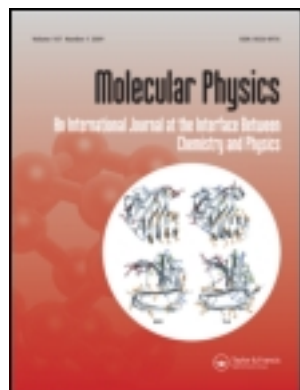


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Multipole moments, polarizabilities and anisotropic long range interaction coefficients for N_2 †

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This paper contains results for the permanent multipoles, the multipole polarizabilities and the related anisotropic long range interaction coefficients C_5 to C_{10} (complete) for the nitrogen molecule. The electrostatic, induction and dispersion interaction coefficients have been calculated using *ab initio* SCF wavefunctions; better estimates for the dispersion terms have been obtained by an approximate procedure, which uses the accurate (semi-) empirical data available for C_6 and the dipole polarizability, in combination with the *ab initio* results. The pure quadrupole-quadrupole anisotropy appears to be substantially modified by the dispersion anisotropy and, to a smaller extent, by the higher multipole electrostatic interactions; the induction energy can be neglected. The dispersion anisotropy factors γ_8 and γ_{10} , are much larger than γ_6 , due to the occurrence of the (completely anisotropic) mixed-pole terms. The recently proposed non-empirical Unsöld method yields results which support applications to larger molecules.

1. INTRODUCTION

In the past few years there has been a rapidly increasing interest in the intermolecular potential for nitrogen. Quite a variety of model potentials with different parameters have been proposed and applied to the calculation of the properties of solid nitrogen [1-16] and, in fewer cases, those of liquid [17-20] and gaseous [12, 21-23] nitrogen. (A review, including an extensive list of references, is given by Scott [24]. Also the recent article by Raich and Gillis [25] is a source of detailed information, in particular with respect to the form of the potential.) All the potentials have in common that most of the parameters have been fitted to experimental quantities, notably the cohesion energy, the crystal equilibrium structure, the lattice frequencies, thermodynamic properties, the liquid structure factors, the second virial coefficient and viscosity data. The most frequently used model is an atom-atom potential of the Lennard-Jones (6- n) [3, 4, 7, 12, 13, 17-19, 22] or the Buckingham (6-exp) type [8, 15]. Often the molecular electrostatic quadrupole-quadrupole interactions [5, 9-11, 14, 20] have been added in order to improve the orientational dependence of the potential. Sometimes this quadrupole-quadrupole term is part of a molecular or semi-molecular approach [1, 2, 6, 16, 21, 23], in which, in a few cases, the

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anisotropies arising from R^{-6} dispersion [1, 6, 16, 23] and R^{-8} induction interactions [16, 21] have also been included.

Nevertheless the intermolecular potential of nitrogen is not satisfactorily established. The remaining discrepancies between the calculated and the experimental data should probably be ascribed mainly to defects in the anisotropy of the potential [15, 20, 23–25]. Although some recent studies have concentrated on this topic [25–28] by computing pair potentials for different relative orientations of the N_2 molecules, the problem is still not settled at all. For instance, Evans [23] concludes that anisotropic corrections to the dispersion interaction have a larger effect upon the second virial coefficient than the inclusion of the electrostatic quadrupole interaction. Cheung and Powles [20] speculate that the dispersion anisotropy, which partly cancels the quadrupole interaction, is required to remove the discrepancies in the specific heat and the thermal pressure coefficient of the liquid. On the other hand, Raich and Gillis [25] state on the basis of their results, that the anisotropic dispersion corrections may be significant for some particular orientations, but that they are quite small for nearest-neighbour pairs in the crystal (for the ethylene crystal we have arrived at a similar conclusion with the aid of *ab initio* computations [29]). At any rate, we can tell, on the basis of our previous results for H_2 -He and H_2 - H_2 [30] and C_2H_4 [29, 31], that important higher multipole anisotropic interactions probably occur, also in N_2 - N_2 , which have not yet been calculated.

