

## Dipole sums and intermolecular interaction coefficients derived from refractive index data

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The old problem of using refractive index measurements to obtain estimates of dipole sums and interaction coefficients is reconsidered. It is found that a consistent numerical procedure for fitting the measured values to a two-term representation of the frequency dependent polarizability enables satisfactory values to be obtained.

**Key words:** Dipole sums — Intermolecular interactions — Refractive index

### 1. Introduction

The dipole oscillator sums  $\{S(-2k)\}$ ,  $k = 1, 2, \dots$ , of an atom or molecule are the coefficients of the Cauchy power series representation of its frequency-dependent dipole polarizability  $\alpha(\omega)$  [1]:

$$\alpha(\omega) = \sum_{k=0}^{\infty} S(-2k-2)\omega^{2k}. \quad (1)$$

An alternative and often more useful expression for  $\alpha(\omega)$  is the Maxwell-Sellmeier (MS)  $n$ -term formula, (or, equivalently, the  $[n, n-1]$  Padé approximant [2])

$$\alpha(\omega) = \sum_{i=1}^n \frac{f_i}{\varepsilon_i^2 - \omega^2}, \quad (2)$$

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where the set  $\{f_i, \varepsilon_i\}$ ,  $i = 1, \dots, n$  are *effective* oscillator strengths and transition frequencies.

Clearly there are relations between constants in (1) and (2) so that the  $\{S(-2k)\}$  can be determined simply from  $\{f_i, \varepsilon_i\}$  by

$$S(-2k) = \sum_{i=1}^n \frac{f_i}{\varepsilon_i^{2k}} \quad (3)$$

and, vice-versa, the  $\{f_i, \varepsilon_i\}$  may be obtained from  $\{S(-2k)\}$  by making (1) and (2) agree to order  $\omega^{4n-2}$ . This equivalence can be very useful. For example, if we first obtain the  $\{f_i, \varepsilon_i\}$ , it is advisable then to transform to the  $\{S(-2k)\}$  for comparison with other theoretical or experimental literature values since the effective oscillator strengths and transition frequencies, in spite of their names, have no actual physical meaning.

There are constraints which the constants in the expressions (1) and (2) have to satisfy. The most important of these arise from the fact that  $\alpha(i\omega)$  is a series of Stieltjes and  $\alpha(\omega)$  has its first pole at the first transition frequency  $\omega_1$ . Because it is very much easier to impose these conditions on (2), by taking  $f_i > 0$  and  $\varepsilon_i > \omega_1$ , rather than on (1) where they take more complicated forms, there are great advantages to working with (2).

In recent years it has become a matter of interest to determine dipole sum values and other quantities such as two- and three-body London dispersion coefficients  $C_6$  and  $\gamma_3$  obtainable from  $\alpha(\omega)$ . The most reliable of such values, essentially state-of-the-art results, are found not by way of (1) but more directly, through the construction of dipole oscillator strength distributions (DOSD). These constructions use and rely on a variety of experimental data. Meath and collaborators have produced DOSD for quite a large number of atoms and molecules, and the associated quantities obtained from their DOSDs can be regarded in most cases as the most accurate available [3-7]. DOSDs are also available for atomic systems [8] not covered in the above works.

A simpler, older, even if invariably less accurate procedure, is to use the relationship between the refractive index of a gas and the  $\alpha(\omega)$  of its constituent atoms or molecules to fit refractive index measurements to a representation of  $\alpha(\omega)$ , that given by (2) being the best choice for reasons previously stated. There are many examples of this available in the literature [9-15]. However, in our view, the method has often been applied in a rather ad hoc way with little or no attempt to evaluate the results by comparison with other work and without the development of a consistent technique which can be applied to a wide variety of cases. It is the purpose of this paper, therefore, to attempt to remedy some of these defects by reconsidering the problem of obtaining  $\{f_i, \varepsilon_i\}$  values from refractive index measurements.

## 2. The fitting procedure

Suppose from refractive index data we can determine the polarizability at  $m$  different frequencies  $\{\omega_i\}$ . Denoting these data points by  $\alpha_i = \alpha(\omega_i)$  ( $i = 1, \dots, m$ ),

a least-squares fit to an  $n$ -term MS formula is found by minimizing

$$F = \sum_{i=1}^m \left\{ \alpha_i - \sum_{j=1}^n \frac{f_j}{\varepsilon_j^2 - \omega_i^2} \right\}^2 \quad (4)$$

However, certain constraints must be placed on the values of  $\{f_j, \varepsilon_j\}$  if the resulting expression for  $\alpha(\omega)$  is to have the correct physical properties (for a discussion, see [16]). As we have stated, one of the most important of these, that  $\alpha(i\omega)$  is monotonic decreasing with  $\omega$ , is automatically satisfied by taking the MS form for  $\alpha(\omega)$ . We now consider what other constraints should be imposed.

