Spherical-Shell Model for the van der Waals Coefficients between Fullerenes and/or Nearly-Spherical Nano-Clusters

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Abstract: Fullerene molecules such as C_{60} are large nearly-spherical shells of carbon atoms. Pairs of such molecules have a strong long-range van der Waals attraction that can produce scattering or binding into molecular crystals. A simplified classical-electrodynamics model for a fullerene is a spherical metal shell, with uniform electron density confined between outer and inner radii (just as a simplified model for a nearly-spherical metallic nano-cluster is a solid metal sphere or filled shell). For the spherical-shell model, the exact dynamic multipole polarizabilities are all known analytically. From them, we can derive exact analytic expressions for the van der Waals coefficients of all orders between two spherical metal shells. The shells can be identical or different, and hollow or filled. To connect the model to a real fullerene, we input the static dipole polarizability, valence-electron number, and estimated shell thickness t of the real molecule. Our prediction for the leading van der Waals coefficient C_6 between two C_{60} molecules $(1.30 \pm 0.22) \times 10^5$ hartree bohr⁶) agrees well with a prediction for the real molecule from time-dependent density functional theory. Our prediction is remarkably insensitive to t . Future work might include the prediction of higher-order (e.g., C_8 and C_{10}) coefficients for C_{60} , applications to other fullerenes or nearly-spherical metal clusters, etc. We also make general observations about the van der Waals coefficients.

1. Introduction

Two spherical objects A and B at rest far apart have an attractive long-range van der Waals attraction

$$E_{\text{vdW}} = -C_6 / r^6 - C_8 / r^8 - C_{10} / r^{10} - \dots, \quad (1)$$

where r is the distance between their centers. Eq. (1) is an asymptotic expansion for $r \rightarrow \infty$, valid when the overlap between the two densities is negligible. Standard semilocal density functionals for the exchange-correlation energy produce interaction only through density overlap, so full nonlocality is needed to capture long-range interactions like those in Eq. (1). Although modern density functional theory is 46 years old, it is only within the past decade or two that it has started to wrestle with Eq. (1). David Langreth and collaborators introduced fully nonlocal functionals that can capture much of the van der Waals interaction [1]. Alternatively, the van der Waals coefficients can be computed in various ways, and then Eq. (1) (multiplied by a function that cuts off the small- r contribution) can be added [2,3,4] to the short-range interaction given by a semilocal functional. We have recently introduced a nonempirical approximation [5,6] that inputs only the static multipole polarizabilities and electron densities of the two objects, and outputs values of C_6 , C_8 , and C_{10} with a mean absolute relative error of only 3% for typical atom pairs [6].

The three coefficients displayed in Eq. (1) arise from second-order perturbation theory in the electron-electron interaction [7]:

$$C_{2k}^{AB} = \frac{(2k-2)!}{2\pi} \sum_{l_1=1}^{k-2} \frac{1}{(2l_1)!(2l_2)!} \int_0^\infty du \alpha_{l_1}^A(iu) \alpha_{l_2}^B(iu) , \quad (2)$$

where $l_2 = k - l_1 - 1$. Here $\alpha_{l_1}^A(iu)$ is the 2^{l_1} -pole dynamic polarizability of system A, evaluated at imaginary frequency $\omega = iu$: $l=1$ (dipole), $l=2$ (quadrupole), $l=3$ (octupole), etc. While $\alpha_l(\omega)$ can have singular behavior for real ω , $\alpha_l(iu)$ is typically a smooth function of u . For example, in a uniform metal the long-wavelength dielectric function $\varepsilon(\omega) = 1 - \omega_p^2 / \omega^2$ has a zero at $\omega = \omega_p$, the plasma frequency, while $\varepsilon(iu) = 1 + \omega_p^2 / u^2$ has a featureless inverse. We use atomic units, in which $\hbar = e^2 = m = 1$, with distances in bohr and energies in hartree.

