employing TDDFT-based complete sum-over-states expressions for the atoms, and direct TDDFT linear response theory for the closed shell dimers and clusters.

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## I. INTRODUCTION

The contribution of the long-range van der Waals force (dispersion force) to the interaction between two many-electron systems is quite significant. This force plays an important role in the description of many physical and chemical phenomena such as adhesion, surface tension, physical adsorption, etc. Physically, this long-range force arises from the correlation between the electron density fluctuations at widely separated spatial locations such that the electronic densities belonging to the different molecules do not overlap significantly. For such a large separation a mathematical expression for the potential corresponding to the long-range dispersion force is obtained by employing perturbation theory for the calculation of the second-order change in energy due to Coulomb interaction between two charge distributions. The first term in the perturbative expansion of the interaction potential (after orientational averages have been performed) decays as  $-C_6/R^6$ , where  $R$  is the intermolecular distance and the van der Waals coefficient  $C_6$  describes the dipole-dipole interaction between the two polarizable systems. The calculation of this coefficient can be performed by using the Casimir-Polder expression [1,2] which relates it to the dynamic dipole polarizability at imaginary frequencies. The dynamic polarizability, which describes the response of an atom or molecule to a weak time-dependent external electric field has been well studied. There exist a number of wave-function-based first-principles methods for calculating this quantity at varying levels of sophistication taking into account electron correlation. Alternatively, time-dependent density-functional theory (TDDFT) represents an efficient tool for first-principles theoretical calculations of dynamic polarizability of atoms and molecules, typically at significantly lower computational cost as compared to the correlated wave-function-based methods. However, it is worth noting that this method fails to provide correct descriptions of long-range charge transfer excitations [3], excitations in solids, multiple excitations, etc., [4] with commonly used approximations for the exchange-correlation (XC) potentials and kernels.

Recently, TDDFT has been applied to calculate van der Waals coefficients of variety of atoms and small molecules [5], an extensive set of polycyclic aromatic hydrocarbons [6,7], fullerene  $\text{C}_{60}$  [6,8], and small sized sodium clusters up to 20 atoms [9,10] by taking into account the actual geometrical arrangement of the atoms in molecules or clusters. The results of these calculations clearly demonstrate that a TDDFT-based method yields results for  $C_6$  which are very close to other theoretical and experimental data (where available). We would like to mention here that along with these *ab initio* works some papers devoted to TDDFT calculations of van der Waals coefficients between sodium, potassium, and sodium-potassium clusters within the jellium background model, ignoring the actual ionic geometry have also been reported in the past [11,12]. In this paper we apply TDDFT to calculate the coefficient  $C_6$  for the interactions of variety of systems containing alkali-metal atoms at *ab initio* level. The choice of alkali-metal atoms and their dimers for our calculations are also driven by the recent development of laser cooling and trapping of these atoms [13]. These advances have rekindled the interest in the knowledge of long-range forces between alkali-metal atoms and clusters thereof as these forces play an important role in the properties of cold gases of atoms and molecules.

We calculate here  $C_6$  for the interactions of Li, Na, and K atoms with themselves and their dimers and also with relatively larger systems consisting of sodium clusters containing even number of atoms ranging from 2 to 20 as well as fullerene  $\text{C}_{60}$ . As mentioned before the calculation of  $C_6$  requires knowledge about the frequency-dependent polarizabilities along the imaginary frequency axis. In this paper we obtain them by employing TDDFT-based complete sum-over-states (SOS) expressions for the atoms, and direct TDDFT linear response theory for the closed shell dimers, clusters, and fullerene  $\text{C}_{60}$ . For any TDDFT-based response property calculations (such as polarizability, hyperpolarizability, excited state energies, etc.) one needs to use approximate forms for the XC potential and kernel. It is well documented in the literature that the nature of XC potential,

especially its behavior in the asymptotic region plays an important role in the calculation of response properties and the accuracies of the results obtained via TDDFT depend crucially on it [14–16]. Keeping this in mind, we choose a model potential called statistical average of orbital potential (SAOP) which affords desirable properties both in the asymptotic and the inner regions of a molecule. It has already been demonstrated that this potential yields accurate results for the response properties of small molecules [16–18]. Recently, we employed SAOP to calculate polarizability and  $C_6$  of small sodium clusters (up to  $\text{Na}_{20}$ ) [10] and obtained results which were quite accurate and very close to the experimental data. These results have played a significant role in our choice to employ SAOP for the present study.