In [30] a closed expression for the orientational dependence of the multipole long range interaction coefficients of Σ state linear molecules was obtained as a specialization of the formula for arbitrary molecules [32, 33]. In this paper we apply the formalism of [30] to the N_2 - N_2 dispersion and induction multipole interaction coefficients C_n for $n=6, 8$ and 10 . The anisotropy factors γ_6, γ_8 and γ_{10} , describing the orientation dependence of the (quadratic and mixed-pole) terms [27–35] occurring in C_6, C_8 and C_{10} , are compared with the anisotropy of the electrostatic interaction coefficients C_5, C_7 and C_9 . The molecules are described by Hartree-Fock LCAO wavefunctions with a specially optimized AO basis.

2. MULTIPOLE MOMENTS AND POLARIZABILITIES

The N_2 molecule has been studied extensively at the SCF level [36–43]. It is well-known from Dunning's work [39–41], that the quadrupole moment of N_2 can be calculated in good agreement with the experimental values only if d functions are included in the AO basis. We have added different sets of atomic polarization functions to Dunning's (9s, 5p) basis set contracted to a [4s, 3p] basis [39]. For the ground state wavefunction occurring in the multipole moments (1) these polarization functions have been optimized by minimizing the SCF energy, this resulted in the basis sets *A* through *G* given in table 1; for the second-order properties which also involve excited states, optimum scaling parameters for the polarization functions have been obtained by maximizing the (quadratic) multipole polarizabilities (in accordance with Hylleraas' variation principle, see [30]). This procedure yielded the basis sets of table 3, which are identical with the basis sets of table 1, except for the exponents of the polarization functions. All calculations have been done with the IBMOL-5 program [44] and the multipole properties program MULTPROP [45].

Table 1. Calculated multipole moments (a) and SCF energies, compared with available literature results.

AO basis (b)	$\langle Q_{2,0} \rangle / e a_0^2$	$\langle Q_{4,0} \rangle / e a_0^4$	$\langle Q_{6,0} \rangle / e a_0^6$	E_{SCF} / E_H
(A) (9, 5) \rightarrow [4, 3], Dunning (c)	-1.792	-6.005	-10.529	-108.8877
(B) $A + 1d$, $\zeta_a = 2.70$	-1.231	-6.774	-14.442	-108.9665
(C) $A + (2d) \rightarrow [1d]$, $\zeta_a = 2.40$	-1.015	-7.160	-16.013	-108.9723
(Dunning, $\zeta_a = 2.40$) (d)	(-1.036)	(—)	(—)	(-108.9716)
(D) $A + (2d) \rightarrow [2d]$, $\zeta_a = 2.40$	-1.000	-7.349	-17.425	-108.9732
(Dunning, $\zeta_a = 2.20$) (d)	(-0.992)	(—)	(—)	(-108.9732)
(E) (9, 6, 2) \rightarrow [5, 4, 2], $\zeta_a = 2.40$ (e)	-0.945	-6.779	-15.575	-108.9752
(F) (9, 6, 3) \rightarrow [5, 4, 3] (e)	-0.850	-6.312	-11.892	-108.9770
(G) $D + 1f$, $\zeta_f = 2.80$	-1.051	-7.782	-17.109	-108.9762
Cade, Sales, and Wahl (f)	-0.947	-6.84	—	-108.9928
Christiansen and McCullough (g)	-0.940	—	—	-108.9939
Experimental (h)	-1.04	—	—	
Experimental (i)	-1.00 ± 0.14	-8.0 ± 2.7	—	

(a) Defined according to formula (1); all computations have been done using the experimental equilibrium distance: $2.068 a_0$ [46].

(b) Convention: () : uncontracted; [] : contracted. The scale factors ζ , which have been varied to minimize the SCF energies, determine the GTO exponents α_i by the scaling relation [47]: $\alpha_i = \zeta^2 \chi_i$ (for χ_i we refer to our own tables of STO- n (GTO) expansions of polarization functions [30]). For the angular part of the GTOs we use (real) spherical harmonic functions.

(c) Reference [39].

(d) Reference [41].

