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Auayporn Jiemchooroj, Bo E. Sernelius and Patrick Norman

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C_6 dipole-dipole dispersion coefficients for the *n*-alkanes: Test of an additivity procedure

A. Jiemchooroj, Bo E. Sernelius, and P. Norman

Department of Physics and Measurement Technology, Linköping University, SE-581 83 Linköping, Sweden

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We report on calculations of the dipole-dipole dispersion coefficients for pairs of *n*-alkane molecules. The results are based on first-principles calculations of the molecular polarizabilities with a purely imaginary frequency argument and which were reported by us in a previous work [P. Norman, A. Jiemchooroj, and Bo E. Sernelius, J. Chem. Phys. **118**, 9167 (2003)]. The results for the static polarizabilities and dispersion coefficients are compared to simple algebraic expressions in terms of the number of C—C and C—H bonds in the two weakly interacting species. The bond additivity procedure is shown to perform well in the present case, and bond polarizabilities of 4.256 and 3.964 a.u. are proposed for the C—H and the C—C bond, respectively.

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Dynamic simulations of the weak dispersion interactions within, or in between, complex molecules, such as, for instance, in protein folding [1], are computationally intensive, and in order to reduce the computational cost it is desirable to use simple, but still accurate, model potentials. Such potentials may be based on quantum chemical calculations, but for large molecules this part of the simulation will become a bottleneck. One may then reduce the problem further by studying contributions to the potentials from different molecular groups, i.e., using a so-called additivity procedure [2]; in the extreme case one adds the contributions from the smallest polarizable entities in the molecules which are atoms or bonds. In the present work we have determined the van der Waals interaction between pairs of *n*-alkane molecules using the polarizabilities obtained from accurate polarization propagator calculations. We have furthermore found simple parametrizations where the result can be expressed in terms of the number of C—C and C—H bonds in each of the two interacting species.

The dipole-dipole interaction between two atoms or molecules i and j is given by the Casimir-Polder potential [3,4]

$$V_{\rm CP}(r) = -\frac{\hbar}{\pi r^6} \int_0^\infty d\omega \alpha_i(i\omega) \alpha_j(i\omega) e^{-2\omega r/c} [3 + 6(\omega r/c) + 5(\omega r/c)^2 + 2(\omega r/c)^3 + (\omega r/c)^4], \qquad (1)$$

where $\alpha_i(i\omega)$ and $\alpha_j(i\omega)$ are the isotropic averages of the dynamic polarizabilities of the two atoms or molecules evaluated on the imaginary frequency axis. This result covers both the van der Waals and Casimir regions of the interaction; the van der Waals region at intermediate separations; the Casimir region at larger separations. We are here concerned with the van der Waals region, and then the integral reduces to

$$V_{\rm vdW}(r) = -\frac{3\hbar}{\pi r^6} \int_0^\infty d\omega \alpha_i(i\omega) \alpha_j(i\omega) = -\frac{C_{6,ij}}{r^6}, \qquad (2)$$

where $C_{6,ij}$ is the dipole-dipole dispersion coefficient.

London [5] was first to correctly explain the van der Waals interaction. He used the so-called London approximation for the atomic polarizability. In this approximation one needs two parameters, only: the static polarizability, $\alpha_i(0)$, and one dominating excitation energy of the atom, $\hbar \omega_{1,i}$. Expressed in terms of these two parameters, the dynamic polarizability is written as

$$\alpha_i(i\omega) = \alpha_i(0)/[1 + (\omega/\omega_{1,i})^2]. \tag{3}$$

Using this approximation in Eq. (2) gives for heteronuclear dimers [6–8]

$$C_{6,ij} = -r^{6}V_{\rm vdW}(r) = 3\hbar\omega_{1,i}\hbar\omega_{1,j}\alpha_{i}(0)\alpha_{j}(0)/[2(\hbar\omega_{1,i} + \hbar\omega_{1,j})]$$
(4)

and for homonuclear dimers it reduces to

$$C_{6,ii} = 3\hbar\omega_{1,i}\alpha_i(0)^2/4.$$
 (5)

Results for the dispersion parameter obtained from this approximation turn out to be very accurate [4,9,10]. In practice, the static polarizability is often well known from experiments or calculations whereas the effective frequency ω_1 is used to fit the potential between the homonuclear dimers. Then the same choice of parameters will also be employed for different combinations of heteronuclear dimers. One should note that the effective or characteristic frequency cannot be identified by a specific electronic transition within the atom. It should be considered a fitting parameter. The reason the very simple London approximation works is that the true polarizability on the imaginary frequency axis is a monotonically decreasing function with suppressed features. The characteristic frequency used in the approximation is a measure of how "broad" the function is. The London approximation would on the real frequency axis give a bad fit to the true polarizability; on this axis the true polarizability has many sharp features associated with the electronic transitions.

