Communication: Non-additivity of van der Waals interactions between nanostructures

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Due to size-dependent non-additivity, the van der Waals interaction (vdW) between nanostructures remains elusive. Here we first develop a model dynamic multipole polarizability for an inhomogeneous system that allows for a cavity. The model recovers the exact zero- and high-frequency limits and respects the paradigms of condensed matter physics (slowly varying density) and quantum chemistry (one- and two-electron densities). We find that the model can generate accurate vdW coefficients for both spherical and non-spherical clusters, with an overall mean absolute relative error of 4%, without any fitting. Based on this model, we study the non-additivity of vdW interactions. We find that there is strong non-additivity of vdW interactions between nanostructures, arising from electron delocalization, inequivalent contributions of atoms, and non-additive many-body interactions. Furthermore, we find that the non-additivity can have increasing size dependence as well as decreasing size dependence with cluster size.

In recent years, there has been an explosive interest in the study of organic nanomaterials. Part of the interest is motivated by microelectronic devices, with the capability to outperform traditional technology. However, due to the strong van der Waals (vdW) interactions between nanostructures, simulation of nanostructured materials presents a challenge to density functional theory (DFT). Therefore, there is a great demand for knowledge of van der Waals interactions between large molecules.

The van der Waals interaction is an important long-range intermolecular interaction arising from instantaneous collective charge fluctuations. It is much weaker than the chemical bond at equilibrium, but it may become dominant in otherwise non-bonded situations. It is ubiquitous, and many phenomena arising from it (e.g., sublimation of solids, high interlayer mobility of layered materials, and physisorption) may be “observed” in our daily life. It determines higher-order structures of biomolecular chains (e.g., DNA double helix structure2) that define biological activities. It affects many properties of molecules and π-π stacking in nucleic bases.3

In the study of vdW interactions, the central task is to calculate the vdW coefficients, which, by second-order perturbation theory, can be expressed in terms of the dynamic multipole polarizability αl(iu).4–6 Since the polarizability is highly sensitive to basis size,7 reliable calculations require a large basis set. This significantly increases computational cost. Development of a simple and yet accurate model dynamic polarizability provides an alternative solution.

Many models have been proposed8–11 to simulate αl(iu) and the vdW coefficients. In particular, Becke and Johnson8 proposed a model for vdW coefficients, based on the assumption that the vdW energy is due to the dipole interaction created by an electron and the associated exchange hole. This model can generate C6 with a mean absolute relative error (MARE) of 3% for free atom pairs. Based on this model, Steinmann and Corminboeuf12 have proposed a density-dependent dispersion correction, which seems promising. Tkatchenko and Scheffler10 proposed a method for intermolecular vdW coefficients, with good accuracy of less than 6%. Recently, Tkatchenko et al.11 developed an accurate αl(iu) to include non-additive many-body (i.e., 3-body, 4-body, ···) interactions, improving the performance of the Tkatchenko-Scheffler method for nanosystems.

It was shown11, 13, 14 that pairwise-based models can make a large error when applied to large nanostructures, due to the non-additive nature of vdW interactions. To overcome this problem, we developed a simple model15 for αl(iu), which extends the original formula16 for the dipole polarizability to the multipole one. Since our model treats the vdW interaction between two whole molecules, not the sum of pair-wise interactions between atomic fragments of the two molecules, it includes all non-additivity effects via the input static polarizability, as discussed below. It was shown10 that this model yields for free atom pairs C6, C8, and C10 in excellent agreement (3%) with accurate reference values. However, the solid-sphere model may not be suitable to cage molecules such as fullerenes.14 The reason is that the cavity affects αl(iu) via both the electron density and the frequency dependence. The solid-sphere model can capture the first effect, but not the second one.

The aim of this work is to study the non-additivity of vdW interactions between nanostructures, such as fullerenes and nanoclusters. For this purpose, we first develop a model αl(iu) for an inhomogeneous system that allows for a cavity. Based on this model, the non-additivity of vdW interactions between nanoclusters is investigated. Let us consider a shell of density, which decays rapidly outside the surface formed...
by the nuclear framework. For such a system, we define an $l$-dependent effective shell thickness by $R_l = R_n + t/2$, with $R_l$ being the $l$-dependent outer radius of the shell and $R_n$ the average radius of the nuclear framework. Then we generalize the exact dynamic polarizability of a conducting spherical shell of uniform density\cite{1,2,6,7} to a shell of inhomogeneous density. Our generalization is made by imposing the following constraints: (i) recovery of the exact static and high-frequency limits, and (ii) respect for two paradigms of condensed matter physics (slowly varying density) and quantum chemistry (one- and two-electron densities). Constraints (i) ensure the correct transfer of physics from one order to another, while constraints (ii) guarantee the consistent accuracy for different densities. A model that satisfies all four constraints is assumed to take the form