(e) The (9s) \rightarrow [5s] contraction of Dunning [39] has been used; an extra diffuse p function ($\alpha_p = 0.0515$) has been added. In basis F an additional diffuse d function ($\alpha_d = 0.2931$; $\zeta_d = 1.50$) has been included.

(f) Reference [38]; the quadrupole and hexadecapole moments have been calculated by Ng *et al.* [48].

(g) The lowest SCF energy for N_2 to date, obtained from numerical HF calculations [43].

(h) From the large variety of measured values this is the most widely quoted result, observed in different experiments [49–51].

(i) These results have been obtained by Birnbaum and Cohen from far-infra-red spectra [52]. The spread in the observed values is connected with the results for different intermolecular N_2-N_2 potentials assumed in [52].

The tabulated permanent multipole moments (table 1) are defined on the basis of Racah spherical harmonic multipole operators [53]:

$$\langle Q_{l,m} \rangle = \langle 0 | \left(\frac{4\pi}{2l+1} \right)^{1/2} \sum_i Z_i r_i^l Y_{l,m}(\hat{r}_i) | 0 \rangle, \quad (1)$$

where the summation over i runs over all particles, electrons and nuclei, in the molecule with charges Z_i and position \mathbf{r}_i ; \hat{r}_i represents the angular coordinates of \mathbf{r}_i (explicit expressions for $Y_{l,m}$ up to $l=6$ inclusive are given in [54]). Table 1 demonstrates once more that the AO basis should contain at least two sets of d functions in order to obtain good agreement with the experimental quadrupole

Table 2. Multipole polarizabilities (*a*), calculated with the optimized AO basis *G'* of table 3, in comparison with available literature values.

	This work		Other theoretical results				Experimental (<i>b</i>)
	π	Total	π	Total	π	Total	
$\alpha_{110}/e^2 a_0^2 E_H^{-1}$	11.81	15.73	14.92 (c),	14.97 (d),	14.39 (d),	14.79 (d)	14.7
$\alpha_{111}/e^2 a_0^2 E_H^{-1}$	4.83	8.76	9.72 (c),	9.46 (d),	9.45 (d),	9.75 (d)	10.3
$\bar{\alpha}_1/e^2 a_0^2 E_H^{-1}$	7.16	11.08	11.45 (c),	11.30 (d),	11.10 (d),	11.43 (d)	11.8
$\alpha_{130}/e^2 a_0^4 E_H^{-1}$	-10.13	22.04	16.05 (e)	16.05 (e)			
$\alpha_{131}/e^2 a_0^4 E_H^{-1}$	-2.77	27.23	27.10 (e)	27.10 (e)			
$\alpha_{220}/e^2 a_0^4 E_H^{-1}$	18.36	64.69	69.35 (e)	69.35 (e)			
$\alpha_{221}/e^2 a_0^4 E_H^{-1}$	18.85	65.97	71.29 (e),	71.29 (e),	53.5 (f)		
$\alpha_{222}/e^2 a_0^4 E_H^{-1}$	17.53	28.19	35.43 (e)	35.43 (e)			
$\bar{\alpha}_2/e^2 a_0^4 E_H^{-1}$	18.22	50.60	56.56 (e)	56.56 (e)			
			This work				
	π	Total	π	Total	π	Total	π
$\alpha_{150}/e^2 a_0^6 E_H^{-1}$	-73.58	76.98	$\alpha_{240}/e^2 a_0^6 E_H^{-1}$	-41.21	339.4	$\alpha_{330}/e^2 a_0^6 E_H^{-1}$	111.0
$\alpha_{151}/e^2 a_0^6 E_H^{-1}$	-33.93	75.60	$\alpha_{241}/e^2 a_0^6 E_H^{-1}$	-26.65	318.1	$\alpha_{331}/e^2 a_0^6 E_H^{-1}$	115.4
			$\alpha_{242}/e^2 a_0^6 E_H^{-1}$	1.05	124.9	$\alpha_{332}/e^2 a_0^6 E_H^{-1}$	200.2
						$\alpha_{333}/e^2 a_0^6 E_H^{-1}$	82.1
						$\bar{\alpha}_3/e^2 a_0^6 E_H^{-1}$	129.5
							412.5

(a) Defined according to formula (2); the isotropic α_s are given by: $\bar{\alpha}_l = (2l+1)^{-1} \sum_{m=-l}^{+l} \alpha_{lm}$. The π contributions to the polarizabilities have been calculated by restricting the sum-over-states formula (2) to excitations from π orbitals only.