The accuracies of the SOS-based TDDFT results for the dynamic polarizabilities of alkali-metal atoms are first assessed by comparing them with published data and then we apply them to calculate  $C_6$  for (i) alkali-metal-atom-alkali-metal-atom (Li, Na, and K) and (ii) alkali-metal-atom-alkali-metal-atom dimer ( $\text{Li}_2$ ,  $\text{Na}_2$ , and  $\text{K}_2$ ) interactions. We compare our results with the data already available in the literature which were obtained by employing correlated wave-function-based methods. After gaining confidence with smaller systems, we then apply the results for the frequency-dependent dipole polarizabilities to calculate the van der Waals coefficient  $C_6$  for the interactions between (iii) alkali-metal atoms and sodium clusters ( $\text{Na}_n$ , where  $n=2-20$ ), (iv) alkali-metal atoms and fullerene  $\text{C}_{60}$ , and (v) sodium clusters and  $\text{C}_{60}$  fullerene. We note here that these calculations involving alkali-metal atoms, sodium clusters, and fullerene  $\text{C}_{60}$  are motivated by a number of experiments performed by Kresin and co-workers [19,20] on the determination of van der Waals coefficient  $C_6$ . These experiments involved measurement of the integral scattering cross sections in low-energy collisions between a beam of sodium clusters and vapors of alkali-metal atoms Li, Na, and K [19] and  $\text{C}_{60}$  molecules [20]. For low-energy collisions, the integral scattering cross section depends on the van der Waals coefficient  $C_6$ . In Ref. [19] van der Waals coefficient could not be determined directly, however, it was found that the experimental results for integral scattering cross section matched quite well with the theoretical predictions which were obtained by employing the London dispersion formula for  $C_6$ . This formula is of approximate nature. It assumes that all the strength of dipole transition is concentrated in a single peak located at an effective frequency and it involves only two parameters [see Eq. (3) below]. We compare our TDDFT-based results with the numbers used in Ref. [19] to reproduce their experimental data. To the best of our knowledge, no first-principles theoretical data for  $C_6$  between alkali-metal atom and sodium clusters have so far been reported in the literature. On the other hand, in Ref. [20] the results for  $C_6$  corresponding to Na- $\text{C}_{60}$  interactions were directly obtained from the data of integral scattering cross section. Since this study also reports data for  $C_6$  between sodium clusters ( $n \geq 2$ ) and  $\text{C}_{60}$  fullerene, we perform the calculation of the van der Waals coefficient for the same. We note here that recently theoretical calculation of  $C_6$  between sodium clusters ( $n \geq 2$ ) and  $\text{C}_{60}$  fullerene has been reported by Jiemchoorj *et al.* [9]. This calculation was carried out by using linear complex

polarization propagator approach within the realm of Hartree-Fock theory and TDDFT formalism with hybrid B3PW91 exchange-correlation (XC) energy functional [21,22]. The experimental and theoretical data available in the literature provide us a good opportunity to test the accuracy of our TDDFT-based results.

For alkali-metal clusters (specially sodium clusters) spherical jellium background model (SJB) has been highly successful in describing the ground-state and optical response properties [23]. As mentioned before this model has also been applied to calculate van der Waals coefficients between all pairs of sodium and potassium clusters containing 1, 2, 8, and 20 atoms [11,12]. It is then natural to make a comparison of these results with our TDDFT-based data to assess the accuracy of jellium model. We conclude from this study that as expected, jellium model grossly underestimates the values of  $C_6$  for atom-atom and atom-dimer interactions.

The paper is organized as follows. In Sec. II, we discuss the theoretical method and the expressions employed to calculate the van der Waals coefficient  $C_6$  from the frequency-dependent dipole polarizability. Results of our calculations are presented in Sec. III.

## II. METHOD OF CALCULATION

As mentioned before we calculate the van der Waals coefficient  $C_6$  by making use of the Casimir-Polder expression which relates  $C_6$  to the frequency-dependent dipole polarizability evaluated at imaginary frequency. In accordance with this expression the orientation averaged dispersion coefficient between two moieties  $A$  and  $B$  is given by [1,2]

$$C_6(A,B) = \frac{3}{\pi} \int_0^\infty d\omega \bar{\alpha}_A(i\omega) \bar{\alpha}_B(i\omega), \quad (1)$$

where  $\bar{\alpha}_j(i\omega)$  is the isotropic average dipole polarizability of the  $j$ th moiety and is given by

$$\bar{\alpha}_j(\omega) = \frac{\alpha_{xx}^j(\omega) + \alpha_{yy}^j(\omega) + \alpha_{zz}^j(\omega)}{3}. \quad (2)$$

In the above expression  $\alpha_{xx}(\omega)$ ,  $\alpha_{yy}(\omega)$ , and  $\alpha_{zz}(\omega)$  are diagonal elements of the dipole polarizability tensor. Therefore, the calculation of dispersion coefficient  $C_6$  involves determining frequency-dependent dipole polarizability tensor at a range of imaginary frequencies followed by the evaluation of Eq. (1) by numerical quadrature. For the determination of the frequency-dependent polarizability we use linear response theory based on TDDFT, as already mentioned. For this work, the frequency dependent polarizabilities of the dimers and clusters were obtained with the Amsterdam density functional (ADF) program package [24]. We refer the reader to Refs. [14,25] for detailed description of the method adopted in this package for obtaining frequency dependent polarizabilities using ADF's RESPONSE module. This module cannot be employed for the calculation of frequency-dependent polarizabilities of open-shell alkali-metal atoms as it is presently restricted to the calculation of response properties of closed-shell systems only. Therefore, for the calculation of the dynamic polarizability of the alkali-metal atoms Li, Na,

and K, we have employed an analytical TDDFT based sum-over-states (SOS) expression for the polarizability [26,27]. We note here that the TDDFT SOS approach employed here is based on the relaxed transition densities. Consequently the polarizabilities obtained from our completely relaxed TD-DFT SOS expression (that is, including all the allowed transitions from the basis set) is formally and numerically equivalent to the results that would be obtained from linear response TDDFT formalism [28]. The SOS approach for the frequency-dependent polarizability requires the computation of the excitation energies for the allowed transitions and their corresponding oscillator strengths. These quantities can also be obtained from TDDFT calculations [29]. For this purpose we make use of the EXCITATIONS module of the ADF program which allows the treatment of open-shell configurations also. The SOS expression was evaluated by considering 85, 407, and 667 dipole-allowed excitations for the Li, Na, and K atom, respectively. These are all of the dipole allowed excitations possible within the chosen Slater-type orbital (STO) basis sets (see below). Due to the requirement of large number of excitations in SOS approach it is impractical for larger systems but quite feasible for atoms or diatomics.

