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Bond and Inner Shell Interaction Coefficients for Hydrocarbons

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Molecular interactions may be broken up into the interaction of bonds and inner shells. Results for bond and inner shell interaction coefficients for pairwise additive terms C_6, C_8, C_{10} and d_4 are given, as well as the non-(pairwise) additive coefficient γ_3. Simple combination rules may be used to estimate these terms with good results. Parameters should be applicable to macromolecules.

Key words: Bond and inner shell interactions - Hydrocarbons - Combination rules

1. Introduction

The long-range temperature-independent interaction energy between two neutral molecules, when averaged over all orientations, may be written [1]

$$\Delta E = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \cdots \tag{1}$$

where R is the intermolecular separation and $C_6, C_8, C_{10}, \ldots$ are constants depending on the particular molecules which are interacting. Each of the terms in Eq. (1) can be divided into orientation, induction and dispersion parts [2] and in this paper we consider the last contribution.

Particularly simple formulae for the dispersion coefficients in Eq. (1) may be obtained using Frost model wavefunctions [3], and recently calculations have been made for $C_6(AB - CD)$, the interaction between bonds AB and CD, for hydrocarbons [4]. For the Frost model [5] the Gaussian orbitals after optimisation tend to position themselves on heavy nuclei or in bonds, and the simple formulae derived for the molecular property may be divided up in a straightforward manner into Inner shell–Inner shell, Inner shell–Bond and Bond–Bond interactions. It turns out that for hydrocarbons the Bond–Bond interactions dominate in the calculation of C_6 [4], though the corrections due to the inner shell electrons may also be calculated easily.

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Often only the coefficient C_6 is calculated for the interaction between two molecules, and this may or may not be a good approximation, depending on the intermolecular separation R. For hydrocarbons it was found that for R between 10 a.u. and 20 a.u. at least the second term in the series in Eq. (1) should be included, whilst for $R >$ 50 a.u. radiative corrections become significant. When three or more molecules interact the interaction energy will not only include the various two-body interactions, but also three-body, γ_3, and higher order nonadditive terms, γ_n, for which the increasing interest in the research field [6–8] reflects the increased importance attached to such interactions.

The term "non-additive" is actually somewhat misleading, as it really means non-pairwise additive, that is the many-body interactions cannot be simply expressed as a sum of pair interactions. However, the expressions for these "non-additive" interaction coefficients γ_n can be written in terms of simple sums [3]. It is the purpose of this paper to demonstrate how these many-body contributions may be calculated by the simple addition of bond and inner shell interactions in the course of considering γ_3 using Frost model parameters for hydrocarbons. Furthermore, corrections to the two-body interaction coefficient C_6 via C_8 and C_{10} or through the inclusion of d_4 for retardation effects may all be included in terms of bond and inner shell interactions.

2. Theory

The Frost model wavefunction for a $2n$-electron molecule consists of a Slater determinant ψ of n doubly occupied floating Gaussian orbitals $\{G_i\}$, i.e.

$$\psi = \det\{G_1\alpha G_1\beta \ldots G_n\alpha G_n\beta\} \tag{2}$$

where

$$G_i(\boldsymbol{r}) = \left(\frac{\omega_i}{\pi}\right)^{3/4} \exp\left(-\tfrac{1}{2}\omega_i|\boldsymbol{r} - \boldsymbol{R}_i|^2\right) \tag{3}$$

is an s-type Gaussian, though p-type Gaussians may also be included in the basis [9]. The exponents $\{\omega_i\}$ and the positions of the centres $\{\boldsymbol{R}_i\}$ of the Gaussians are found by using the variational principle. Thus all parameters are obtained in an *ab initio* fashion and are not determined empirically.

Previously an expression for the C_6 interaction coefficient for bonds AB and CD was given [4], obtained from frequency-dependent bond polarizabilities from the Frost model

$$C_6(AB - CD) = \frac{6}{\omega_{AB}\omega_{CD}(\omega_{AB} + \omega_{CD})}. \tag{4}$$

Inner shell–bond interaction coefficients may be computed simply by replacing one of the exponents in Eq. (4) by ω_{IS}, the inner shell exponent. For hydrocarbons the carbon inner shell exponents vary very little from atom to atom and so if ω_{IS} is the carbon inner shell exponent the inner shell–inner shell interaction can be written

$$C_6(\mathrm{IS–IS}) = \frac{3}{\omega_{\mathrm{IS}}^3}. \tag{5}$$

A summation of all the three types of interaction mentioned above yields the total molecular C_6 interaction coefficient.

