

# Long-Range Molecular Interaction Coefficients Computed from Frost-Model Wave Functions

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The average long-range interaction energy between two molecules can be written as an inverse asymptotic series in the intermolecular separation distance  $R$ . Using Frost-model wave functions, the dispersion coefficients of the first three ( $R^{-6}$ ,  $R^{-8}$ ,  $R^{-10}$ ) terms in the series are obtained. Coefficients of three- and four-body non-additive interaction energies are also calculated and the form of the dispersion interaction when retardation effects are included is examined.

**Key words:** Dispersion coefficients - Intermolecular forces - Frost model

## 1. Introduction

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

$$\Delta E = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \dots \quad (1)$$

where  $R$  is the intermolecular separation distance and  $C_6, C_8, C_{10} \dots$  are constants depending on the particular molecules which are interacting. The important contributions to  $\Delta E$  arise from applying second-order perturbation theory and each of the terms in (1) can be subdivided into two parts one of which - the induction part - depends on the moments and polarizabilities of the molecules. This is usually very much smaller than the second part which is the London dispersion interaction. In this paper, we shall ignore the induction part and assume that the coefficients  $C_6, C_8, C_{10}$  can be adequately estimated from the dispersion part alone.

The most convenient expression for  $C_6$  relates it to the average frequency-dependent polarizabilities at imaginary frequencies,  $\alpha_A(i\omega)$  and  $\alpha_B(i\omega)$  of the two interacting molecules [1, 2]. The result is

$$C_6 = \frac{3}{\pi} \int_0^{\infty} \alpha_A(i\omega) \alpha_B(i\omega) d\omega \quad (2)$$

Thus if reasonable estimates of  $\alpha_A$  and  $\alpha_B$  can be found,  $C_6$  can be evaluated. Actually it seems to be the case that to obtain really accurate values of  $C_6$  it is best to use experimental information to determine  $\alpha_A$  and  $\alpha_B$ , for example from measurements of refractive indices [3]. However, for some large molecules not enough experimental data is available

for this to be done and, in any case, it is desirable that purely theoretical estimates of  $C_6$  should be attempted.

Recently we have shown how the frequency-dependent polarizability of a molecule can be estimated if its Frost-model wave function is known [4]. Although, due to deficiencies of the Frost model the resulting expression for the polarizability is far too simple, nevertheless it seems worthwhile investigating whether it can be used to give reasonable values of the  $C_6$  coefficients. In the first part of this paper we show that, in the main, satisfactory numerical values can be found in this way. A preliminary account of these results has been given elsewhere [5].

As well as giving an expression for  $C_6$ , it turns out to be a simple matter to use Frost-model perturbation theory to find the higher coefficients  $C_8$  and  $C_{10}$ . Although they are not so important as the  $C_6$  coefficient, it is useful to have estimates of their values in order to discuss the convergence properties of the series for  $\Delta E$ .

Previous calculations of dispersion coefficients for molecular interactions have usually been based on approximate methods such as those of London [6] or Slater and Kirkwood [7]. The Frost-model results can be used to analyse these methods and to investigate their accuracy. In the main we find that none of the approximate methods is uniformly successful although empirical values based on a simple one-term fitting of refractive-index data are usually very satisfactory.

As already explained, Eq. (1) is obtained using second-order perturbation theory. Extra terms arise when the perturbation theory is carried through higher order [8, 9]. For interactions between pairs of molecules these terms are not so very important but for interactions between three or more molecules they lead to non-additive forces. The leading term in the long-range non-additive interaction between the  $n$  molecules  $A_1, A_2, \dots, A_n$  depends on the coefficient [8]:

$$\gamma_n = \gamma(A_1, A_2 \dots A_n) = \frac{3}{\pi} \int_0^\infty \alpha_{A_1}(i\omega) \alpha_{A_2}(i\omega) \dots \alpha_{A_n}(i\omega) d\omega \quad (3)$$

Using the Frost-model expression for the polarizabilities we can, in principle, evaluate  $\gamma$  although it turns out to be sufficiently accurate and much more convenient to employ approximations to the  $\alpha_{A_i}(i\omega)$ .

Although  $\Delta E$  in Eq. (1) is usually described as the long-range interaction energy, the formula is not valid when  $R$  becomes very large. For very long-range interactions relativistic retardation effects have to be taken into account as was first shown in the famous work of Casimir and Polder [10]. In the final section of this paper we examine the behaviour of the more general formula in the context of the Frost model.

## 2. Theory

The Frost-model [11] wave function for a  $2n$ -electron molecule consists of a Slater determinant  $\Psi$  of  $n$  doubly occupied floating spherical Gaussian orbitals (FSGO's)  $\{G_i\}$  i.e.

$$\Psi = \det(G_1\alpha G_1\beta \dots G_n\alpha G_n\beta) \quad (4)$$

where

$$G_i(\mathbf{r}) = \left( \frac{\omega_i}{\pi} \right)^{3/4} \exp - \frac{1}{2} \omega_i |\mathbf{r} - \mathbf{R}_i|^2 \quad (5)$$

The exponents  $\{\omega_i\}$  and the positions of the centres  $\{\mathbf{R}_i\}$  of the Gaussians are found by using the variational principle. Thus all the parameters are obtained in an *ab initio* fashion and are not determined empirically.