For the calculations of response properties by TDDFT one needs to choose approximations for the XC potential and for the XC response kernel. The static XC potential is needed to calculate the ground-state Kohn-Shan (KS) orbitals and their energies. The XC response kernel  $f_{XC}(\mathbf{r}, \mathbf{r}', \omega)$  determines the XC contribution to the screening of an applied electric field. For the XC kernel, we have used the adiabatic local density approximation (ALDA) which was shown to be reasonably accurate for atoms [30]. On the other hand, for the static XC potential needed to calculate the ground-state orbitals and energies, we use a model potential, called statistical average of orbital potentials (SAOP) which has desirable properties both in the asymptotic and the inner regions of a molecule [17,18]. The SAOP yields improved results in particular for Rydberg excitations where the asymptotic behavior of the XC potential becomes important. For the sake of comparisons, we also use the standard local density approximation (LDA) as parameterized by Vosko, Wilk, and Nusair (VWN) [31].

All calculations of the frequency-dependent polarizabilities were carried out by using large Slater-type orbital (STO) basis sets. It is well known that for accurate calculations of response properties it is necessary to have large basis sets with both polarization and diffuse functions. For alkali-metal atoms (Li, Na, and K) we choose the quadruple- $\zeta$  triply polarized all electron even tempered basis set (ET-QZ3P-3DIFFUSE) from the ADF basis set library which has three sets of diffuse functions. For dimers of alkali-metal atoms and clusters of sodium atoms a slightly smaller all electron basis set ET-QZ3P-2DIFFUSE has been used to reduce the computational time and cost. We expect from our previous work [10] that even with this slightly smaller basis set, our results will be quite close to the basis-set limit. The application of highly flexible atomic orbital basis sets with diffuse functions often leads to the problem of linear dependencies. Such problem have been circumvented by removing linear combinations of functions corresponding to small eigenvalues of the overlap matrix. For the calculation of the

frequency-dependent polarizability of fullerene  $C_{60}$  a triple- $\zeta$  Slater-type basis with two sets ( $3d, 4f$ ) of polarization functions (TZ2P) has been employed. The capability of this basis set in obtaining accurate results for the static polarizabilities of fullerenes has already been demonstrated [32].

The Casimir-Polder integral Eq. (1) has been evaluated by employing a thirty point Gauss-Chebyshev quadrature scheme as described in Ref. [33]. The convergence of the results have been checked by comparing the results for increasing numbers of frequency points.

In order to perform the TDDFT calculations of the frequency-dependent polarizabilities of the dimers and clusters, we needed to choose their ground-state geometries. For the dimers, we used experimental bond lengths 2.6725 Å for  $Li_2$ , 3.0786 Å for  $Na_2$ , and 3.923 Å for  $K_2$  as in Ref. [34]. On the other hand, for larger clusters (4-to 20-atom clusters), we use structures which have been obtained via geometry optimizations employing a triple- $\zeta$  STO basis with two added polarization functions (TZ2P basis from the ADF basis set library) along with the Becke-Perdew (BP86) energy functional [35,36]. This XC potential is known to yield reliable geometries. All the optimizations have been carried out with the convergence criteria for the norm of energy gradient and energy, fixed at  $10^{-4}$  atomic units (a.u.) and  $10^{-6}$  a.u., respectively. In case of a cluster having more than one isomers, we choose the one possessing the lowest energy for our calculations of the dipole polarizability.

### III. RESULTS AND DISCUSSION

Before proceeding with the detailed discussion on our results for the dispersion coefficients we shall first assess the accuracy of the TDDFT based analytical SOS expression and of the SAOP XC potential in predicting the dynamic polarizabilities of alkali-metal atoms. To this end we have calculated the frequency-dependent linear polarizabilities  $\alpha(\omega)$  for Li, Na, and K atoms over wide range of frequencies and compared with theoretical results available in the literature. We begin by comparing the results for the static polarizabilities of Li, Na, and K atoms obtained by us with other theoretical results [37–45] and experimental data of Ref. [46]. The compilation of these results are presented in Table I. In Refs. [39–41] the calculations were performed by employing a configuration interaction (CI) method for the valence orbitals. The core electrons were treated using a pseudopotential approach. Other quantum chemical methods such as Møller-Plesset perturbation theory based on quasienergy derivative [37], coupled cluster approach with nonrelativistic [42] and relativistic [44,45] Hamiltonians, and an *ab initio* time-dependent gauge invariant method coupled with a CI method [43] have been employed to calculate the frequency-dependent polarizabilities.

