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Electric Polarizabilities, Magnetic Susceptibilities and Dispersion Coefficients for Hydrocarbons

II. Bond Values

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Using wavefunctions given in the companion paper bond properties and interactions are computed. Results are in agreement with other theoretical estimates and provide good molecular results. Differences between similar bonds can be accounted for by change in bond length. Simple formulae can be used to normalize bond contributions according to bond length. Parameters should be applicable to macromolecules.

Key words: Bond properties – Bond interactions – Hydrocarbons

1. Introduction

In the companion paper Frost-model exponents for wavefunctions of various hydrocarbons are given and selected properties of the molecules are calculated. *Ab initio* molecular calculations, even of the simple type represented by the Frost model, are obviously limited in size to those that are sufficiently small for the computer in question. Because the majority of molecules of real biological and industrial significance fall outside the present-day capabilities of most computers, alternative methods must be found. The molecular fragmenting technique of Christoffersen [1] is one method of dealing with the problem where the large molecule is split up into smaller parts which are optimized. Certain properties, however, may be calculated by adding together the contributions from the bonds and atoms in molecules [2] and this type of procedure is particularly successful when dealing with hydrocarbons. The contribution from the sigma electrons normally poses few problems, but that due to pi-bonding electrons is not strictly additive because of the electron delocalization. However, certain computational procedures for molecules do provide a kind of localized picture even for pi-electrons. One such example is the Frost model

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[3], in which orbitals after optimization tend to position themselves on heavy nuclei or in bonds and thus conform with chemical intuition. This localization onto atoms and bonds makes the Frost model an ideal candidate to attempt calculations of bond and atom properties, and in this paper we consider bond and atom electric polarizabilities and magnetic susceptibilities.

It is of considerable biological importance to be able to estimate intermolecular forces between macroscopic systems, particularly hydrocarbons and hydrocarbons with substituted groups or side chains. Although there have been criticisms of such a procedure [4], it seems to be generally accepted that this can best be done by summing pairwise interactions between individual components of the molecules, particularly for saturated systems [5, 6]. Since we may also calculate pi-bond contributions using the Frost-model localized picture, we may treat unsaturated systems as well. It is the frequency-dependent bond polarizabilities that are used to calculate bond–bond interaction dispersion coefficients, and in view of the excellent results obtained for the static polarizability of pi-bonding molecules using localized orbitals, we feel it is reasonable to compute intermolecular forces using similar methods.

That bond parameters for small systems can be transferred to larger systems is due to the fact that most bonds and especially CH and CC single bonds have much the same properties independent of the molecule in which they are found. This is largely because the bond lengths are so similar; CH bond lengths vary very little, and what small variations do occur for C—C and C═C bond lengths can be predicted from Stoicheff's empirical rules [7] in terms of linear functions of the number of bonds adjacent to the CC bond in question. More recently Kuchitsu [8] has proposed a simple empirical parabola to fit the C—C bond lengths, again in terms of the number of adjacent bonds. Whether one considers theoretical estimates of bond lengths in macromolecules using formulae such as mentioned above, or actual experimental results, the bond contribution to the property of interest may be adjusted, or normalized, if necessary according to its bond length provided the property can be expressed as some simple function of bond length. The dependence of the different parameters to be optimized, as well as associated properties, on the change in bond length is considered taking CH_4 as a simple example, and the value of normalized bond contributions is discussed.

2. Electric Polarizabilities and Magnetic Susceptibilities of CH and CC Bonds

The electric polarizability, $\bar{\alpha}$, and magnetic susceptibility, $\bar{\chi}$, of a molecule can both be expressed in terms of orbital exponents in the molecules' Frost-model wavefunction, and so it is a simple matter to find the contribution of each bond and atom. For $\bar{\alpha}$, we obtain [9]

$$\begin{aligned}\bar{\alpha}\,(\mathrm{BOND}) &= \tfrac{1}{2}\alpha_{\mathrm{B}}^{-2}\\ \bar{\alpha}\,(\mathrm{ATOM}) &= \tfrac{1}{2}\alpha_{\mathrm{IS}}^{-2}\end{aligned} \qquad (1)$$

where α_B and α_{IS} are the bond and inner shell exponents respectively. For $\bar{\chi}$ we find [10]

$$\begin{aligned} \bar{\chi}\,(\text{BOND}) &= -\frac{1}{4\alpha_B} \quad \text{for } s\text{-type and aromatic } p\text{-type Gaussians} \\ &= -\frac{1}{6\alpha_B} \quad \text{for double bond } p\text{-type Gaussians} \\ &= -\frac{1}{3\alpha_B} \quad \text{for triple bond } p\text{-type Gaussians} \\ \bar{\chi}\,(\text{ATOM}) &= -\frac{1}{4\alpha_{IS}}. \end{aligned} \tag{2}$$

When there is more than one orbital in a bond, for example a C=C bond, the bond value is made up of the sum of the individual contributions from the orbitals on it.