In a previous paper [4], by setting up a point-charge model and using a classical approach we obtained the following expression for the frequency-dependent molecular polarizability:

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

Not surprisingly the same result can be obtained quantum-mechanically if symmetry-adapted double perturbation theory [12] is applied as is shown in the appendix.

Substituting Eq. (6) into Eq. (2) gives the result:

$$C_6 = 6 \sum_{i=1}^{n_A} \sum_{j=1}^{n_B} \frac{1}{\omega_i^A \omega_j^B (\omega_i^A + \omega_j^B)} \quad (7)$$

in an obvious notation. Expressions can also be derived for  $C_8$  and  $C_{10}$  and they are

$$C_8 = 45 \sum_{i=1}^{n_A} \sum_{j=1}^{n_B} \frac{1}{\omega_i^A \omega_j^B} \left\{ \frac{1}{\omega_i^A (2\omega_i^A + \omega_j^B)} + \frac{1}{\omega_j^B (\omega_i^A + 2\omega_j^B)} \right\} \quad (8)$$

and

$$C_{10} = 315 \sum_{i=1}^{n_A} \sum_{j=1}^{n_B} \frac{1}{(\omega_i^A)^2 (\omega_j^B)^2 (\omega_i^A + \omega_j^B)} + 420 \sum_{i=1}^{n_A} \sum_{j=1}^{n_B} \left\{ \frac{1}{\omega_i^A (\omega_j^B)^3 (\omega_i^A + 3\omega_j^B)} + \frac{1}{(\omega_i^A)^3 \omega_j^B (3\omega_i^A + \omega_j^B)} \right\} \quad (9)$$

These expressions are very similar to those found from the oscillator model [1] (i.e. from the Drude theory). This follows because we take only the leading term of the symmetry-adapted perturbation theory which amounts to replacing the molecular Hamiltonian by a sum of one-electron harmonic oscillator Hamiltonians. For many harmonic oscillator properties of which the frequency dependent polarizability is one, classical and quantum theory give identical results. Thus Eq. (6) and, hence the dispersion coefficients deduced from it, have the same form as in the Drude theory. Where Eq. (6) differs from the Drude theory is that the parameters  $\{\omega_i\}$  are obtained from the quantum-mechanical variational principle rather than found empirically. Moreover, while there is no way to correct the Drude theory, even in principle, Eq. (6) is to be regarded as the leading term in a perturbation expansion which, if sufficient terms could be computed, would give the exact result.

### 3. Values of the Dispersion Coefficients

In Table 1 we list values of  $C_6$ ,  $C_8$ ,  $C_{10}$  to three significant figure accuracy as found from Eqs. (7)–(9) for a number of different pairs of interacting species. The wave functions used

were taken from Refs. [11] except  $\text{H}_2\text{O}$  which was taken from Ref. [4]. The results for  $C_6$  are compared with the best estimates available in the literature [3, 13]. The latter are found by employing considerable experimental information to determine empirical formulae for  $\alpha_A(i\omega)$  and  $\alpha_B(i\omega)$  from which  $C_6$  can be obtained by means of Eq. (2). The error in these best estimates is thought to be less than 5% and in some cases considerably less. It is clear from the table that in the case of molecules the results of this paper are in very satisfactory agreement with these best estimates. Water is an exception, our results being about 80% of the best value. This could have been anticipated in view of the low values for other properties of water found from the Frost model [4, 12]. Even so the Frost-model value for  $C_6$  is rather better than values found by more elaborate calculations ( $C_6 = 60.2$  a.u. [14];  $C_6 = 66.7$  a.u. [16]) and by semi-empirical methods (see, for example, the final paragraph of Ref. [16]). Although there seems to be no reliable estimate for the  $C_6$  dispersion coefficient between two ammonia molecules with which to compare our value we expect ammonia to follow the same pattern as water and so our result will probably be too low.

The values of the dispersion coefficients for helium and for helium interacting with molecules are much too low. This is almost entirely due to the poor Frost-model representation of  $\alpha(\omega)$  for the helium atom. In order to obtain better estimates of the He- $\text{H}_2$  and He- $\text{CH}_4$  interactions, we can take an empirical formula  $\alpha(\omega) = 2/(1.27^2 - \omega^2)$  for helium which gives the correct value for  $C_6$  (He-He). When this is used with the Frost-model expressions for  $\text{H}_2$  and  $\text{CH}_4$  the results in brackets in Table 1 are obtained. These are in good agreement with the best estimates.

Apart from methane, there are also no really satisfactory best estimates of the first dispersion coefficients between hydrocarbons although there are some calculated and semi-empirical values available in the literature. For example, in the case of ethane, Amos and Crispin [14] have recently obtained  $C_6 = 443$  a.u. in good agreement with the result of this paper but older semi-empirical estimates are about 25% higher [17]. In their classic paper, Haugh and Hirschfelder [18] found an average value of  $C_6 = 303$  a.u. for ethylene and  $C_6 = 363$  a.u. for acetylene. Their ethylene result is in reasonable agreement with ours but their acetylene value is about 50% larger.

Also in Table 1 we give a set of semi-empirical values of  $C_6$  which we have calculated using up-to-date values of polarizabilities, susceptibilities and ionization potentials in various approximate formulae. As a rule the Frost-model results lie between the semi-empirical ones and, on the whole, are much more reliable.