Now for C_8 and C_{10}, using Frost model formulae [3], similar terms to Eq. (4) may be given for interactions between bonds AB and CD:

$$C_8(AB - CD) = \frac{45}{\omega_{AB}\omega_{CD}}\left\{\frac{1}{\omega_{AB}(2\omega_{AB} + \omega_{CD})} + \frac{1}{\omega_{CD}(2\omega_{CD} + \omega_{AB})}\right\} \tag{6}$$

and

$$C_{10}(AB - CD) = \frac{315}{\omega_{AB}^2\omega_{CD}^2(\omega_{AB} + \omega_{CD})} + \frac{420}{\omega_{AB}\omega_{CD}}\left\{\frac{1}{\omega_{CD}^2(\omega_{AB} + 3\omega_{CD})} + \frac{1}{\omega_{AB}^2(3\omega_{AB} + \omega_{CD})}\right\}. \tag{7}$$

For inner shell–inner shell interactions we find

$$C_8(\mathrm{IS{-}IS}) = \frac{30}{\omega_{\mathrm{IS}}^4} \tag{8}$$

and

$$C_{10} = \frac{735}{2\omega_{\mathrm{IS}}^5} \tag{9}$$

whilst for inner shell–bond interactions simply replace one of the bond exponents by ω_{IS} in Eqs. (6) and (7).

When relativistic corrections are included for large (but not very large) R the interaction energy becomes

$$\Delta E = -R^{-6}\{C_6 - \sigma^2 R^2 d_4 + O(\sigma^3 R^3)\} \tag{10}$$

where σ is the fine structure constant ($\sigma = 1/137$). Then d_4, from the Frost model formula [3], may also be written in terms of bond and inner shell interactions:

$$d_4(AB - CD) = \frac{2}{\omega_{AB} + \omega_{CD}} \tag{11}$$

for bond–bond interactions and for inner shell–inner shell interactions merely

$$d_4(\mathrm{IS{-}IS}) = \frac{1}{\omega_{\mathrm{IS}}} \tag{12}$$

whilst ω_{IS} replaces one of the bond exponents in Eq. (11) for the bond–inner shell interaction.

In principle the interaction between n bonds may be calculated and hence the leading term in the n-body non-(pairwise) additive interaction derived. Again we associate a frequency-dependent polarizability with bond AB:

$$\bar{\alpha}_{AB}(\omega) = \frac{2}{\omega_{AB}^2 - \omega^2} \tag{13}$$

and then the coefficients γ_n for the interaction between the n bonds $AB, CD, \ldots, YZ$ is just

$$\gamma_n(AB - CD - \cdots - YZ) = \frac{3}{\pi}\int \bar{\alpha}_{AB}(i\omega)\bar{\alpha}_{CD}(i\omega)\cdots\bar{\alpha}_{YZ}(i\omega)\, d\omega. \tag{14}$$

When n molecules $A_1, A_2, \ldots, A_n$ interact, the total non-additive n-body interaction energy can be written [10]

$$\Delta E_n = \Theta(A_1, A_2, \ldots, A_n)\gamma_n \tag{15}$$

where γ_n is just a sum of all interactions between bonds and inner shells given by terms similar to Eq. (14). Θ depends on the distances between the molecules and their configurations relative to each other, whilst γ_n depends on the type of molecules that interact. The configuration and distance dependent term Θ varies as the inverse $3n$th power of the separation distances. For instance, when $n = 3$

$$\Theta = R_1^{-3}R_2^{-3}R_3^{-3}(3\cos\theta_1\cos\theta_2\cos\theta_3 + 1) \tag{16}$$

where the molecules are placed at the vertices of a triangle with angles θ_1, θ_2, θ_3 and sides R_1, R_2, R_3. The dependence on the intermolecular separations means that ΔE_n decreases rapidly as n increases and we consider γ_3 here, though higher orders can also be calculated. The coefficient for the interaction between three bonds *AB*, *CD*, *EF* is

$$\gamma_3(AB - CD - EF) = \frac{12(\omega_{AB} + \omega_{CD} + \omega_{EF})}{\omega_{AB}\omega_{CD}\omega_{EF}(\omega_{AB} + \omega_{CD})(\omega_{CD} + \omega_{EF})(\omega_{EF} + \omega_{AB})} \tag{17}$$

whilst for the interaction between bonds and inner shells we merely replace the bond exponents by inner shell ones where appropriate. For the inner shell–inner shell–inner shell coefficient, Eq. (17) reduces to

$$\gamma_3(\text{IS–IS–IS}) = \frac{9}{2\omega_{\text{IS}}^5}\cdot \tag{18}$$

3. Results and Discussion

The exponents used in the calculations were taken from wave-functions given previously [4]:

$\omega_{\text{IS}} = 18.6013$ taken from C_2H_6

$\omega_{\text{CH}} = 0.7098$ taken from C_2H_6

$\omega_{\text{C—C}} = 0.7067$ taken from C_2H_6

$$\omega_{\text{C=C}} = \begin{cases} 0.8890 \\ 0.3986 \end{cases} \text{taken from } C_2H_4$$

$$\omega_{\text{C}\equiv\text{C}} = \begin{cases} 0.9435 \\ 0.5065 \\ 0.5065 \end{cases} \text{taken from } C_2H_2$$

$$\omega_{\text{CC}_A} = \begin{cases} 0.8316 \\ 0.3988 \\ 0.8911 \end{cases} \text{taken from } C_6H_6$$

We have taken ω_{CH} to be the exponent from C_2H_6 and results for interactions using the CH exponents of either C_2H_4 or C_2H_2 will be similar, though smaller as $\omega_{\text{CH}}(C_2H_2) > \omega_{\text{CH}}(C_2H_4) > \omega_{\text{CH}}(C_2H_6)$. For interactions involving double or triple

Table 1. Bond and inner shell two-body interaction coefficients

Interaction	C_6	C_8	C_{10}	d_4
IS–IS	0.000	0.000	0.000	0.054
–CH	0.024	0.245	3.141	0.104
–C—C	0.024	0.247	3.183	0.104
–C=C	0.061	0.947	19.88	0.208
–C≡C	0.084	1.111	18.95	0.312
–CC_A	0.041	0.561	10.89	0.155
CH–CH	8.390	118.2	2040	1.409
–C—C	8.444	119.2	2062	1.412
–C=C	25.08	463.7	10800	3.055
–C≡C	32.86	537.5	10880	4.498
–CC_A	15.82	274.7	6082	2.175
C—C–C—C	8.499	120.3	2084	1.415
–C=C	25.25	467.5	10900	3.063
–C≡C	33.08	542.0	10990	4.509
–CC_A	15.93	277.0	6141	2.180
C=C–C=C	77.92	1745	49190	6.740
–C≡C	100.5	2057	52790	9.867
–CC_A	48.62	1043	28390	4.762
C≡C–C≡C	130.5	2408	55130	14.47
–CC_A	63.00	1225	30150	6.988
CC_A–CC_A	30.43	621.9	16320	3.376

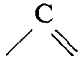
bonds where there is more than one orbital in the bond the interactions are calculated as a simple sum of the orbital interactions. For interactions involving aromatics we take the interaction with the fragment  and multiply by 2^{-n} for $n = 1, 2, 3$ where n is the number of CC_A involved in the interaction in question. For example, for the interaction CH—CH—CC_A we will multiply by $\frac{1}{2}$, whilst for CH—CC_A—CC_A by $\frac{1}{4}$ and CH—CC_A by $\frac{1}{2}$.

Table 1 gives values of Bond–Bond, Bond–Inner shell and Inner shell–Inner shell interaction coefficients in atomic units and certainly the most obvious conclusion that can immediately be drawn is that for all four coefficients the interactions involving inner shells are much smaller than those involving just bonds, except for d_4 which is hardly surprising, as this only involves $\omega_{\mathrm{IS}}^{-1}$; see Eqs. (11) and (12). For the other three coefficients the largest bond–inner shell interaction coefficient is less than 1% of the smallest bond–bond interaction coefficient.

The interactions involving CH and C—C bonds are very similar, which again is hardly surprising in view of the similar exponents, whilst it is interesting to note that for interactions involving CC bonds an approximate relationship is

$$I(AB - \mathrm{C{-}C}) + I(AB - \mathrm{C{=}C}) \approx I(AB - \mathrm{C{\equiv}C}) \approx 2I(AB - \mathrm{CC}_A) \qquad (19)$$

where I is C_6, C_8, C_{10} or d_4. A combination rule for estimating molecular interactions between unlike species from like species has been suggested by Moelwyn-Hughes [11] and a similar formula may be used for bond interactions. However, we prefer the simpler formula [12]

$$I(AB - CD) = [I(AB - AB)I(CD - CD)]^{1/2} \tag{20}$$

where I is as before. When $I = C_6$ in Eq. (20) estimates obtained in this way for bond–bond interactions lie within 2% of the actual value obtained from Eq. (4) providing an upper bound to the actual result [13]. For $I = C_8$ and $I = C_{10}$ in Eq. (20) results lie below the actual values obtained from Eqs. (6) and (7) by under 2% and under 7% respectively. For $I = d_4$ results lie less than 1% above values obtained using Eq. (11) and results using Eq. (20) seem to prove rather more successful for bond interaction coefficients than for molecular ones [14] because of the fewer electrons involved. However, the use of Eq. (20) for interactions involving inner shells is far less successful.