On the other hand, the calculation of frequency-dependent polarizabilities at imaginary frequencies and  $C_6$  of alkali-metal atoms have been performed in Ref. [38] by constructing precise single-electron model potentials to represent the motion of the valence electron in the field of the closed-shell alkali-metal positive-ion core. First of all we note from Table I that both SAOP and LDA results for the static polarizabil-

TABLE I. Comparison of theoretical and experimental values of static polarizabilities of Li, Na, and K atoms (in atomic units). For methods see the text.

Source	Li	Na	K
Present (LDA)	141.92	140.48	262.12
Present (SAOP)	162.97	157.65	276.89
Ref. [37]	165.01	166.88	285.23
Ref. [40]	163.7	162.2	286.1
Ref. [39]	163.7	162.4	287.1
Ref. [41]	164.3	162.6	298.0
Ref. [38]	164.0	159.2	292.8
Ref. [42]	167.7	167.6	299.2
Ref. [44]		162.88	
Ref. [45]		162.88	
Ref. [43]	166.0	163.0	
Expt. Ref. [46]	164.0 ± 3	159.2 ± 3.4	292.8 ± 6.1

ities of Li atom are higher than the corresponding Na atom numbers. This observation is consistent with the majority of the theoretical data presented in Table I (except for Ref. [37]) and also experimental values of Ref. [46]. It can also be seen from Table I that SAOP result for Li and Na atom lie well within the range of values predicted by various theoretical approaches and also quite close to the experimental data. For the case of K atom, however, SAOP result for the static polarizability lie below the range of values presented in Table I. The SAOP result for the polarizability of K atom is around 5% lower than the most accurate theoretical result of Ref. [38] as well as experimental data [46].

Having compared our results for the static polarizability of Li, Na, and K atoms with other theoretical and experimental data we now focus our attention on the frequency dependence of the polarizabilities. In Figs. 1–3 we display the frequency-dependent linear polarizability of Li, Na, and K atoms, respectively, for real frequencies. In each figure we consider two different ranges of frequencies. In part (a) a frequency range spanning  $\omega=0-0.035$  Hartree (a.u.) has been chosen to compare our the results with those of Refs. [47] (Hylleraas approach), [37] (Møller-Plesset perturbation theory), and [48] (configuration interaction approach). A wider frequency range is chosen in part (b) of each figure, which is similar to the one considered in Ref. [49] for the calculation of dynamic polarizabilities of alkali-metal atoms. The authors of Ref. [49] used the random-phase approximations for the core electrons and the contribution of valence electrons were obtained using very accurate oscillator strength and transition energy data. For clarity we display the results for each atom in two separate graphs as the frequency mesh used for the above two ranges are quite different. Along with SAOP results we also display the results obtained with LDA XC potential for completeness. It can be clearly seen from these figures that LDA results for the frequency-dependent polarizabilities for all the atoms are always lower than the SAOP data throughout the whole frequency range. Both the static values of the polarizabilities and their frequency dependence are underestimated by LDA XC poten-

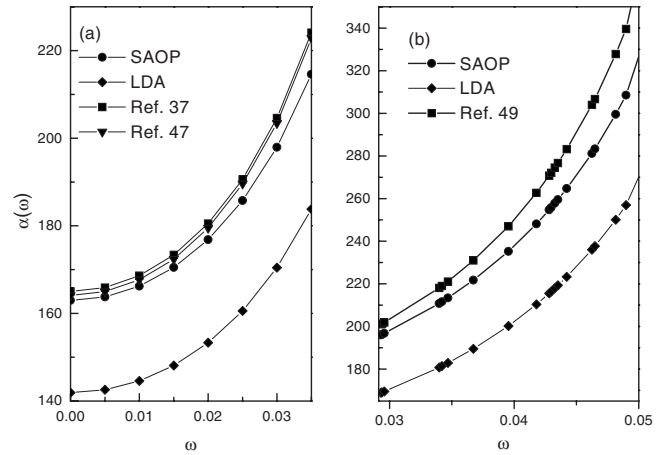


FIG. 1. Comparison of linear polarizability  $\alpha(\omega)$  (in Hartree atomic units) of the Li atom as a function of frequency obtained by different methods: TDDFT (SAOP and LDA, this work), Møller-Plesset perturbation theory (Ref. [37]), Hylleraas wave function approach (Ref. [47]), and Random-phase approximation and SOS expression (Ref. [49]). The lines joining the points were added to guide the eye.

tial. This is consistent with the fact that the LDA potential fails to exhibit the correct behavior both in the inner and asymptotic regions of the molecule—which is required for accurate determination of the frequency-dependent dipole polarizability. In comparison, the SAOP XC potential possesses much improved properties both in the asymptotic and the inner region of a molecule and consequently it is expected that the results obtained with this potential will be in better agreement with the other accurate theoretical results available in the literature. We observe from Figs. 1–3 that the frequency-dependent polarizability obtained with SAOP XC potential are still slightly lower than the results of Refs. [37,47–49] except for the case of the K atom. The differ-

