Calculation of van der Walls coefficients of alkali metal clusters
by hydrodynamic approach to time-dependent density-functional theory

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Abstract

In this paper we employ the hydrodynamic formulation of time-dependent density functional theory to obtain the van der Waal coefficients $C_6$ and $C_8$ of alkali-metal clusters of various sizes including very large clusters. Such calculation becomes computationally very demanding in the orbital-based Kohn-Sham formalism, but quite simple in the hydrodynamic approach. We show that for interactions between the clusters of same sizes, $C_6$ and $C_8$ sale as the sixth and the eighth power of the cluster radius respectively, and approach the respective classically predicted values for the large size clusters.
I. INTRODUCTION

The long-range van der Waals forces play an important role in the description of many physical and chemical phenomena such as adhesion, surface tension, physical adsorption, etc. The correlations between electron density fluctuations at widely separated locations give rise to these long range forces. For clusters the knowledge of coefficients of van der Waals interaction is useful in describing the cluster-cluster collisions and also for characterizing the orientation of clusters in bulk matter. The van der Waals interaction coefficients, namely $C_{6}^{AB}$ and $C_{8}^{AB}$ between small alkali metal particles within the spherical jellium background (SJBM) model of have been theoretically calculated in the past using time dependent density functional theory (TDDFT) [1, 2, 3]. In Refs. [1, 2], time-dependent Kohn-Sham (TDKS) formalism of TDDFT was employed to obtain $C_{6}^{AB}$ and $C_{8}^{AB}$. On the other hand, in Ref. [3], we employed density based method within TDDFT formalism to obtain the van der Waals coefficient $C_{6}^{AB}$ for the clusters. The TDKS formalism is an orbital based theory and involves calculation of these orbitals in a self-consistent manner. Thus, as the size of system increases these calculations tend to become computationally cumbersome. In such cases, our approach [3] is much easier to as it makes calculations size independent with hardly any loss in accuracy.

The main aim of this paper is to extend our previous study by applying the density based hydrodynamic approach to calculate the higher-order van der Waals coefficient $C_{8}^{AB}$ of alkali atom clusters characterizing dipole-quadrupole interaction of long-range force and study its evolution with the size of clusters. In addition to this we also calculate $C_{6}^{AB}$ and $C_{8}^{AB}$ coefficients for the pair interaction between potassium clusters of various sizes and between potassium and sodium clusters of different sizes as well.

Before proceeding further, it is necessary to note that the density functional theory (DFT) in principle should give the exact ground-state properties including long range van der Waals energies. However, the frequently used local density approximation (LDA) [7, 8] and generalized gradient approximations (GGA) [9, 10, 11] fail to reproduce the van der Waals energies. This is due to the fact that LDA and GGA cannot completely simulate the correlated motion of electrons arising from coulomb interaction between distant non overlapping electronic systems. It is only recently that several attempts [12, 13, 14] have been made to obtain van der Waals energies directly from the ground-state energy functional by correcting
the long range nature of the effective Kohn-Sham potential. On the other hand, it is possible to make reliable estimates of the van der Waals coefficients by using expressions which relate these coefficients to the frequency dependent multipole polarizabilities at imaginary frequencies [15, 16]. We follow this route for the calculation of these coefficients.

The paper is organized as follows: In section II we express \( C_6 \) and \( C_8 \) in terms the dipole and the quadrupole dynamic polarizabilities. We then briefly describe our method of obtaining these polarizabilities employing hydrodynamic approach of TDDFT. Results of our calculations are presented and discussed in section III.

