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# Electric Polarizabilities, Magnetic Susceptibilities and Dispersion Coefficients for Hydrocarbons

## I. Molecular Values

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Frost-model wavefunctions for $CH_4$, $C_2H_6$, cyclo-$C_3H_6$, $C_2H_4$, $C_2H_2$, allene, transbutadiene and benzene are given using experimental rather than optimized geometries. Results for electric polarizabilities and magnetic susceptibilities are computed using several different optimizations, and results are in good agreement with experiment. Dispersion coefficients $C_6$, $C_8$ and $C_{10}$ are given for all pair interactions, as are values for $\gamma_3$, the three-body interaction, and $d_4$, a retardation correction term, for several interacting species. Results should be fairly reliable.

**Key words:** Hydrocarbons – Frost model – Electric polarizabilities – Magnetic susceptibilities – Dispersion coefficients

## 1. Introduction

In calculations using floating Gaussians, e.g. as in the Frost model, certain molecular computational procedures, such as those of Frost [1] and Blustin and Linnett [2], optimize nuclear geometry as well as orbital positions and sizes to obtain the energy minimum, whilst others, such as OPIT [3], do an energy minimization for a fixed geometry which normally is taken to be experimental.

In Frost's procedure all orbital positions are allowed to float except in the case of pi-bonding or molecules containing lone pairs, when there may be coalescence of two or more *s*-type orbitals causing singularity problems. In such cases the use of actual *p*-type functions, which are automatically orthogonal to *s*-type orbitals, to represent out-of-plane electrons, rather than that simulated by *s*-type functions, alleviates any difficulties. Since inner shell orbitals position themselves extremely close to nuclei, these orbitals are often actually held fixed on the nuclei, whilst certain other orbitals may also be held fixed through symmetry considerations. For

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instance, the bonding orbital in a homonuclear diatomic such as $Li_2$ would be held fixed at the centre of the bond. Sometimes similar parameters are allocated the same value, for example inner shell exponents for the same atom, say carbon, as they do not vary very much and so carbon atoms in different environments will often be given the same exponent.

In all cases, whether it be reducing the number of parameters to be optimized by holding them fixed, or allocating them the same value as another similar parameter, the reduction obviously means a simplification in the optimization routine and a reduction in computational time and expense. But how do various properties vary according to the various optimisations that are undertaken and which geometry should be used, optimized or experimental? The optimized geometry has certain attractions in that the geometry criterion is implicit in the energy minimization and means also that predictions of bond lengths and angles may be made. However, if one is not interested in predicting these properties but is concerned with others, then certainly the actual experimental geometry has its attractions, as well as reducing the number of parameters to be optimized. Different properties can obviously depend on different parameters. Some, such as total energy, depend mainly on the inner shell orbital sizes, whilst others, such as electric polarizabilities, $\bar{\alpha}$, and magnetic susceptibilities, $\bar{\chi}$, depend mainly on bond and lone pair orbital sizes, and inner shell contributions may effectively be ignored [4]. Dipole moments depend on nuclear and orbital positions and so it can be seen that the nature of the property must be taken into consideration before attempting to reduce the number of parameters to be optimized.

In the case of hydrocarbons, molecular geometries using the Frost model are normally predicted fairly accurately and usually in a uniform way, CH bond lengths are normally slightly larger than experiment and C—C slightly smaller [2]. When optimized and experimental geometries are in reasonable agreement, it is to be expected that properties should be fairly similar as well. However, certain properties are more sensitive to geometric changes than others, and this paper will consider the effect of taking experimental geometry, rather than optimized, for several hydrocarbons in the calculation of electric polarizabilities and magnetic susceptibilities. Results may be compared directly with those using the optimized geometries and wavefunctions of Frost and Rouse [5] and also with the experimental values of Bridge and Buckingham [6]. Both allene and butadiene provide ideal examples of molecules where parameters may be optimized separately or together, and, along with benzene, a pi-bonding ring system, provide further examples of pi-bonding molecules with which to test our formulae.