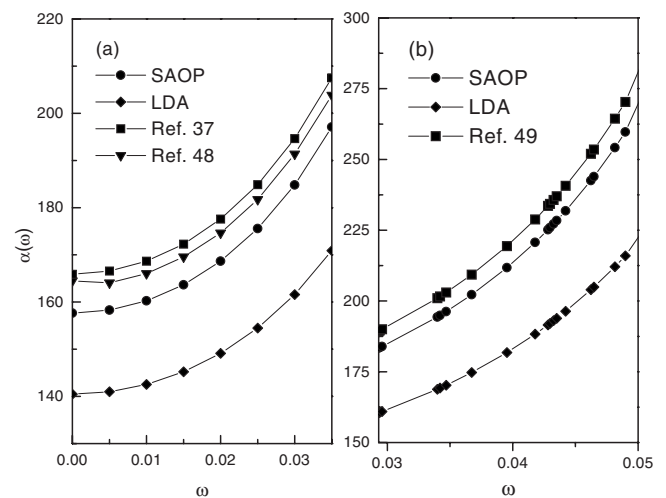


FIG. 2. Same as Fig. 1 but for Na atom. TDDFT (SAOP and LDA, this work), Møller-Plesset perturbation theory (Ref. [37]), CI approach (Ref. [48]), and random-phase approximation and SOS expression (Ref. [49]). The lines joining the points were added to guide the eye.

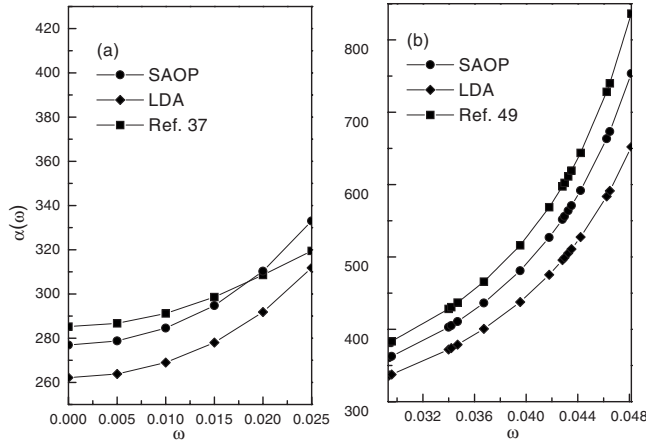


FIG. 3. Same as Fig. 1 but for K atom. TDDFT (SAOP and LDA, this work), Møller-Plesset perturbation theory (Ref. [37]), and random-phase approximation and SOS expression (Ref. [49]). The lines joining the points were added to guide the eye.

ences between SAOP and the other results shown in Figs. 1–3 are uniform over whole frequency range for Li and Na atoms. A SAOP XC kernel has not yet been implemented, therefore we are unable to make a direct comparison but it is likely that the ALDA approximation for the XC kernel, along with differences in the basis sets applied, is responsible for the remaining small differences between our and the literature data.

Having demonstrated the applicability and assessed the accuracy of the analytical SOS expression within TDDFT for the calculation of frequency-dependent polarizabilities of alkali-metal atoms Li, Na, and K, we now proceed with the discussions of the results for  $C_6$ . First we present the results for  $C_6$  between different pairs of alkali-metal atoms obtained by employing the SAOP and LDA XC potentials. These results are presented in Table II and compared with other theoretical results available in the literature [38–43]. We note that, as it was the case for the polarizability, the  $C_6$  coefficients obtained with SAOP are systematically higher than the corresponding LDA data. The comparison of other theoretical results compiled in Table II with the corresponding SAOP data clearly shows that SAOP value of  $C_6$  for Li-Li interaction is slightly higher (around 2.5%) relative to all the results presented in Table II except for the data of Ref. [42].

TABLE II. Results for  $C_6$  between different pairs of alkali-metal atoms, in atomic units.

Source	Li-Li	Na-Na	K-K	Li-Na	Li-K	Na-K
Present (LDA)	1117.65	1243.51	3320.71	1176.73	1922	2019
Present (SAOP)	1426	1473	3590	1448	2257	2288
Ref. [40]	1385	1527	3637	1452	2238	2336
Ref. [39]	1386	1518	3574	1448	2219	2309
Ref. [41]	1389	1540	3945	1460	2333	2443
Ref. [38]	1388	1472	3813	1427	2293	2348
Ref. [42]	1439	1639	4158	1532	2441	2595
Ref. [43]	1419	1554		1479		

TABLE III. Results for  $C_6$  between different alkali-metal atoms and alkali dimers, in atomic units. For each pair the first and second row numbers are obtained with LDA and SAOP XC potentials, respectively. The number in the parenthesis for each pair is taken from Refs. [40].

Dimers/Atoms	Li <sub>2</sub>	Na <sub>2</sub>	K <sub>2</sub>
Li	1696	2018	3338
	2108	2513	3967
	(1935)	(2394)	(3791)
Na	1794	2138	3516
	2148	2562	4029
	(2039)	(2524)	(3966)
K	2910	3459	5759
	3327	3969	6302
	(3102)	(3838)	(6144)

As a matter of fact for all the diatom pairs, results of Ref. [42] are higher than all other results displayed in Table II. In contrast to the Li-Li case, for Na-Na and K-K interactions SAOP results are slightly lower than the corresponding numbers obtained with other theoretical methods except for the results of Refs. [38,39] for Na-Na and K-K cases, respectively. In particular for the Na-Na interaction the SAOP value of  $C_6$  differs slightly (higher by around 1 atomic unit) as compared to the data of Ref. [38]. For heteronuclear cases of Li-Na and Li-K interactions, the agreement between SAOP and the other theoretical results presented in Table II is quite good. For Na-K interaction, SAOP number for  $C_6$  is lower than all the results and a maximum difference (around 6%) is found with result of Ref. [41]. These results then clearly demonstrate that the TDDFT approach used here (with the SAOP potential) is capable of predicting reasonably accurate  $C_6$  of alkali-metal diatoms as these results lie well within the range of values produced by other correlated wave-function-based first-principles methods.

