Theoret. Chim. Acta (Berl.) 52, 155–161 (1979)

THEORETICA CHIMICA ACTA

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Intermolecular Interaction Coefficients Using Point Charge Models

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Values of the two-body interaction coefficients $C6$ and $d4$ between like species, as well as the three-body term $\gamma 3$, are obtained from point charge model formulae. Lewis set results may be compared with atomically centered wavefunction values as well as results obtained using an experimental point charge model. Generally results are in good agreement with experiment and when theoretical values differ wildly from experiment they may be normalized using theoretical and experimental static polarizability values.

Key words: Interaction coefficients – Point charge models

1. Introduction

Recently dipole oscillator strength distributions (DOSDs) have been constructed from extensive experimental information and used to calculate the dispersion energy constant $C6$ for a number of atomic and molecular interactions [1] as well as a number of one- and two-body properties [2–5]. Because the DOSDs are either completely continuous, or contain a substantial continuum contribution, the computational numerical integrations involved can prove prohibitively expensive and consequently pseudospectral DOSDs (PDOSDs) were constructed providing a discrete representation of the original DOSDs. The use of the PDOSDs greatly simplifies the calculation of interaction coefficients and reliably reproduces the values obtained for $C6$ using the DOSDs [6]. Related two-body interactions, such as the relativistic correcting term $d4$ [6], as well as higher order interactions, like the triple dipole energy coefficient $\gamma 3$ [7], can also be calculated simply from the PDOSDs.

The results obtained for the various interaction coefficients using PDOSDs may be termed experimental and used as standards with which to compare *ab initio* theoretical calculations. Results for H_2, H_2O, NH_3 and CH_4 using Frost model

0040-5744/79/0052/0155/$01.40

[8–10] Lewis set wavefunctions, that is one orbital per electron pair, have been in good agreement with DOSD and PDOSD results considering the simplicity of the wavefunctions used [11]. Further calculations on a number of hydrocarbons have also been carried out [12] but again these were restricted to Lewis basis sets.

The expression for the frequency-dependent polarizability used in the calculation of the interaction coefficients can not only be derived quantum mechanically but also classically in terms of a point charge model [13]. The use of more general point charge models of Hall [14, 15] and Shipman [16] lead to expressions for the frequency-dependent polarizability that are not only applicable to Lewis set wavefunctions but also to non-Lewis set wave functions as well [17]. Essentially for each model the methodology is to associate frequencies obtained from Gaussian exponents to the set of point charges of each model. The central properties of all three point charge models are that the total electronic charge and the dipole moment are conserved. The PDOSDs can be thought of as an "experimental" point charge model where again the total charge is conserved but instead of the dipole moment various dipole oscillator strength sums are reproduced. Thus we can compare directly values obtained using the Hall, Shipman and Amos-Yoffe models for the static polarizability $\alpha(0)$ as well as interaction coefficients $C6$, $d4$, and $\gamma3$ with the experimentally derived Margoliash-Meath point charge model results.

2. Point Charge Model Formulae for $\alpha(0)$, $C6$, $d4$ and $\gamma3$

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	$Z_{ij} = 2P_{ij}S_{ij}$	$\omega_{ij} = \alpha_i + \alpha_j = 2\alpha_{ij}$	
Shipman	$q_i = \sum_j \frac{2\alpha_i Z_{ij}}{\alpha_i + \alpha_j}$	$\omega_i = 2\alpha_i$	(1)
Amos-Yoffe	2	$\omega_i = 2\alpha_i$	
Margoliash-Meath	f_i	ε_i	

Properties and 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 on to 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. Each molecule in the Margoliash-Meath model (MM) is represented by ten point charges with associated frequencies that reproduce experimentally known dipole oscillator strength sums $S(k)$ where

$$S(k) = \sum_{i=1}^{10} \varepsilon_i^k f_i \tag{2}$$

and where, for instance $S(0) = Z$, conserving the total charge, and $S(-2) = \alpha(0)$, conserving the experimental static polarizability. The formulae for the properties or 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). Firstly the static electric polarizability has already been given [17] and the result is

$$\alpha(0) = \sum_u \frac{Z_u}{\omega_u^2} \tag{3}$$

The frequency-dependent polarizability is a natural extension of the static case and can be written [17]