(b) Experimental results from [61], where $\alpha(\omega)$ has been extrapolated to zero frequency for each component separately.

(c) Reference [62] (method: solution of the SCF equations with an additional point charge at large distance).

(d) Finite field perturbation method [63] results from [64], [56] and [65] respectively. Other theoretical results are: $(\alpha_{110}, \alpha_{111}, \bar{\alpha}_1) = (15.06, 8.82, 10.90) e^2 a_0^2 E_H^{-1}$ (Electric Field Variant basis method [66]) and $(22.88, 6.21, 11.77) e^2 a_0^2 E_H^{-1}$ (Hartree-Fock-Slater method [67]).

(e) Calculated by Coulon *et al.* [68] with the generalized Kirkwood method [69] using our basis *E'* (table 3). Their corresponding values for the dipole polarizabilities are: $(\alpha_{110}, \alpha_{111}, \bar{\alpha}_1) = (16.32, 8.28, 10.96) e^2 a_0^2 E_H^{-1}$.

(f) Reference [70] (equations-of-motion method); if we convert our values to the cartesian quadrupole polarizabilities [34] we can compare all the components, given in [70]: $(C_{xx,xx}, C_{xx,zz}, C_{zz,zz}) = (11.1, -10.7, 17.8) e^2 a_0^4 E_H^{-1}$ [70] and $(24.8, -21.6, 23.8) e^2 a_0^4 E_H^{-1}$ (our results). The corresponding calculated dipole polarizabilities of [70] are: $\alpha_{zz} = \alpha_{110} = 13.22$, $\alpha_{xx} = \alpha_{111} = 8.21$, $\bar{\alpha}_1 = 9.88 e^2 a_0^2 E_H^{-1}$.

moment, $\langle Q_{2,0} \rangle$. (The exponents of these polarization functions are determined by applying the scaling relation [47] to our tabulated GTO expansions of STO's [30], which are slightly more diffuse (for a fixed ζ) than the corresponding functions listed by Dunning [41]. The SCF energy decreases slightly by using the polarization functions of [30] rather than those of [41], quite similarly to the H_2 case [30].) The hexadecapole moment, $\langle Q_{4,0} \rangle$, is also in good agreement with the proposed experimental range of values [52], but it should be mentioned that the latter are subject to rather large uncertainties. The addition of an f polarization function (AO basis G) was not really necessary; such an enlarged AO basis is essential, however, for the calculation of higher multipole polarizabilities, as will become clear in the sequel. In the AO basis sets E or F we had hoped to find an AO basis which describes both the permanent multipole moments and the multipole polarizabilities equally well; neither of these attempts was really successful and since we did not want to extend the AO basis even more, we left this idea. In tables 1 and 2 we compare our results with other *ab initio* calculations at the SCF level. Among the several studies of N_2 including electron correlation two papers have considered the effect of correlation on the permanent multipoles. They find opposite effects, however. An MCSCF calculation [55] yields a reduction of $Q_{2,0}$ from -0.97 to $-0.91 e a_0^2$; the CI computation of [56] leads to an increase of $Q_{2,0}$ from -1.16 to $-1.35 e a_0^2$ (the results of [56] for $Q_{4,0}$ are: -8.86 (SCF) and $-8.42 e a_0^4$ (CI)).