Turning now to the higher-order terms, we find that  $C_8 \approx 15C_6$  and  $C_{10} \approx 18C_8$  although the ratios for ammonia are rather smaller and for water are much smaller. (Following our earlier remarks concerning the  $C_6$  coefficients for these two molecules we believe that their  $C_8$  and  $C_{10}$  coefficients should also be scaled upwards.) The ratios 15 and 18 are not dissimilar to those found for atoms [19] although they are larger than those found in the oscillator model [20] and if we accept them as typical of molecular interactions it follows that the dispersion energy takes the form:

$$\Delta E = -\frac{C_6}{R^6} \left\{ 1 + \frac{15}{R^2} + \frac{270}{R^4} + O(R^{-6}) \right\}$$

Consequently for values of  $R$  between 10 a.u. and 20 a.u. it is a poor approximation to take only the first,  $-C_6/R^6$ , term in  $\Delta E$  and at least the second,  $-C_8/R^8$ , ought to be included. For  $R > 20$  a.u. it is sufficient to use the first term only.

Table 1. Values of the dispersion coefficients  $C_6$ ,  $C_8$ ,  $C_{10}$  in atomic units

Interacting Atoms or Molecules	$C_6$ (Hartree-Bohr <sup>6</sup> )		Best Estimate	S-K <sup>a</sup>	K-M <sup>b</sup>	L <sup>c</sup>	R1 <sup>d</sup>	Others	$C_8$ (Hartree-Bohr <sup>8</sup> )	$C_{10}$ (Hartree-Bohr <sup>10</sup> )
	This Paper	Ref. [13]								
He-He	0.83		1.46 <sup>e</sup>						5.42, (11.5)	43.3, (111)
He-H <sub>2</sub>	2.83 (3.89)		4.0 <sup>e</sup>					(48.1)	(726)	(726)
He-CH <sub>4</sub>	10.1 (13.8)		14 <sup>f</sup>					(159)	(2240)	(2240)
H <sub>2</sub> -H <sub>2</sub>	11.6		12 <sup>e</sup>	14	14	13	15	182	3500	3500
H <sub>2</sub> -CH <sub>4</sub>	40.6		43 <sup>f</sup>					610	11200	11200
CH <sub>4</sub> -CH <sub>4</sub>	142		149 <sup>f</sup>	152	134	104	147	134 <sup>g</sup> , 195 <sup>h</sup> , 152 <sup>i</sup>	2040	33800
H <sub>2</sub> O-H <sub>2</sub> O	36.5		45.4 <sup>j</sup>	65	81	33	46	60 <sup>g</sup> , 67 <sup>k</sup>	333	3720
NH <sub>3</sub> -NH <sub>3</sub>	90.9		-	123	154	63	88	1130	17100	17100
C <sub>2</sub> H <sub>6</sub> -C <sub>2</sub> H <sub>6</sub>	426		-	465	521	288	435	443 <sup>g</sup> , 567 <sup>h</sup> , 443 <sup>i</sup>	6070	106000
C <sub>2</sub> H <sub>4</sub> -C <sub>2</sub> H <sub>4</sub>	321		-	395	275	235	304	303 <sup>l</sup> , 357 <sup>m</sup>	4660	83300
C <sub>2</sub> H <sub>2</sub> -C <sub>2</sub> H <sub>2</sub>	231		-	271	186	174	194	363 <sup>l</sup>	3430	62600

<sup>a</sup> Slater-Kirkwood approximation: Eqs. (13) and (10).

<sup>b</sup> Kirkwood-Muller approximation: Eqs. (15) and (10).

<sup>c</sup> London approximation: Eqs. (18) and (10).

<sup>d</sup> From refractive index data using Eqs. (17) and (10). Values of  $C_A$  and  $\bar{\Omega}_A$  taken from Ref. [22].

<sup>e</sup> Ref. [3]. <sup>f</sup> Ref. [13]. <sup>g</sup> Ref. [14]. <sup>h</sup> Ref. [17]. <sup>i</sup> Computed from atom-atom dispersion coefficients using the values of Ref. [26].

<sup>j</sup> Ref. [16]. <sup>k</sup> Ref. [15]. <sup>l</sup> Ref. [18]. <sup>m</sup> Computed from atom-atom dispersion coefficients using the values of Ref. [27].

#### 4. Approximate and Empirical Formulae

For all the molecules considered here, the exponents  $\{\omega_i\}$  fall into two classes. Those associated with inner-shell orbitals on C, N and O atoms are relatively large and so contribute little to the summations in Eqs. (6)–(9). The remaining exponents are from bond or lone-pair orbitals and are much smaller. Moreover their numerical values tend to be very similar. Thus it is a reasonable approximation to replace the bond and lone-pair orbital exponents by an average value  $\bar{\omega}_A$  for each molecule and to neglect the inner-shell orbital exponents. As a consequence the equations of the previous section take simpler forms; for example  $C_6$  becomes:

$$C_6 = \frac{3}{2} \frac{N_A N_B}{\bar{\omega}_A \bar{\omega}_B (\bar{\omega}_A + \bar{\omega}_B)} \quad (10)$$

where  $N_A$  is the number of valence electrons (i.e. the total number minus the number in inner shells) in molecule A.