Long-range intermolecular forces are of central importance to the understanding of how molecules interact with each other. Using the electric polarizability formula, it is a simple matter to derive Frost model values of dispersion coefficients. Previously calculations have been mainly restricted to atoms and small molecules [7] and only a few *ab initio* calculations have been performed on hydrocarbons [8]. Of course, theoretical estimates may be made using the Slater–Kirkwood [9], Kirkwood–Muller [10] or London [11] formulae, though perhaps the most accurate values are found from refractive index data which are generally in reasonable agreement with Frost model values [12]. For this reason we believe that the values given in this paper for dispersion coefficients are fairly reliable and do provide *ab initio* rather than semi-empirical estimates of the forces involved.

## 2. Electric Polarizabilities, Magnetic Susceptibilities and Dispersion Coefficients for Frost Model Wavefunctions

For the Frost model the ground-state wavefunction using a Lewis basis set, that is one orbital per electron pair, is the antisymmetrized product of $n$ doubly occupied floating Gaussian orbitals. Then we can write the zero order function as $\psi_0 = \mathscr{A}\phi_{00}$, where

$$\phi_{00} = G_1(1)G_1(2)G_2(3)\cdots G_n(2n)\alpha(1)\beta(2)\alpha(3)\cdots\beta(2n), \tag{1}$$

with an $s$-type Gaussian of the form

$$G_i(j) = \left(\frac{2\alpha_i}{\pi}\right)^{3/4} \exp\left(-\alpha_i r_i^2(j)\right), \tag{2}$$

where $r_i^2(j) = |\boldsymbol{r}_j - \boldsymbol{R}_i|^2$ with $\boldsymbol{R}_i$ the position of the centre of the $i$th Gaussian. The non-linear parameters $\{\alpha_i, \boldsymbol{R}_i\}$ are chosen to minimize the variational energy. Particularly simple expressions for $\bar{\alpha}$ and $\bar{\chi}$ can be obtained using perturbation theory in conjunction with the Frost model [13], where using $\phi_{00}$ rather than $\psi_0$, we find

$$\bar{\alpha} = \frac{1}{2}\sum_{i=1}^{n}\frac{1}{\alpha_i^2} \tag{3}$$

and

$$\bar{\chi} = -\frac{1}{4}\sum_{i=1}^{n}\frac{1}{\alpha_i}, \tag{4}$$

with $n$ the number of orbitals. Eq. (3) is true for a mixed $s$- and $p$-type Lewis Gaussian basis set [4] whilst Eq. (4) is true for $s$-type sets only. It can be argued that Eq. (4) is also true for mixed $s$- and $p$-type sets [14], but another formula also suggested for hydrocarbons is [14]

$$\bar{\chi} = -\frac{1}{4}\sum_{s,p_A=i}\frac{1}{\alpha_i} - \frac{1}{6}\sum_{p_D=i}\frac{1}{\alpha_i} - \frac{1}{3}\sum_{p_T=i}\frac{1}{\alpha_i}, \tag{5}$$

where the first sum is over $s$-type and aromatic $p$-type functions, whilst $p_D$ and $p_T$ correspond to $p$-type functions in double and triple bonds respectively.

Previously it has been shown classically by setting up a point charge model [15] or quantum mechanically using perturbation theory [12] that the average frequency-dependent molecular polarizability is a natural extension of Eq. (3), namely

$$\bar{\alpha}(\omega) = \sum_{i=1}^{n}\frac{2}{\omega_i^2 - \omega^2} \tag{6}$$

with $\omega_i = 2\alpha_i$. This plays an important role in the theory of intermolecular forces. For, the long-range temperature-independent interaction energy between two neutral molecules, when averaged over all orientations, may be written as an asymptotic series [16]

$$\Delta E = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \cdots, \tag{7}$$

where $R$ is the intermolecular separation distance and $C_6$, $C_8$, $C_{10}, \ldots$ are constants depending on the particular molecules which are interacting. Each of the terms in Eq. (7) may be divided into two parts, the induction and dispersion parts. The induction part depends on the permanent dipole moments, $\mu_A$, $\mu_B$, and static polarizabilities, $\bar{\alpha}_A$, $\bar{\alpha}_B$ [17], and there will also be an additional orientation or Keesom term dependent on the $\mu_A$ and $\mu_B$. However, for all the hydrocarbons considered in this paper, $\mu = 0$ and so these contributions are zero. Thus $C_6$ may be expressed by the dispersion part alone, which can be written in terms of the average frequency-dependent polarizabilities at imaginary frequencies, $\alpha_A(i\omega)$ and $\alpha_B(i\omega)$, of the two interacting molecules [18]. The result is

$$C_6 = \frac{3}{\pi} \int_0^\infty \alpha_A(i\omega)\alpha_B(i\omega)\, d\omega. \tag{8}$$