II. METHODS OF CALCULATION

The nonretarded electrostatic interaction energy between two spherically symmetric electronic systems \( A \) and \( B \) separated by interaction distance \( R \) can be written as [15, 16]

\[
V_{AB}(R) = -\frac{C_{6}^{AB}}{R^6} - \frac{C_{8}^{AB}}{R^8} - \cdots
\]  

(1)

The above expression has been obtained by assuming that \( R \) is very large so that the charge distributions corresponding to the two systems do not overlap. The coefficient \( C_{6}^{AB} \) describes the dipole-dipole interaction, and \( C_{8}^{AB} \) corresponds to the dipole-quadrupole interaction between system \( A \) and \( B \). These coefficients can be expressed in terms of the dynamic multipole polarizability \( \alpha_l(\omega) \) (where \( l \) denotes the index of multipolarity) by following relations [17, 18]:

\[
\begin{align*}
C_{6}^{AB} &= C(A, 1; B, 1) \\
C_{8}^{AB} &= C(A, 1; B, 2) + C(A, 2; B, 1)
\end{align*}
\]  

(2)

with

\[
C(A, l_1; B, l_2) = \frac{(2l_1 + 2l_2)!}{2\pi(2l_1)!(2l_2)!} \int_0^\infty d\omega \alpha_{l_1}^A(i\omega)\alpha_{l_2}^B(i\omega)
\]  

(3)

where \( \alpha_{l}^X(i\omega) \) is the multipole polarizability of system \( X \) (\( X = A \) or \( B \)) at imaginary frequency \( u = i\omega \). Although \( \alpha_{l}^X(i\omega) \) does not have any physical significance, expressions given by Eqs. (2) and (3) make the computation of \( C_{6}^{AB} \) and \( C_{8}^{AB} \) straightforward. Moreover, mathematically \( \alpha_{l}^X(i\omega) \) is better behaved than its real frequency counterpart \( \alpha(\omega) \): it does not have any singularity and decreases monotonically from its static value \( \alpha_{l}^X(0) \) to zero as
$\omega \to \infty$. Consequently, the quadrature in Eq. (3) can be computed quite accurately. To determine the frequency dependent polarizabilities appearing in Eq. (3), we employ variation-perturbation method within the hydrodynamic approach of TDDFT. We now describe the theory in brief. For details the reader is referred to the literature [3, 5, 6].

The basic dynamical variables of the hydrodynamic theory are the time dependent density $\rho(r, t)$ and the velocity potential $S(r, t)$. Thus the total time-averaged energy can be expressed in terms of these two variables. For our purpose we need to evaluate the second-order change in the time-averaged energy as this is directly related to the frequency dependent multipole polarizability by the relation

$$\alpha_l(\omega) = -4E_l^{(2)}$$

The second-order time-averaged energy $E_l^{(2)}$ in turn can be expressed as

$$E_l^{(2)} = \left\{ \frac{1}{2} \int \frac{\delta^2 F[\rho]}{\delta \rho(r, t) \delta \rho(r', t)} \rho^{(1)}(r, t) \rho^{(1)}(r', t) dr dr' + \int v_{\text{app}}^{(l)}(r, t) \rho^{(0)}(r) dr \right\}$$

$$+ \int \frac{\partial S^{(1)}(r, t)}{\partial t} \rho^{(1)}(r, t) dr + \frac{1}{2} \int (\nabla S^{(1)} \cdot \nabla S^{(1)}) \rho^{(0)}(r) dr$$

where the curly bracket denotes the time averaging over a period of the applied oscillating field and $\rho^{(0)}(r)$ represents the ground-state density. It is easily shown [3] that $E_l^{(2)}$ is stationary with respect to the variations in the first-order induced density $\rho^{(1)}(r, t)$ and the induced current-density $S^{(1)}(r, t)$. Consequently, $E_l^{(2)}$ can be determined by choosing appropriate variational forms for $\rho^{(1)}(r, t)$ and $S^{(1)}(r, t)$ and making $E_l^{(2)}$ stationary with respect to the variations in the parameters of $\rho^{(1)}(r, t)$ and $S^{(1)}(r, t)$. In the above expression the functional

$$F[\rho] = T_s[\rho] + E_H[\rho] + E_{XC}[\rho],$$

where $T_s[\rho]$, $E_H[\rho]$ and $E_{XC}[\rho]$ denote the kinetic, Hartree and the exchange-correlation (XC) energy functionals respectively. The exact forms of $T_s[\rho]$ and $E_{XC}[\rho]$ are not known. Consequently to perform any calculation one needs to use approximate forms for these functionals. On the other hand, the hartree energy functional $E_H[\rho]$ representing classical coulomb energy is exactly known and it given by

$$E_H[\rho] = \frac{1}{2} \int \int \frac{\rho(r, t) \rho(r', t)}{|r - r'|} dr dr'.$$