There are a number of ways in which the average exponents could be chosen from the  $\{\omega_i\}$ . The most obvious is to take  $\bar{\omega}_A = (3N_A^2/4C_6)^{1/3}$  where  $C_6$  has the Frost-model value. This choice ensures that for interactions between like molecules, the simplified (Eq. (10)) and exact (Eq. (7)) Frost-model expressions give identical results. Taking the  $\bar{\omega}_A$  values obtained in this way, it seems also to be the case that Eqs. (10) and (7) lead to nearly identical results even for interactions between different molecules; in addition, the same choice of  $\bar{\omega}_A$  when used in the approximate formulae (analogous to Eq. (10)) for  $C_8$  and  $C_{10}$  give results in very good agreement with the exact Frost-model results obtained from Eqs. (8) and (9). The values of these  $\bar{\omega}_A$  are given in Table 2. Frost-model values for various molecular properties can also be used to determine  $\bar{\omega}_A$ , or, indeed, a straightforward average of the  $\{\omega_i\}$  ignoring inner shell exponents can be taken. In all cases the results are almost identical to the Frost-model values given in Table 2.

It is immediately obvious from Table 2 that the  $\bar{\omega}_A$  for the hydrocarbons have almost exactly the same value. This suggests that good estimates of the dispersion coefficients for interactions between hydrocarbons can be obtained by assuming that for every hydro-

Table 2. Values of the average exponents  $\bar{\omega}_A$ , in atomic units

Molecule	Frost Model	S-K <sup>a</sup>	K-M <sup>b</sup>	L <sup>c</sup>	Average <sup>d</sup>	RI <sup>e</sup>	From $C_6$ <sup>f</sup>
H <sub>2</sub>	0.64	0.60	0.60	0.61	0.60	0.58	0.63
H <sub>2</sub> O	1.10	0.91	0.84	1.13	0.96	1.02	1.02
NH <sub>3</sub>	0.81	0.73	0.68	0.91	0.77	0.82	—
CH <sub>4</sub>	0.70	0.68	0.71	0.77	0.72	0.69	0.69
C <sub>2</sub> H <sub>6</sub>	0.70	0.68	0.66	0.80	0.71	0.70	—
C <sub>2</sub> H <sub>4</sub>	0.70	0.65	0.73	0.77	0.72	0.71	—
C <sub>2</sub> H <sub>2</sub>	0.69	0.65	0.74	0.76	0.72	0.73	—

<sup>a</sup> Slater-Kirkwood approximation: from Eq. (13).

<sup>b</sup> Kirkwood-Muller approximation: from Eq. (15).

<sup>c</sup> London approximation: from Eq. (18).

<sup>d</sup> Average of three previous columns.

<sup>e</sup> From refractive index data of Ref. [22] using Eqs. (16) and (17).

<sup>f</sup> From "best estimates" of  $C_6$ , quoted in Tab. 1, and Eq. (19).

carbon  $\bar{\omega}_A = 0.70$  a.u. With this approximation the coefficients will depend only on the number of valence electrons in each hydrocarbon. The results are:

$$\begin{aligned} C_6 &= 2.19N_A N_B \\ C_8 &= 31.2N_A N_B \\ C_{10} &= 547N_A N_B \end{aligned} \quad (11)$$

in atomic units.

Instead of using the Frost model to determine  $\bar{\omega}_A$ , it can be chosen empirically using experimental values for various molecular properties. One such procedure is to approximate Eq. (6) by

$$\alpha(\omega) = \frac{N_A}{\bar{\omega}_A^2 - \omega^2} \quad (12)$$

and take the limit as  $\omega \rightarrow 0$ , giving the static polarizability  $\alpha_A(0)$  as

$$\alpha_A(0) = \frac{N_A}{\bar{\omega}_A^2} \quad (13)$$

The values of  $\bar{\omega}_A$ , which in conjunction with Eq. (13) would give static polarizabilities in agreement with experiment, are listed in Table 2. Alternatively, since the formula for the molecular susceptibility  $\chi_A$  can be approximated by

$$\chi_A = -\frac{N_A}{4\bar{\omega}_A} \quad (14)$$

the experimental values of  $\chi_A$  can be used to obtain the  $\bar{\omega}_A$ . However, the  $\bar{\omega}_A$  found in this way are not very satisfactory and it is much better to combine (13) and (14) and estimate the average exponent by

$$\bar{\omega}_A^3 = -\frac{N_A^2}{4\chi_A \alpha_A} \quad (15)$$

Eqs. (13) and (15) are interesting because the use of the empirical  $\bar{\omega}_A$  determined from them to find  $C_6$  via Eq. (10) is equivalent to the well-known approximations due to Slater and Kirkwood [7] (Eq. (13)) and to Kirkwood and Muller [21] (Eq. (15) although this gives the Kirkwood-Muller approximation only for the dispersion coefficient between like molecules). It can be seen from Table 2 that, except in a few cases, the  $\bar{\omega}_A$  obtained from Eqs. (13) and (15) do not agree particularly well either with each other or with the Frost-model values.