Then, substituting Eq. (6) into Eq. (8) we find

$$C_6 = 6 \sum_{i=1}^{n_A} \sum_{j=1}^{n_B} \frac{1}{\omega_i^A \omega_j^B (\omega_i^A + \omega_j^B)} \tag{9}$$

in an obvious notation. Similar expressions may be obtained for $C_8$, $C_{10}$ and $\gamma_3$, the 3-body interaction energy coefficient, and these are given elsewhere [12]. Again, it can be seen from Eq. (9) that bond and lone pair orbital contributions will dominate as in the case of $\bar{\alpha}$ and $\bar{\chi}$.

## 3. The Wavefunctions and Geometries

The calculations of the wavefunctions were performed using the OPIT program at Nottingham [3] which has been modified to include $p$-type Gaussians by Brailsford and Schnuelle, see for example Brailsford *et al.* [19]. Details of the Lewis set exponents for $CH_4$, $C_2H_6$, cyclo-$C_3H_6$, $C_2H_4$ and $C_2H_2$ are given in Table 1, and total energies may be compared with the values of Frost and Rouse [5] and the more accurate calculations of Snyder and Basch (SB) [20]. In all cases CH orbital positions were optimized and all other bond orbitals were held fixed through symmetry considerations, and all exponents were optimized. The inner shell orbitals were held fixed on the nuclei since that should not affect the results for the properties considered in view of remarks made earlier. Experimental geometries, as used by SB, were taken throughout. Details for $C_2H_2$ and $C_2H_4$ have been given previously [4], but are included for completeness. The energies for these molecules are very similar to Frost's values and give about 84% of the SB results. Frost's values are slightly better for the saturated systems, but the energies for pi-bonding systems show that there is an improvement through using actual $p$-type functions.

Also given in Table 1 are three examples of larger pi-bonding hydrocarbons, allene, transbutadiene and benzene. SB geometries were taken for $C_3H_4$ and $C_4H_6$ whilst

**Table 1.** Molecular wavefunctions with experimental geometries[a]

| Molecule[b] | Inner shell | Exponents | | | Distance | | Energy | |
|---|---|---|---|---|---|---|---|---|
| | | CH[c] | $CC_s$[d] | $CC_p$ | C–CH orbital | This paper | SB[e] | Frost[f] |
| $CH_4$ | 9.3073 | 0.3562 | — | — | 1.2361 | 33.991 | 40.182 | 33.992 |
| $C_2H_6$ | 9.3006 | 0.3549 | 0.3534 | — | 1.2712 | 67.001 | 79.198 | 67.005 |
| $C_3H_6$ (cyclo) | 9.3158 | 0.3621 | 0.3172 | — | 1.2523 | 98.888 | 117.010 | 98.895 |
| $C_2H_4$ | 9.3350 | 0.3868 | 0.4445 | 0.1993 | 1.2449 | 65.957 | 78.005 | 65.835 |
| $C_2H_2$ | 9.3563 | 0.4126 | 0.4718 | 0.2533 | 1.1611 | 64.793 | 76.792 | 64.678 |
| $C_3H_4$ (F) | 9.3426 | 0.3888 | 0.4524 | 0.2344 | 1.2145 | 97.849 | 115.820 | — |
| $C_3H_4$ (O)[g] | 9.3434 | 0.3903 | 0.4540 | 0.2328 | 1.2190 | 97.850 | 115.820 | — |
| $C_4H_6$ (FS) | 9.3507 | 0.3671 | 0.3903 (S)<br>0.4279 (D) | 0.1982 | 0.9808 | 130.637 | 154.865 | — |
| $C_4H_6$ (FD) | 9.3472 | 0.3888 (I)<br>0.3644 (O) | 0.4042 (S)<br>0.4303 (D) | 0.2000 | 0.8899 (O)<br>1.2563 (I) | 130.707 | 154.865 | — |
| $C_4H_6$ (OD) | 9.3460 | 0.3940 (I)<br>0.3602 (O) | 0.4102 (S)<br>0.4247 (D) | 0.2016 | 0.8759 (O)<br>1.2547 (I) | 130.717 | 154.865 | — |
| $C_6H_6$ (BOND) | 9.3353 | 0.3923 | 0.4455 (S)<br>0.4158 (D) | 0.1994 | 1.2384 | 194.814 | — | — |
| $C_6H_6$ (ATOM) | 9.3351 | 0.3840 | 0.4290 | 0.2352 | 1.2203 | 194.873 | — | — |

[a] Atomic units.