$$\alpha(\omega) = \sum_u \frac{Z_u}{\omega_u^2 - \omega^2}. \tag{4}$$

Now the long-range temperature independent orientation averaged dispersion energy coefficient $C6$ may be written in terms of the frequency-dependent polarizabilities at imaginary frequencies $\alpha^{A}(i\omega)$ and $\alpha^{B}(i\omega)$ of the two interacting species A and B. The result is [18]

$$C6(\mathrm{A{-}B}) = \frac{3}{\pi}\int_0^\infty \alpha^{A}(i\omega)\alpha^{B}(i\omega)\, d\omega \tag{5}$$

and substituting the point-charge expression of Eq. (4) into Eq. (5) yields

$$C6(\mathrm{A{-}B}) = \frac{3}{2}\sum_{u,v} \frac{Z_u^A Z_v^B}{\omega_u^A \omega_v^B(\omega_u^A + \omega_v^B)} \tag{6}$$

in an obvious notation.

The relativistic correcting term $d4$ given by [19]

$$d4(\mathrm{A{-}B}) = \frac{1}{\pi}\int_0^\infty \omega^2\alpha^{A}(i\omega)\alpha^{B}(i\omega)\, d\omega \tag{7}$$

also assumes a particularly simple form when Eq. (4) is used, namely

$$d4(\mathrm{A{-}B}) = \frac{1}{2}\sum_{u,v} \frac{Z_u^A Z_v^B}{(\omega_u^A + \omega_v^B)}. \tag{8}$$

Non-(pairwise) additive energies are of importance when three or more molecules interact and the dispersion interaction constant $\gamma 3$ given by [20]

$$\gamma 3(\mathrm{A{-}B{-}C}) = \frac{3}{\pi}\int \alpha^{A}(i\omega)\alpha^{B}(i\omega)\alpha^{C}(i\omega)\, d\omega \tag{9}$$

again takes on a simple form using Eq. (4)

$$\gamma 3(\mathrm{A{-}B{-}C}) = \frac{3}{2}\sum_{u,v,w} \frac{(\omega_u^A + \omega_v^B + \omega_w^C) Z_u^A Z_v^B Z_w^C}{(\omega_u^A + \omega_v^B)(\omega_v^B + \omega_w^C)(\omega_w^C + \omega_u^A)\omega_u^A\omega_v^B\omega_w^C}. \tag{10}$$

3. Results

Results for the static polarizability $\alpha(0)$ and like interaction coefficients $C6$(A–A), $d4$(A–A) and $\gamma 3$(A–A–A) are given in Tables 1–4 for a variety of species. In Tables

Table 1. Static electric polarizabilities $\alpha(0)$ in atomic units

Atom/ molecule	Frost wavefunction[a]	Pople wavefunction[b]		Experiment
	α_{AY}	α_{H}	α_{S}	α_{MM}
He	0.850	1.23	1.26	1.38
O	—	4.96	5.32	4.96
H_2	4.93	6.96 (5.38)	7.29 (5.65)	5.43
N_2	—	11.0 (13.2)	11.1 (13.3)	11.7
O_2	—	15.6 (9.00)	14.3 (9.02)	10.6
H_2O	6.07	8.73 (8.86)	9.56 (9.29)	9.64
NH_3	12.3	12.8 (14.5)	13.7 (15.3)	14.6
CH_4	16.5	21.1 (17.9)	22.2 (18.8)	17.3

[a] Refs. [8–10].

[b] Exponents of Ref. [21]. Values in brackets using wavefunction exponents of Ref. [23].

Table 2. Values of $C6(A\text{–}A)$ in atomic units

Atom/ molecule	Frost wavefunction	Pople wavefunction		Experiment
	$C6_{AY}$	$C6_{H}$	$C6_{S}$	$C6_{MM}$
He	0.832	1.24	1.28	1.46
O	—	16.5	17.3	14.9
H_2	11.6	15.5 (10.8)	16.5 (11.5)	12.1
N_2	—	76.7 (102)	77.3 (102)	73.3
O_2	—	109 (62.4)	104 (62.5)	61.6
H_2O	36.5	41.0 (46.1)	43.9 (48.4)	45.3
NH_3	90.9	78.9 (95.3)	83.2 (101)	89.0
CH_4	142	173 (134)	182 (142)	130