Values computed for $\bar{\alpha}$ using experimental and optimized geometries are compared with the values obtained by Amos and Crispin [11] in Table 1. For all the molecules the inner shell contribution was 0.0085 or 0.0086 (10^{-25} cm^3) and can really be ignored, and so for $\bar{\alpha}$ the molecular value can be made up simply of bond contributions and atomic terms may be neglected, though the values given in Table 1 for $\bar{\alpha}$ (TOTAL) do include these terms. The values obtained using optimized geometries are in better agreement with Amos and Crispin, though the CH bond values, from Eq. (1), show more variation than their values. There is a significantly larger CC contribution using the experimental geometries, which is reflected in the improved agreement with the experimental values. The molecular values of Amos and Crispin are similar to those using optimized geometries, but only in the case of C_2H_6, when there is only a small difference, are they superior to experimental geometry Frost-model wavefunctions, the difference being particularly marked for C_2H_4 and C_2H_2. Other values for bond polarizabilities include the rather old values

Table 1. Bond polarizabilities[a]

	Method[b]	CH_4	C_2H_6	C_2H_4	C_2H_2
CH	EG	5.84	5.88	4.95	4.35
	OG	6.10	6.12	5.39	4.63
	Amos–Crispin	5.81	6.15	6.03	6.05
CC	EG	—	5.93	22.40	26.43
	OG	—	5.44	15.35	22.36
	Amos–Crispin	—	4.94	13.78	20.61
$\bar{\alpha}$ (TOTAL)	EG	23.4	41.3	42.2	35.2
	OG	24.4	42.1	36.9	31.6
	Amos–Crispin	23.2	41.8	37.9	31.8
	Experiment[c]	25.6	44.7	42.2	34.9

[a] Units 10^{-25} c.c.

[b] EG = Experimental Geometry; OG = Optimized Geometry.

[c] See previous paper.

Table 2. Comparison of bond polarizabilities with other results[a]

Method	C—H	C—C	C=C	C≡C
EG	5.88	5.93	22.40	26.43
OG	6.12	5.44	15.35	22.36
Amos–Crispin [11]	6.15	4.94	13.78	20.61
Denbigh [2]	6.6	5.1	16.4	—
Syrkin–Dyatkina [13]	6.7	5.0	16.5	25.4
Bolton [12]	—	4.87	16.2	26.1

[a] Units 10^{-25} c.c.

given by Bolton [12] which are similar to those given by Syrkin and Dyatkina [13] from molar refractions and the almost identical results of Denbigh *et al.* [2, 14]. These are given in Table 2, together with C—H, C—C parameter values taken from C_2H_6, C=C from C_2H_4 and C≡C from C_2H_2 for experimental and optimized geometries as well as the results of Amos and Crispin. Note that the C—H bond value does vary for the different species, and we have taken the alkane value. The other estimates for C—H are somewhat larger and C—C somewhat smaller than both experimental and optimized geometry results. The C=C bond value using the optimized geometry is in good agreement with the other values, whilst the result using the experimental geometry is some 40% higher, although the C≡C value is in good agreement with the other values whilst the optimized geometry result is lower. Of course, the ultimate test is the molecular results obtained using the parameters, and results given in Table 1 certainly indicate that satisfactory results may be obtained using them. We would, however, suggest the use of the different C—H values for the different environments for the C—H bond.

Values for $\bar{\chi}$ using Eqs. (2) are given in Table 3, and it can be seen immediately that atomic contributions are constant, but can no longer really be considered negligible, due to the dependence on $\alpha_{\bar{\mathrm{IS}}}^{1}$ rather than $\alpha_{\bar{\mathrm{IS}}}^{2}$ as for $\bar{\alpha}$ and so ought to be included in the total molecular value. Normally contributions are considered as atomic sums, for example Pascal constants given by Pople [15] or those used by Davies [16], with corrections to allow for multiple bonds and so comparison cannot be made directly.