[b] F = Fixed CC orbital positions; O = Optimized CC orbital positions; S = All CH bonds considered to be the same; D = Outer and inner CH bonds treated differently; BOND = *p*-orbitals in bonds; ATOM = *p*-orbitals on atoms.

[c] I = Inner; O = Outer.

[d] S = Single bond; D = Double bond.

[e] Ref. [20].

[f] Ref. [5].

[g] $C_3H_4$: central C to C=C orbitals = 1.2154; $R_{C=C}$ = 2.4786. $C_4H_6$: inner C to C=C orbitals = 1.3503; $R_{C=C}$ = 2.5266.

for $C_6H_6$ we take $R_{CH} = 2.0409$ and $R_{CC} = 2.6457$ bohrs. The effects of various different optimizations were considered as follows:

1. All cases:
   a) CH orbital positions and exponents optimized
   b) Inner shell orbitals held fixed, exponents optimized
   c) All other exponents optimized.
2. $C_3H_4$:
   a) C=C orbitals held fixed at the centre of the bonds ($C_3H_4$(F))
   b) C=C orbital positions optimized ($C_3H_4$(O)).
3. $C_4H_6$:
   a) C=C orbitals optimized or held fixed (O or F); C—C orbital fixed
   b) The same or different parameters (S or D) used for inner and outer CH orbital exponents and positions.
4. $C_6H_6$:
   a) *p*-type Gaussian fixed at the centre of every other CC bond; *s*-type Gaussian fixed at the centre of every CC bond ($C_6H_6$ (BOND))
   b) *p*-type Gaussian fixed on every other atom; *s*-type Gaussian fixed at the centre of every CC bond ($C_6H_6$ (ATOM)).

For $C_3H_4$ it can be seen from the table that the exponents for $C_3H_4$ (F) and $C_3H_4$ (O) only differ slightly and $C_3H_4$ (O) gives a slightly lower energy, but not by much. The CC orbitals only move slightly from the centre of the CC bond towards the central carbon atom for $C_3H_4$ (O).

The differences in the various optimizations are far more pronounced for $C_4H_6$ than $C_3H_4$. Unlike $C_3H_4$, the CC orbitals move towards the outer carbon atoms and the exponents differ by more. The CH orbital positions, when they are optimized independently, differ considerably and it is the end CH orbitals which have the bigger radius (smaller exponent), although one might expect that as the C=C orbitals move towards them the greater overlap would cause them to contract. It should, however, be pointed out that an extremely shallow minimum was found for this molecule, and different starting values do yield slightly different optimized parameters, and so it is difficult to say unequivocally that the true minimum has been reached in each case.

For $C_6H_6$ there has always been a problem in how to treat the delocalized pi-electrons using a Lewis set wavefunction. In addition, there is the basic philosophic question of representing delocalized electrons using localized orbitals, and this becomes even more of a problem due to the especially diffuse nature of pi-electrons in ring systems. The first method, $C_6H_6$ (BOND), corresponds effectively to creating alternate single and double bonds as for the Kekulé structure, whilst $C_6H_6$ (ATOM) at least ensures that all the *s*-type CC bond orbitals should be the same. In both instances the molecule does not possess the full rotational symmetry. Yet another method is to put a *p*-type Gaussian on every CC bond, thus ensuring full symmetry. However, this is now a non-Lewis wavefunction, and we must assume single occupancy of each $p$-type Gaussian. This and other methods for non-Lewis basis sets will be discussed more fully in a forthcoming paper.