Table 3. Values of $d4(A\text{–}A)$ in atomic units

Atom/ molecule	Frost wavefunction	Pople wavefunction		Experiment
	$d4_{AY}$	$d4_{H}$	$d4_{S}$	$d4_{MM}$
He	0.652	0.593	0.572	0.664
O	—	6.77	6.51	6.09
H_2	1.57	1.30 (1.21)	1.23 (1.15)	1.44
N_2	—	22.6 (25.9)	22.5 (25.8)	21.4
O_2	—	27.8 (27.7)	28.5 (27.7)	23.9
H_2O	15.1	12.6 (13.3)	12.0 (12.8)	12.3
NH_3	20.4	16.3 (17.0)	15.6 (16.1)	16.3
CH_4	23.8	20.9 (19.8)	20.0 (18.9)	20.4

Table 4. Values of $\gamma 3$(A–A–A) in atomic units

Atom/ molecule	Frost wavefunction $\gamma 3_{\mathrm{AY}}$	Pople wavefunction		Experiment $\gamma 3_{\mathrm{MM}}$
		$\gamma 3_{\mathrm{H}}$	$\gamma 3_{\mathrm{S}}$	
He	0.531	1.13	1.21	1.47
O	—	58.9	65.5	52.3
H_2	42.9	79.5 (42.9)	89.3 (48.2)	48.5
N_2	—	628 (1000)	638 (1008)	618
O_2	—	1196 (417)	1065 (418)	454
H_2O	179	253 (299)	295 (330)	308
NH_3	826	729 (1010)	818 (1140)	921
CH_4	1710	2683 (1760)	2969 (1970)	1630

1–4 we compare values obtained from Frost model Lewis set wavefunctions using the Amos-Yoffe model formulae (AY) with values obtained from atomically centred wavefunctions, whose exponents are given by Pople *et al.* [21], in conjunction with the Hall (H) and Shipman (S) model formulae. The exponents used for these atomically centred wavefunctions were the unconstrained set but the contraction coefficients were not used and the density matrix was found using all the Gaussians from OPIT [22]. Two Gaussians for each of the $1s$, $2s$, $2p_x$, $2p_y$ and $2p_z$ orbitals, making a total of ten, were centred on every heavy atom whilst two Gaussians were centred on every hydrogen. For Helium, however, two Gaussians with exponents 4.0978 and 0.5321, found using OPIT, were placed on the atomic centre. All results can then be compared with the "experimental" results of Margoliash and Meath (MM).

For Helium the values in all four tables using OPIT (though under the column marked Pople wavefunction) and the Hall and Shipman models are in much better agreement with the experimental values than the Frost wavefunction Amos-Yoffe values except for $d4$ when the single Gaussian value is fortuitously good. The results for oxygen are very reasonable using the Pople exponents but those for H_2 are poor and not as good as those obtained using the Frost wavefunction. Values for N_2 are generally in good agreement with experiment but those for O_2 are much too large particularly for $\gamma 3_{\mathrm{H}}$ and $\gamma 3_{\mathrm{S}}$. Results using the non-Lewis set atomically centred wavefunctions for H_2O show considerable improvement over the Frost wavefunction values in all four tables whilst for NH_3 values show improvement for $\alpha(0)$ and $d4$ but not for $C6$ or $\gamma 3$. For CH_4, Frost wavefunction results are superior except for $d4$. General results which hold in all cases, except for O_2, are that $\alpha_{\mathrm{H}} < \alpha_{\mathrm{S}}$, $C6_{\mathrm{H}} < C6_{\mathrm{S}}$, $d4_{\mathrm{H}} > d4_{\mathrm{S}}$ and $\gamma 3_{\mathrm{H}} < \gamma 3_{\mathrm{S}}$.