Using the multipole operators $Q_{l,m}$ of formula (1), we define the multipole polarizabilities by:

$$\alpha_{ll'm} = 2 \sum_k \langle 0 | Q_{l,m} | k \rangle \langle k | Q_{l',-m} | 0 \rangle (E^k - E^0)^{-1}, \quad (2)$$

where we distinguish between quadratic ($l=l'$) and cross or mixed-pole ($l \neq l'$) polarizabilities. The best results for N_2 were obtained with method I of [30], (uncoupled Hartree-Fock) in which the states $|k\rangle$ are represented by single configuration wavefunctions and the excitation energies ($E^k - E^0$) are replaced by differences of orbital energies. For other small molecules the alternative and theoretically better methods II and III of [30] have yielded the best results, whereas the values of method I were smaller by a factor of 0.7 (He, H_2 [30], ethylene [31], formic acid [57, 58]). For N_2 the same ratio has been found [59], and hence the polarizabilities calculated with the methods II and III are too large. It is evidently somewhat fortuitous that method I yields the best results for N_2 . Results obtained by methods I-III are to be regarded as approximations to the coupled Hartree-Fock SCF values. (Method II represents the states $|k\rangle$ in (2) by the eigenvectors of a Configuration Interaction calculation over singly excited states and E^k by the corresponding eigenvalues; method III uses single configuration wavefunctions $|k\rangle$ but takes expectation values over the exact hamiltonian including electron repulsion for the E^k (for references see [30] and [31]).) We note that the finite field method [63], which is a coupled Hartree-Fock method, yields reasonable values for the dipole polarizability of N_2 (see table 2). There is the further question of how the results might be modified by inclusion of electron correlation. The only CI calculation of the dipole polarizability of N_2 [56] known to us predicts that the effect is of the order of 5 per cent [$\alpha_{110}(\text{CI}) - \alpha_{110}(\text{SCF}) = -0.47 e^2 a_0^2 E_H^{-1}$; $\alpha_{111}(\text{CI}) - \alpha_{111}(\text{SCF}) = +0.46 e^2 a_0^2 E_H^{-1}$], although the authors point out uncertainties in currently-available methods of calculation of this effect. These

results are in agreement with the conclusion of Werner and Meyer [60] that, in the finite field method, electron correlation changes the dipole polarizability of small molecules by not more than 10 per cent. Werner and Meyer also predict that the CI dipole polarizability will be larger than SCF, which is correct for the average dipole polarizability of [56] but not for both components.

Our results for the dipole polarizability of N_2 , obtained with the largest optimized AO basis set in the orbital energy differences method, are not as good as the finite field values (listed in table 2). In particular the anisotropy is overestimated to a larger extent. This could equally apply to our calculated

Table 3. Quadratic multipole polarizabilities and completeness ratios (*a*) for different optimized AO basis sets (*b*).

	<i>A</i>	<i>B'</i> $\zeta_a=1.35$	<i>C'</i> $\zeta_a=1.25$	<i>D'</i> $\zeta_a=1.50$	<i>E'</i> $\zeta_a=1.50$	<i>F'</i> $\zeta_a=1.50$ $\zeta_a'=2.40$	<i>G' (c)</i> $\zeta_a=1.50$ $\zeta_f=1.25$
$\alpha_{110}/e^2 a_0^2 E_H^{-1}$	17.36 (18.13)	15.71 (16.24)	15.11 (15.65)	15.60 (15.78)	15.68 (15.87)	15.69 (15.78)	15.73 (15.91)
$\alpha_{111}/e^2 a_0^2 E_H^{-1}$	4.08 (8.95)	8.13 (9.19)	8.72 (9.66)	8.66 (8.86)	8.73 (8.94)	8.78 (8.92)	8.76 (8.94)
$\alpha_{220}/e^2 a_0^4 E_H^{-1}$	36.7 (64.7)	54.2 (60.1)	57.2 (62.1)	58.4 (61.2)	60.8 (63.5)	61.3 (63.6)	64.7 (65.9)
$\alpha_{221}/e^2 a_0^4 E_H^{-1}$	33.8 (73.3)	56.6 (61.3)	60.4 (63.2)	64.2 (65.2)	65.7 (66.9)	65.5 (66.6)	66.0 (66.6)
$\alpha_{222}/e^2 a_0^4 E_H^{-1}$	6.3 (32.8)	15.0 (27.9)	16.2 (30.5)	16.0 (28.8)	18.2 (32.2)	18.5 (32.6)	28.2 (30.9)
$\alpha_{330}/e^2 a_0^6 E_H^{-1}$	276 (632)	449 (575)	465 (587)	527 (624)	551 (664)	555 (658)	669 (695)
$\alpha_{331}/e^2 a_0^6 E_H^{-1}$	175 (694)	353 (524)	374 (541)	450 (595)	494 (648)	497 (645)	574 (618)
$\alpha_{332}/e^2 a_0^6 E_H^{-1}$	121 (556)	217 (392)	213 (385)	257 (451)	284 (501)	287 (503)	408 (437)
$\alpha_{333}/e^2 a_0^6 E_H^{-1}$	0 (0)	58 (232)	78 (285)	80 (258)	82 (275)	87 (283)	128 (c) (236)
\overline{CR}_1	0.71	0.92	0.93	0.98	0.98	0.99	0.98
\overline{CR}_2	0.42	0.81	0.84	0.88	0.87	0.88	0.97
\overline{CR}_3	0.28	0.63	0.60	0.65	0.65	0.65	0.88 (c)