Overall, the inner shell exponents only vary between 9.3006 and 9.3563, which is a small variation for the properties we are concerned with. The CH and CC exponents are much more variable if we consider the variation as a percentage of the value. For the CH bond exponents the general trend is for smaller exponents, and hence larger radii, for longer bonds as is to be expected. The only exceptions really are $C_4H_6$ (FD) and $C_4H_6$ (OD) which have already been discussed. The $CC_s$-type Gaussians in single bonds and the pseudo-single bond in benzene follow a similar pattern with the cyclo-$C_3H_6$ exponent being much smaller, as it is a strained small ring system. The $CC_s$-type Gaussian exponents in double bonds tend to be larger than their single bond counterparts, again probably because $R_{C=C} < R_{C-C}$. For benzene, when the bond lengths are in fact the same, the $s$-type Gaussian in the pseudo C=C bond actually has a smaller exponent than the C—C exponent. As far as the $p$-type Gaussians are concerned, those for $C_2H_4$, $C_4H_6$ and $C_6H_6$ (BOND) are very similar, whilst the $C_3H_4$ and $C_6H_6$ (ATOM) exponents are similar; again for $C_3H_4$ the bond length is that much shorter than for the other molecules. The $C_2H_2$ $p$-type Gaussian exponents are larger because the bond length is about 10% shorter than for $C_2H_4$ and also the two $p$-orbitals in the bond probably cause the other to contract a little. The CH bond orbital tends to position itself slightly nearer the hydrogen than the carbon except for $C_4H_6$ in some cases (see Table 1).

## 4. Discussion of the Results for the Properties

In Table 2 values are given for $\bar{\alpha}$, using Eq. (3), and $\bar{\chi}$, using Eq. (4) with values from Eq. (5) in brackets. The polarizability results tend to be the more accurate, and optimized geometry wavefunction values for $C_2H_6$ and $CH_4$ are slightly better than those using experimental geometries, the reverse applying to cyclo $C_3H_6$, $C_2H_4$ and $C_2H_2$, with the last two results also demonstrating the benefit of using real $p$-type functions. The value for $C_6H_6$ is slightly overestimated using the bond wavefunction and underestimated using the atom one, whilst the non-Lewis procedure mentioned in the previous section yields results slightly lower than for $C_6H_6$ (ATOM). For $C_3H_4$ and $C_4H_6$ the experimental values are possibly less reliable than for the other molecules, but even so all values are in reasonable agreement with experiment. We would expect the $C_4H_6$ result to be reasonably accurate, but the Frost model value for $C_3H_4$ is probably rather low and other experimental values are as high as 63 [21]. There is only a small difference between the fixed and optimized values for $C_3H_4$, whilst for $C_4H_6$ it would seem to be the use of different exponents for inner and outer CH orbitals that causes the difference.

For $\bar{\chi}$ the values for the first five molecules using Eq. (4) are in reasonable, but not excellent, agreement with experiment and are much the same as those obtained using optimized wave-functions. Values using Eq. (5) given in brackets are normally in better agreement with experiment than those using Eq. (4). The results for $C_4H_6$ are in worst agreement with experiment, though they are close to the value of 35.6 obtained by Barter *et al.* [22] for 1,2-$C_4H_6$ rather than 1,3-$C_4H_6$, which is the value

**Table 2.** Electric polarizabilities and magnetic susceptibilities

| Molecule | $\bar{\alpha}^a$ | | | $-\bar{\chi}^b$ | | |
|---|---|---|---|---|---|---|
| | Experimental geometry[c] | Optimized geometry[d] | Experiment | Experimental geometry | Optimized geometry | Experiment |
| $CH_4$ | 23.36 | 24.4 | 25.6 | 13.47 | 13.76 | 17.4 |
| $C_2H_6$ | 41.25 | 42.1 | 44.7 | 23.70 | 23.95 | 26.8 |
| $C_3H_6$ (cyclo) | 56.03 | 57.5 | 56.4 | 31.31 | 31.74 | 39.2 |
| $C_2H_4$ | 42.22 | 36.9 | 42.2 | 21.17 (19.19) | 20.71 | 18.8 |
| $C_2H_2$ | 35.15 | 31.6 | 34.9 | 17.91 (21.04) | 17.50 | 20.8 |
| $C_3H_4$ (F) | 53.85 | — | 55[e], 60[f] | 27.99 (24.61) | — | 25.3 |
| $C_3H_4$ (O) | 54.00 | — | 55[e], 60[f] | 27.99 (24.59) | — | 25.3 |
| $C_4H_6$ (FS) | 83.68 | — | 84[f] | 40.51 (36.51) | — | 32.1 |
| $C_4H_6$ (OD) | 81.51 | — | 84[f] | 40.01 (36.08) | — | 32.1 |
| $C_4H_6$ (FD) | 81.72 | — | 84[f] | 40.00 (36.04) | — | 32.1 |
| $C_6H_6$ (BOND) | 108.89 | — | 104 | 53.38 | — | 54.8 |
| $C_6H_6$ (ATOM) | 94.52 | — | 104 | 51.09 | — | 54.8 |

[a] $10^{-25}$ c.c. units.