The simplest case of Eq. (2),

$$C_6^{AB} = \frac{3}{\pi} \int_0^\infty du \alpha_1^A(iu) \alpha_1^B(iu) , \quad (3)$$

requires only the dipole polarizabilities, which describe the induced linear response p of the electric dipole moment to a weak external uniform electric field E oscillating at frequency ω :

$$p(\omega) = \alpha_1(\omega)E(\omega). \quad (4)$$

The physical picture behind Eq. (1) is that zero-point fluctuations of the electron density on A correlate with and interact coulombically with those on B, and vice versa.

In this work, we will discuss a spherical-shell model for objects A and B, in which all the dynamic polarizabilities have exact analytic expressions (within the limitations of classical electrodynamics) and all the integrals in Eq. (2) can be evaluated analytically. The model is relevant to fullerene molecules and to nearly-spherical metallic clusters. After we find an explicit analytic expression for C_6^{AB} , we will apply it to compute this leading van der Waals coefficient for the interaction of two C_{60} buckyballs, demonstrating reasonable agreement with the predictions of costly time-dependent density functional theory for the real molecules, and so supporting the validity of the model. Finally, we will discuss possible future applications of the model.

2. Spherical Metal Shell Model and Its Dynamic Multipole Polarizabilities

Let each object be a classical spherical metal shell of thickness t , with an electron density that is a constant n between an outer radius R and an inner radius $R-t$ with $0 \leq t \leq R$, and 0 otherwise. The dynamic multipole polarizabilities are given exactly by Eq. (5) of Ref. [8]. Setting $\varepsilon_i = \varepsilon_e = 1$ and $\varepsilon = 1 + \omega_p^2 / u^2$, where $\omega_p^2 = 4\pi n$ is the plasma frequency, we find

$$\alpha_l(iu) = R^{2l+1} \frac{\omega_l^2}{\omega_l^2 + u^2} \frac{1 - \rho_l}{1 - \beta_l \rho_l}, \quad (5)$$

where

$$\beta_l = \frac{\omega_l^2 \tilde{\omega}_l^2}{(\omega_l^2 + u^2)(\tilde{\omega}_l^2 + u^2)}, \quad (6)$$

$$\rho_l = \left(\frac{R-t}{R} \right)^{2l+1}. \quad (7)$$

Here

$$\omega_l = \omega_p \sqrt{l/(2l+1)} \quad (8)$$

Is the natural frequency of the l -th normal mode or surface plasmon in a solid metal sphere, and

$$\tilde{\omega}_l = \omega_p \sqrt{(l+1)/(2l+1)}. \quad (9)$$

Some limiting cases of Eq. (5) are worth noting. If the density n and the outer radius R are held fixed, then

$$\lim_{t \rightarrow 0} \alpha_l(iu) = 0 \quad (\text{vanishing shell, } u > 0), \quad (10)$$

$$\lim_{t \rightarrow R} \alpha_l(iu) = R^{2l+1} \frac{\omega_l^2}{\omega_l^2 + u^2} \quad (\text{solid sphere}), \quad (11)$$

$$\lim_{u \rightarrow 0} \alpha_l(iu) = R^{2l+1} \quad (\text{universal static limit}), \quad (12)$$

$$\lim_{u \rightarrow \infty} \alpha_l(iu) \sim R^{2l+1} (1 - \rho_1) \omega_l^2 / u^2 \rightarrow 0 \quad (\text{high-frequency limit}). \quad (13)$$

For Eq. (13), note that $R^3(1 - \rho_1)\omega_1^2 = N$.

The universal static limit of Eq. (12) is at first surprising: The static polarizability persists even in the limits $n \rightarrow 0$ or $t \rightarrow 0$ in which the shell vanishes. But the same kind of effect is also evident in the familiar classical static dipole polarizability R^3 of a solid sphere of metal with radius R and density n . The classical-physics formulas of course may fail when pushed too hard. They are designed for simple metals, and should also work best when R , n , and t are all large enough.