In his excellent review article on the subject Ditchfield [17] mentions that though very approximate methods such as Pople's prove highly successful there have been criticisms; for instance, Hameka [18] disagrees with the theoretical justification and prefers instead to consider $\bar{\chi}$ as the sum of bond contributions as in this paper. His results [18], however, include corrections for interactions between adjacent bonds and for atomic inner shell electrons, and so are not directly comparable with ours. Table 3 gives the various bond contributions from Frost-model wavefunctions as well as molecular values for $\bar{\chi}$. It can be seen that for the saturated molecules there is reasonable but not excellent agreement with experiment and that the bond contributions are too small. For C_2H_4 and C_2H_2 there is good agreement using the bond values given, whilst for cyclo-C_3H_6 again the values should be larger due to

Table 3. Bond magnetic susceptibilities[a]

	Method	CH_4	C_2H_6	C_2H_4	C_2H_2	cyclo C_3H_6
IS	EG	−0.13	−0.13	−0.13	−0.13	−0.13
	Baudet	−0.15	−0.15	−0.15	−0.15	−0.15
CH	EG	−3.34	−3.35	−3.07	−2.88	−3.28
	OG	−3.41	−3.41	−3.20	−2.97	−3.36
	Baudet	−4.05	−4.05	−3.74	−3.33	−4.05
CC	EG	—	−3.36	−6.65	−15.02	−3.75
	OG	—	−3.22	−7.65	−11.30	−3.72
	Baudet	—	−3.10	−6.03	−12.30	−3.10
$\bar{\chi}$	EG	−13.5	−23.7	−19.2	−21.0	−31.3
(Total)	OG	−13.8	−24.0	−20.7	−17.5	−31.7
	Pople [15]	−17.7	−29.6	−20.8	−17.8	−35.6
	Davies [16]	−16.3	−28.5	−17.3	−18.8	−34.4
	Experiment[b]	−17.4	−26.8	−18.8	−20.8	−39.2
	Baudet [20]	−16.4	−27.7	−21.3	−19.3	−34.1

[a] 10^{-6} c.g.s. units.

[b] See previous paper.

its being a strained ring system. The CC bond in cyclo-C_3H_6 does in fact display certain characteristics similar to those in a system like C_2H_4, and it is interesting to note that the result using the parameters for C_2H_4 gives a value of −38.8, in good agreement with experiment. The values using Pascal constants are in much better agreement for CH_4 and cyclo-C_3H_6, slightly better for C_2H_6 but worse for C_2H_4 and C_2H_2. Hameka's values for CH_4 and C_2H_6 are −18.9 and −29.6, which are better than those given in this paper for CH_4 and comparable for C_2H_6, tending to overestimate rather than underestimate the magnitude of the result. It is worth mentioning, however, that the older experimental result given by Bitter [19] for CH_4 of −12.4 is in good agreement with our result. Theoretical values which are directly comparable with Frost-model results are also given in Table 3 due to Baudet [20], who treats the molecular value as a sum of inner shell and bond contributions. Though his values for CH bonds are slightly larger and for CC bonds slightly smaller than Frost-model results, the molecular results are reasonably close. The overall picture of the results for $\bar{\chi}$ from Table 3 is that there seems little to choose between procedures involving sums of bond contributions with inner shell corrections, such as that of Baudet and the method of this paper, and methods involving sums of atomic terms with corrections due to multiple bonds. On the whole, however, results seem slightly less accurate for $\bar{\chi}$ than for $\bar{\alpha}$, though there is the problem of deciding how accurate and reliable experimental values are.

3. Bond Values for Some Other Molecules

The main criterion which must be satisfied to justify the use of bond and atomic properties to estimate molecular values is that the parameters involved should be transferable. Previous results [21, 22] indicate that this is indeed the case for

Table 4. Bond properties for some other molecules[a]

	$\bar{\alpha}$		$\bar{\chi}$	
Molecule	CH	CC[b]	CH	CC[b]
cyclo-C_3H_6	5.65	7.36	3.28	3.75
C_3H_4	4.90	17.11	3.06	6.00
C_4H_6	5.50	4.86, 22.90	3.24	3.04, 6.77
C_6H_6 (BOND)	4.81	3.73, 22.91	3.03	2.67, 8.81
C_6H_6 (ATOM)	5.02	10.72	3.09	5.29

[a] Units as for Tables 1 and 3.