The same expression, Eq. (3), can also be used for molecules. A straightforward extension or refinement of Eq. (3) in the case of molecules would be to sum over the contributions from the most polarizable entities of the molecule.



FIG. 1. Static polarizabilities for the n-alkanes The filled circles are from first-principles quantum chemical calculations [11], while the straight line is the fit to Eq. (6).

These are known to be the covalent bonds [2]. Thus the summation runs over the bonds, not over the atoms making up the molecule. In this summation each term is of the type given in Eq. (3).

In Fig. 1 we have plotted the angular averaged static polarizabilities for the *n*-alkanes. The filled circles are the results from a polarization propagator calculation based on density-functional theory with the hybrid B3LYP exchange correlation functional [11]. These results are in close agreement with experimental results, see Ref. [11] for a comparison. It is our intention in the present work to investigate the applicability of a simple bond additive procedure to obtain the static polarizabilities for the members of the *n*-alkanes. We will employ a model for the polarizability as follows:

$$\alpha_i(0) = n_i \alpha_0 + m_i \alpha_1, \tag{6}$$

where n_i and m_i are the number of C—H and C—C bonds, respectively, of molecule *i*. When fitted to the results in Table I, the values of the two parameters become α_0 =4.256 a.u. and α_1 =3.964 a.u., respectively. The polarizabilities obtained from the bond additive procedure are included in Table I and Fig. 1 (solid line). We note that these parameters representing the polarizabilities for the C—H and C—C bonds in saturated compounds differ from the ones found in Ref. [2]. The values quoted there are 4.4 a.u. and 3.2 a.u., respectively. Thus, in our calculation the polarizability of the C—C bond has increased on expense of the C—H bond polarizability.

If one applies the expression for the London atomic polarizability in Eq. (3) to the molecular case and uses this to represent the polarizabilities of the *n*-alkanes, there is a very small spread in the so obtained characteristic frequencies. The values of $\omega_{1,i}$ are in the range of 0.569–0.579 a.u. when determined from the relation $\omega_{1,i}=4C_{6,ii}/3\hbar\alpha_i(0)^2$, i.e., the inverse of Eq. (5). This fact gives us the possibility to represent the complete set of molecules by the same characteristic frequency; we choose the average value ($\bar{\omega}_1=0.573$ a.u.) of the found characteristic frequencies. From Eq. (4), with one and the same characteristic frequency, we thereby obtain

TABLE I. Static polarizabilities $\alpha_i(0)$ and dipole-dipole dispersion coefficients $C_{6,ii}$ for the *n*-alkanes. All quantities are given in atomic units.

		$\alpha_i(0)$		C _{6,ii}			
Molecule	DFT ^a	DOSD ^b	Fitted ^c	DFT ^a	DOSD ^b	Predicted ^d	
CH ₄	17.20	17.27	17.02	127.1	129.6	124.5	
C_2H_6	29.37	29.61	29.50	372.6	381.8	374.0	
C_3H_8	41.84	42.09	41.98	752.6	768.1	757.4	
$C_{4}H_{10}$	54.41	54.08	54.45	1269	1268	1274	
$C_{5}H_{12}$	67.06	66.07	66.93	1922	1905	1925	
$C_{6}H_{14}$	79.53	78.04	79.40	2704	2650	2709	
C7H16		90.02	91.88		3525	3628	
$C_{8}H_{18}$		102.0	104.4		4521	4684	

^aReference [11].

^bCH₄—Ref. [12]. For the rest see Ref. [13].

^cThe fit to the DFT/B3LYP result using Eq. (6).

^dThe predicted result by using Eq. (8).

$$C_{6\,ii} = 3\hbar\bar{\omega}_1 \alpha_i(0)\alpha_i(0)/4 \tag{7}$$

and our parametrized expression for the dispersion coefficient becomes

$$C_{6,ii} = 3\hbar \bar{\omega}_1 (n_i \alpha_0 + m_i \alpha_1) (n_i \alpha_0 + m_i \alpha_1)/4.$$
(8)

In Table I we present the static polarizabilities and the dipole-dipole dispersion coefficients for a pair of identical molecules. The first column of the results for the static polarizability is our result from the polarization propagator calculation [11]; the second is from a pseudospectral dipoleoscillator-strength-distribution calculation based on experimental results [12,13]; the third is from the bond additivity procedure as expressed in Eq. (6). From these results it is clear that the molecular polarizability can be accurately decomposed into bond polarizabilities. We recall, however, that the present study is concerned only with saturated hydrocarbons, and the same attempt is likely to be less successful for unsaturated, π -conjugated, systems.