Other limits are

$$\lim_{n \rightarrow \infty} \alpha_l(iu) = R^{2l+1} \quad (\text{high-density limit}), \quad (14)$$

$$\lim_{n \rightarrow 0} \alpha_l(iu) = 0 \quad (\text{low-density limit, } u > 0). \quad (15)$$

3. Evaluation of C_6 between Two Spherical Shells

Inserting Eqs. (5)-(7) into Eq. (3) yields

$$C_6^{AB} = \frac{3}{2}(1-\rho_1^A)(1-\rho_1^B)\alpha_1^A(0)\alpha_1^B(0)F^{AB}, \quad (16)$$

$$F^{AB} = \frac{\omega_{1A}^2 \omega_{1B}^2}{E^{AB}} \sum_{i=1}^3 \left[\frac{f_i^{AB}(a_A, a_B; b_A, b_B)}{D(a_A, a_B)} + \frac{f_i^{AB}(b_A, b_B; a_A, a_B)}{D(b_A, b_B)} \right], \quad (17)$$

$$E^{AB} = (a_A^2 - b_A^2)(a_A^2 - b_B^2)(a_B^2 - b_A^2)(a_B^2 - b_B^2). \quad (18)$$

In Eqs. (17) and (18),

$$a = \frac{1}{\sqrt{2}} \left[(\omega_1^2 + \tilde{\omega}_1^2) - \sqrt{(\omega_1^2 - \tilde{\omega}_1^2)^2 + 4\rho_1 \omega_1^2 \tilde{\omega}_1^2} \right]^{1/2}, \quad (19)$$

$$b = \frac{1}{\sqrt{2}} \left[(\omega_1^2 + \tilde{\omega}_1^2) + \sqrt{(\omega_1^2 - \tilde{\omega}_1^2)^2 + 4\rho_1 \omega_1^2 \tilde{\omega}_1^2} \right]^{1/2}. \quad (20)$$

$$D(x, y) = xy(x + y), \quad (21)$$

$$f_1^{AB}(p, q; s, t) = (pq)^4 + (pq)^3(s^2 + t^2) - pq(st)^2(p^2 + pq + q^2), \quad (22)$$

$$f_2^{AB}(p, q; s, t) = -(\tilde{\omega}_{1A}^2 + \tilde{\omega}_{1B}^2)[(pq)^2(p^2 + pq + q^2 - s^2 - t^2) - pq(st)^2], \quad (23)$$

$$f_3^{AB}(p, q; s, t) = \tilde{\omega}_{1A}^2 \tilde{\omega}_{1B}^2 [p^4 + p^3q + p^2q^2 + pq^3 + q^4 - (p^2 + pq + q^2)(s^2 + t^2) + (st)^2]. \quad (24)$$

Note the expected symmetry between A and B in the expression for C_6^{AB} .

As a check on Eq. (16), we have evaluated it in the limit where both shells become solid spheres ($\rho_1^A = \rho_1^B = 0$). The result is simple,

$$C_6^{AB} = \frac{3}{2} \alpha_1^A(0) \alpha_1^B(0) \omega_1^A \omega_1^B / (\omega_1^A + \omega_1^B) \quad (\text{solid spheres}), \quad (25)$$

and agrees with the exact formula of Eq. [S5] of Ref. 6.

Our Eq. (16) for C_6^{AB} properly vanishes when the density or thickness of either spherical shell vanishes at fixed R , but it becomes very large when the product

$\alpha_1^A(0)\alpha_1^B(0)=R_A^3R_B^3$ becomes large for fixed densities and thicknesses. Thus the large size of fullerene molecules suggests large C_6 coefficients between them.

If C_6^{AB} could be found by adding up pairwise van der Waals interactions of atoms in object A with atoms in object B, then we would expect the right side of Eq. (16) to be proportional to the product of the shell volume of A with that of B. The first factors in Eq. (16) show this expected behavior, but the F^{AB} factor has its own dependence upon ρ_1^A and ρ_1^B , i.e., upon the shapes of the two spherical shells. Aside from this dependence, F^{AB} depends only upon the densities n_A and n_B . When $A=B$, $F^{AB} \sim n^{1/2}$.