### 2.1. Constraints on the values of $f_j$ and $\varepsilon_j$

As  $n$  becomes large the  $\varepsilon_j$  should tend to the exact transition frequencies  $\bar{\omega}_j$  from above. This implies the condition  $\varepsilon_j \geq \bar{\omega}_1$ , which should certainly be applied as we have emphasized in a previous publication [16]. On the other hand, in some calculations the  $\varepsilon_j$  have been constrained to be exactly equal to the experimental values of the  $\bar{\omega}_j$ . For example, Dalgarno et al [12] fit a two term MS equation to refractive index data subject to  $\varepsilon_1 = \bar{\omega}_1$ , with  $\bar{\omega}_1$  the experimental first allowed dipole transition frequency. However, using the exact dipole sum values for the hydrogen atom and working backwards from these to the  $\{f_i, \varepsilon_i\}$ , it is not until a five-term MS formula is used that  $\varepsilon_1$  coincides with the exact  $\omega_1$ , and with  $n$  in the MS formula smaller than 5,  $\varepsilon_1 > \bar{\omega}_1$  [17]. Therefore, we conclude that only the condition  $\varepsilon_1 \geq \bar{\omega}_1$  should be applied and that  $\varepsilon_1 = \bar{\omega}_1$  should not.

In a similar way, the  $f_j$  should tend to true oscillator strengths, but to constrain them to equal experimental values in the case of a MS formula with few terms does not give the optimum fit and is not justifiable.

### 2.2. The Thomas-Reiche-Kuhn sum rule

The TRK sum rule is

$$S(0) = N, \quad (5)$$

where  $N$  is the number of electrons in the system. Via (3) this becomes

$$\sum_{i=1}^n f_i = N. \quad (6)$$

Strictly speaking this equality holds only in so far as (2) is an accurate representation of  $\alpha(\omega)$  which, in practice, means  $n$  relatively large. For small values of  $n$ , (6) ought to be replaced by an inequality

$$\sum_{i=1}^n f_i < N. \quad (7)$$

However, some authors have imposed the equality constraint (6) on their calculations, scaling the  $f_i$  where necessary to ensure it is satisfied, even in cases where  $n$  is as small as one or two. Evidence which suggests this procedure is incorrect is provided by considering the case of the hydrogen atom where exact values of

the sums  $S(-2k)$  are available [17]. In [17] the exact sums are used to determine  $f_i$  values, and we find that taking  $n = 1$  to  $n = 5$  the value of  $\sum_i f_i$  is 0.7618, 0.9023, 0.9490, 0.9694, and 0.9798, so that even with  $n = 5$  the expression has not converged to the TRK sum rule value  $N = 1$ . Thus we consider that only (7) and not (6) should be applied. Moreover, as we have argued elsewhere [16], with  $n$  small,  $N$  should in practice be the number of valence electrons rather than the total number of electrons.

### 2.3. Refractive index data

The values of the  $\alpha_i$  to be used in (4) are obtained from refractive index measurements [18-35]. If  $n_i$  is the refractive index at wavelength  $\lambda_i$  (measured in Å at temperature  $T$  in °K) then

$$\alpha_i = \frac{3}{4\pi\zeta} \frac{(n_i^2 - 1)}{(n_i^2 + 2)}, \quad \omega_i = \frac{\delta}{\lambda_i}, \quad (8)$$

with  $\alpha_i$  and  $\omega_i$  in atomic units and

$$\begin{aligned} \delta &= hc/2R = 455.6321 \\ \zeta &= 0.08923743/(82.05624T + B), \end{aligned} \quad (9)$$

where  $B$  is the second virial coefficient in  $\text{cm}^3 \text{mol}^{-1}$ .

As was pointed out by Leonard [36], there are difficulties in the non-uniform way refractive index data is presented by different authors. These include the use of different constants in the reduction to standard conditions (STP), in some cases it not being entirely clear how the reduction has been made. In addition some authors take vacuum and some air wavelengths while others round off their wavelength values, all of which can alter the fitted values in one way or another.

