Time dependent density functional theory calculation of van der Waals coefficient $C_6$ of alkali-metal atoms Li, Na, K, alkali dimers Li$_2$, Na$_2$, K$_2$ and sodium clusters Na$_n$

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Abstract

In this paper we employ all-electron 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 Li$_2$, Na$_2$, K$_2$ and sodium clusters containing even number of atoms ranging from 2 to 20 atoms. The dispersion coefficients are 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.
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 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 electrons belonging to the different molecules are distinguishable. 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 wavefunction-based ab-initio 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 correlated wavefunction-based methods. TDDFT often yields an accuracy similar to wave function based correlated methods as long as long-range charge transfer excitations are not overly important for the property under consideration. Recently, TDDFT has been applied to calculate van der Waals coefficients of variety of atoms and small molecules \([3]\) extensive set of polycyclic aromatic hydrocarbons \([4, 5]\), C\(_{60}\) and C\(_{70}\) molecules \([4, 6]\) and small sized sodium clusters up to 20 atoms \([7, 8]\). The results of these calculations are quite encouraging and clearly demonstrate that TDDFT based method yields results for \(C_6\) which are very close to other theoretical and experimental data (where available). This success has motivated us to further apply all-electron TDDFT based method to calculate the coefficient \(C_6\) to variety of systems containing alkali-metal atoms.
In this paper, we calculate $C_6$ for following interactions (i) alkali atom-alkali atom (Li, Na, and K), (ii) alkali atom-alkali atom dimer (Li$_2$, Na$_2$, and K$_2$), and (iii) alkali atom-sodium cluster (Na$_n$, where $n \leq 20$). The choice of alkali-metal atoms and their molecules for our calculations are also motivated by the recent development of laser cooling and trapping of these atoms [9]. These advances have rekindled the interest in the knowledge of long range forces between alkali atoms and clusters thereof as these forces play an important role in the properties of cold gases of atoms and molecules. Moreover, the results of the calculations of $C_6$ for systems (i) and (ii) give a good opportunity to assess the accuracy of TDDFT to calculate $C_6$ for alkali atoms and diaomics as for these systems accurate theoretical data obtained by correlated wave-function based methods exist in the literature. Moreover, the calculations of $C_6$ for the alkali atom – Na$_n$ interactions is motivated by an experiment performed by Kresin and co-workers [10]. Kresin et al. measured the integral scattering cross section in low energy collisions between a beam of sodium clusters and vapours of alkali-metal atoms Li, Na, and K. For low energy collisions, the integral scattering cross section depends on the van der Waals coefficient $C_6$. 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 $C_6$. The London dispersion formula assumes that all the strength of dipole transition is concentrated in a single peak located at an effective frequency and the formula involves only two parameters. (see Eq. (3) below). We will compare our TDDFT based results with the numbers used in Ref. [10] to reproduce their experimental data. We note that, 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.

Before we proceed with the main plan of the paper, we wish to mention here that in principle ground state density functional theory (DFT) should yield the exact ground-state properties including the long range van der Waals energies. However, the widely used local density approximation (LDA) and generalized gradient approximations (GGA) [11, 12, 13] exchange-correlation (XC) functionals as well as popular hybrid functionals fail to reproduce the van der Waals energies. This is due to the fact that the LDA and GGA functionals cannot describe the correlated motion of electrons arising from Coulomb interaction between distant non overlapping electronic systems. It is only recently that attempts [14, 15, 16, 17, 18] have been made to obtain van der Waals energies directly from the ground-state energy functional through systematic improvements of the effective Kohn-Sham potential. On the other hand,
it is possible to make reliable estimates of the van der Waals coefficient $C_6$ directly by using expressions which relate this coefficient to the frequency dependent dipole polarizabilities at imaginary frequencies [3] which can be computed from TDDFT using common functionals. We follow the latter route for the calculation of these coefficients.

The paper is organized as follows: In section 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 Section III.

II. METHOD OF CALCULATION

In order to calculate the van der Waals coefficient $C_6$, we make 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]

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

(1)

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

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

(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 [19]. We refer the reader to Ref. [3, 20] for detailed description of the method adopted in this package for obtaining frequency dependent polarizabilities using ADF’s RESPONSE module. This module is restricted to the calculation of response properties of closed–shell systems. 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 [21, 22]. 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 \[23\]. For this purpose we made 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 STO basis sets (see below). The SOS TDDFT results reported here are therefore equivalent to the corresponding full linear response data for \(\alpha(i\omega)\) (because of the large number of excitations using the SOS 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 KS orbitals and their energies. The XC response kernel \(f_{XC}(r, r', \omega)\) 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 \[24\]. On the other hand, for the static XC potential needed to calculate the ground-state orbitals and energies, two different choices have been made. These are (i) the standard local density approximation (LDA) as parameterized by Vosko, Wilk and Nusair \[25\] and (ii) 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 \[26, 27\]. The results obtained by these two XC potentials are compared in order to investigate the effect of the XC potential on the dispersion coefficient \(C_6\). The SAOP yields improved results in particular for Rydberg excitations where the asymptotic behavior of the XC potential becomes important.