4. Choice for the Inputs R , n , and t

To apply Eqs. (5) or (16) to real fullerenes and other nearly-spherical molecules or clusters, we need to know how to choose R , n , and t . In view of the critical role [5,6] played by the static dipole polarizability, it is natural to invoke Eq. (12):

$$R = \alpha_1(0)^{1/3}. \quad (26)$$

Since our model density is a better model for the polarizable valence electrons than for the localized and rigid core electrons, we take the number N of electrons within the spherical shell to be the number of valence electrons. If the object is made up of atoms labeled by index i , each with valence z_i , then

$$N = \sum_i z_i, \quad (27)$$

so that $N=60(4)=240$ for C_{60} . The volume of the shell is $V = (4\pi/3)[R^3 - (R-t)^3]$, so

$$n = N/V = 3N / [(4\pi)t(3R^2 - 3Rt + t^2)]. \quad (28)$$

The thickness t is not so easy to define. Perhaps the best approach would be to adjust t to recover the static quadrupole polarizability of the nearly-spherical object of interest, if known. Below we will take a simpler approach to estimate t for C_{60} .

5. Application to C_6 for a Pair of Buckyballs, and for a Pair of Carbon Atoms

The experimental value [9] for the static dipole polarizability of C_{60} is 516 ± 54 bohr³. This quantity is difficult to calculate accurately for such a large molecule, using for example the GAUSSIAN code [10], because it is remarkably sensitive to method and basis set. The valence electron number is $N = 60(4) = 240$ from Eq. (28). Since in the local density approximation all nuclei are at a distance $R_n = 6.68$ bohr from the center, we estimate $t = 2(R - R_n)$. Then from Eq. (16) we find $C_6 = 130,00 \pm 22,000$ hartree bohr⁶ between two C_{60} molecules ($A=B$) from our spherical-shell model, which agrees well with the adiabatic LDA (ALDA) [14] value of 126,500 hartree bohr⁶ from time-dependent density functional theory [15]. The ALDA value contains atomistic details not present in the spherical-shell model, but it also makes physical and computational approximations whose accuracy we cannot assess.

A single free C atom is small enough that we can calculate its static dipole polarizability (11.7 bohr³) by an accurate correlated-wavefunction method (CCSD(T)-frozen core) with a large basis set (aug-cc-pvtz). This value is well converged with respect to basis set and correlation method. It agrees well with Moeller-Plesset second-order perturbation theory MP2/aug-cc-pVQZ (11.6 bohr³) and Hartree-Fock HF/aug-cc-pVQZ (12.0 bohr³) results. We have also compared MP3, MP4 and core correlated results, and all support our value. Within the solid-sphere model for the free C atom, we then find $C_6 = 60.0$ hartree bohr⁶ between two such atoms. The crude model of pairwise van der Waals interactions between constituent free atoms gives $C_6(C_{60}) = (60)^2 C_6(C) = 216,000$ hartree bohr⁶, which is as expected [2,16] much too large. It is expected that the polarizability per atom in the molecule will be smaller than the polarizability of the free atom, an effect which (in the limited basis sets for which we can handle C_{60}) we observe for the Hartree-Fock and correlated-wavefunction methods but *not* for the local density approximation (LDA) or the generalized gradient approximation. The C_6 value estimated in Ref. [2] for a non-free carbon atom in an sp^2 hybridization state is 27.3 hartree bohr⁶, and a larger value (up to 33 hartree bohr⁶) has been proposed in Ref. [16]. This larger value gives $C_6(C_{60}) = (60)^2(33) = 118,800$ hartree bohr⁶.

For the free C atom, a sophisticated calculation [17] gives $C_6 = 46.6$ hartree bohr⁶, 22% less than our solid-sphere model. We might expect the spherical-shell model to be more accurate for a large molecule like C_{60} than for a single atom like free C.