We have pointed out earlier that the best estimates of  $C_6$  are obtained by using refractive index data to fit an empirical formula for  $\alpha_A(\omega)$ . The simplest of such formulae is a one-term function

$$\alpha_A(\omega) = \frac{C_A}{\bar{\Omega}_A^2 - \omega^2} \quad (16)$$

where  $C_A$  and  $\bar{\Omega}_A$  are empirical parameters which can be obtained from tables of refractive index measurements [22]. Eq. (16) is not quite the same as Eq. (12) since it usually

turns out that  $C_A$  is less than  $N_A$ . However, for the interaction of like molecules, the use of (16) to find  $C_6$  will give the same result as the use of (12) with  $\bar{\omega}_A$  chosen to be

$$\bar{\omega}_A = \bar{\Omega}_A (N_A/C_A)^{2/3} \quad (17)$$

Values of  $\bar{\omega}_A$  found from this equation are given in Table 2 and it is pleasing to note that they are generally in reasonable agreement with the Frost-model values.

Perhaps the best known of all approximate methods for finding  $C_6$  is due to London [6]. This can be obtained from (16) by noting that  $\bar{\Omega}_A$  is roughly the same as the ionization potential  $I_A$  for many atoms and molecules. Setting  $\bar{\Omega}_A = I_A$ , therefore, and taking the limit as  $\omega \rightarrow 0$  of Eq. (16) so that  $\alpha_A(0) = C_A/I_A^2$ , enables Eq. (17) to be rewritten to give the average exponent corresponding to the London approximation, viz.

$$\bar{\omega}_A = I_A^{-1/3} (N_A/\alpha_A(0))^{2/3} \quad (18)$$

The results of using Eq. (18) are in the fourth column of Table 2.

Table 2 now contains five sets of average exponents. Four are empirical of which one - the set found from Eq. (17) - is a special case since it is the first approximation in the procedure which leads to the best estimates of  $C_6$ . The remaining three correspond to the most used methods for finding approximate values of  $C_6$  and we had hoped, by relating them to making particular choices of the  $\bar{\omega}_A$  and by considering the values of the  $\bar{\omega}_A$  thus obtained, to be able to decide unambiguously which of the three it is best to use. However, it is not easy to do this on the basis of the results in Table 2 since the approximate values fall into no easily recognizable pattern. On the whole, the Slater-Kirkwood, Kirkwood-Muller and London approximations seem to be less reliable individually than the *ab initio* procedure based on the Frost-model. However, perhaps fortuitously due to cancellation of errors, the average of the three semi-empirical values of  $\bar{\omega}_A$  is in much more satisfactory agreement with both the Frost-model values and those obtained from refractive index data. We are certainly of the opinion that more reliable sets of  $C_6$  values can be obtained by this type of averaging than by using any single one of the empirical methods.

Finally, we note that where good estimates rather than Frost-model values of  $C_6$  are available then, of course,  $\bar{\omega}_A$  can be chosen to satisfy

$$\bar{\omega}_A^3 = 3N_A^2/4C_6 \quad (19)$$

and then used to find  $C_8$  and  $C_{10}$ . The best estimates of  $C_6$  quoted in Table 1 for  $H_2$ - $H_2$ ,  $H_2O$ - $H_2O$ ,  $CH_4$ - $CH_4$  interactions have been used to find  $\bar{\omega}_A$  for these molecules from Eq. (19) and the results can be seen in Table 2. Except for the hydrogen molecule they are in good agreement with values found from the refractive index data using Eq. (17). For  $H_2$  and  $CH_4$  they are in good agreement with the Frost-model  $\bar{\omega}_A$  but for water there is a significant difference.

## 5. Non-additive Interaction Energies

In general, when  $n$  molecules  $A_1, A_2, \dots, A_n$  interact, the non-additive  $n$ -body interaction energy can be written in the form [8]:

$$\Delta E_n = \Theta(A_1, \dots, A_n) \gamma_n \quad (20)$$

Where  $\Theta$  depends on the distances between the molecules and their configurations relative to each other and  $\gamma_n$  depends on the type of molecules which interact. On averaging over



all orientations of the interacting molecules,  $\gamma_n$  can be expressed in terms of the frequency-dependent polarizabilities of the molecules by means of Eq. (3).

The configuration and distance dependent term  $\Theta$  varies as the inverse  $3n$ th power of the separation distances. For example, when  $n = 3$ ,

$$\Theta = R_1^{-3} R_2^{-3} R_3^{-3} (3 \cos \theta_1 \cos \theta_2 \cos \theta_3 + 1) \quad (21)$$

where the molecules are placed at the vertices of a triangle with angles  $\theta_1, \theta_2, \theta_3$  and sides  $R_1, R_2, R_3$ . The dependence on intermolecular separations means that  $\Delta E_n$  decreases rapidly as  $n$  increases so that it usually suffices to consider three- and four-body energies.

Using the Frost-model expressions for  $\alpha(i\omega)$  it is possible to express  $\gamma_3$  and  $\gamma_4$  in terms of the orbital exponents. The formula for  $\gamma_3$  is given in Ref. [5] and that for  $\gamma_4$  (and the higher coefficients) has the same form as is found in the oscillator model (cf. Ref. [23] Sect. 3.3). However, these formulae are fairly complicated and it turns out to be accurate enough to simplify them by introducing average exponents.