All calculations of the frequency dependent polarizabilities of sodium clusters 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. On the other hand, for dimers of alkali-metal atoms and clusters of sodium atoms a slightly smaller yet accurate all electron basis set ET-QZ3P-2DIFFUSE has been used to reduce the computational time.
and cost. 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. We expect that the size of the chosen basis set will make our results quite close to the basis-set limit.

The Casimir-Polder integral Eq. (11) has been evaluated by employing a thirty point Gauss-Chebyshev quadrature scheme as described in Ref. [28]. 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 Li₂, 3.0786 Å for Na₂, and 3.923 Å for K₂ as in Ref. [29]. 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-ζ STO basis with two added polarization functions (TZ2P basis from the ADF basis set library) along with the Becke-Perdew (BP86) XC potential [30, 31]. 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 Ref. [8], we employed these geometries to calculate C₆ for sodium clusters. 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 (compared to the LDS) 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. 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. [32] (Hylleraas approach), [33] (Moller-Plesset perturbation theory), and [34] (CI approach). A wider frequency range is chosen in part (b) of each figure, which is similar to the one considered in Ref. [35] for the calculation of dynamic polarizabilities of alkali-metal atoms by using a combination of 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. 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 potential. 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. The improvement of SAOP results over the LDA results obtained with the same STO basis are clearly elucidated in Figs. 1-3. We also observe from Figs. 1 -3 that the frequency dependent polarizability obtained with SAOP XC potential are still slightly lower than the results of Refs. [32, 33, 34, 35] except for the case of K atom. The differences 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 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 LDA and SAOP XC potentials. These results are presented in Table I and compared with other theoretical results available in the literature [36, 37, 38, 39, 40, 41]. In Refs.
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 a couple cluster approach and an *ab initio* time dependent gauge invariant method coupled with a CI method have been employed to calculate the dynamic polarizability at imaginary frequencies. On the other hand, 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 the calculation of frequency dependent polarizabilities at imaginary frequencies and $C_6$ of alkali-metal atoms have been performed in Ref. [36].

First 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 I 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 I except for the data of Ref. [40]. As a matter of fact for all the diatom pairs results of Ref [40] are higher than all other results displayed in Table I. 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 Ref. [36] and Ref. [37] for Na-Na and K-K cases respectively. In particular for Na-Na interaction the SAOP value of $C_6$ differs slightly ( higher by around 1 atomic unit) as compared to the data of Ref. [36]. For heteronuclear cases of Li-Na and Li-K interactions the agreement between SAOP and the other theoretical results presented in Table I 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. [39]. These results then clearly demonstrate that the TDDFT approach used here (with the SAOP potential) is capable of predicting quite accurate $C_6$ of alkali-metal diatoms as these results lie well within the range of values produced by other correlated wavefunction based methods. Mostly, our results compare very well with other data listed in Table I.

We now present $C_6$ for the interactions between alkali-metal atoms and alkali dimers. These results are displayed in Table II and compared with the results of Ref. [38]. We mention here that Ref. [38] employed slightly different values of bond lengths for the dimers of alkali atoms in comparison to the ones used in our calculations. Like 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. [38]. The largest difference of around 8% is found for Li-Li$_2$ interaction whereas the difference is the smallest for Na-Na$_2$ (around 1%). In general it appears that the differences between our SAOP results and the data of Ref. [38] for the interaction between alkali atoms and the Li$_2$ dimer are somewhat larger than the corresponding differences for Na$_2$ and K$_2$. For example, the difference between the results for K-Na$_2$ and K-K$_2$ are of the order of 3% whereas for K-Li$_2$ it is around 7%. Similarly for Na-Na$_2$ and Na-K$_2$ the discrepancy between the results are just 1% while it is around 5% for Na-Li$_2$ case. Overall, however, the agreement between our data and those of Ref. [38] is very encouraging.

Finally, we discuss the results for $C_6$ pertaining to the Li-Na$_n$, Na-Na$_n$, and K-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 Na$_n$ (2 ≤ $n$ ≤ 20) and the alkali atoms Li, Na and K was performed by Kresin et al. [10]. It has been shown in Ref. [10] that the values of $C_6$ calculated from the London dispersion formula given by

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

(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 which show a 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. [10].

In this paper, we compare the London–formula based $C_6$ coefficients with our first–principles results (using the SAOP data). In Figs. 4a, 4b and 4c we display $C_6$ coefficient for the pairs $Li - Na_n$, $Na - Na_n$, and $K - Na_n$, 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 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 $Li - Na_{16}$, $Na - Na_{16}$, and $K - Na_{16}$. These results are consistent with the fact that the London’s 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 [8] are well described by London’s formula. The overall agreement of
the $C_6$-coefficients obtained here from the TDDFT computations with those derived from the London formula may be attributed to the fact that for alkali-metal atoms and sodium clusters \footnote{42, 43, 44, 45} 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.