The reduction to STP involves multiplication of the polarizabilities by a constant, which is essentially equivalent to multiplying  $n_i - 1$  by the same constant (since  $n_i \approx 1$  so that  $\alpha_i \approx (n_i - 1)/2\pi\zeta$ ). Similarly the inclusion or not of the virial coefficient  $B$  in (9), the former treating the gas as non-ideal and the latter as ideal, is equivalent to a scaling of the  $\alpha_i$  and  $n_i - 1$  values. Scaling or normalizing the  $\alpha_i$  values in this way corresponds to a vertical shift if we plot  $\alpha_i$  against  $\omega_i$ . As a consequence, the  $f_i$  values in (2) when fitted, will be scaled by the same amount while the  $\varepsilon$ -values will be unaffected. Thus it seems best to fit the MS formula to the unnormalized data, any required normalization can be applied afterwards. Similarly a change from air to vacuum wavelengths corresponds to a horizontal shift by a constant of all the data. In the fit to the MS formula, the  $f_i$  will be unchanged while the  $\varepsilon_i$  values are scaled by this same constant. Here, too, any scaling can be performed after the fitting.

The only real problems in either case arise when different sets of data are being mixed to give an extended range for fitting, when both types of renormalization must be made. Marrying different sets of data can be dangerous as different gas properties etc. can affect results, and where there is an overlap in data ranges

there can be non-monotonicity in the data. On the other hand, it can be tempting to do so since, when data is only available in the long wave length region, there are problems in obtaining good values for higher sums  $S(-6)$ ,  $S(-8)$  from the  $\{f_i, \varepsilon_i\}$ , while for short wavelength data the problems can arise in determining correct behaviour for  $S(-2)$  and  $S(-4)$ .

The position we have adopted is to fit data from a single paper. We have specified what  $T$  and  $B$  values have been taken to find the  $\alpha_i$  using the data quoted by the original experimentalists for both  $\lambda_i$  and  $n_i$ .

#### 2.4. Numerical procedure

Eq. (2) was fitted for appropriate values of  $n$  subject to constraints (7) (with  $f_i \geq 0$ ) and  $\varepsilon_i \geq \bar{\omega}_1$  using routine E04WAF from the NAG library [37]. This routine includes both first and second derivatives of the objective function.

Problems can occur when the optimization procedure reaches the parameter boundary edge, e.g. if  $n = 2$ ,  $f_1 + f_2 = N$  or  $\varepsilon_1 = \omega_1$ , where it is sometimes possible to get trapped. By restarting the procedure some distance away, one can obtain some indication of whether a spurious minimum has been found. In some cases it is not possible to get off the boundary.

The number of terms in (2) which can be fitted depends on the data available and, in particular, on the range of values of  $\omega$ . When only one term can be fitted it is usually due to lack of curvature in the  $\alpha(\omega)$  because of a small data range. For systems where the data range approaches the first transition, a three-term fit can often be obtained but usually no higher. In these cases we invariably found  $\varepsilon_1 = \omega_1$  with  $f_1$  very small and this had the effect of decreasing  $S(-4)$  and increasing  $S(-6)$  and  $S(-8)$  values, yielding results closer to DOSD values.

### 3. Results

For various sets of refractive index data we have applied the numerical procedure described in the previous section. In some cases only one term MS functions could be fitted, usually because the measurements were made for a restricted range of low frequencies, i.e. in a region of small curvature. Almost always the sum values and other quantities obtained from one-term functions are of poor quality and so we have excluded them from further consideration. For a few other cases, the experimental refractive indices were not monotonic in  $\omega$  and any attempt to fit such data led to poor results and, sometimes, to difficulties with the numerical procedure. These data sets, too, were not considered further. A final group of data which we decided to exclude were those with fewer than ten data points since as a rule these led to unsatisfactory results when compared with other theoretical and empirical calculations. The remaining sets of data, therefore, were those with not less than ten measured values per set and those which could be fitted by a two-term MS formula. The results obtained from these are given in Table 1.