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

[c] From Table 1.

[d] Ref. [5].

[e] Ref. [29], refractive index data.

[f] Ref. [30], bond refractions.

in the table. The value for $C_6H_6$ (BOND) is again better than that for $C_6H_6$ (ATOM) and on the whole we would recommend the use of this wavefunction in this context on the basis of the results for these properties. For $C_4H_6$ the choice is more difficult, $C_4H_6$ (FS) for simplicity's sake or $C_4H_6$ (OD) if individual constituent subtleties are required. For $C_3H_4$ we suggest $C_3H_4$ (F), as there is really a negligible difference in the values for the two properties.

Turning now to the dispersion coefficients, values for $C_6$ for all possible pair interactions of the molecules considered are given in Table 3 to three significant figures. The values of 133 and 413 atomic units for $C_6$ ($CH_4$—$CH_4$) and $C_6$ ($C_2H_6$—$C_2H_6$) are similar though a little lower than those obtained using optimized geometries of 142 and 426 respectively, as well as the values given by Amos and Crispin of 134 and 443 [8]. The result for $C_6$ ($CH_4$—$CH_4$) is reasonably close to the recommended value of Dalgarno [23] of 150 and the recent value of 129.6 given by Margoliash *et al.* [24], but that for $C_6$ ($C_2H_6$—$C_2H_6$) is slightly lower than the other estimates, due to theoretical and experimental polarizabilities differing by almost 8%. Results for $C_6$ ($C_2H_4$—$C_2H_4$) and $C_6$ ($C_2H_2$—$C_2H_2$) are larger than those using optimized geometries, the former being greater and the latter smaller than the values given by Haugh and Hirschfelder [25] of 303 and 363 respectively. It is worth reiterating that in view of the good agreement with refractive index results we feel that the values given in Table 3 provide reasonably reliable *ab initio* estimates of $C_6$.

In Table 4 values for $C_8$ and $C_{10}$ for all pair interactions are given and for a discussion on which regions these terms become important see reference [12]. Estimates are suggested in that same paper of $C_8 \approx 15C_6$ and $C_{10} \approx 18C_8$, which again provide good results for interactions between saturated molecules using experimental geometries, though perhaps coefficients of 14 and 17, respectively, provide more accurate results. However, for interactions between two pi-bonding systems $C_8 \approx 17C_6$ and $C_{10} \approx 23C_8$ will give improved results, whilst for the interaction between a saturated molecule and a pi-bonding molecule we'd suggest $C_8 \approx 16C_6$ and $C_{10} \approx 20C_8$.

In Tables 5 and 6 results are given for several three-body interactions, again to three significant figures; others of interest can easily be computed using the wavefunctions in Table 1 from the formula for $\gamma_3$. Results for comparison are scarce, but our value for $CH_4$ in Table 5 is in good agreement with the value of 16.31 given recently [26]. Bearing in mind that a good approximation is [12, 27, 28],

$$\gamma_3 = \tfrac{3}{4}\bar{\alpha}C_6 \qquad (10)$$

for interactions between like molecules, it can be seen that reasonable estimates of correcting terms, such as $C_8$, $C_{10}$ and $\gamma_3$, can be made from knowledge of $C_6$ and $\bar{\alpha}$ alone. Not only can these correcting terms be calculated, but retardation effects may also be included by considering expansions for very large $R$ and for relatively small values of $R$. For the latter we can write [12]

$$\Delta E = -R^{-6}\{C_6 - \sigma^2R^2d_4 + O(\sigma^3R^3)\} \qquad (11)$$

**Table 3.** $C_6$ Coefficients[a]

| Molecule[b] | $CH_4$ | $C_2H_6$ | $C_3H_6$ | $C_2H_4$ | $C_2H_2$ | $C_3H_4$ (O) | $C_4H_6$ (OD) | $C_6H_6$ (BOND) |
|---|---|---|---|---|---|---|---|---|
| $CH_4$ | 133 | | | | | | | |
| $C_2H_6$ | 234 | 413 | | | | | | |
| $C_3H_6$ | 313 | 552 | 738 | | | | | |
| $C_2H_4$ | 217 | 383 | 512 | 357 | | | | |
| $C_2H_2$ | 184 | 324 | 434 | 302 | 256 | | | |
| $C_3H_4$ (O) | 285 | 502 | 671 | 467 | 396 | 612 | | |
| $C_4H_6$ (OD) | 416 | 732 | 980 | 683 | 579 | 894 | 1310 | |
| $C_6H_6$ (BOND) | 550 | 970 | 1300 | 905 | 767 | 1180 | 1730 | 2300 |

[a] Atomic units.