For the purpose of calculation the multipolar applied potential $v_{\text{app}}^{(l)}(r, t)$ is chosen to be

$$v_{\text{app}}^{(l)}(r, t) = \mathcal{E}r^lY_{l0}(\theta, \phi) \cos \omega t$$
where $E$ and $\omega$ represent the amplitude and the frequency of the applied periodic electromagnetic field. In accordance with the above form of the applied potential the variational forms for $\rho^{(1)}(r, t)$ and $S^{(1)}(r, t)$ are chosen to be

$$
\rho^{(1)}(r, t) = \rho^{(1)}(r, \omega) \cos \omega t \\
S^{(1)}(r, t) = \omega S^{(1)}(r, \omega) \sin \omega t
$$

with

$$
\rho^{(1)}(r, \omega) = \sum_i c_i r^i \rho^{(0)}(r) Y_l^0(\theta, \phi) \\
S^{(1)}(r, \omega) = \sum_i d_i r^i (r) Y_l^0(\theta, \phi)
$$

where $\rho^{(0)}(r)$ is the ground-state density and $c_i$ and $d_i$ are the variational parameters obtained by minimizing time-averaged second-order energy $E^{(2)}$. On substituting Eq. (9) in Eq. (5) and taking average over time we get

$$
E^{(2)} = \frac{1}{4} \int \frac{\delta^2 F[\rho]}{\delta \rho(r) \delta \rho(r')} \rho^{(1)}(r, \omega) \rho^{(1)}(r', \omega) dr dr' + \frac{1}{2} \int v_{app}^{(1)}(r) \rho^{(1)}(r, \omega) dr + \frac{\omega^2}{2} \int S^{(1)}(r, \omega) \rho^{(1)}(r, \omega) dr + \frac{\omega^2}{4} \int (\nabla S^{(1)} \cdot \nabla S^{(1)}) \rho^{(0)}(r) dr,
$$

At this point it is important to point out that the VP method discussed above is also applicable for the imaginary frequencies with $\omega^2$ replaced by $-\omega^2$ in Eq. (11). This allows us to determine dynamic multipolarizability at imaginary frequencies ($\alpha(i\omega)$) by exactly the same procedure as employed for getting $\alpha(\omega)$. All that is required for this is to change $\omega^2$ to $-\omega^2$ in Eq. (11). This is done very easily in the numerical code written for determining dynamic polarizability at real frequencies.

As mentioned earlier the calculation of $E^{(2)}$ requires approximating the functionals $T_s[\rho]$ and $E_{XC}[\rho]$. To this end we choose the von Weizsacker form for $T_s[\rho]$ which is given as

$$
T_W[\rho] = \frac{1}{8} \int \nabla \rho \cdot \nabla \rho dV.
$$

Our previous experience with the calculation of response properties has led us to choose von Weizsacker KE functional for the polarizability calculation. For the XC energy, adiabatic local-density approximation (ALDA) is accurate enough to describe the energy changes.
Thus the exchange energy is approximated by the Dirac exchange functional \[ E_x[\rho] = C_x \int \rho^{3/2}(r) d\mathbf{r} \]

\[ C_x = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3}. \]  

(13)

and for the correlation energy functional we employ the Gunnarsson-Lundqvist (GL) parametrized form for it.

In the present paper the ground-state densities \( \rho^{(0)}(\mathbf{r}) \) of clusters are obtained by employing purely density-based extended Thomas-Fermi (ETF) method within the spherical jellium background model (SJBM) of metal clusters. This approach yields the ground-state densities of very large clusters (containing up to 1000 atoms) easily thereby allowing us to study the evolution of van der Waals coefficients with the size of clusters. For details of the ETF method and its application to study alkali-metal cluster, we refer the reader to [5, 6, 22, 23, 24]. In the next section we present the results for \( C_{6}^{AB} \) and \( C_{8}^{AB} \) of alkali metal clusters by employing the method describe above.