In Table 2, values for 3-body interactions involving bonds and inner shells are given, with values for the same interaction only given once, e.g. $\gamma_3(\mathrm{CH{-}CH{-}CC_A}) = \gamma_3(\mathrm{CH{-}CC_A{-}CH})$. The three-body interaction involving at least two inner shells is effectively zero, whilst the largest value for interactions involving just a single inner shell is only 3% of the smallest bond–bond–bond interaction coefficient. A similar result to Eq. (19) again holds for CC bonds, where

$$\gamma_3(AB - CD - \mathrm{C{-}C}) + \gamma_3(AB - CD - \mathrm{C{=}C}) \approx \gamma_3(AB - CD - \mathrm{C{\equiv}C}) \approx 2\gamma_3(AB - CD - \mathrm{CC}_A). \tag{21}$$

Table 2. Bond and inner shell γ_3 interaction coefficients

Interaction	IS	CH	C—C	C=C	C≡C	CC_A
IS-IS	0.000					
-CH	0.000					
-C—C	0.000					
-C=C	0.000					
-C≡C	0.000					
-CC_A	0.000					
CH-CH	0.048	24.98				
-C—C	0.049	25.16				
-C=C	0.145	79.34				
-C≡C	0.190	101.6				
-CC_A	0.091	49.17				
C—C-C—C	0.049	25.34	25.52			
-C=C	0.146	79.93	80.52			
-C≡C	0.191	102.4	103.1			
-CC_A	0.092	49.53	49.90			
C=C-C=C	0.450	258.9	260.9	864.5		
-C≡C	0.581	327.9	330.4	1084		
-CC_A	0.281	159.4	160.6	529.1		
C≡C-C≡C	0.754	417.4	420.5	1366	1728	
-CC_A	0.364	202.4	203.9	665.3	840.2	
CC_A-CC_A	0.176	98.26	99.00	324.3	408.8	199.0

Several combination rules have been suggested [15–17] and tested [18] for the estimation of γ_3 from $\bar{\alpha}$ and C_6 values for several atoms and molecules. It turns out, however, that

$$\gamma_3(AB - CD - EF) = [C_6(AB - AB)C_6(CD - CD)C_6(EF - EF)]^{1/2} \quad (22)$$

will give values to within 19% of those in Table 2, whilst

$$\begin{aligned}&\gamma_3(AB - CD - EF)\\ &\quad = [\gamma_3(AB - AB - AB)\gamma_3(CD - CD - CD)\gamma_3(EF - EF - EF)]^{1/3} \quad (23)\end{aligned}$$

only overestimates the results by at most 3%, though the other formulae will provide good estimates as well.

Unfortunately, bond values or indeed molecular values with which to compare our results are very few and far between. A discussion on C_6 has been given previously [4], but it is worth noting that using the values in Table 1 we find $C_6(CH_4—CH_4) = 134$, in good agreement with the value of Margoliash and Meath of 129.6 [14]. For $d_4(CH_4—CH_4)$ we obtain a value of 22.6 compared with their result of 20.36, whilst we find $\gamma_3(CH_4—CH_4—CH_4) = 1600$ compared with their value of 1631 [18]. For any other hydrocarbon interactions, including unsaturated as well as saturated molecules, the results are readily obtainable from Table 1 or 2 simply by adding up the various bond interactions, for example $C_6(C_2H_6—C_2H_6) = 413$ a.u. We would expect parameters obtained in this paper to be applicable to macromolecules[1], making it possible to consider not only C_6 values but also corrections to pairwise interactions as well as non-(pairwise) additive terms. Higher order interaction coefficients γ_n, for $n > 3$, can also be calculated in a similar way if so desired, but for the inclusion of anisotropic effects anisotropic polarizabilities must be considered.

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[1] For a macromolecule when its size is comparable or greater than intermolecular distances, the simple expression $-\sum_{ij} C_n^{ij}/r^n$ should be replaced by $-\sum_{ij} C_n^{ij}/r_{ij}^n$ in an obvious notation.

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