[b] For details of the wavefunctions see Table 1.

Table 4. $C_8$ and $C_{10}$ values[a]

| Molecule | $CH_4$ | $C_2H_6$ | $C_3H_6$ | $C_2H_4$ | $C_2H_2$ | $C_3H_4$ (O) | $C_4H_6$ (OD) | $C_6H_6$ (BOND) |
|---|---|---|---|---|---|---|---|---|
| $CH_4$ | 18.7<br>321 | 32.9 | 44.8 | 34.3 | 28.3 | 43.6 | 66.1 | 88.6 |
| $C_2H_6$ | 567 | 58.1<br>1000 | 79.0 | 60.5 | 50.0 | 76.9 | 117 | 156 |
| $C_3H_6$ | 785 | 1390 | 107<br>1920 | 82.1 | 67.9 | 104 | 158 | 212 |
| $C_2H_4$ | 690 | 1220 | 1680 | 62.4<br>1420 | 51.7 | 79.5 | 120 | 161 |
| $C_2H_2$ | 544 | 961 | 1320 | 1130 | 42.8<br>900 | 65.9 | 99.7 | 134 |
| $C_3H_4$ (O) | 838 | 1480 | 2040 | 1750 | 1390 | 101<br>2140 | 153 | 205 |
| $C_4H_6$ (OD) | 1340 | 2360 | 3250 | 2750 | 2190 | 3380 | 232<br>5320 | 311 |
| $C_6H_6$ (BOND) | 1830 | 3230 | 4440 | 3740 | 2990 | 4600 | 7240 | 416<br>9840 |

[a] $C_8$ values in the upper triangle, $C_{10}$ values in the lower triangle. Both in atomic units × $10^{-2}$, e.g. $C_8$ ($CH_4$–$CH_4$) = 1870 atomic units. Wavefunctions from Table 1.

**Table 5.** $\gamma_3$ and $d_4$ for interactions between like molecules in atomic units

| Molecule | $\gamma_3 \times 10^{-2}$ | $d_4$ |
|---|---|---|
| $CH_4$ | 15.7 (17.1) | 23.3 (23.8) |
| $C_2H_6$ | 86.1 (91.8) | 72.2 (72.9) |
| $C_3H_6$ | 209 | 123.0 |
| $C_2H_4$ | 74.1 (57.8) | 53.4 (54.2) |
| $C_2H_2$ | 44.8 (36.0) | 38.1 (38.3) |
| $C_3H_4$ (O) | 164 | 95.2 |
| $C_4H_6$ (OD) | 526 | 185.8 |
| $C_6H_6$ (BOND) | 1220 | 336.3 |

[a] Values using optimized geometries in brackets.

with $\sigma$ the fine structure constant and $d_4$ having the simple form, using Frost model wavefunctions, of

$$d_4 = 2 \sum_{i=1}^{n_A} \sum_{j=1}^{n_B} \frac{1}{\omega_i^A + \omega_j^B} \tag{12}$$

for the interaction of two molecules A and B. We include values for the interactions between like atoms in Table 5, but it is a simple matter to compute other values of $d_4$ from Eq. (12) using the wavefunctions of Table 1. Again, values for comparison are rare, but for $CH_4$ the agreement with the values 20.4, given once more by Ref. [26], is good.