III. RESULTS AND DISCUSSION

We have performed calculations for the coefficients \( C_{6}^{AB} \) and \( C_{8}^{AB} \) between clusters of alkali metal atoms of various sizes. In this paper we consider clusters made up of sodium (\( r_s = 4.0 a.u. \)) and potassium (\( r_s = 4.86 a.u. \)) atoms (where \( r_s \) is the Wigner-Seitz radius of the cluster species). First we discuss the results for the sodium clusters. For completeness we also include \( C_{6}^{AB} \) numbers of sodium clusters in this paper. As in our previous study, Table I and II we present the results for \( C_{6}^{AB} \) and \( C_{8}^{AB} \) respectively, between sodium clusters containing 2, 8, 20, and 40 atoms. For comparison we also show the corresponding TDKS results of Ref. [2] in parenthesis. Table I and II clearly show that the numbers obtained by employing the hydrodynamic approach for small clusters are quite close to the corresponding numbers obtained by the TDKS method. The numbers for \( C_{6}^{AB} \) obtained in this paper are systematically lower than the orbital-based TDKS results. The difference between the two results is slightly more for larger clusters than the smaller ones, the maximum difference being of the order of 10\%. Now we discuss the main results of this paper, that is, numbers for \( C_{8}^{AB} \) between clusters of sodium clusters.
In Table II we present the results for the coefficient $C_{8A}^{B}$. This table clearly shows that our numbers for $C_{8A}^{B}$ are quite close to the corresponding TDKS results. In comparison to the results for $C_{6A}^{B}$ our numbers for $C_{8A}^{B}$ are closer to the corresponding TDKS values. Moreover, unlike $C_{6A}^{B}$ case, the numbers for $C_{8A}^{B}$ are not always lower than the corresponding TDKS results. The values of $C_{8A}^{B}$ between 2 and 2 and, 2 and 8 atom sodium clusters obtained by the hydrodynamic method are slightly more than the corresponding TDKS results. We next apply hydrodynamic approach to calculate the van der Waals coefficients between potassium clusters of various sizes.

In Table III and IV we present the results for $C_{6A}^{B}$ and $C_{8A}^{B}$ respectively, between potassium clusters of different sizes. Again two tables clearly show that both $C_{6A}^{B}$ and $C_{8A}^{B}$ between potassium clusters are obtained quite accurately with the hydrodynamic approach. The numbers obtained by us for potassium clusters are all lower than the corresponding TDKS results. Table III and IV also clearly show that the difference between the hydrodynamic and the TDKS results is lower for the larger clusters than than the smaller ones. On the other hand, for sodium clusters the difference between the two results shows the opposite trend.

Next we now present in Table V and VI the results for $C_{6A}^{B}$ and $C_{8A}^{B}$ respectively, for the pair interaction between sodium and potassium clusters with 2, 8, and, 20 constituent atoms. Once again we see from these two table that hydrodynamic numbers quite close to the corresponding TDKS results barring few exceptions like the number for $C_{6A}^{B}$ between two types of clusters containing 8 atoms each. Table V and VI also show that like the pair interaction between clusters of identical atoms the value of $C_{8A}^{B}$ for two different clusters obtained by hydrodynamic approach is closer to the TDKS as compared to the corresponding $C_{6A}^{B}$ results.

With favourable comparison between the numbers obtained by our approach and those by the TDKS approach for small clusters we now employ the hydrodynamic approach to evaluate the van der Waal coefficients for much larger clusters. This allows us to study the size dependence of van der Waals coefficients and how they approach the asymptotic classical values. In the present paper we have performed calculations for clusters containing up to 1000 atoms without any increase in computational effort. To study the size dependence of van der Waals coefficients we plot in Figs. 1 and 2, $C_{6A}^{B}/R_{0}^{6}$ and $C_{8A}^{B}/R_{0}^{8}$ respectively, as functions of $R_{0}$ ( where $R_{0} = r_{s}N^{1/3}$ and N denotes number of atoms). These two figures
clearly exhibit that as the size of cluster increases the values of coefficients $C_{6}^{AA}/R_0^6$ and $C_{8}^{AA}/R_0^8$ saturate to constants numbers, indicating that $C_{6}^{AA}$ and $C_{8}^{AA}$ scale as the sixth and the eight power of the radius $R_0$ of the cluster respectively. This trend is consistent with the fact that the properties of metal clusters approach their corresponding classical values as the size of cluster is increased. The classical expressions for $C_{6}^{AA}/R_0^6$ and $C_{8}^{AA}/R_0^8$ between clusters of same sizes can be written as \[2\]

\[
C_{6}^{AA}/R_0^6 = \frac{3}{4} \omega_{Mie}
\]

\[
C_{8}^{AA}/R_0^8 = \frac{15}{2} \sqrt{\frac{5}{5 + \sqrt{6}}} \omega_{Mie}.
\]  