Table 1. Effective oscillator strengths and transition frequencies obtained from index of refraction data<sup>a</sup>

Atom/ Molecule <sup>b</sup>	Data Reference	Number of points <sup>c</sup>	$\omega$ Data Range	Convergence Factor	$f_1$	$f_2$	$\epsilon_1$	$\epsilon_2$	S(0)	S(-2)	S(-4)	S(-6)	S(-8)
H <sub>2</sub>	[18]	20	0.0834 0.1979	6.73 (-5)	0.9433	1.0567	0.4759	0.9094	2.0	5.443	19.94	83.09	360.9
B = 14.34	[19]	11	0.0834 0.1979	7.19 (-5)	0.9949	1.0051	0.4802	0.9441	2.0	5.443	19.98	82.57	353.5
$\bar{\omega}_1 = 0.4110$	[20]	26	0.1581 0.2713	6.04 (-4)	0.8426	1.1574	0.4671	0.8589	2.0	5.431	19.83	84.00	375.7
N <sub>2</sub>	[3]	DOSD							2.0	5.428	19.96	82.94	367.0
	[21]	21	0.0834 0.1915	1.65 (-4)	2.2385	11.7615	0.5273	1.7803	14	11.76	30.13	104.5	374.7
B = -10.04	[22] <sup>d</sup>	19	0.0221 0.0974	3.31 (-5)	1.6940	4.1765	0.5215	0.8708	5.871	11.74	30.17	93.83	322.5
$\bar{\omega}_1 = 0.4487$	[3]	DOSD							14	11.74	30.11	101.8	384.6
O <sub>2</sub>	[20]	22	0.1581 0.2472	2.83 (-3)	0.2472	15.7528	0.3127	1.3901	16	10.68	30.06	266.4	2703
B = -21.66	[23]	42	0.0772 0.2373	3.94 (-4)	0.1500	4.8647	0.3012	0.7379	5.015	10.59	34.64	231.1	2271
$\bar{\omega}_1 = 0.2249$	[3]	DOSD							16	10.59	34.75	237.1	2196
NO	[24]	18	0.0834 0.1862	1.92 (-4)	0.0254	3.9262	0.2343	0.5958	3.952	11.52	39.59	241.4	3045
B = -23.2 $\bar{\omega}_1 = 0.2014$	[3]	DOSD							15	11.52	38.46	276.2	3194
CO	[25]	20	0.0834 0.1915	1.88 (-4)	0.3445	4.8759	0.3312	0.7006	5.220	13.07	48.87	302.3	2465
B = -13.65	[20]	28	0.1581 0.2725	1.31 (-3)	0.1557	3.9190	0.3065	0.5869	4.075	13.04	50.67	283.7	2277
$\bar{\omega}_1 = 0.2950$	[45]	DOSD							14	13.08	48.27	296.5	2387
CO <sub>2</sub>	[25]	20	0.0834 0.1915	2.82 (-4)	0.0442	6.1299	0.3089	0.5996	6.174	17.52	52.30	182.9	900.6

$B = -151.4$ $\bar{\omega}_1 = 0.3089$	[26]	11	0.0682 0.1655	4.46 (-3)	1.7080	20.2920	0.4418	1.5342	22	17.37	48.51	231.3	1178
$N_2O$	[45]	DOSD							22	17.51	50.99	211.4	1030
$B = -160.4$ $\bar{\omega}_1 = 0.2503$	[24]	21	0.0834 0.1979	9.71 (-4)	0.8946	8.2966	0.3638	0.8023	9.191	19.65	71.12	417.3	2967
$NH_3$	[3]	DOSD							22	19.70	72.11	410.7	2847
$B = -345$ $\bar{\omega}_1 = 0.2102$	[27]	18	0.0834 0.1942	4.52 (-4)	0.0691	3.5803	0.2314	0.5189	3.649	14.59	73.45	632.7	9069
$CH_4$	[3]	DOSD							10	14.56	71.44	684.0	9527
$B = -53.9$ $\bar{\omega}_1 = 0.3132$	[27]	21	0.0834 0.1979	3.50 (-4)	0.7325	5.1360	0.3850	0.6480	5.869	17.17	62.47	294.2	1682
$C_2H_6$	[5]	DOSD							10	17.27	62.41	298.3	1714
$B = -221.4$ $\bar{\omega}_1 = 0.3000$	[28]	15	0.0787 0.1979	3.96 (-4)	1.0826	9.4502	0.3696	0.6586	10.533	29.71	108.3	540.7	3378
$C_3H_8$	[6]	DOSD							18	29.61	108.1	531.4	3149
$B = -465.1$ $\bar{\omega}_1 = 0.2800$	[28]	15	0.0787 0.1979	4.43 (-4)	2.6440	15.4486	0.3873	0.7960	18.09	42.01	156.0	844.4	5321
$He$	[6]	DOSD							26	42.09	157.1	804.2	5046
$B = 11.8$	[21] <sup>c</sup>	21	0.0834 0.1978	3.14 (-5)	0.9848	0.4301	0.9012	1.5761	1.415	1.386	1.563	1.867	2.276
$\bar{\omega}_1 = 0.7797$	[29]	14	0.0834 0.1655	1.30 (-5)	0.5731	1.1134	0.8129	1.4672	1.687	1.385	1.553	2.098	3.058
	[20]	25	0.1581 0.2713	1.97 (-4)	0.4934	1.2035	0.7797	1.4552	1.697	1.380	1.603	2.323	3.672
	[8]	DOSD							2	1.384	1.546	2.048	2.939