We now present  $C_6$  for the interactions between alkali-metal atoms and alkali-metal dimers. These results are displayed in Table III and compared with the results of Ref. [40]. We mention here that Ref. [40] employed slightly different values of bond lengths for the dimers of alkali-metal atoms in comparison to the ones used in our calculations. As for our other results, we find that the LDA values for the atom-dimer interactions are again systematically lower than the corresponding SAOP results. For both the homonuclear and heteronuclear cases the SAOP results are a little higher than the corresponding data of Ref. [40]. The largest difference of around 8% is found for Li-Li<sub>2</sub> interaction whereas the difference is the smallest for Na-Na<sub>2</sub> (around 1%). In general it appears that the differences between our SAOP results and the data of Ref. [40] for the interaction between alkali atoms and the Li<sub>2</sub> dimer are somewhat larger than the corresponding differences for Na<sub>2</sub> and K<sub>2</sub>. For example, the difference between the results for K-Na<sub>2</sub> and K-K<sub>2</sub> are of the order of 3% whereas for K-Li<sub>2</sub> it is around 7%. Similarly for Na-Na<sub>2</sub> and Na-K<sub>2</sub> the discrepancy between the results are just 1% while it is around 5% for the Na-Li<sub>2</sub> case. However,

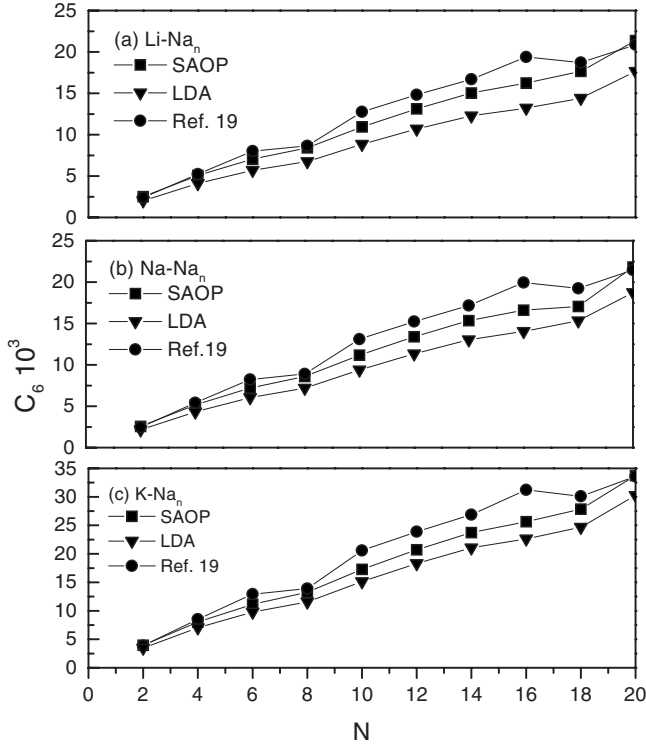


FIG. 4. Comparison of TDDFT and London formula based results for the van der Waals coefficient  $C_6$  corresponding to the alkali-atom-cluster pairs (a) Li- $\text{Na}_n$ , (b) Na- $\text{Na}_n$ , and (c) K- $\text{Na}_n$ . The numbers for  $C_6$  are in atomic units. The London formula results (represented by solid circles) were taken from Ref. [19]. The lines joining the points were added to guide the eye.

these results show that there is a reasonably good general agreement between our data and those of Ref. [40].

Next we discuss the results for  $C_6$  pertaining to the Li- $\text{Na}_n$ , Na- $\text{Na}_n$ , and K- $\text{Na}_n$  interactions. As mentioned before an experiment involving the measurement of the integral scattering cross section in low-energy collisions between neutral sodium clusters  $\text{Na}_n$  ( $2 \leq n \leq 20$ ) and the alkali-metal atoms Li, Na, and K was performed by Kresin *et al.* [19]. It has been shown in Ref. [19] that the values of  $C_6$  calculated from the London dispersion formula given by

$$C_6 = \frac{3}{2} \alpha_A(0) \alpha_B(0) \frac{\omega_A \omega_B}{\omega_A + \omega_B}, \quad (3)$$

with  $\omega_i$  and  $\alpha_i(0)$  denoting the characteristic frequency and static polarizability of the collision partners yield results for the integral scattering cross sections in good agreement with the experimental data. For details on the values of dipole transition frequencies and static polarizabilities employed to calculate  $C_6$  we refer the reader to Ref. [19]. In this paper, we compare the London-formula based  $C_6$  coefficients of Ref. [19] with our first-principles results (using the SAOP XC potential). In Figs. 4(a)–4(c) we display  $C_6$  coefficient for the pairs Li- $\text{Na}_n$ , Na- $\text{Na}_n$ , and K- $\text{Na}_n$ , respectively, as functions of the number of atoms present in the cluster. It can be clearly seen from Fig. 4 that for all the three cases of atom-cluster interactions, the TDDFT and London formula

TABLE IV. Comparison of *ab initio* and jellium results for  $C_6$  (in atomic units) between various pairs. For each pair the first entry is *ab initio* result and the number in the parenthesis is jellium based result taken from Ref. [11].