**Table 6.** $\gamma_3$ in atomic units $\times$ $10^{-2}$ for some other interactions

| Molecules | $\gamma_3 \times 10^{-2}$ |
|---|---|
| $C_2H_6$—$C_2H_6$—$CH_4$ | 48.8 |
| $C_3H_6$—$C_3H_6$—$C_2H_6$ | 155 |
| $C_2H_4$—$C_2H_4$—$C_2H_2$ | 62.6 |
| $C_2H_2$—$C_2H_2$—$CH_4$ | 31.5 |
| $C_3H_4$—$C_3H_4$—$C_2H_4$ | 126 |
| $C_4H_6$—$C_4H_6$—$C_3H_4$ | 356 |
| $C_6H_6$—$C_6H_6$—$CH_4$ | 285 |
| $C_6H_6$—$C_6H_6$—$C_2H_6$ | 503 |
| $C_6H_6$—$C_6H_6$—$C_3H_6$ | 676 |
| $C_6H_6$—$C_6H_6$—$C_2H_4$ | 481 |
| $C_6H_6$—$C_6H_6$—$C_2H_2$ | 406 |
| $C_6H_6$—$C_6H_6$—$C_3H_4$ | 626 |
| $C_6H_6$—$C_6H_6$—$C_4H_6$ | 924 |

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## References

1. Frost, A. A.: J. Chem. Phys. **47**, 3707 (1967)
2. Blustin, P. H., Linnet, J. W.: Trans. Faraday Soc. II **70**, 274 (1974)
3. Ford, B., Hall, G. G., Packer, J. C.: Intern. J. Quantum Chem. **4**, 533 (1970)

4. Yoffe, J. A.: Chem. Phys. Letters **54**, 562 (1978)
5. Frost, A. A., Rouse, R. A.: J. Am. Chem. Soc. **90**, 1965 (1968)
6. Bridge, N. J., Buckingham, A. D.: Proc. Roy. Soc. **A295**, 334 (1966)
7. Dalgarno, A., Morrison, I. H., Pengelly, R. M.: Intern. J. Quantum Chem. **1**, 161 (1967)
8. Amos, A. T., Crispin, R. J.: Mol. Phys. **31**, 159 (1976)
9. Slater, J. C., Kirkwood, J. G.: Phys. Rev. **37**, 682 (1931)
10. Kirkwood, J. G.: Physik. Z. **33**, 57 (1932); Muller, A.: Proc. Roy. Soc. **A154**, 624 (1936)
11. London, F.: Z. Physik. Chem. **B11**, 222 (1930)
12. Amos, A. T., Yoffe, J. A.: Theor. Chim. Acta (Berl.) **42**, 247 (1976)
13. Amos, A. T., Yoffe, J. A.: J. Chem. Phys. **63**, 4723 (1975)
14. Yoffe, J. A.: Theor. Chim. Acta (Berl.) (Ms. 1165)
15. Amos, A. T., Yoffe, J. A.: Theor. Chim. Acta (Berl.) **40**, 221 (1975)
16. Margenau, H., Kestner, N. R.: Theory of intermolecular forces. New York: Pergamon Press 1969
17. Israelachvili, J. N., Tabor, D.: Progr. Surface Membrane Sci. **7**, 1 (1973)
18. Landau, L., Lifshitz, E. M.: Electrodynamics of continuous media, p. 368. New York: Pergamon Press 1960
19. Brailsford, D. F., Hall, G. G., Hemming, N., Martin, D.: Chem. Phys. Letters **35**, 437 (1975)
20. Snyder, L. C., Basch, H.: Molecular wavefunctions and properties: tabulated from SCF calculations in a Gaussian basis set. New York: Wiley 1972
21. Smith, J. W.: Electric dipole moments. London: Butterworth 1955
22. Barter, C., Meisenheimer, R. G., Stevenson, D. P.: J. Phys. Chem. **64**, 1312 (1960)
23. Dalgarno, A.: Advan. Chem. Phys. **12**, 164 (1967)
24. Margoliash, D. J., Meath, W. J.: J. Chem. Phys. **68**, 1426 (1978)
25. Haugh, E. F., Hirschfelder, J. O.: J. Chem. Phys. **23**, 1778 (1955)
26. Margoliash, D. J., Proctor, T. R., Zeiss, G. D., Meath, W. J.: Mol. Phys. **35**, 747 (1978)
27. Kihara, T.: Advan. Chem. Phys. **1**, 267 (1958)
28. Davison, W. D., Dalgarno, A.: Advan. Atomic Mol. Phys. **2**, 1 (1966)
29. Watson, H. E., Ramaswamy, K. L.: Proc. Roy. Soc. **A156**, 144 (1936)
30. Syrkin, Y. K., Dyatkina, M. E.: Structure of molecules and the chemical bond, p. 201. New York: Dover 1964

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