Table 1. Continued

Atom/ Molecule <sup>b</sup>	Data Reference	Number of points <sup>c</sup>	$\omega$ Data Range	Convergence Factor	$f_1$	$f_2$	$\epsilon_1$	$\epsilon_2$	S(0)	S(-2)	S(-4)	S(-6)	S(-8)
Ar	[30]	21	0.1981 0.4105	8.75 (-4)	0.2703	4.3038	0.4297	0.6706	4.574	11.04	29.21	90.28	337.8
$B = -21.4$	[31]	17	0.0803 0.1979	1.03 (-4)	1.5404	6.6943	0.5027	1.1582	8.235	11.09	27.84	98.19	379.6
$\bar{\omega}_1 = 0.4272$	[32] <sup>d</sup>	17	0.0221 0.0974	1.44 (-5)	1.0240	5.1800	0.4784	0.8855	6.204	11.08	27.98	96.18	387.0
Kr	[8]	DOSD							18	11.08	27.98	94.56	382.1
	[20]	28	0.1581 0.2712	9.19 (-3)	1.3889	9.0678	0.4174	1.0144	10.46	16.78	54.33	271.0	1516
$B = -62.4$	[33]	21	0.1981 0.3505	1.34 (-3)	0.2717	4.2394	0.3716	0.5402	4.511	16.50	64.04	273.8	1332
$\bar{\omega}_1 = 0.3687$	[34]	19	0.0679 0.2249	9.64 (-4)	0.4309	5.6952	0.3687	0.6490	6.126	16.69	55.42	247.8	1443
	[35]	20	0.0731 0.1979	1.74 (-4)	2.2370	33.7630	0.4498	2.4400	36	16.73	55.59	270.2	1335
Xe	[8]	DOSD							36	16.78	56.65	251.5	1317
	[33]	17	0.1981 0.3038	3.29 (-3)	0.2784	5.0682	0.3103	0.4620	5.343	26.60	140.9	829.3	5641
$B = -157.8$	[34]	18	0.0679 0.2125	2.05 (-3)	1.5702	12.9837	0.3519	0.9482	14.55	27.13	118.5	845.5	6705
$\bar{\omega}_1 = 0.3100$	[35]	20	0.0731 0.1979	1.57 (-4)	1.2250	6.5943	0.3464	0.6285	7.819	26.91	127.4	816.3	6182
	[8]	DOSD							54	27.11	128.3	820.3	6219

<sup>a</sup> All values reported in atomic units: Shull H, Hall GG (1959) Nature 184:1559

<sup>b</sup>  $B$  is the second virial coefficient in  $\text{cm}^3 \text{mol}^{-1}$ ;  $\bar{\omega}_1$  is the estimated first transition frequency [43, 44] in atomic units (see text for further discussion)

<sup>c</sup> DOSD refers to dipole sum values obtained through the construction of dipole oscillator strength distributions. S(0) is obtained directly by the TRK sum rule (5)

<sup>d</sup> For [22] in the case of  $\text{N}_2$ ,  $T = 288.15^\circ\text{K}$  and  $B = -6.64 \text{ cm}^3 \text{mol}^{-1}$ , and for [32] in the case of Ar,  $T = 288.15^\circ\text{K}$  and  $B = -17.9 \text{ cm}^3 \text{mol}^{-1}$ , otherwise  $T = 273.15^\circ\text{K}$

<sup>e</sup> The minimization routine may not have completely converged for this set of data



In Table 1, we list for each data set the temperature and second virial coefficient used to transform between  $n(\omega)$  and  $\alpha(\omega)$  and, for each atom and molecule, the value used for the first transition  $\bar{\omega}_1$  frequency applied as a constraint in the numerical procedure. We must emphasize that there can be problems in choosing  $\bar{\omega}_1$ , e.g. whether to take the onset or middle of the band and what to do when band overlap occurs (see O<sub>2</sub> when both sets of data appear to go through the first transition). However, we do not believe that any of our results have been significantly affected by these difficulties.