(a) The isotropic completeness ratios \overline{CR}_l are defined according to formula (3), in which both STM and CM are taken isotropically. The values in parentheses have been obtained by the theoretical Unsöld procedure [29, 31], which corrects for the incompleteness of the AO basis sets.

(b) The AO basis sets have been optimized by varying ζ (see text). They are described in more detail in table 1; for the *F'* basis $\zeta_a=1.50$ applies to a double uncontracted *d* set, whereas $\zeta_a'=2.40$ belongs to a single *d* function.

(c) The basis is far from complete for the octupole component $Q_{3,3}$, since atomic *g* functions should be included in order to make $Q_{3,3}$ transitions possible from the occupied π orbitals. This is also the main reason why \overline{CR}_3 is still relatively low.

higher multipole polarizabilities, listed in table 2. As a consequence we must be cautious in the interpretation of our results for the anisotropic long range interactions. The π contributions to the quadratic multipole polarizabilities, which are also presented in table 2, decrease from 65 per cent (for $\bar{\alpha}_1$), via 36 per cent (for $\bar{\alpha}_2$) to 31 per cent (for $\bar{\alpha}_3$). The mixed-pole polarizabilities have π and σ parts, which have opposite signs for most of the components.

The optimum AO basis set G' , used to obtain the results of table 2, has been determined by searching the exponents ζ of the atomic polarization functions which maximize the quadratic multipole polarizabilities [30], giving priority to the lower multipoles. In addition we have aimed at a complete AO basis set for the different multipole operators by calculating the completeness ratios (CR) :

$$CR_{l'm} = \frac{STM_{l'm}}{CM_{l'm}} = \frac{\sum_k \langle 0|Q_{l,m}|k\rangle \langle k|Q_{l',-m}|0\rangle}{\langle 0|Q_{l,m}Q_{l',-m}|0\rangle - \langle 0|Q_{l,m}|0\rangle \langle 0|Q_{l',-m}|0\rangle}, \quad (3)$$

which should approach unity as close as possible [30] (STM stands for sum of transition moments, CM for closure moments). Some results of the examination of a number of AO basis sets (of the same type as those of table 1) have been collected in table 3. It can be seen that d functions are required for a satisfactory description of dipole transitions, in particular for the $Q_{1,1}$ component; the optima occur for rather diffuse d functions. The quadrupole and especially the octupole properties are improved significantly when (rather diffuse) f functions are included in the basis. For the $Q_{2,2}$ and $Q_{3,2}$ operators this is strictly necessary, since only then are $\pi \rightarrow \phi^*$ transitions possible; similarly, g functions are required in order to describe the $Q_{3,3}$ transitions properly, but we did not actually include such functions. It appears from table 3 that the polarizabilities are much less sensitive to the quality of the AO basis when the non-empirical Unsöld procedure [29, 31] is applied, which confirms our earlier conclusions for the ethylene molecule [31]. This applies both to the quadratic (see table 3) and the mixed-pole polarizabilities. For instance, basis B' yields polarizabilities which are smaller than those of basis G' by at most 50 per cent (for α_{222} , α_{332} and α_{242}), calculated in the sum-over-states approach. The use of the Unsöld procedure reduces these deviations to 10 per cent for α_{222} and α_{332} and 20 per cent for α_{242} , the latter deviation being the largest observed between the Unsöld results for the basis sets B' and G' .