We then find:

$$\gamma_3(A, B, C) = \frac{3N_A N_B N_C}{2} \frac{\bar{\omega}_A + \bar{\omega}_B + \bar{\omega}_C}{\bar{\omega}_A \bar{\omega}_B \bar{\omega}_C (\bar{\omega}_A + \bar{\omega}_B) (\bar{\omega}_B + \bar{\omega}_C) (\bar{\omega}_C + \bar{\omega}_A)} \quad (22)$$

$$\begin{aligned} \gamma_4(A, B, C, D) = & \frac{3N_A N_B N_C N_D}{2} \{ \bar{\omega}_A \bar{\omega}_B \bar{\omega}_C \bar{\omega}_D (\bar{\omega}_A + \bar{\omega}_B) \dots (\bar{\omega}_C + \bar{\omega}_D) \}^{-1} \times \\ & \times \{ (\bar{\omega}_A^2 + \bar{\omega}_B^2 + \bar{\omega}_C^2 + \bar{\omega}_D^2) (\bar{\omega}_A + \bar{\omega}_B + \bar{\omega}_C + \bar{\omega}_D) - \bar{\omega}_A^3 - \\ & - \bar{\omega}_B^3 - \bar{\omega}_C^3 - \bar{\omega}_D^3 + 2\bar{\omega}_A \bar{\omega}_B \bar{\omega}_C \bar{\omega}_D \times (\bar{\omega}_A^{-1} + \bar{\omega}_B^{-1} + \bar{\omega}_C^{-1} + \\ & + \bar{\omega}_D^{-1}) \} \end{aligned} \quad (23)$$

For interactions between like molecules these formulae simplify considerably to become:

$$\gamma_3(A, A, A) = \frac{9 N_A^3}{16 \bar{\omega}_A^5} \quad (24)$$

$$\gamma_4(A, A, A, A) = \frac{15 N_A^4}{32 \bar{\omega}_A^7} \quad (25)$$

Values of  $\gamma_3$  and  $\gamma_4$  computed from Eqs. (24) and (25) for a number of molecules are given in Table 3.

Table 3.  $\gamma_3$  and  $\gamma_4$  in atomic units for interactions between like molecules

Molecule	$\gamma_3 \times 10^{-2}$	$\gamma_4 \times 10^{-3}$
H <sub>2</sub>	0.42	0.171
H <sub>2</sub> O	1.79	0.985
NH <sub>3</sub>	8.26	8.39
CH <sub>4</sub>	17.1	23.3
C <sub>2</sub> H <sub>6</sub>	91.8	219
C <sub>2</sub> H <sub>4</sub>	57.8	118
C <sub>2</sub> H <sub>4</sub>	36.0	63

Using the formulae in the previous section relating  $\bar{\omega}_A$  to experimentally measurable quantities, it is possible to obtain many approximations to Eqs. (25) and (26). However it appears that the best of these use the dispersion coefficient  $C_6$  - through Eq. (19) - either alone or in conjunction with  $\alpha_A(0)$  via Eq. (13). The corresponding expressions are:

$$\gamma_3(A, A, A) = \left(\frac{3}{4}\right)^{1/3} N_A^{-1/3} C_6^{5/3} \quad (26)$$

$$\gamma_4(A, A, A, A) = \frac{5}{8} \left(\frac{3}{4}\right)^{-4/3} N_A^{-2/3} C_6^{7/3} \quad (27)$$

and

$$\gamma_3(A, A, A) = \frac{3}{4} \alpha_A(0) C_6 \quad (28)$$

$$\gamma_4(A, A, A, A) = \frac{5}{8} \alpha_A^2(0) C_6 \quad (29)$$

At the moment there seems no way of testing these approximate formulae in the case of molecular interactions. However, for rare gas atoms, Eq. (28), which has previously been derived by Kihara [9], has been shown to be surprisingly accurate [24]. Unfortunately it is not possible to test Eq. (26) in a similar way since  $N_A$  is defined only for first-row atoms.

## 6. Retardation Effects

When radiative corrections are taken into account the leading term in the interaction energy is more complicated than the simple  $-C_6/R^6$  dispersion term of Eq. (1) (see, for example, [1], [10]). The correct expression is

$$\Delta E = -\frac{1}{\pi R^6} [3I_0 + 6\sigma R I_1 + 5\sigma^2 R^2 I_2 + 2\sigma^3 R^3 I_3 + \sigma^4 R^4 I_4] \quad (30)$$

where we have used  $\sigma$  for the fine-structure constant ( $\sigma = 1/137$ ) and  $I_n$  is the integral

$$I_n = \int_0^\infty \omega^n \alpha_A(i\omega) \alpha_B(i\omega) \exp(-2\sigma R\omega) d\omega \quad (31)$$

For very large  $R$  an asymptotic expansion of  $\Delta E$  can be obtained. This is easy to do since the integrals  $I_n$  are in precisely the form to which Watson's lemma can be applied (see, for example, chapter 17 of Ref. [25]). If we write

$$\alpha_A(i\omega) \alpha_B(i\omega) = a_0 - a_2 \omega^2 + a_4 \omega^4 - \dots \quad (32)$$

for small  $\omega$ , then applying the lemma gives the asymptotic formula:

$$\Delta E \sim -\frac{23}{4\pi\sigma} a_0 R^{-7} + \frac{129}{8\pi\sigma^3} a_2 R^{-9} - \frac{639}{4\pi\sigma^6} a_4 R^{-11} + \dots \quad (33)$$

a result which has been obtained by many authors (for references, see [1]). To find the coefficients  $a_0, a_2, a_4 \dots$  we expand  $\alpha_A(i\omega), \alpha_B(i\omega)$  separately. For example:

$$\alpha_A(i\omega) = \sum_{k=0}^{\infty} S_A(-2k-2)(-1)^k \omega^{2k} \quad (34)$$