For a measure of accuracy of the fit, we give a convergence factor  $\sqrt{F/m}$ ,  $F$  being the function of Eq. (4) and  $m$  the number of points used. The ratio of this to an average value for the polarizability is usually considerably better than two parts in 10<sup>4</sup>, which is generally thought to be the order of the experimental error in refractive index measurements. Values of  $S(-2k)$  and the interaction coefficients fitted from different data sets of the same system from a single paper showed only small changes which would indicate that values are not materially affected by random error.

We have noticed, as was pointed out also by Gerhart [38], that there can be difficulties with short wavelength measurements. In particular, those of Kirn [19] on H<sub>2</sub> below  $\lambda = 2300 \text{ \AA}$  (above  $\omega = 0.2 \text{ au}$ ) lead to fitted values that differ quite dramatically from those given by other data as well as from the DOSD results and have been omitted in the fit. This reinforces the view that measurements at short wave length are hard to do accurately and shows, also, that fitted values do depend significantly on the data range taken.

The bulk of Table 1 consists of the values of  $f_1$ ,  $f_2$ ,  $\epsilon_1$ ,  $\epsilon_2$  obtained from the numerical fit. From these the associated sums  $S(0), \dots, S(-8)$  are easily evaluated and are listed in the table. Where accurate sum values are available from DOSD these are given for comparison. It is clear that a two-term MS fit to refractive index data does indeed allow very reasonable values for  $S(-2)$  and  $S(-4)$  to be obtained and quite satisfactory values for  $S(-6)$  and  $S(-8)$ . For systems where we have fitted data below  $2300 \text{ \AA}$  (above  $\omega = 0.2 \text{ au}$ ), notably from the measurements of Smith et al [20], values for O<sub>2</sub>, He and Kr are not in particularly good agreement with DOSD results, but H<sub>2</sub> values are reasonable.

Chaschina et al. [30, 33] also give data below  $2300 \text{ \AA}$  for the inert gases which yield overestimates of  $S(-4)$  contributions. Leonard [36] points out that their values have already been subjected to a degree of smoothing and data from other papers has been incorporated. Therefore, their values may not be reliable. Other authors who include values below  $2300 \text{ \AA}$ , are Ladenburg [23], giving excellent results for O<sub>2</sub> and Kronjager [34], where  $S(-4)$  values are underestimated for the inert gases.

When the data range of  $\omega$  values was small compared to the experimental  $\bar{\omega}_1$ , i.e. He with  $\bar{\omega}_1 = 0.7797$  and Ne with  $\bar{\omega}_1 = 0.6127$ , it was not possible to obtain good [2, 1] fits for any of the data sets considered, except perhaps [29] for He. We include the He values, although convergence was similar to a [1, 0] fit, in

order to illustrate that surprisingly good interaction coefficients can still be obtained.

In view of earlier remarks it is not surprising that, in most cases, the TRK sum rule,  $S(0) = N$ , is not satisfied. This has important consequences when interatomic and intermolecular interaction coefficients  $C_6$  and  $\gamma_3$  and also,  $d_4$ , the coefficient of the long-range relativistic interaction are computed. If  $f_1 + f_2 = N$ , then upper bounds only to those coefficients can be obtained [2] and these tend to be far from those predicted by DOSD methods. On the other hand, if  $f_1 + f_2 < N$ , then both upper and lower bounds can be obtained. The difference between these can be large and usually neither is close to the DOSD value. This particularly applies to the calculation of  $d_4$ . However, it does seem to be the case empirically that the average of the two is quite close to accurate values. Therefore, in Table 2 we give these average values for  $C_6$ ,  $d_4$  and  $\gamma_3$  obtained from the  $\{f_b, \epsilon_i\}$ , in Table 1.