Figure 1: Plot of the spherical-shell-model C_6 for a pair of buckyballs, as a function of the thickness t of the shell, for fixed C_{60} inputs $\alpha_1(0) = 516 \pm 54$ bohr³ and $N = 240$ electrons. The solid-sphere limit has $t = R \sim 8$ bohr.

Figure 1 plots our spherical-shell model value for C_6 as a function of shell thickness t for fixed static dipole polarizability $\alpha_1(0)$ and fixed valence electron number N . The result is fortunately not sensitive to t . The reason is that, under these conditions, different values of t correspond to different ways of connecting fixed zero-frequency and high-frequency behaviors, as can be seen from Eqs. (10) and (11).

6. Conclusions and Future Directions

The model of a spherical metal shell provides a simplified but quasi-realistic electron density for a fullerene or a nearly-spherical metal particle. For this model, we have presented analytic expressions for the dynamic multipole polarizabilities (Eq. (5)) and van der Waals C_6 coefficient (Eq. (16)), which are exact at the level of classical

electrodynamics. Our model inputs the static dipole polarizability (a quantity that can be calculated for a real molecule or cluster within ground-state density functional theory), the valence electron number, and the static dipole polarizabilities of the constituent atoms.. Applied to the buckyball C_{60} , it predicts $C_6 = 130,000 \pm 22,000$ a.u., with an accuracy possibly comparable to that of the computationally much more demanding but inexact ALDA ($C_6 = 126,500$ a.u.) [14]. As expected, these values are vastly greater than those for atom pairs [6], and can be estimated only very roughly from free-atom pair interactions.

A natural next step would be to evaluate the higher-order van der Waals coefficients C_8 and C_{10} for the interaction between two C_{60} molecules, which are of current interest [18,19]. This presents a greater challenge to the model. If we do not input atomistically-calculated static quadrupole and octupole polarizabilities ($\alpha_2(0)$ and $\alpha_3(0)$), then we must rely more on the model density itself or on the insensitivity of the van der Waals coefficients to details of the density. Since Eq. (1) is expected to be valid for $r > R_A + R_B$, we can investigate the importance of the higher-order terms and the summability of the infinite series in this region.

A further step would be to test the model for other fullerenes, spherical metal clusters, etc. Moreover, the analytic nature of the model may suggest useful semi-empirical estimates for the van der Waals coefficients.

A final step would be to use this model to test the expressions we have presented recently [5,6] for C_6 , C_8 , and C_{10} between any two spherical densities. Those nonempirical expressions interpolate the multipole polarizabilities between exact zero- and high-frequency limits, are surprisingly accurate (within about 3%) for atom pairs, and are exact by construction for solid metal spheres but *not* for hollow spherical metal shells. They include atomistic details washed out in the spherical-shell model.

The expressions we have presented in Refs. [5,6] are explicit, nonlocal density functionals for the van der Waals coefficients. But in them the static multipole polarizabilities are inputted from correlated-wavefunction calculations, or at least from Kohn-Sham orbital calculations. Eq. (12) of this paper shows clearly that the static multipole polarizabilities, although they are ground-state properties, cannot be expressed in any general and usefully simple way as explicit functionals of the density, since for a spherical metal shell they are R^{2l+1} , independent of both n and t .

For a real atom or molecule, the static multipole polarizabilities are remarkably sensitive to method and basis set, while the electron density is not. For example, we find that the LDA static dipole polarizability of the C atom is 9.1 bohr^3 with a 6-311+G*

basis and 13.5 bohr^3 with an aug-cc-pvqz basis; neither is very close to the accurate 11.7 bohr^3 from CCSD(T) with an aug-cc-pvtz basis. We suggest that the variation of the van der Waals coefficients with method or basis set can be found from our expressions of Refs. [5,6] by inputting the respective multipole polarizabilities.

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