[b] For two entries, the first refers to C—C, the second to C=C.

hydrocarbons and here we consider the other hydrocarbon molecules of the previous paper and consider slightly larger ring and pi-bonding systems with a view to checking this premise.

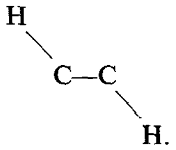
In Table 4 values for bond contributions to $\bar{\alpha}$ and $\bar{\chi}$ for cyclo-C_3H_6 (repeated in the case of $\bar{\chi}$), C_3H_4, C_4H_6 and C_6H_6 are given. The wavefunctions for C_3H_4 and C_4H_6 were taken with CC orbital positions fixed at the centre of each bond, and the same exponent for inner and outer CH exponents for C_4H_6, whilst both wavefunctions for benzene are used, that is *p*-type Gaussians in the bonds or on atoms. For further details see the previous paper.

For $\bar{\alpha}$ inner shell contributions are again all 0.0085, while that for $\bar{\chi}$ is again 0.13, clearly indicating the inner shell contributions are transferable and are independent of the environment. The C—H contribution is not independent of the environment, and for $\bar{\alpha}$ the slightly smaller contribution for cyclo-C_3H_6 than for C_2H_6 is a consequence of smaller bond length. For C_3H_4 the C—H contribution is very similar to the C_2H_4 value, as is that for both the C_6H_6 wavefunctions. The C—H value for C_4H_6 is in between the C_2H_6 and C_2H_4 values as to be expected as the molecule bears certain obvious similarities to both species. For C_6H_6 both wavefunctions give results similar to C_2H_4 and so we can say that C—H values are transferable for π systems. Indeed, exactly the same comments as above can be made for the C—H contributions to $\bar{\chi}$ as well.

For CC values the situation is slightly different. In the case of $\bar{\alpha}$ for cyclo-C_3H_6 there is an increase in the CC value for C_2H_6 of about 25%, due to the strained ring system and the almost pi nature of the bond, and so the two are not strictly comparable. For C_3H_4 the C=C value is some 20% lower than the corresponding C_2H_4 result, and we would imagine this rather underestimates the contribution. A value of around 20 would probably be more realistic, not only putting it in better agreement with the C=C value for C_2H_4 but also putting the molecular value closer to experimental values of around 60 [13, 23]. However, it should be noted that the bond length used for C_3H_4 is shorter than for C_2H_4 and that the molecular result obtained with the values given in Table 4 is in good agreement with another experimental value of 55 [24]. On the whole we would be inclined to think that the C=C value for C_3H_4 should be increased. For C_4H_6 the C=C value is close to that for C_2H_4, whilst the C—C value is smaller than for C_2H_6, again because of the shorter bond length. Benzene produces a slightly different problem, and the C_6H_6 (BOND) method gives a value for the pseudo double bond very similar to the C_2H_4 value. The pseudo single bond value, however, is much smaller than the value for C_2H_6 as a consequence of the bond length being almost 10% smaller. For C_6H_6 (ATOM) the CC term is taken as a result of dividing the atomic p-contribution onto the adjacent CC bonds and adding the CC_σ term. The value for this of 10.72 is rather too small, and a better result would be obtained by averaging the single and double bond contributions for C_6H_6 (BOND) to give 13.32, though this probably slightly overestimates the value for aromatic CC. Overall we would consider that parameters were transferable even to ring systems, and where values do show variations they can be directly attributed to bond length changes, which will be discussed further in Sect. 5. For the $\bar{\chi}$ CC parameters much the same can be said as for $\bar{\alpha}$, though for benzene the C=C formula is different from that for C_2H_4 and so values are not comparable.

4. Bond Interactions

The most influential work that has been done using the summation of pairwise interactions between individual components was due to Salem [25]. He expressed the interaction between two paraffin chains as the sum of interactions between units in each chain, each unit consisting of four atoms and three bonds



The interaction between these units, which is chemically equivalent to CH_2, was broken down into dispersion interactions between bonds which were calculated using approximate formulae and semi-empirical estimates. Basically, therefore, Salem can be considered to have taken the interaction between saturated hydrocarbons as the sum of bond dispersion interactions. Recently Amos and Crispin [26] have used a more sophisticated version of the same approach and have evaluated bond dispersion coefficients using quite accurate Hartree–Fock wavefunctions for methane and ethane. It should be emphasized that not all the interaction energy comes from dispersion coefficients; there will be orientation-dependent terms due to the CH bond dipole moment as well as smaller induction terms. These terms may be zero for the molecular interaction treated as a whole by considering the interacting molecules as two points, but if bond interactions are considered these may well be non-vanishing. These terms can be included if it is thought necessary, but it is the estimation of the dispersion terms which is the difficult problem and which will be considered here.