(14)

Here $\omega_{Mie}$ is the Mie resonance frequency given by

\[
\omega_{Mie} = \sqrt{\frac{1}{r_s^3}}
\]  

(15)

and it is equal to $1/\sqrt{3}$ bulk plasmon frequency. The classical expressions for $C_{6}^{AA}/R_0^6$ and $C_{8}^{AA}/R_0^8$ given above are derived in Ref. \[2\] by assuming that all the strength of respective multipole resonance is concentrated in a single peak. By substituting the values of $r_s$ in Eq. (14) we get following numbers for sodium clusters $C_{6}^{AA}/R_0^6 = 0.094$ and $C_{8}^{AA}/R_0^8 = 0.49$ whereas for potassium clusters $C_{6}^{AA}/R_0^6 = 0.07$ and $C_{8}^{AA}/R_0^8 = 0.37$. These classical numbers for $C_{6}^{AA}/R_0^6$ and $C_{8}^{AA}/R_0^8$ are shown by asymptotic straight lines in Figs. 1 and 2. We see from Figs. 1 and 2 that the hydrodynamic approach yields correct asymptotic values of the van der Waals coefficients or the values to which these coefficient saturate as the size of cluster grows.

To conclude, we have extended the applicability of the hydrodynamic approach within TDDFT to the calculation of higher order van der Waals coefficient $C_{8}^{AB}$ between clusters of various sizes and different species. Our results for both $C_{6}^{AB}$ and $C_{8}^{AB}$ are quite close to more accurate orbital based TDKS approach. In particular we have found that the numbers obtained by hydrodynamic approach for $C_{8}^{AB}$ are more accurate than that of $C_{6}^{AB}$. For both sodium and potassium clusters we have been able to calculate $C_{6}^{AB}$ and $C_{8}^{AB}$ coefficients for clusters containing up to 1000 atoms. Thus we have been able to get the evolution of these coefficients as a function of cluster size and have shown that they approach their respective classical values for large clusters.
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TABLE I: Dispersion coefficient $C_6$ for sodium atom clusters in atomic units (a.u.). The numbers follow the notation $3.60(3) = 3.60 \times 10^3$. The numbers in parenthesis are results of Refs. \cite{1,2}

| N  | 2     | 8     | 20    | 40    |
|----|-------|-------|-------|-------|
| 2  | 2.56(3) | 9.47(3) | 2.27(4) | 4.42(4) |
|    | (2.62(3)) | (1.02(4)) | (2.45(4)) | (4.74 (4)) |
| 8  | 3.51(4) | 8.42(4) | 1.64 (5) |
|    | (4.01(4)) | (9.55(4)) | ( 1.86 (5)) |
| 20 | 2.02(5)  | 3.93 (5) |
|    | (2.29(5)) | ( 4.45 (5)) |
| 40 |         | 7.63 (5) |
|    |         | (8.60 (5)) |

TABLE II: Dispersion coefficient $C_8^{AB}$ for sodium atom clusters in atomic units (a.u.). The numbers follow the notation $3.60(3) = 3.60 \times 10^3$. The numbers in parenthesis are results of Refs. \cite{1,2}

| N  | 2     | 8     | 20    | 40    |
|----|-------|-------|-------|-------|
| 2  | 3.08 (5) | 2.28 (6) | 8.95 (6) | 2.58 (7) |
|    | (2.97(5)) | (2.27(6)) | (9.08(6)) | (2.69 (7)) |
| 8  | 1.26(7) | 4.33 (7) | 1.15 (8) |
|    | (1.32(7)) | (4.59 (7)) | (1.25 (8)) |
| 20 | 1.35 (8) | 3.37 (8) |
|    | (1.44 (8)) | (3.67 (8)) |
| 40 |         | 8.00 (8) |
|    |         | (8.82 (8)) |
TABLE III: Dispersion coefficient $C_{6}^{AB}$ for potassium atom clusters in atomic units (a.u.). The numbers follow the notation $3.60(3) = 3.60 \times 10^3$. The numbers in parenthesis are results of Ref. [2].