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 and their dimers, and sodium atom clusters containing an even number of atoms ranging from 2 to 20. The calculations were performed by employing all-electron TDDFT methods. The van der Waals coefficient 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 polarizability of the atoms were obtained by employing a TDDFT-based analytical complete SOS expression while for all other systems (dimers and clusters) direct linear response theory within TDDFT has been used. The calculations were performed by using a model XC potential (SAOP) having the correct behavior in the asymptotic region (as well as improved behavior in the valence and core regions of the molecules, compared to LDA). The calculations were carried out with one of the largest STO basis sets available in ADF basis set library; therefore, the results are expected to be reasonably close to the complete basis limit. In this paper the performance of the SAOP and LDA XC potentials for the calculations of the frequency dependent polarizability of alkali-metal atoms have been compared against other theoretical results available in the literature. We found that SAOP results are in much better agreement with published data than the LDA results and compare well with results obtained by employing \textit{ab initio} correlated wave-function based methods. Motivated by these encouraging results we then carried out calculations of the coefficient $C_6$ for different atom/diatomic - cluster pairs as mentioned above and compared our results with other theoretical data where available. The results presented in this paper clearly showed that
TDDF with the SAOP XC potential performs very well in the computation of van der Waals coefficient $C_6$ also. For atom-atom and atom-dimer interactions, we found that SAOP 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.\cite{Kresin10} by using the London dispersion formula which is valid under the approximation that the absorption spectra exhibits single strong resonance peak at an effective frequency. These comparisons clearly reveal that the overall agreement is quite good and specially for magic–number clusters with 2, 8, and 20 atoms the approximate London formula yields values for $C_6$ which are very 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.

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Figure captions

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), Moller-Plesset perturbation theory (Ref. [33]), Hyleraas wavefunction approach (Ref. [32]), and Random-phase approximation and SOS expression (Ref. [35]). The lines joining the points were added to guide the eye.

Fig.2 Same as Fig. 1 but for Na atom. TDDFT (SAOP and LDA, this work), Moller-Plesset perturbation theory (Ref. [33]), CI approach (Ref. [34]), and Random-phase approximation and SOS expression (Ref. [35]). 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), Moller-Plesset perturbation theory (Ref. [33]), and Random-phase approximation and SOS expression (Ref. [35]). The lines joining the points were added to guide the eye.

Fig.4 Comparison of TDDFT and London formula based results for the van der Waals coefficient $C_6 \times 10^{-3}$ corresponding to the alkali-atom-cluster pairs (a) $Li - Na_n$, (b) $Na - Na_n$, and (c) $K - Na_n$. The numbers for $C_6$ are in atomic units. The London formula results (represented by solid circles) were taken from Ref. [10]. The lines joining the points were added to guide the eye.
### TABLE I: Results for $C_6(\times10^{-3})$ 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. [38]          | 1385   | 1527   | 3637   | 1452   | 2238   | 2336   |
| Ref. [37]          | 1386   | 1518   | 3574   | 1448   | 2219   | 2309   |
| Ref. [39]          | 1389   | 1540   | 3945   | 1460   | 2333   | 2443   |
| Ref. [36]          | 1388   | 1472   | 3813   | 1427   | 2293   | 2348   |
| Ref. [40]          | 1439   | 1639   | 4158   | 1532   | 2441   | 2595   |
| Ref. [41]          | 1419   | 1554   |        | 1479   |        |        |

### TABLE II: Results for $C_6(\times10^{-3})$ 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. [38]

| DIMERS ATOMS | Li$_2$ | Na$_2$ | K$_2$ |
|--------------|--------|--------|-------|
| 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)|
FIGURE 3

(a) SAOP
LDA
Ref. 31

(b) SAOP
LDA
Ref. 33

ω(ω)

0.000 0.005 0.010 0.015 0.020 0.025

ω

0.032 0.036 0.040 0.044 0.048

ω

260 280 300 320 340 360 380 400 420

400 380 360 340 320 300 280 260

800 700 600 500 400 300 200 100 0

0.00 0.01 0.02 0.03 0.04 0.05 0.06 0.07 0.08

0.00 0.02 0.04 0.06 0.08 0.10 0.12 0.14 0.16

0.00 0.02 0.04 0.06 0.08 0.10 0.12 0.14 0.16
FIGURE 4

(a) Li-Na$_n$
- ■ SAOP
- ▼ LDA
- • Ref. 10

(b) Na-Na$_n$
- ■ SAOP
- ▼ LDA
- • Ref. 10

(c) K-Na$_n$
- ■ SAOP
- ▼ LDA
- • Ref. 10

$C_6 \times 10^{-3}$ vs. $N$