$$\alpha_l(iu) = \frac{2l + 1}{4 \pi d_l} \int_{R_l - t_l}^{R_l} d^3 r \left( \frac{r^{2l-2} d_l^4 \omega_l^2}{d_l^4 \omega_l^2 + u^2} \right) (1)$$

where $\alpha_l(iu)$ is the static multipole polarizability $\alpha_l(0)$, which can be found from the literature (e.g., Ref. 7), is needed as input. (For large systems, $\alpha_l(0)$ can be estimated from $\alpha_l(0)$; see discussion below.) Since the model respects the two paradigms, it is expected to be accurate for systems of any size. This expected size-independent performance can be understood from the energy-gap viewpoint. A remarkable feature of the present model is that it is valid for any value of $t_l$, including the $t_l/R_l = 1$ (solid-sphere) and $t_l/R_l = 0$ (large-size) limits. The general validity and nearly the same accuracy for all orders allow us to study on the same footing the vdW interactions for systems that may or may not have a cavity. The model may be simplified with the single-frequency approximation (SFA), which assumes that (i) only valence electrons are polarizable, and (ii) the density is uniform within the shell and zero otherwise. This simplified SFA takes the same expression as the full hollow-sphere model [Eq. (1)], but with $n(r)$ replaced by the average valence electron density $\bar{n} = N/V_f$. Here $N$ is the number of valence electrons, and $V_f$ is the $l$-dependent shell volume. Note that our SFA is different from the shell model (CSM).\cite{6} In SFA, the cutoff radius is determined by $R_l = |\alpha_l(0)|^{1/2l+1}$, rather than by the sharp single boundary $R_l = R_1$. While less accurate than the full hollow-sphere expression (1), it requires no detailed knowledge of the density and no numerical integration (see the supplementary material).\cite{19}

It is worth pointing out that our model is not limited to spherical systems. The non-spherical effect can enter the model via the exact static and high-frequency limits. For non-spherical systems, we use the isotropic $\alpha_l(0)$. In addition, since the energy gap is related to system size and since the energy gap can be also accounted for via $\alpha_l(0)$, the model should be valid for any system size and the accuracy should be size-independent. The general validity of the model is the most appealing feature and has been demonstrated by applying it to non-spherical H-terminated silicon cluster $H_34Si_{14}$. These and other results are reported in detail in the supplementary material.\cite{19}

Now we apply SFA to $Na_{14}-Na_{14}$ (no cavity) and $C_{60}-Na_{14}$ cluster pairs. We find that the mean absolute relative deviations of $C_6$ from the TD Hartree-Fock (TDHF) values\cite{18} are only 6% and 7%, respectively, for $N = 2$–20. To make a comparison, we repeat calculations for $C_{60}-Na_{14}$ pairs with the solid-sphere model within SFA. We find that MARE increases to 22%, which is significantly larger than that for the hollow-sphere model-SFA by a factor of 3. For a $C_{60}$ dimer, the solid-sphere model predicts $C_6 = 86.6 \times 10^2$ and $C_8 = 365.5 \times 10^2$, which are 32% and 27% smaller than the TDHF values ($C_6 = 126.5 \times 10^2$, $C_8 = 498.7 \times 10^2$).\cite{21} Next we compare the full hollow-sphere expression with SFA for $C_{60}-Li$ pair. Our calculation shows that the full hollow-sphere model ($C_6 = 8.31 \times 10^3$) is indeed closer to the experimental value $8.05 \times 10^3$ (Ref. 22) than SFA ($9.14 \times 10^3$). Finally, we apply SFA to H-terminated Si clusters from $Si_{171}H_{120}$. Calculation shows that our $C_6$ are in excellent agreement (2%) with more expensive TDFT values.\cite{22} The overall performance of the model is nearly size-independent for the clusters considered here (see Tables S5, S6, and S8 of the supplementary material), with a mean absolute relative deviation of only 4%. (TDHF has an error of 5%,\cite{22} while the error of TDHF is smaller. So they are reliable and can be used as standard for comparison.)