It is possible to associate with each bond a frequency-dependent polarizability which is just a natural extension of Eq. (1):

$$\bar{\alpha}_{\mathrm{AB}}(\omega) = \frac{1}{\omega_{\mathrm{AB}}^2 - \omega^2} \tag{3}$$

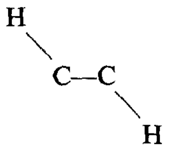
with $\omega_{\mathrm{AB}} = 2\alpha_{\mathrm{AB}}$ for bond AB. The average dispersion coefficient C_6 (AB − CD) between bonds AB and CD can then be written

$$C_6(\mathrm{AB} - \mathrm{CD}) = \frac{3}{\pi} \int \bar{\alpha}_{\mathrm{AB}}(i\omega)\bar{\alpha}_{\mathrm{CD}}(i\omega)\, d\omega. \tag{4}$$

In the previous section the Frost-model static polarizabilities $\bar{\alpha}$ (CC) and $\bar{\alpha}$ (CH) were in satisfactory agreement with other results and led to good molecular results, and so it is to be hoped that the frequency-dependent results will be just as accurate. Using the formulae of Eqs. (3) and (4) we obtain

$$C_6(\mathrm{AB} - \mathrm{CD}) = \frac{6}{\omega_{\mathrm{AB}}\omega_{\mathrm{CD}}(\omega_{\mathrm{AB}} + \omega_{\mathrm{CD}})} \tag{5}$$

which for interactions between like bonds reduces to $3/\omega_{\mathrm{AB}}^3$. Using this formula bond–bond dispersion coefficients given in Table 5 are in good agreement with Amos and Crispin, whose values for saturated hydrocarbons are CH—CH between 8.39 and 9.39, CH—CC 8.16 and CC—CC 7.13, though the CC—CC result in Table 5 is somewhat higher. Salem's semi-empirical values are given in brackets in the table and generally interactions involving CH are larger than our values and C═C are smaller. When our values are combined together we find $C_6 = 75.8$ a.u. for the interaction between



fragments as compared with the value 96.9 a.u. used by Salem. Interactions involving C≡C are also given in the table, as well as interactions between the different sorts of CH bonds. In the case of multiple bonds, contributions are considered to be sums of the individual constituent orbital interactions.

The inner shell correcting terms are small, dispersion coefficients using the C_2H_6 inner shell exponent are IS—IS = 0.00047, IS—CH(C_2H_6) = 0.0235, whilst for interactions with C—C, C═C and C≡C the values are 0.0236, 0.0612 and 0.084. Amos and Crispin [27] quote IS—CH and IS—IS interactions as 0.0308 and 0.00061, which are in reasonable agreement with our values, but really they are so small as to be readily ignored.

The bond interaction method is not the only way to evaluate the interaction energy between large molecules. It is often more convenient to write the energy as the sum of atom–atom interactions, the dispersion part of which will involve terms such as $-C_6(\mathrm{C—H})/R_{\mathrm{CH}}^6$ for the dispersion energy between a carbon atom and a hydrogen

Table 5. Bond–bond dispersion coefficients[a]

Bond	$CH(C_2H_6)$	$CH(C_2H_4)$	$CH(C_2H_2)$	C—C	C=C	C≡C	CC_A
$CH(C_2H_6)$	8.39 (12.20)						
$CH(C_2H_4)$	7.37	6.48					
$CH(C_2H_2)$	6.67	5.88	5.34				
C—C	8.44 (9.99)	7.41	6.72	8.50 (8.20)			
C=C	25.08 (27.27)	21.84	19.68	25.25 (22.20)	77.92 (61.55)		
C≡C	32.86	28.71	25.92	33.08	100.54	130.54	
CC_A[b]	15.79, 13.90	14.10, 12.17	12.46, 11.00	15.93, 13.99	48.63, 42.15	62.99, 54.90	30.44, 23.15

[a] In atomic units.