**Table 2.** Calculated dispersion interaction coefficients<sup>a</sup>

Atom/Molecule <sup>b</sup>	U <sup>c</sup> /A <sup>d</sup> /DOSD <sup>e</sup>	$C_6$	$d_4$	$\gamma_3$
H <sub>2</sub>	U	12.29	1.494	49.27
	U	12.25	1.485	49.10
	U	12.31	1.505	49.20
	DOSD	12.11	1.436	48.47
N <sub>2</sub>	U	80.48	33.21	656.2
	A	72.12	20.70	607.8
	DOSD	73.39	21.43	618.3
O <sub>2</sub>	U	86.57	46.96	637.2
	A	64.47	25.53	473.2
	DOSD	62.01	23.89	453.8
NO	A	68.66	22.65	553.8
	DOSD	69.78	22.87	565.4
CO	A	84.56	23.48	773.9
	A	77.88	20.53	714.4
	DOSD	81.40	21.55	753.5
CO <sub>2</sub>	A	145.7	40.02	1839
	U	188.5	86.29	2235
	DOSD	158.7	49.41	1973
N <sub>2</sub> O	A	196.0	58.07	2684
	DOSD	184.9	51.15	2568
NH <sub>3</sub>	A	87.90	15.43	908.9
	DOSD	89.08	16.30	920.6
CH <sub>4</sub>	A	129.1	20.27	1609
	DOSD	129.6	20.36	1631
C <sub>2</sub> H <sub>6</sub>	A	393.3	64.85	8454
	DOSD	381.8	61.57	8221
C <sub>3</sub> H <sub>8</sub>	A	808.5	146.1	24 340
	DOSD	768.1	124.9	23 480

Table 2. Continued

Atom/Molecule <sup>b</sup>	U <sup>c</sup> /A <sup>d</sup> /DOSD <sup>e</sup>	$C_6$	$d_4$	$\gamma_3$
He	A	1.405	0.549	1.439
	A	1.473	0.653	1.491
	A	1.457	0.653	1.465
	DOSD	1.461	—	1.481
Ar	A	61.99	21.83	490.4
	A	72.21	30.98	557.0
	A	69.51	27.89	541.3
	DOSD	64.20	—	517.4
Kr	A	160.7	91.26	1816
	A	112.6	48.06	1329
	A	141.4	74.92	1621
	U	171.5	145.7	1837
	DOSD	127.9	—	1554
Xe	A	254.0	107.0	4794
	A	386.6	210.8	6919
	A	320.0	165.1	5801
	DOSD	290.5	—	5605

<sup>a</sup> All values reported in atomic units: Shull H, Hall GG (1959) Nature 184:1559.  $C_6$  and  $\gamma_3$  are the two-body and three-body London dispersion interaction coefficients.  $d_4$  is the coefficient of the long-range relativistic interaction.

<sup>b</sup> Sets of values are in the order as in Table 1

<sup>c</sup> U means upper bound and applies when  $S(0) = N$

<sup>d</sup> A means average of upper and lower bounds

<sup>e</sup> DOSD values for the inert gases from [8]. For  $C_2H_6$  and  $C_3H_8$  pseudo-DOSD values are given for  $C_6$ ,  $d_4$  and  $\gamma_3$  [39] which are known to reproduce DOSD results accurately and simply. All the rest of the  $d_4$  values are pseudo-DOSD [40]. The remaining DOSD results for  $C_6$  are taken from [41], [45] and [5] and for  $\gamma_3$  from [42]

For comparison, DOSD results are also given where available, and it can be seen that our results do compare well with them.

On the other hand, the interaction coefficients for the inert gases seem rather less good than those for molecules and less good than might be expected in view of the reasonable  $S(-2k)$  values. In general, where average values have been taken, results are within 5% for  $C_6$  and  $\gamma_3$  but  $d_4$  is less accurate. The results are always either all above or all below DOSD values.

#### 4. Conclusion

We believe the results in Tables 1 and 2 indicate that excellent results can be obtained from a simple two-term MS fit to refractive index data. The results seem most reliable when obtained from measurements in the frequency range 0.08 to 0.20 and for atoms and molecules where  $\bar{\omega}_1$  lies between 0.25 and 0.45. From the fitted values it is possible to obtain good estimates of interaction coefficients, which are important in the study of intermolecular forces. Results of this kind

would be particularly useful in the case of alkanes and unsaturated hydrocarbons. At the moment there is a dearth of accurate experimental refractive index data for these systems so that experimental work in this area would be most welcome.

