Theoret. Chim. Acta (Berl.) 55, 219–224 (1980)

THEORETICA CHIMICA ACTA

Hydrocarbon Long-Range Interaction Coefficients from Point Charge Model Formulae

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Two-body interaction coefficients *C*6 and *d*4 and the three-body coefficient $\gamma 3$ are calculated for interactions between like species for a variety of hydrocarbons. Three different point charge models are employed and results are similar when Frost model Lewis set wavefunctions are used and in agreement with other literature values where available. We also consider simple Slater–Kirkwood type formulae for the coefficients and it turns out that very similar results to the *ab initio* model values are found for *d*4. The formulae can also be used in conjunction with molecular fragment wavefunctions.

Key words: Dispersion coefficients – Point charge models – Hydrocarbons.

1. Introduction

Intermolecular interaction coefficients have been calculated using point charge models [1] from expressions for the frequency dependent polarizability. Results were in good agreement with the results of Margoliash and Meath [2, 3] obtained using pseudospectral dipole oscillator strength distributions (PDOSDs). The PDOSDs can themselves be thought of as an "experimental" point charge model and provide a discrete representation of the original DOSDs constructed from extensive experimental information [4, 5]. Previously [6] coefficient values have been given for hydrocarbon Frost model Lewis set wavefunctions using the simple Amos–Yoffe point charge model [7] and we now consider the values obtained for these wavefunctions using the more general point charge models of Hall [8, 9] and Shipman [10]. Unfortunately, of the molecules considered here, a PDOSD is only available for CH_4, but in view of the close agreement between experimental and theoretical polarizabilities using these models in conjunction with these wavefunctions [11] we feel that the interaction coefficients should be reasonably accurate.

In addition we consider the use of Hall and Shipman models in conjunction with molecular fragment wavefunctions for C_2H_6 and C_2H_4.

2. Point Charge Model Formulae for Interaction Coefficients

We consider the general case of point charges $\{Z_u\}$ with associated frequencies $\{\omega_u\}$ and the point charge models correspond to specific choices of these quantities.

Model	**Charges**	**Frequencies**	
Hall [8, 9]	$Z_{ij} = 2P_{ij}S_{ij}$	$\omega_{ij} = \alpha_i + \alpha_j = 2\alpha_{ij}$	
Shipman [10]	$q_i = \sum_j \frac{2\alpha_i Z_{ij}}{\alpha_i + \alpha_j}$	$\omega_i = 2\alpha_i$	(1)
Amos–Yoffe [7]	2	$\omega_i = 2\alpha_i$	

Interaction coefficients calculated from the Hall model are denoted by the subscript H and the charges and frequencies are calculated using Gaussian wavefunctions with density and overlap matrices P and S and Gaussian exponents $\{\alpha_i\}$. The Shipman model (denoted by S) reallocates off-centre charges in the Hall model onto Gaussian centres whilst the Amos–Yoffe model (AY), unlike the Hall and Shipman models restricted to Lewis basis sets, allocates charges of 2 on each Gaussian centre.

The formulae for interaction coefficients can now be given for the general point charge case and the specific model results are obtained simply by substituting in the appropriate charges and frequencies given in Eqs. (1).

The formulae have been given before [1] and so are merely listed below for interacting species A, B and C

$$C6(\mathrm{A}-\mathrm{B}) = \tfrac{3}{2} \sum_{u,v} \frac{Z_u^{\mathrm{A}} Z_v^{\mathrm{B}}}{\omega_u^{\mathrm{A}} \omega_v^{\mathrm{B}} (\omega_u^{\mathrm{A}} + \omega_v^{\mathrm{B}})} \tag{2}$$

$$d4(\mathrm{A}-\mathrm{B}) = \tfrac{1}{2} \sum_{u,v} \frac{Z_u^{\mathrm{A}} Z_v^{\mathrm{B}}}{(\omega_u^{\mathrm{A}} + \omega_v^{\mathrm{B}})} \tag{3}$$