Table 4. Frost-model values of the sums  $S(-2)$ ,  $S(-4)$ ,  $S(-6)$  in atomic units

Molecule	$S(-2)^a$	$S(-4)$	$S(-6)$
H <sub>2</sub>	4.93	12.15	29.95
H <sub>2</sub> O	6.66	5.55	4.63
NH <sub>3</sub>	12.28	18.89	29.35
CH <sub>4</sub>	16.48	33.91	69.80
C <sub>2</sub> H <sub>6</sub>	28.44	57.83 <sup>1</sup>	117.81
C <sub>2</sub> H <sub>4</sub>	24.90	53.25	117.48
C <sub>2</sub> H <sub>2</sub>	21.35	47.72	110.73

<sup>a</sup> Note that  $S(-2) = \alpha(0)$  and  $S(0) = 2n$ , the number of electrons so that the Thomas-Reiche-Kuhn sum rule is satisfied by the Frost-model expression.

where the  $S_A(-2k - 2)$  are oscillator-strength sums. The first four coefficients are given by

$$\begin{aligned} a_0 &= S_A(-2)S_B(-2) \\ a_2 &= S_A(-2)S_B(-4) + S_A(-4)S_B(-2) \\ a_4 &= S_A(-2)S_B(-6) + S_A(-6)S_B(-2) + S_A(-4)S_B(-4) \end{aligned} \quad (35)$$

These results are quite general.

If we use the Frost model to estimate the sums we find

$$S_A(-2k - 2) = 2 \sum_{i=1}^{n_A} \omega_i^{-2(k+1)} \quad (36)$$

and values of the first few of the sums for a number of molecules are given in Table 4.

Note that for the hydrocarbons each successive term is approximately double the previous one. This happens because  $S_A$  can be approximated by  $N_A \bar{\omega}_A^{-2(k+1)}$  so that  $S_A(-2k - 2) \approx \bar{\omega}_A^{-2} S_A(-2k)$ . Since, for the hydrocarbons,  $\bar{\omega}_A \approx 0.7$  we have  $S_A(-2k - 2) \approx 2S_A(-2k)$ . Of course, this result is valid only within the Frost model and it appears to underestimate the values of the higher sums<sup>1</sup>.

In spite of this, we can get at least a rough estimate of the values of  $a_0, a_2, a_4$  by using the results from Table 4. For example, using the estimate  $S_A(-2k - 2) \approx 2S_A(-2k)$  for hydrocarbons we find that Eq. (33) is approximately

$$\Delta E \approx -\frac{27}{4\pi\sigma} a_0 R^{-7} [1 - 2 \cdot 10^5 R^{-2} + 10^{11} R^{-4} + O(R^{-6})] \quad (37)$$

which should be a good approximation to Eq. (30) for  $R > 1500$  a.u.

It is much less easy to obtain a useful expansion of  $\Delta E$  for relatively small values of  $R$ . However, by seeking a Taylor series in  $\sigma R$  we find

$$\Delta E = -R^{-6} \{C_6 - \sigma^2 R^2 d_4 + O(\sigma^3 R^3)\} \quad (38)$$

<sup>1</sup> For H<sub>2</sub>, Starkschall and Gordon [3] find  $S(-4) = 19.91 \pm 0.35$  a.u. and  $S(-6) = 80.4 \pm 2.7$  a.u. so that the Frost-model value for  $S(-6)$  is less than 40% of the accurate value.

Table 5. Frost-model values of  $d_4$  in atomic units

Molecule	$d_4$
H <sub>2</sub>	1.57
H <sub>2</sub> O	15.07
NH <sub>3</sub>	20.40
CH <sub>4</sub>	23.84
C <sub>2</sub> H <sub>6</sub>	72.92
C <sub>2</sub> H <sub>4</sub>	54.18
C <sub>2</sub> H <sub>2</sub>	38.34

where  $C_6$  is the usual dispersion coefficient and

$$d_4 = \frac{1}{\pi} \int_0^{\infty} \omega^2 \alpha_A(i\omega) \alpha_B(i\omega) d\omega \quad (39)$$

Using the Frost-model formula for the polarizabilities it follows that

$$d_4 = 2 \sum_{i=1}^{n_A} \sum_{j=1}^{n_B} \frac{1}{(\omega_i^A + \omega_j^B)} \quad (40)$$

Though an averaging process has proved successful for treating  $C_6$  and  $\gamma_n$  it must be noted that for  $d_4$  individual terms are of the order  $1/\omega_i$  and it is not nearly as good an approximation to neglect inner shell contributions which are no longer entirely negligible. Therefore, for the interaction of like molecules, values of  $d_4$  found directly from Eq. (40), rather than an approximate formula, are given in Table 5. The figures in that table show that when  $R$  becomes greater than 50 a.u. it is not sufficiently accurate to consider  $C_6$  alone but radiative corrections due to the  $\sigma^2 R^2 d_4$  term begin to become significant.