[b] $CC_A = CC(C_6H_6)$; first entry using C_6H_6 (BOND), second C_6H_6 (ATOM).

atom. For saturated hydrocarbons we require three atom–atom dispersion coefficients $C_6(\text{C—H})$, $C_6(\text{C—C})$, $C_6(\text{H—H})$ which can be obtained by redistributing the bond interaction coefficients amongst the atoms in the bonds according to the formulae [6]:

$$\begin{aligned} C_6(\text{C—C}) &= 4C_6(\text{CC—CC}) \\ C_6(\text{C—H}) &= 2C_6(\text{CH—CC}) - C_6(\text{CC—CC}) \\ C_6(\text{H—H}) &= C_6(\text{CH—CH}) - C_6(\text{CH—CC}) + \tfrac{1}{4}C_6(\text{CC—CC}). \end{aligned} \tag{6}$$

The values of the atom–atom coefficients are 34, 8.4 and 2.1 a.u. respectively compared with values used by Abe *et al.* [28] in the study of conformations, configuration statistics and crystal structures of 26.3, 9.2 and 3.3 calculated using Slater-Kirkwood atom polarizabilities.

For the interaction between aromatic hydrocarbons it is possible to estimate the interaction using the pseudo single and double bonds of the C_6H_6 (BOND) wavefunction to calculate the various bond interactions. Alternatively the C_6H_6 (ATOM) wavefunction can be used where the CC bond interactions will come from the *s*-type Gaussian in the bond and there will be additional atomic contributions from the *p*-type Gaussians, or they may be shared between adjacent bonds. In Table 5 values for interactions using both C_6H_6 (BOND) and C_6H_6 (ATOM) are given. For C_6H_6 (BOND) the value in each case is the average of the interaction with the single bond and with the double bond except for $\text{CC}_\text{A}\text{—CC}_\text{A}$, which is taken to be $\frac{1}{4}((\text{C=C} - \text{C=C}) + (\text{C—C} - \text{C—C}) + 2(\text{C=C} - \text{C—C}))$. For C_6H_6 (ATOM) the atomic contribution is reallocated onto the adjacent CC bonds which effectively assume a singly occupied *p*-orbital of the same exponent as the atomic function in each bond. The values obtained using both methods not surprisingly lie between the corresponding results for CC single and CC double bonds. As the results for the molecular polarizabilities using the two wavefunctions are either side of the experimental result, we are inclined to believe that a more accurate interaction coefficient lies between the two values given. Though it is difficult to guess the exact accuracy of the procedures mentioned above, we believe that because of the success of a localized picture in predicting molecular properties for ring systems there is no reason why bond properties and interactions cannot be estimated from the localized orbitals as well. Care must be taken in the approximations made, but the localized picture provides a useful tool in the calculation of properties for ring systems.

5. Properties as Functions of Bond Length; Methane as a Simple Example

Frost-model formulae for bond values for $\bar{\alpha}$ and $\bar{\chi}$ have been given in terms of orbital exponents in Eqs. (1) and (2). Alternatively, for the Frost model we may rewrite the formulae in terms of orbital radii $\{\rho_i\}$ which are simply related to the exponents $\{\alpha_i\}$ by [3]

$$\alpha_i = \frac{1}{\rho_i^2}. \tag{7}$$

Substitution of Eq. (7) into Eqs. (1) and (2) yields a dependence on ρ^4 for $\bar{\alpha}$ and ρ^2 for $\bar{\chi}$, and so in an obvious way the longer the bond length R the larger the orbital radius becomes, and hence there is a corresponding increase in the value of $\bar{\alpha}$ and $\bar{\chi}$. This is borne out by statements made in previous sections and in this section the variation with bond length of various parameters to be optimized, as well as associated properties, is investigated.

An ideal example to demonstrate these changes is methane, where we take a tetrahedral geometry and simply hold the CH bond length fixed at different values close to the experimental and optimized values. There are three parameters to be optimized, the inner shell and CH exponents and the CH orbital position. The CH exponent and hence radius is related to $\bar{\alpha}$(CH) and $\bar{\chi}$(CH) as mentioned before, whilst the inner shell exponent mirrors changes in the total energy E, though not of course with as simple a formula as for $\bar{\alpha}$ or $\bar{\chi}$. The CH orbital position determines the CH bond dipole, for, using perturbation theory [9] we may write the x-component of the dipole moment for a molecule as

$$\mu_x = \sum_r \bar{X}_r \bar{Z}_r - 2 \sum_{i=1}^{n} X_i \tag{8}$$

where the nuclei have x-coordinates $\bar{X}_r$ and nuclear charges $\bar{Z}_r$ and X_i is the position of the ith Gaussian relative to a fixed molecular axis. Again, as for $\bar{\alpha}$ and $\bar{\chi}$, it is the unantisymmetrized product of Gaussians that is used to determine μ. For CH_4 $\mu = 0$ from symmetry considerations, but we can consider instead the distance of the orbital along the bond which is related to the CH dipole moment.