$$\gamma 3(\mathrm{A}-\mathrm{B}-\mathrm{C}) = \tfrac{3}{2} \sum_{u,v,w} \frac{(\omega_u^{\mathrm{A}} + \omega_v^{\mathrm{B}} + \omega_w^{\mathrm{C}}) Z_u^{\mathrm{A}} Z_v^{\mathrm{B}} Z_w^{\mathrm{C}}}{\omega_u^{\mathrm{A}} \omega_v^{\mathrm{B}} \omega_w^{\mathrm{C}} (\omega_u^{\mathrm{A}} + \omega_v^{\mathrm{B}})(\omega_v^{\mathrm{B}} + \omega_w^{\mathrm{C}})(\omega_w^{\mathrm{C}} + \omega_u^{\mathrm{A}})}. \tag{4}$$

Again it is assumed that any redistribution of charges can be neglected.

3. Results

The formulae of Eqs. (2–4) in conjunction with the various point charge models of Eqs. (1) are tested on Frost model Lewis basis set wavefunctions for hydrocarbons whose details have been given previously [6]. Some of the wavefunctions contain p-type Gaussians as well as s-type ones and we may use exactly the same formulae as before [11].

We can compare the results using the point charge models with other literature values for $C6$ but for $\gamma 3$ and $d4$ these are not so numerous. We can, however, consider another point charge model which we shall call the Slater–Kirkwood model (SK) and use that for comparison. This model consists of a single charge N_v for each molecule, the number of valence electrons, and a single average frequency $\bar{\omega}$ which is calculated using N_v and α_0, the experimental static polarizability as

$$\bar{\omega} = (N_v/\alpha_0)^{1/2}. \tag{5}$$

Substituting Eq. (5) into Eqs. (2)–(4) leads to the following simple formulae for interactions between like species

$$C6_{\mathrm{SK}} = \tfrac{3}{4} N_v^{1/2} \alpha_0^{3/2} \tag{6}$$

$$d4_{\mathrm{SK}} = \tfrac{1}{4} N_v^{3/2} \alpha_0^{1/2} \tag{7}$$

$$\gamma 3_{\mathrm{SK}} = \tfrac{9}{16} N_v^{1/2} \alpha_0^{5/2}. \tag{8}$$

In fact Eqs. (6) and (8) are the leading two- and three-body long-range interaction coefficients and the expression for the leading n-body term will be of the form $M_n N_v^{1/2} \alpha_0^{(2n-1)/2}$ for like interactions in the SK model, where $M_2 = \frac{3}{4}$, $M_3 = \frac{9}{16}$ etc.

All results in the tables are given in atomic units. In Table 1 values of $C6$ for interactions between like species are given for the three *ab initio* models and compared with other literature values and SK model results. The agreement in the Table is very reasonable, with the model results lower than the SK values apart

Table 1. Values of the intermolecular interaction coefficient $C6$(A–A) for interactions between like species

Molecule	$C6_{\mathrm{AY}}$	$C6_{\mathrm{H}}$	$C6_{\mathrm{S}}$	Other values	$C6_{\mathrm{SK}}$
CH_4	132.9	135.0	134.9	129.6[a], 134[b]	152
C_2H_6	412.5	419.6	419.1	406[c], 443[b]	465
C_2H_4	356.9	363.9	363.3	341.3[d]	395
C_2H_2	256.1	261.3	260.9	—	271
cyclo C_3H_6	737.6	759.0	757.3	—	747
C_3H_4	610.8	624.1	623.0	—	678
C_4H_6	1308	1339	1337	—	1501
C_6H_6(BOND)[f]	2296	2344	2340	2670[e]	2415
C_6H_6(ATOM)[f]	1962	2007	2004	2670[e]	2415

[a] Ref. [2].
[b] Ref. [15].
[c] Ref. [12].
[d] Ref. [16].
[e] Ref. [17].
[f] p-type Gaussian on alternate CC bonds (BOND) or alternate C atoms (ATOM).