3. ANISOTROPIC LONG RANGE INTERACTIONS

According to [30] we can write the long-range interaction energy of two Σ state linear molecules as follows :

$$\Delta E(R, \theta_A, \phi_A, \theta_B, \phi_B) = \sum_n \sum_{L_A, L_B} \sum_{M=0}^{\min(L_A, L_B)} C_n^{L_A L_B M} R^{-n} \times P_{L_A}^M(\cos \theta_A) P_{L_B}^M(\cos \theta_B) \cos M(\phi_A - \phi_B), \quad (4)$$

where $P_L^M(\cos \theta)$ are associated Legendre functions [53] and $C_n^{L_A L_B M}$ are long range interaction coefficients. The polar angles (θ_A, ϕ_A) and (θ_B, ϕ_B) define the orientations of the molecular axes with respect to a global coordinate system. The latter is chosen such that the z axis coincides with the vector \mathbf{R} which

connects the centres of mass of both molecules (pointing from *A* to *B*). We can distinguish between (first-order) electrostatic interaction coefficients and (second-order) dispersion and induction-interaction coefficients. For molecules which have a centre of inversion the electrostatic interactions occur only for odd *n*; the second-order interactions occur only for even *n*. The electrostatic coefficients are given by [30]:

$$C_{L_A+L_B+1}^{L_A L_B M} = (-1)^{L_B+M} (2 - \delta_{M,0}) \left(\frac{(L_A + L_B)!}{(L_A + M)! (L_B + M)!} \right) \langle Q_{L_A,0} \rangle \langle Q_{L_B,0} \rangle, \quad (5)$$

whereas the second-order interaction coefficients are summations of different terms:

$$C_n^{L_A L_B M} = \sum_{l_A, l'_A, l_B, l'_B}^{(l_A+l'_A+l_B+l'_B+2=n)} C_n^{l_A l'_A L_A; l_B l'_B L_B; M}. \quad (6)$$

The coefficients contributing to the summation (6) are:

$$C_{l_A+l'_A+l_B+l'_B+2}^{l_A l'_A L_A; l_B l'_B L_B; M} = - \zeta_{L_A L_B M}^{l_A l'_A l_B l'_B} \sum_{k_A, k_B} (E^{k_A} - E^{0_A} + E^{k_B} - E^{0_B})^{-1} \times T_{(l'_A) L_A, 0}^{0 k_A} T_{(l'_B) L_B, 0}^{0 k_B}, \quad (7)$$

where $\zeta_{L_A L_B M}^{l_A l'_A l_B l'_B}$ are algebraic coefficients (tabulated completely up to $l_A + l'_A + l_B + l'_B + 2 = 10$ inclusive in appendix A 1 of [30]). In the quantities $T_{(l') L, 0}^{0 k}$ either transition multipoles (in the dispersion and induction coefficients) or permanent multipoles (only in the induction coefficients, where $|k\rangle = |0\rangle$ for one of the molecules) are coupled:

$$T_{(l') L, 0}^{0 k} = \sum_m \langle 0 | Q_{l, m} | k \rangle \langle k | Q_{l', -m} | 0 \rangle (l, m; l', -m | L, 0) \quad (8)$$

with $L = |l - l'|$, $|l - l'| + 2, \dots, l + l'$, and $(l, m; l', -m | L, 0)$ is a Clebsch-Gordan coefficient [53]. In expression (7) we distinguish two different classes of terms, quadratic ones ($l_A = l'_A$ and $l_B = l'_B$) and mixed-pole or cross terms (all other cases) [27–35]. Only the former contribute to the isotropic part of the interactions, C_n^{000} , whereas the latter are completely anisotropic [32, 33, 35] and strongly enhance the anisotropies due to the quadratic terms [29–31]. Usually the anisotropies of the interactions are expressed as fractions of the isotropic coefficients (anisotropy factors):