The experimental bond length is 2.067 a.u. [29], whilst the optimized value given by Frost is 2.107 [21] and so the range considered is 2.05 to 2.15 with increments of 0.01. Values of $R_{\mathrm{CH}} = 2.00$ and 2.20 were also used, but it is only really worthwhile looking at values in the given range, as methyl-like CH bond lengths tend to be well within these values [8]. Simple linear fits for the orbital radii ρ_{IS} and ρ_{CH} as well as D_{CH}, the distance of the CH orbital along the CH bond, are obtained using a regression program on a Texas TI programmable 57 hand calculator, that is

$$\rho = AR + B \tag{9}$$

with a similar expression for D, with A and B constants. The closeness of the correlation coefficient r to unity is an indication of the goodness of fit. Results are given in Table 6; the fit is obtained from the values for $R = 2.05$ to 2.15. First, it can be seen that the minimum total energy falls somewhere between $R = 2.10$ and 2.11, which is in agreement with Frost's value, though the energy minimum is extremely shallow, with only an overall change of about 0.04% with a 10% change in R. Excellent linear fits for both ρ_{IS} and D_{CH} are obtained, but we would not claim accuracy to the number of figures given but have merely given what was on the calculator display. Normally one would expect some rounding errors from the calculator and so to all intents and purposes one could almost say that the fit was exact. Certainly results are often only published to three decimal places [21] for orbital radii, and over the range ρ_{IS} remains constant at 0.328 to three decimal places. The almost negligible change is reflected by the small change in energy, though there is no minimum for ρ_{IS}. The position of the orbital is about 60% along

Table 6. Inner shell radius and CH orbital position as functions of bond length for CH_4[a]

		ρ_{1S}		D_{CH}[b]	
R	Energy	Actual	Predicted	Actual	Predicted
2.05	−33.98875	0.3277311	0.3277330	1.2280535	1.2282258
2.06	−33.98986	0.3277636	0.3277646	1.2329745	1.2330508
2.07	−33.99074	0.3277965	0.3277962	1.2378465	1.2378757
2.08	−33.99140	0.3278283	0.3278278	1.2427702	1.2427007
2.09	−33.99185	0.3278608	0.3278595	1.2476475	1.2475256
2.10	−33.99209	0.3278927	0.3278911	1.2525117	1.2523505
2.11	−33.99212	0.3279237	0.3279227	1.2572902	1.2571755
2.12	−33.99195	0.3279555	0.3279543	1.2620579	1.2620004
2.13	−33.99159	0.3279860	0.3279859	1.2668621	1.2668254
2.14	−33.99103	0.3280165	0.3280175	1.2715652	1.2716503
2.15	−33.99029	0.3280469	0.3280491	1.2762767	1.2764753
2.00	−33.97964	0.3275615	0.3275750	1.2026759	1.2041011
2.20	−33.98392	0.3281943	0.3282071	1.2993507	1.3006000
Function (Eq. (9))	A		0.0031604		0.4824944
	B		0.3212543		0.2391123
	r		0.9998513		0.9999723

[a] In atomic units.

[b] Distance measured from the carbon atom.

the bond, that is closer to H than to C, giving a value of about −0.4 a.u. taking $\overrightarrow{CH}$ as positive direction.

In Table 7 actual and predicted values from Eq. (9) are given for ρ_{CH}, $\bar{\alpha}$(CH) and $\bar{\chi}$(CH). Again, there is excellent agreement using the simple linear fits, the change in ρ_{CH} of about 5% or 6% is reflected by 10% to 12% change for $\bar{\chi}$(CH) and 20% to 24% change for $\bar{\alpha}$(CH), with a 10% change in R. So the effect is far more pronounced with this parameter and these properties. Using the formula of Eq. (9), it is possible to estimate a parameter for a different bond length from a known value at a given bond length provided that either the slope or intercept is known. Alternatively we may fit a formula of the form