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### Appendix: A Symmetry-Adapted Perturbation Theoretic Expansion of $\alpha(\omega)$

Consider a molecule with Hamiltonian  $\mathcal{H}$  and ground-state wavefunction  $\psi_0$  and energy  $E$  so that

$$(\mathcal{H} - E)\psi_0 = 0 \quad (A1)$$

If the system is perturbed by a time-dependent sinusoidal perturbation  $\mathcal{W} \cos \omega t$  where  $\mathcal{W}$  is independent of  $t$  and  $\omega$  is the frequency then following Langhoff, Epstein, and Karplus [28] the first-order change in the wavefunction  $\psi_1$ , can be written in terms of the spatial functions  $\psi_1^+$ ,  $\psi_1^-$  in the form

$$\psi_1(t) = \frac{1}{2} e^{i\omega t} \psi_1^+ + \frac{1}{2} e^{-i\omega t} \psi_1^- \quad (A2)$$

where

$$(\mathcal{H} - E \pm \omega)\psi_1^\pm = (E_1 - \mathcal{W})\psi_0 \quad (A3)$$

which is time-independent.

In the case where  $\mathcal{W}$  is the dipole-moment operator, and since all the functions are real, the frequency-dependent polarizability is given by

$$\alpha(\omega) = -\langle \psi_0 | \mathcal{W} | \psi_1^+ + \psi_1^- \rangle \quad (A4)$$

In order to obtain a perturbation-theoretic expansion of  $\alpha$  it is convenient to define it by means of an equation similar to that which determines the static polarizability in the time-independent case. Such an equation is

$$(\mathcal{H} - E)\psi_2 = -\alpha\psi_0 + (E_1 - \mathcal{W})(\psi_1^+ + \psi_1^-) \quad (\text{A5})$$

If  $\mathcal{H}$  is written as the sum of a zero-order Hamiltonian  $\mathcal{H}_0$  and a correcting internal perturbation  $\lambda\mathcal{V} = \mathcal{H} - \mathcal{H}_0$  then Eqs. (A1)–(A5) can be used to obtain  $\alpha(\omega)$  as a series in  $\lambda$ .

Suppose, however, that  $\mathcal{G}$  is an idempotent symmetry operator which commutes with  $\mathcal{H}$  and  $\mathcal{W}$  and which is such that  $\mathcal{G}\psi_0 = \psi_0$ ;  $\mathcal{G}\psi_1^\pm = \psi_1^\pm$ ;  $\mathcal{G}\psi_2 = \psi_2$  but that  $\mathcal{G}$  does not commute with  $\mathcal{H}_0$  and  $\mathcal{V}$  separately. Then the equations can be solved by symmetry-adapted perturbation theory. If, in particular, we extend Hirschfelder's method [29] we introduce the equations

$$[\mathcal{H}_0 - E_0 + \mathcal{G}(\mathcal{V} - \bar{E} + E_0)]\phi = 0 \quad (\text{A6})$$

$$[\mathcal{H}_0 - E_0 \pm \omega + \mathcal{G}(\mathcal{V} - \bar{E} + E_0)]\chi^\pm = (E_1 - \mathcal{W})\phi \quad (\text{A7})$$

$$[\mathcal{H}_0 - E_0 + \mathcal{G}(\mathcal{V} - \bar{E} + E_0)]\xi = \bar{\alpha}\phi + (E_1 - \mathcal{W})(\chi^+ + \chi^-) \quad (\text{A8})$$

Clearly in terms of the solutions to (A6)–(A8) the solution to (A1)–(A5) will be given by  $\psi_0 = \mathcal{G}\phi$ ,  $\psi_1^\pm = \mathcal{G}\chi^\pm$ ,  $\psi_2 = \mathcal{G}\xi$  and  $E = \bar{E}$ ,  $\alpha = \bar{\alpha}$ . Thus Eqs. (A6)–(A8) can be used to obtain a symmetry adapted perturbation theoretic expansion of  $\alpha(\omega)$ .

We now apply this theory to the Frost model and we take  $\mathcal{G}$  to be the antisymmetrizer and  $\mathcal{H}_0$  the sum of harmonic oscillator Hamiltonians as described in Ref. [12]. The relevant equations we require from (A6)–(A8) to obtain the leading term in the expansion of  $\alpha(\omega)$ , i.e. the term independent of  $\lambda$ , are

$$(\mathcal{H}_0 - E_0)\phi_0 = 0 \quad (\text{A9})$$

$$(\mathcal{H}_0 - E_0 \pm \omega)\chi_0^\pm = (E_1 - \mathcal{W})\phi_0 \quad (\text{A10})$$

$$(\mathcal{H}_0 - E_0)\xi_0 = -\alpha\phi_0 + (E_1 - \mathcal{W})(\chi_0^+ + \chi_0^-) \quad (\text{A11})$$

For the Frost model, taking  $\phi_0$  as a single Gaussian centred at the origin (for simplicity), we find when  $\mathcal{W} = -x$ , i.e. the field is in the  $x$ -direction,

$$\chi_0^\pm = \frac{1}{\omega_0 \pm \omega} x\phi_0 \quad (\text{A12})$$

and so

$$\alpha = \left\langle \phi_0 \left| x^2 \right| \frac{1}{\omega_0 + \omega} \phi_0 + \frac{1}{\omega_0 - \omega} \phi_0 \right\rangle \quad (\text{A13})$$

whence

$$\alpha = \frac{1}{\omega_0^2 - \omega^2} \quad (\text{A14})$$

The leading term for the total polarizability is just a sum of such expressions yielding Eq. (6).

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