As an important application, we study the vdW coefficients for fullerene ($C_{N}$) pairs. For small fullerenes, $\alpha_l(0)$ can be calculated accurately from TDFT,\cite{7} while $\alpha_2(0)$ and $\alpha_3(0)$ may be estimated from CSM. For a $C_{60}$ dimer, SFA yields $C_6 = 136.7 \times 10^3$ and $C_8 = 545.2 \times 10^3$, which agree well (about 8%) with the TDHF values. However, there is a large discrepancy of $C_{10}$ between the SFA (1495 $\times 10^3$) and the literature value (446.0 $\times 10^3$)\cite{22} which arises from the error in estimating $\alpha_3(0)$. This is similar to sodium clusters.\cite{24} For instance, for $Na_{20}-Na_{20}$ SFA predicts...
$C_8 = 239 \times 10^6$ and $C_{10} = 157 \times 10^6$, while CSM (with $t=R$) yields $C_8 = 246 \times 10^6$ and $C_{10} = 169 \times 10^6$. For large fullerenes ($N \geq 110$), evaluation of $R_{np}$ is more reliable$^{25,26}$ than actual calculation of $\alpha_t(0)$, due to the basis size issue. Here instead of taking $\alpha_t(0)$ from the literature,$^{26,27}$ we estimate it from $\alpha_t(0) = (R_{np} + t_1/2)^3$, in which $t_1$ is obtained from $t_1 = 3.24 + 0.16(N - 110)/N + 1$, an interpolation between the thickness of $C_{110} (3.24)$ and the large-$N$ limit (3.4).$^{27}$ We apply this formula to calculate $\alpha_t(0)$ for $C_{50}$ ($t_1$), $C_{70}$ ($D_{5h}$), $C_{78}$ ($C_{2v}$), and $C_{84}$ ($D_2$), using the $R_{np}$ estimated from Ref. 25. The results are 525, 638, 733, and 811, respectively, which are in good agreement (about 2%) with TDHF$^{28}$ ($537, 659, 748, 806$). This simple method provides the best estimates of $\alpha_t(0)$ for large fullerenes. They are tabulated as input in Table S1 of the supplementary material.$^{19}$ An error in the estimate of $\alpha_t(0)$ may carry over twice that error to $C_6$ and slightly more to $C_8$.

The atom pairwise picture$^{26,30}$ is perhaps the most popular method for the evaluation of $C_{N}$ between large systems. In this picture, the $C_{2k}$ are obtained as a sum of atom pair interactions, where each pair involves one atom from each of the two systems. Because of simplicity, it has been widely used$^{8,29,31,32}$ in chemistry and physics. However, examination of its validity has been focused on small molecules. Here we will examine it for a variety of nanocluster pairs. For a cluster pair with $M$ atoms in cluster A and $N$ in cluster B, the vdW coefficients per atom pair is$^{33}$ $C_{2k}/MN$. If all the atoms of a cluster make equal contributions (as for $C_{2k}$ in the simplest version of the atom pairwise picture), $C_{2k}$ per atom pair should be nearly size-independent.$^{14}$ To our surprise, this picture only works fairly well with $C_6$ for Si$_{4N}$-Si$_N$ (no cavity), but not for other cluster pairs, as shown in Fig. 1. From Figs. 1(a) and 1(b) we see that $C_6$ per atom pair for $C_{A}$-$C_{N}$ exhibits very strong non-additivity, leading to a rapidly increasing trend with $N$,$^{11,14,28}$ while the trend is opposite for Na$_{A}$-Na$_{N}$. Figure 1(d) shows an oscillating increasing trend for Ge$_N$-Ge$_N$, suggesting a very possible failure of this picture, as $N$ increases. Our calculation also shows that, for $C_{60}$-Na$_{N}$, $C_6$ per atom pair displays a decreasing trend with $N$, like Na$_{A}$-Na$_{N}$, while for a fixed $N$, C$_M$-Na$_{N}$ shows an increasing trend with $M$. The failure to follow the normal $N \times M$ size dependence is more serious for Na$_M$-Na$_{N}$, C$_M$-Na$_{N}$, and C$_N$-C$_X$ than for Ge$_N$-Ge$_N$. In the bulk ($N \rightarrow \infty$) limit, in which the energy gap in C$_X$ (graphene) and Na$_{N}$ vanishes, the (valence) electrons are nonlocal and the non-additivity of vdW interactions is so strong that the pairwise picture completely fails.$^{14,34}$ Even with finite energy gap, it may produce a large error, as observed in H-terminated Si clusters$^{11}$ and other systems.$^{35-37}$

From this study, we see that non-additivity of vdW interactions may arise from electron delocalization (or energy gap) and/or from nonadditive many-body interactions,$^{11,13}$ and/or from inequivalent contributions of each atom pair,$^{14}$ in which atoms further from the center contribute more, and this inequivalence increases from the leading-order to higher-order coefficients. While these effects have strong size-dependence and are included in our model via the input $\alpha_t(0)$, they are missing in the standard atom pairwise picture. Consequently, the error of this picture grows with system size and may affect the performance of other pairwise-based models for nanostructures.$^{11}$