$$\bar{\alpha}(\mathrm{CH}) = AR^{B} \tag{10}$$

with a similar function for $\bar{\chi}$(CH); simply by taking logarithms of both sides B becomes the slope and A the intercept. For the range 2.05 to 2.15 for CH_4 again a good fit was obtained, with $r = 0.9999851$, $A = 0.768353$ and $B = 2.2521774$ for $\bar{\alpha}$(CH) and $r = 0.9999846$, $A = 0.3099097$ and $B = 1.1260893$ for $\bar{\chi}$(CH). This means that $\bar{\alpha}(\mathrm{CH})'$, $\bar{\chi}(\mathrm{CH})'$ for known R' may be estimated from known $\bar{\alpha}$(CH) and $\bar{\chi}$(CH) by the simple approximate formulae

$$\bar{\alpha}(\mathrm{CH})' = \left(\frac{R'}{R}\right)^{9/4} \bar{\alpha}(\mathrm{CH}) \tag{11}$$

Table 7. Bond orbital radius and bond properties as functions of bond length for CH_4[a]

	ρ_{CH}		$\bar{\alpha}$ (CH)		$\bar{\chi}$ (CH)	
R	Actual	Predicted	Actual	Predicted	Actual	Predicted
2.05	1.6680726	1.6680037	3.8710591	3.8677751	0.6956165	0.6954817
2.06	1.6725448	1.6725373	3.9127405	3.9116013	0.6993515	0.6993142
2.07	1.6770797	1.6770710	3.955349	3.9554275	0.7031491	0.7031467
2.08	1.6815771	1.6816046	3.997948	3.9992537	0.7069254	0.7069792
2.09	1.6861002	1.6861382	4.0411365	4.04308	0.7107335	0.7108117
2.10	1.6906191	1.6906719	4.0846334	4.0869062	0.7145482	0.7146442
2.11	1.6951753	1.6952055	4.1288439	4.1307324	0.7184048	0.7184768
2.12	1.6997349	1.6997391	4.1734457	4.1745586	0.7222747	0.7223093
2.13	1.7042565	1.7042728	4.2180317	4.2183849	0.7261226	0.7261418
2.14	1.7088318	1.7088064	4.2635099	4.2622111	0.7300265	0.7299743
2.15	1.7133987	1.7133400	4.3092703	4.3060373	0.7339338	0.7338068
2.00	1.6457643	1.6453356	3.6680948	3.648644	0.677135	0.6763191
2.20	1.7363817	1.7360082	4.5451770	4.5251684	0.7537554	0.7529694
Function (Eq. (9))	A	0.4533633		4.3826223		0.3832517
	B	0.738609		−5.1166006		−0.0901843
		0.9999971		0.9999059		0.9999804

[a] In atomic units.

and

$$\bar{\chi}(\mathrm{CH})' = \left(\frac{R'}{R}\right)^{9/8} \bar{\chi}(\mathrm{CH}). \tag{12}$$

To test these formulae the CH bond from which the known values of $\bar{\alpha}$(CH) and $\bar{\chi}$(CH) are to be taken must be in exactly the same environment as the CH bond for which the properties are to be predicted. The only two molecules in the previous paper for which this occurs are C_2H_4 and C_3H_4 where there is a small difference in bond lengths. If Eqs. (11) and (12) are assumed to be true for all CH bond lengths, to be used in the way suggested above, then values predicted for CH bond properties for C_3H_4, simply from knowledge of its bond length and complete knowledge of C_2H_4, are $\bar{\alpha}(\mathrm{CH}) = 4.91$ and $\bar{\chi}(\mathrm{CH}) = 3.06$ compared with actual values of 4.90 and 3.06.

6. Conclusions

Ab initio bond properties for $\bar{\alpha}$ and $\bar{\chi}$ as well as interactions computed using Frost-model wavefunctions are in agreement with other theoretical and empirical estimates. Where there are differences between contributions of similar bonds in different molecules they can normally be attributed to changes in bond length. In Sect. 5 it is demonstrated how contributions may be normalized according to bond length using simple formulae if so desired. On the whole, rather than actually normalize bond contributions we feel that the bond lengths should provide an approximate guide to relative property results rather than a definitive result. Certainly in the case of bond interactions where anisotropic effect and higher order terms are not included the accuracy of the procedure would not really warrant normalization, though it is worth bearing in mind. The bond values given in this paper should be useful in estimating interactions between larger hydrocarbons, including ring systems.

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