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## References

1. Hirschfelder JO, Byers Brown W, Epstein ST (1964) *Adv Quantum Chem* 1:255
2. Langhoff PW, Karplus M: In: (1970) Baker Jr GA Gammel JL (eds) *The Padé Approximant in Theoretical Physics* Chap. 2. Academic Press, New York
3. (a) Zeiss GD, Meath WJ, MacDonald JCF, Dawson DJ (1975) *Radiat Res* 63:64. (b) *ibid* (1977) *Can J Phys* 55:2080
4. Zeiss GD, Meath WJ (1975) *Mol Phys* 30:161
5. Thomas GF, Meath WJ (1977) *Mol Phys* 34:113
6. (a) Jhanwar BL, Meath WJ, MacDonald JCF (1980) *Can J Phys* 59:185. (b) *ibid* (1983) 61:1027
7. Meath WJ, Margoliash DJ, Jhanwar BL, Koide A, Zeiss GD (1981) In: Pullman B (ed) *Intermolecular forces*. D. Reidel, Dordrecht, pp. 101-115
8. Leonard PJ, Barker JA *Theor Chem NY* (1975) 1:117
9. Parker GA, Pack RT (1976) *J Chem Phys* 64:2010
10. Pack RT (1974) *J Chem Phys* 61:2091
11. Dalgarno A, Kingston AE (1960) *Proc Roy Soc A* 259:424
12. Dalgarno A, Morrison IH, Pengelly RM (1967) *Int J Quantum Chem* 1:161
13. Langhoff PW, Karplus M (1969) *J Opt Soc Am* 59:863.
14. Neilson GC, Parker GA, Pack RT (1976) *J Chem Phys* 64:2055.
15. Starkschall G, Gordon RG (1971) *J Chem Phys* 54:663
16. Yoffe JA, Maggiora GM, Amos AT (1981) *Theor Chim Acta* 58:137
17. Langhoff PW, Karplus M (1970) *J Chem Phys* 52:1435
18. Koch J (1912) *Ark Mat Astron Fys* 8:No. 20, 1
19. Kirn M (1921) *Ann Phys* 64:566
20. Smith PL, Huber MCE, Parkinson WH (1976) *Phys Rev A* 13:1422
21. Koch J (1913) *Ark Mat Astron Fys* 9:No. 6, 1
22. Peck ER, Khanna BN (1966) *J Opt Soc Am* 56:1059
23. Ladenburg R, Wolfsohn G (1932) *Z Phys* 79:42
24. Koch J (1924) *Ark Mat Astron Fys* 18:No. 3, 1
25. Koch J (1914) *Ark Mat Astron Fys* 10:No. 1, 1
26. Howell JT (1915) *Phys Rev* 6:81
27. Friberg S (1927) *Z Phys* 41:378
28. Friberg S (1931) *Z Phys* 73:216
29. Cuthbertson C, Cuthbertson M (1932) *Proc Roy Soc A* 135:40
30. Chashchina GI, Gladushchak VI, Schreider E Ya (1967) *Opt Spectrosc* 24:542
31. Larsen T (1934) *Z Phys* 88:389
32. Peck ER, Fisher DJ (1964) *J Opt Soc Am* 54:1362
33. Chashchina GI, Shreider EYa (1968) *Opt Spectrosc* 25:79
34. Kronjäger W (1936) *Z Phys* 98:17
35. Koch J (1949) *Kungl Fysiograf Sällskap Lund Forh* 19:173
36. Leonard PJ (1974) *At Data Nuc Data Tables* 14:21
37. NAG (Numerical Algorithms Group) *Library Manual-Mark 7*, December 1978
38. Gerhart DE (1975) *J Chem Phys* 62:821
39. Jhanwar BL, Meath WJ (1980) *Mol Phys* 41:1061
40. Margoliash DJ, Meath WJ (1978) *J Chem Phys* 68:1426

41. Zeiss GD, Meath WJ (1977) *Mol Phys* 33:1155
42. Margoliash DJ, Proctor TR, Zeiss GD, Meath WJ (1978) *Mol Phys* 35:747
43. Herzberg G (1966) *Spectra of diatomic molecules*. D van Nostrand, New York
44. Herzberg G (1966) *Electronic spectra and electronic structure of polyatomic molecules*. D van Nostrand, New York
45. Jhanwar BL, Meath WJ (1982) *Chem Phys* 67:185