In order to get a fuller understanding of the shape and size effects, we imagine modifying $C_6$ in each of four ways that change the vdW coefficients (or the vdW coefficients per atom pair) between two modified fullerenes. (a) First, we fix the number of valence electrons $N$ and the outer radius $R_l$ of the shell, while varying $t_1$ from 0 to $R_l$. This corresponds to compressing or expanding the material in the shell without changing the outer radius. The result is plotted in Fig. 2(a). It is observed from Fig. 2(a) that, relative to the $t_1 = 0$ case, $C_6$ (or $C_7$ per atom pair) monotonically increases with $t_1$ and reaches a maximum as the shell evolves into a solid sphere, suggesting that the non-additivity increases with shell thickness. However, $C_6$ and $C_{10}$ display a local maximum and then drop to a minimum, which is slightly larger than the $t_1 = 0$ value. (b) Then we hold $N$ and the valence electron density fixed, while varying $t_1$ and $R_l$. When $t_1$ is equal to $R_l$, the shell collapses into a solid sphere. This corresponds to changing

![FIG. 1. $C_6$ per atom pair in SFA and CSM vs. cluster size for (a) Na$_{4N}$-Na$_N$, (b) C$_N$-C$_X$, (c) Si$_{4N}$-Si$_N$, and (d) Ge$_N$-Ge$_N$. $C_6/N^2$ tends to increase or decrease with $N$ according as $\alpha_t(0)/N$ does.](image)

![FIG. 2. Effects on the vdW coefficients in CSM due to identical modifications of each half of a C$_{60}$-C$_{60}$ pair. Panel (a): $N$ and $R_l$ are held fixed. At $t = 0$, $C_6 = 0.033 \times 10^6$, $C_8 = 0.123 \times 10^6$, $C_{10} = 0.382 \times 10^6$. Panel (b): $N$ and the average valence electron density $n$ are held fixed. Panel (c): $R_l$ and $n$ are held fixed. Panel (d): $R_l$ and $R_l$ are held fixed. The parameters fixed at their C$_{60}$ values are $N = 240$, $t = 2.8$, $R_l = 8.1$, $n = 0.150$.](image)
the way in which the uncompressed and unexpanded material is shaped. The vdW coefficients reach a minimum at $t_i = R_i$, because the radius of the shell is smallest in this case and so is the static polarizability. When $t_i$ tends to zero, $R_i \to \infty$ as $(1/t_i)^{1/2}$. This makes the polarizability grow rapidly and so do the vdW coefficients, as shown in Fig. 2(b). This leads to the decrease of non-additivity. (c) Next, we hold $R_i$ and the valence electron density at our $C_{60}$ value, but vary $t_i$ from its $C_{60}$ value to $R_i$. This shows the effect on $C_6$, $C_8$, and $C_{10}$ of gradually filling in the cavity with about 23 additional atoms. From Fig. 2(c) we see that all the coefficients increase with $t_i$, but with the strongest effect on $C_6$, followed by $C_8$ and $C_{10}$. In particular we observe that atoms further from the center contribute more to the vdW coefficients, and especially to the higher-order ones. This results in the increase of non-additivity. (d) Finally we fix $R_i$ and $t_i$ at our $C_{60}$ values, but vary the atom number $M$ from 0 to 60. This shows the effect of filling in vacancies in the single-walled fullerene. We observe from Fig. 2(d) that the ratio of the vdW coefficients to their $M = 60$ values grows with $M$ rapidly, leading to the increase of non-additivity as well.

In conclusion, we have developed a model $\alpha_{ij}(iu)$ for inhomogeneous systems that allow for a cavity. The vdW coefficients generated from this model are consistently accurate for both small and large molecules (i.e., no size dependence). The coefficients generated from this model are consistently accurate.


33. There is a small additional contribution for $C_6$ and $C_{10}$ given by $21C_j \Sigma_{M_i} \Sigma_{\mu_\lambda} \Sigma_{\mu_\lambda} \Sigma_{\mu_\lambda} \Sigma_{\mu_\lambda} \Sigma_{\mu_\lambda} \Sigma_{\mu_\lambda} \Sigma_{\mu_\lambda}$ and $\Sigma_{M_i} \Sigma_{\mu_\lambda} \Sigma_{\mu_\lambda} \Sigma_{\mu_\lambda} \Sigma_{\mu_\lambda} \Sigma_{\mu_\lambda} \Sigma_{\mu_\lambda} \Sigma_{\mu_\lambda}$ respectively. Here $\delta_i = |R_i - r_j|$ and $r_j$ is the distance of atom pairs.