Atoms/ $X_n$	Na	K
Na	1243.5 (915.0)	2019.0 (1385.3)
$\text{Na}_2$	2138 (1745)	3459 (2440)
$\text{Na}_8$	7177 (6688)	11 557 (9334)
$\text{Na}_{20}$	18 731 (15 545)	30 246 (21 682)
K		3320 (2131)
$\text{K}_2$	3516 (2583)	5759 (3660)

results for  $C_6$  are quite close to each other for magic-number clusters containing 2, 8, and 20 sodium atoms. For other pairs, the match between the two data are still reasonably good. The largest differences are found for the pairs Li- $\text{Na}_{16}$ , Na- $\text{Na}_{16}$ , and K- $\text{Na}_{16}$ . These results are consistent with the fact that the London formula does not take anisotropic nature of the clusters into account. As a result of this the magic-number clusters which show less anisotropy than the non-magic ones [10] are well described by London's formula. The reasonably good agreement between our TDDFT-based results for  $C_6$  coefficients and those obtained by employing London formula may be attributed to the fact that for alkali-metal atoms and sodium clusters [23,50–52] the optical absorption spectra exhibit one strong resonance carrying essentially all the transition strength, which is also the basic assumption made in deriving the London formula. This is confirmed by our first-principles computations, i.e., our results show that the approximate London dispersion formula is indeed well suited for calculating the dispersion coefficient  $C_6$  for interactions between alkali atoms and magic number sodium clusters.

Let us now compare the jellium model based results for  $C_6$  available in the literature [11] between various pairs with the corresponding TDDFT-based *ab initio* results. A compilation of jellium and *ab initio* results for interactions between various relevant systems are presented in Table IV. Before discussing the results we note here that the SJBm based results were obtained with Gunnarsson and Lundqvist (GL) parametrization [53] of LDA XC potential and therefore we compare them with our LDA results. The VWN (XC functional employed in this paper) and GL parametrizations of the LDA XC functional use the same Dirac form for the exchange part but different parametrizations are used for the correlation part. We expect that the deviation in the results due to application of different correlation energy functionals will be significantly smaller than the difference in the two results, arising due to the consideration of the true nuclear potential or ionic structures in *ab initio* calculations. It can be

seen from Table IV that the SJBM results for  $C_6$  are lower than the corresponding *ab initio* values by around 30%. The discrepancies between the two results arise mainly due to the fact that one of the partners in all these interactions is an atom and the jellium model does not describe the nuclear potential of atoms correctly. However, this model appears to be well suited for larger clusters and yields fairly accurate results for their polarizability [54] and van der Waals coefficient between them [55].

Finally, we focus our attention on the results for  $C_6$  for the interactions between alkali-metal atoms and fullerene  $C_{60}$  and between sodium clusters containing even number of atoms ranging from 2 to 20 and  $C_{60}$ . Before discussing the results for  $C_6$ , we first present the results for the static polarizability of  $C_{60}$  molecule obtained by us with TZ2P/SAOP to ascertain the quality of this approach in determining response properties of  $C_{60}$ . Our TZ2P/SAOP calculation yields  $\alpha(0)=542.84$  a.u. This result is quite close to the experimental result of  $\alpha(0)=516.20 \pm 54.0$  a.u. [56] and also theoretical results  $\alpha(0)=545.5$  a.u. obtained with SAOP and a basis set different from TZ2P [32], and  $\alpha(0)=557.2$  a.u. obtained with the B3PW91 XC potential [6,9]. In order to assess the accuracy of the frequency-dependent polarizabilities of  $C_{60}$  obtained with TZ2P/SAOP, we have also calculated  $C_6$  between a pair of  $C_{60}$  fullerenes and compared the result with the values already available in literature [6,8,57,58]. With TZ2P/SAOP, we obtain  $C_6=115.5 \times 10^3$  a.u., which compares well with the TDDFT/DFT results  $C_6=101.0 \times 10^3$  a.u. [6] obtained with the hybrid XC functional B3PW91, and  $C_6=126.5 \times 10^3$  a.u. [8] obtained by employing a SOS technique along with the LDA XC functional.

Having assessed the accuracy of the results for polarizability of  $C_{60}$ , we now discuss the results for  $C_6$  between alkali-metal atoms and fullerene  $C_{60}$ . With SAOP, we find  $C_6=8.07 \times 10^3$  a.u.,  $8.52 \times 10^3$  a.u., and  $12.95 \times 10^3$  a.u. for Li- $C_{60}$ , Na- $C_{60}$ , and K- $C_{60}$  interactions respectively. We note here that only for the case Na- $C_{60}$  experimental result for  $C_6$  is available in the literature [20]. The value reported by Kresin *et al.* is  $(8.05 \pm 1.931) \times 10^3$  a.u. Thus we find that a very good agreement is achieved between the experimental data and theoretical result for the van der Waals coefficient between Na atom  $C_{60}$  fullerene. For the other two pairs (Li- $C_{60}$  and K- $C_{60}$ ) we are not aware of other theoretical results in the literature. However, the accuracies of the results for the polarizabilities of alkali-metal atoms and  $C_{60}$  indicate that TDDFT results for  $C_6$  between Li and K atoms and  $C_{60}$  obtained by us should also be quite accurate.