| N  | 2     | 8   | 20   |
|----|-------|-----|------|
| 2  | 5.35 (3) | 2.03 (4) | 4.93 (4) |
|    | (6.28 (3)) | (2.34 (4)) | (5.48 (4)) |
| 8  | 7.70 (4) | 1.87 (5) |
|    | (8.71 (4)) | (2.02 (5)) |
| 20 | 4.55 (5) |
|    | (4.74 (5)) |

TABLE IV: Dispersion coefficient $C_{8}^{AB}$ for potassium atom clusters in atomic units (a.u.). The numbers follow the notation $3.60(3) = 3.60 \times 10^3$. The numbers in parenthesis are results of Ref. [2].

| N  | 2     | 8   | 20   |
|----|-------|-----|------|
| 2  | 8.69 (5) | 6.87 (6) | 2.77 (7) |
|    | (1.10 (6)) | (7.81 (6)) | (3.03 (7)) |
| 8  | 3.97 (7) | 1.38 (8) |
|    | (4.37 (7)) | (1.43 (8)) |
| 20 | 4.36 (8) |
|    | (4.55 (8)) |
TABLE V: Dispersion coefficient $C_6^{AB}$ for the pair interaction between sodium clusters (values of $N$ along the column) and potassium clusters (values of $N$ along row) in atomic units (a.u.). The numbers follow the notation $3.60(3) = 3.60 \times 10^3$. The numbers in parenthesis are results of Ref. [2].

| $N$ | 2    | 8    | 20   |
|-----|------|------|------|
| 2   | 3.68 (3) | 1.40 (4) | 3.40 (4) |
|     | (4.01 (3)) | (1.50 (4)) | (3.49 (4)) |
| 8   | 1.35 (4) | 5.16 (4) | 1.26 (5) |
|     | (2.16 (4)) | (8.05 (4)) | (1.88 (5)) |
| 20  | 3.25 (4) | 1.24 (5) | 3.00 (5) |
|     | (3.75 (4)) | (1.40 (5)) | (3.26 (5)) |

TABLE VI: Dispersion coefficient $C_8^{AB}$ for the pair interaction between sodium clusters (values of $N$ along the column) and potassium clusters (values of $N$ along row) in atomic units (a.u.). The numbers follow the notation $3.60(3) = 3.60 \times 10^3$. The numbers in parenthesis are results of Ref. [2].

| $N$ | 2    | 8    | 20   |
|-----|------|------|------|
| 2   | 5.21 (5) | 4.44 (6) | 1.84 (7) |
|     | (5.77 (5)) | (4.41 (6)) | (1.84 (7)) |
| 8   | 3.55 (6) | 2.23 (7) | 8.29 (7) |
|     | (4.52 (6)) | (2.91 (7)) | (1.12 (8)) |
| 20  | 1.35 (7) | 7.30 (7) | 2.45 (8) |
|     | (1.51 (7)) | (7.75 (7)) | (2.57 (8)) |
Figure captions

**Fig. 1** Plot of van der Waals coefficient $C^{AA}_{6}$ in units of $R_{0}^{6}$ of alkali-metal clusters: sodium (solid circles) and potassium (solid squares) as a function of $R_{0}$. The lines are drawn as a guide to eye and horizontal lines represent corresponding classical values of van der Waals coefficient.

**Fig. 2** Plot of van der Waals coefficient $C^{AA}_{8}$ in units of $R_{0}^{8}$ of alkali-metal clusters: sodium (solid circles) and potassium (solid squares) as a function of $R_{0}$. The lines are drawn as a guide to eye and horizontal lines represent corresponding classical values of van der Waals coefficient.