Of course the exponents of Pople are not the only values that can be used and atomically optimized wavefunctions may well overemphasize the core electrons when set in a molecular context. Several different sets of exponents optimized in a molecular situation for a variety of molecules for H, C, N and O are to be published shortly [23] and the resulting wavefunctions should provide an improved valence description. Using exponents from these wavefunctions, again ignoring contraction coefficients and obtaining density matrix elements using all the Gaussians from OPIT, we obtain the values given in brackets in the tables for the various coefficients. These alternative wavefunction results are given for H_2, N_2, O_2, H_2O, NH_3 and CH_4 using real *p*-type Gaussians where appropriate. For H_2 improved values are obtained over the Pople results except for $d4$ and over the Frost results except for $d4$ and $C6$. For O_2 there is a great improvement over the Pople values for $\alpha(0)$, $C6$ and $\gamma3$ whilst in the case of H_2O results are much better than those using Frost wavefunctions and are comparable to the Pople wavefunction values. The results for NH_3 are also in as good agreement with experiment as the Pople wavefunction values but the Frost values for $C6$ and $\gamma3$ are better. Finally the CH_4 results are much improved for $\alpha(0)$, $C6$ and $\gamma3$ but are slightly worse for $d4$. The only failure, really, is for N_2 when results are too high and not in as good agreement with the experimental values as Pople's wavefunction.

4. Discussion

Generally speaking the methods employed are too approximate to provide accurate atomic results. Even so reasonable estimates may be obtained for $\alpha(0)$ and the interaction coefficients for He and O. For molecules the transference of parameters obtained in an atomic environment to a molecular context gives good results for N_2, H_2O and NH_3, and rather poorer results for H_2, CH_4 and, in particular O_2. Improved values can be obtained using exponents optimized from a molecular environment for these three molecules. It is worth bearing in mind, however, that extremely good results are obtained from simple Frost model wavefunctions particularly for H_2, NH_3 and CH_4. However, atomic non-Lewis sets can provide a description of a molecule, or atom such as O, when the Lewis set orbital description is by no means obvious.

Since interaction coefficients $C6$, $d4$ and $\gamma3$ depend on $\alpha(i\omega)$, an alternative method when results are poor is to normalize values according to the ratio of the theoretical and experimental polarizabilities. We express $\alpha(0)$ as

$$\alpha(0) = k/\bar{\omega}^2 \tag{11}$$

where k is a constant and $\bar{\omega}$ the average valence exponent for the molecule or atom in question. Then, for the Hall model, for instance, we find

$$\bar{\omega}_{\mathrm{H}} = \bar{\omega}_{\mathrm{EXP}}(\alpha_{\mathrm{EXP}}(0)/\alpha_{\mathrm{H}}(0))^{1/2} \tag{12}$$

and results for $C6_{\mathrm{H}}$, $d4_{\mathrm{H}}$ and $\gamma3_{\mathrm{H}}$ may be normalized by taking their dependence on $\bar{\omega}_{\mathrm{H}}$ as $\bar{\omega}_{\mathrm{H}}^{-3}$, $\bar{\omega}_{\mathrm{H}}^{-1}$ and $\bar{\omega}_{\mathrm{H}}^{-5}$ respectively. According to this scheme using the results from Tables 1–4 for Pople's wavefunctions in conjunction with the Hall model formulae we find for O_2 results of $C6_{\mathrm{H}} = 61.1$, $d4_{\mathrm{H}} = 22.9$ and $\gamma3_{\mathrm{H}} = 455$ in excellent agreement with experiment. For CH_4 we find $C6_{\mathrm{H}} = 128$, $d4_{\mathrm{H}} = 18.9$ and $\gamma3_{\mathrm{H}} = 1624$ showing considerable improvement over the raw results except for $d4_{\mathrm{H}}$. Generally results using this procedure in conjunction with the Pople wavefunctions provides better results for $C6$ and $\gamma3$ but worse for $d4$. So even when results differ widely from experiment they need not be dismissed as useless as ratios are reproduced.

In conclusion, then, *ab initio* values for $\alpha(0)$ and interaction coefficients can be obtained for a variety of species using point charge model formulae. The interaction coefficient can be considered reliable when static polarizability results are in good agreement with experiment and otherwise normalized according to a procedure involving the ratios of experimental and theoretical polarizability values.

Point charge models provide an ideal *ab initio* method to estimate properties, such as $\alpha(0)$, and the interaction coefficients, mentioned in this paper, which is readily applicable to macromolecules, a field hitherto generally restricted to atoms and small molecules. Currently we are considering the use of point charge models for other properties and interaction coefficients as well as more accurate procedures especially for atomic system.

Acknowledgements. I would like to thank Professor R. E. Christoffersen for allowing me to use exponents for wavefunctions prior to publication as well as Colin Smith for computational assistance. I would also like to thank the SRC for the award of a Postdoctoral Fellowship.

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Received January 12, 1979