Once we have established the possibility to obtain a quantitatively correct decomposition of the molecular static polarizability, the dispersion interaction potential can be addressed. If being accurate, Eq. (8) represents a powerful means to determine the interaction between extended n-alkanes. Table I includes a comparison between dispersion coefficients obtained in the bond additive procedure and those obtained from first-principles quantum chemical calculations as well as experiment. The first column of the table is from Eq. (2) where the dynamic polarizabilities on the imaginary frequency axis were obtained in our polarization propagator calculation [11]; the second column is from Refs. [12,13]; the third column is the result of Eq. (8). The accuracy of the predicted results is striking.

Table II displays the results for the dispersion coefficients for all combinations of pairs of n-alkane molecules with six or fewer carbon atoms. These values were obtained from Eq. (2) where the dynamic polarizabilities on the imaginary fre-

TABLE II. Dipole-dipole dispersion coefficients $C_{6,ij}$ (a.u.) for the *n*-alkanes. Results are obtained at the DFT/B3LYP level of theory and with use of Eq. (2).

Molecule	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C ₆ H ₁₄
CH ₄	127.1	217.6	309.2	401.5	494.2	586.1
C_2H_6		372.6	529.5	687.5	846.4	1004
C ₃ H ₈			752.6	977.1	1203	1426
$C_{4}H_{10}$				1269	1562	1852
C ₅ H ₁₂					1922	2280
C_6H_{14}						2704

quency axis were obtained in our polarization propagator calculation [11]. In order to visualize how well the results from the expression in Eq. (8) agree with those from the full quantum chemical calculation we have constructed Fig. 2. The horizontal axis represents the values of Table II and the vertical axis the values obtained from Eq. (8). Both sets of values are given in atomic units (hartree $\times a_0^6$). It is again clear that the results obtained with the bond additive procedure are in perfect agreement with the reference data.

In summary, we present accurate results for the dipoledipole dispersion coefficients for pairs of *n*-alkane molecules with six or less carbon atoms. These calculations are based on the dynamic polarizabilities of the molecules on the imaginary frequency axis. The dynamic polarizabilities in turn were obtained from Kohn-Sham density-functional theory polarization propagator calculations using the hybrid B3LYP exchange-correlation functional. Furthermore, a

- R. Bonneau and D. Baker, Annu. Rev. Biophys. Biomol. Struct. 30, 173 (2001).
- [2] J. Israelachvili, Intermolecular & Surface Forces, 2nd ed. (Academic Press, London, 1992).
- [3] H. B. G. Casimir and D. Polder, Phys. Rev. 73, 360 (1948).
- [4] Bo E. Sernelius, Surface Modes in Physics (Wiley-VCH, Berlin, 2001).
- [5] F. London, Z. Phys. Chem. Abt. B 11, 222 (1930); Z. Phys. 63, 245 (1930).
- [6] E. A. Moelwyn-Hughes, Physical Chemistry (Pergamon, New



FIG. 2. The predicted dipole-dipole dispersion coefficients for pairs of n-alkane molecules as obtained from Eq. (8) vs those obtained from Eq. (2) based on the polarizabilities from first-principles quantum chemical calculations [11].

bond additive procedure for the interaction potential of the n-alkanes is proposed. The results for the static polarizabilities of each molecule are decomposed into bond polarizabilities and values for the polarizabilities of the C—H and C—C bonds are reported. The London approximation is used to obtain the dynamic polarizabilities and thereby also the dispersion interaction potential. The final formula for the dipole-dipole dispersion coefficient makes a mere reference to the number of C—H and C—C bonds in the interacting species but is, despite its simplicity, proven to be highly accurate for the *n*-alkanes.

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York, 1957), p. 332.

- [7] K. T. Tang, Phys. Rev. 177, 108 (1969).
- [8] A. J. Thakkar, J. Chem. Phys. 81, 1919 (1984).
- [9] G. D. Mahan, J. Chem. Phys. 76, 493 (1982).
- [10] G. D. Mahan and K. R. Subbaswamy, *Local Density of Polar-izability* (Plenum, New York, 1990).
- [11] P. Norman, A. Jiemchooroj, and Bo E. Sernelius, J. Chem. Phys. **118**, 9167 (2003).
- [12] G. F. Thomas and W. J. Meath, Mol. Phys. 34, 113 (1977).
- [13] B. L. Jhanwar and W. J. Meath, Mol. Phys. 41, 1061 (1980).