With the results for the frequency dependent dipole polarizabilities of sodium clusters and  $C_{60}$  molecule at our disposal it is quite natural to perform calculations of the van der Waals coefficients between these two systems and demonstrate the feasibility and applicability of TDDFT-based calculations to very large systems for which correlated wavefunction-based calculations are computationally prohibitive. We have already mentioned in the Introduction that both theoretical and experimental results for the van der Waals coefficient  $C_6$  between sodium clusters containing 2 to 20 atoms and fullerene  $C_{60}$  are available in the literature and we compare them with our SAOP results to assess the accuracy of the results obtained by us. In Table V, we present the results

TABLE V. Results for  $C_6$  ( $\times 10^{-3}$ ) between sodium clusters and  $C_{60}$  molecule in atomic units. The theoretical results obtained via B3PW91 are taken from Ref. [9] and the experimental results are taken from Ref. [20].

$Na_n$	SAOP	B3PW91	Experimental
2	15.27	15.36	$17.62 \pm 5.11$
4	30.55	29.94	$25.05 \pm 7.44$
6	43.42	43.33	$38.91 \pm 12.06$
8	53.36	54.33	$55.01 \pm 15.95$
10	68.39	65.67	$63.71 \pm 19.75$
12	82.00	81.81	$92.52 \pm 28.68$
14	94.38	98.25	$108.3 \pm 33.56$
16	103.7		$117.8 \pm 37.72$
18	113.7	111.7	$139.0 \pm 43.10$
20	134.7	124.0	$169.2 \pm 52.45$

obtained by employing SAOP along with the theoretical and experimental results of Refs. [9,20], respectively. We note here that the geometries of all the clusters used for theoretical calculations in Ref. [9] are similar to the ones used in this paper except for  $Na_{20}$ . Table V clearly shows that the results obtained with SAOP are quite close to B3PW91 data and they are also well within the experimental error bars (about 30%). It is important to note that similar to the B3PW91 data the difference between SAOP results and experimental data increases with the size of the clusters. In this respect we agree with Jiemchoorj *et al.* [9] that the enhancement of discrepancy of theoretical and experimental data may be due the presence of other isomers at finite temperature in the experiment, in addition to the ones we have considered here for the theoretical calculations of van der Waals coefficient  $C_6$ .

#### IV. SUMMARY AND CONCLUSIONS

This paper is devoted to the calculation of long-range van der Waals coefficient  $C_6$  for the interactions between alkali-metal atoms Li, Na, and K, their dimers, sodium atom clusters containing an even number of atoms ranging from 2 to 20, and fullerene  $C_{60}$ . The van der Waals coefficient  $C_6$  has been obtained by using the Casimir-Polder expression which needs frequency-dependent dipole polarizabilities of the two interacting species as input. The frequency-dependent polarizabilities of all the systems have been obtained by employing TDDFT formalism at the *ab initio* level. For alkali-metal atoms, we have used a TDDFT-based analytical SOS expression while for all other systems (dimers, clusters, and  $C_{60}$ ) direct linear response theory within TDDFT has been used. The calculations have been performed by using a model XC potential (SAOP) having correct behavior both in the inner and the asymptotic regions of a molecule. The calculations on the alkali-metal systems were carried out with one of the largest STO basis sets available in ADF basis set library; therefore, the results are expected to be close to the complete basis limit. In this paper the performance of TDDFT method

for the calculations of the frequency-dependent polarizability of alkali-metal atoms have been compared against other theoretical results available in the literature. We have found that TDDFT results, especially with SAOP agree well with the published data obtained by employing *ab initio* correlated wave-function-based methods. Motivated by these encouraging results we have then carried out calculations of the van der Waals coefficient  $C_6$  for different atomic- and diatomic-cluster pairs as mentioned above and compared our results with other theoretical data where available. The results presented in this paper clearly demonstrate that TDDFT with an asymptotically correct local XC potential performs well in the computation of van der Waals coefficient  $C_6$  also. For atom-atom and atom-dimer interactions, we found that our TDDFT results are quite close to the data available in literature obtained by employing various correlated wave-function-based methods. As no theoretical results are available for  $C_6$  between alkali-metal atoms and sodium clusters, we made comparisons of our TDDFT-based results with those obtained by Kresin *et al.* [19] which were arrived at by fitting the experimental data with the London dispersion formula. These comparisons clearly reveal that the overall agreement is quite good. Especially for magic-number clusters with 2, 8, and 20 atoms the approximate London formula yields values for  $C_6$  which are close to our first-principles

results. We attribute the agreement of the results obtained with TDDFT and with the London formula to the fact that a single strong resonance peak dominates the absorption spectra of the alkali-metal atoms and sodium clusters.

For interaction between Na atom and fullerene  $C_{60}$  the value of  $C_6$  obtained by employing the TDDFT agree well with the experimental data [19]. Using the frequency-dependent polarizabilities of sodium clusters and  $C_{60}$  we have also calculated van der Waals coefficient  $C_6$  for  $Na_n-C_{60}$  interactions. The TDDFT results obtained by us match with the theoretical data calculated with hybrid XC functional. They also agree well with the experimental results as they all lie within the experimental error bars.

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