Table 2. Values of the intermolecular interaction coefficient $d4(A-A)$ for interactions between like species

Molecule	$d4_{AY}$	$d4_H$	$d4_S$	$d4_{SK}$
CH_4	23.3	23.6	23.6	23.5
C_2H_6	72.2	73.2	73.2	71.9
C_2H_4	53.4	54.3	54.4	55.5
C_2H_2	38.1	38.9	39.0	38.4
cyclo C_3H_6	123	125	125	118
C_3H_4	95.3	97.1	97.3	102
C_4H_6	186	189	190	194
C_6H_6(ATOM)	329	336	336	344
C_6H_6(BOND)	336	343	343	344

from the Hall and Shipman results for cyclo C_3H_6. Since the SK formula usually overestimates $C6$, see for instance reference [12], the *ab initio* model results appear to be very satisfactory.

In Table 2 results are given for $d4$ and we note that the PDOSD result for CH_4 of $d4 = 20.31$[2] is in reasonable agreement with all the model results. Interestingly enough the SK values give excellent estimates of the *ab initio* model results apart from the cyclo C_3H_6 value which, in actual fact, is only about 6% lower than the $d4_H$ result. since the accurate value of $d4$ for CH_4 is lower than the model results by some 15% it may well be that the SK estimate for cyclo C_3H_6 is the most accurate value.

The values of $\gamma 3$ are given in Table 3 and the three *ab initio* model values for CH_4 are in excellent agreement with the PDOSD result of 1630 [3]. Once again, as for C6, the SK values are higher than the other model results, apart from the cyclo C_3H_6 value, and for C_3H_4 much higher.

For these hydrocarbon Lewis set wavefunctions a general result for interaction coefficient I is that

$$I_{AY} < I_S < I_H \tag{9}$$

Table 3. Values of the intermolecular interaction coefficient $\gamma 3(A-A-A)$ for interactions between like species

Molecule	$\gamma 3_{AY}$	$\gamma 3_H$	$\gamma 3_S$	$\gamma 3_{SK}$
CH_4	1571	1608	1606	1974
C_2H_6	8609	8831	8817	10520
C_2H_4	7407	7620	7599	8434
C_2H_2	4483	4616	4604	4789
cyclo C_3H_6	20890	21850	21760	21330
C_3H_4	16320	16850	16800	23470
C_4H_6	52660	54520	54330	63830
C_6H_6(ATOM)	92110	95320	95030	127100
C_6H_6(BOND)	122500	126200	125900	127100

Table 4. Results for molecular fragment wavefunctions

Molecule	Model	$C6$	$d4$	$\gamma 3$
C_2H_6	HALL	443.8	74.7	9693
	SHIPMAN	443.7	74.8	9688
C_2H_4	HALL	318.5	54.6	5897
	SHIPMAN	317.3	54.8	5843

for $I = C6$ and $\gamma 3$, as indeed for the molecular polarizability [11], and, apart from cyclo C_3H_6, $I_H < I_{SK}$ can be added to Eq. (9). For $d4$, however, we find

$$d4_{AY} < d4_H < d4_S \tag{10}$$

for all the molecules considered.

In Table 4 values for the various coefficients are given for molecular fragment wavefunctions for C_2H_6, using the orbital parameters and geometry of reference [13] with optimised density matrix elements found from OPIT, and for C_2H_4 using an experimental geometry. Results may be compared with the values given in the previous tables for these molecules and it can be seen that there is satisfactory agreement.

4. Conclusion

The results for the various models using the Lewis set wavefunctions are extremely close and follow a uniform pattern and so we would recommend, perhaps not without bias, the use of the simplest formulae, that is those of Amos and Yoffe. For non-Lewis set wavefunctions of this paper the Shipman model appears to give a good estimate of the Hall values and involves considerably less point charges.

It should perhaps be mentioned that the formulae of Eqs. (9) and (10) apply only to the wavefunctions of this paper. The SK approximation gives a very reasonable order of magnitude approximation to the model $C6$ and $\gamma 3$ results and a more accurate estimate of the $d4$ values, providing a simple method of checking results. It will be easier to gauge the exact accuracy of the interaction coefficients of this paper following the completion of further DOSDs and PDOSDs for a variety of molecules including hydrocarbons [14].

Acknowledgement. This work was supported partially by an SRC postdoctoral research fellowship and by a program project grant (GM 22357) from the National Institutes of General Medical Sciences, National Institutes of Health.

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Received November 12, 1979