$$\gamma_n^{L_A L_B M} = C_n^{L_A L_B M} / C_n^{000}. \quad (9)$$

With the now-available monomer multipole moments (in basis *G*, table 1), transition moments and excitation energies (in basis *G'*, table 3) we have calculated the long range interactions, contributing to (4) up to C_{10} inclusive, with our program VDWAALS [71], which can deal with molecules of arbitrary symmetries in arbitrary orientations. In table 4 we have listed the isotropic and the lowest ($L_A L_B$) anisotropic terms of the dispersion and induction interactions. Table 4 is another illustration of the crucial role of the mixed-pole terms in determining the anisotropy factors γ_8 and γ_{10} . The relative contributions of these mixed-pole terms to the γ s are approximately the same as we have found for H_2 [30], i.e. 65–70 per cent (almost equal ratios have recently been found by Meyer for H_2 with correlated wavefunctions [75]). The convergence of the dispersion anisotropy factors $\gamma^{L_A L_B M}$ with respect to L_A and L_B , although slightly slower than for H_2 , is still very fast: the first higher ($L_A L_B M$) anisotropy

Table 4. The isotropic dispersion and induction interaction coefficients and their lowest (L_{ALB}) anisotropy factors (a), calculated with the AO basis sets G and G' (b).

	$-C_n^{000}/$ $E_H a_0^n$ (isotropic)	γ_n^{200}	γ_n^{220}	γ_n^{221}	γ_n^{222}
Dispersion					
$n=6$	92.66	0.165	0.087	-0.019	0.0024
(Lit.)	(73.39)(c)	(0.106)(d)	(0.036)(d)	(-0.0080)(d)	(0.0010)(d)
$n=8$	2303	0.689	0.214	-0.030	0.0013
mixed-pole	—	0.459	0.148	-0.016	-0.0020
(Lit.)	(1625)(e)				
$n=10$	62545	1.025	0.759	-0.083	0.0027
mixed-pole	—	0.722	0.669	-0.067	-0.0032
Induction					
$n=8$	29.69	0.655	0.300	-0.060	0.015
$n=10$	632.6	1.923	1.602	-0.169	0.001
mixed-pole	—	1.263	1.208	-0.101	-0.025

(a) Defined according to (6) and (9); the cross or mixed-pole contributions to the anisotropy factors have been given separately.

(b) The AO basis sets are described in tables 1 (basis G , for the permanent multipoles) and 3 (basis G' , for the transition multipoles).

(c) Accurate semi-empirical value of Zeiss and Meath [72], which is very close to the earlier semi-empirical result of Langhoff and Karplus [73]: $73.8 E_H a_0^6$; other recent theoretical values are: $97.80 E_H a_0^6$ [68] (Kirkwood method, see caption (e) of table 2); $61.9 E_H a_0^6$ [70] (equations-of-motion method, see caption (f) of table 2).

(d) Semi-empirical estimates of Langhoff, Gordon and Karplus [74]; other recent theoretical values are: $\gamma_6^{200}=0.176$, $\gamma_6^{220}=0.106$, $\gamma_6^{221}=-0.024$, $\gamma_6^{222}=0.0029$ [68].

(e) This value has been proposed by Thakkar and Smith [21]; another theoretical value is: $2620 E_H a_0^8$ [68].

factors, which have been omitted from table 4, are: $\gamma_8^{400}=-0.045$, $\gamma_8^{420}=-0.032$ ($\ll \gamma_8^{220}$) and $\gamma_{10}^{400}=0.111$, $\gamma_{10}^{420}=-0.021$ ($\ll \gamma_{10}^{220}$). The more strongly anisotropic induction terms show a significantly slower convergence of the anisotropy factors, but fortunately the induction energy itself is very small (table 4) and can safely be neglected (a similar conclusion was drawn for H_2 [30]).

Only for C_6 are data available, which can be used to check the accuracy of the results of table 4. Both the isotropic C_6 and its anisotropy factors γ_6 are too large; in particular the anisotropy factors show substantial deviations from the previous semi-empirical estimates of Langhoff, Gordon and Karplus [74]. These deviations can be understood and, at the same time, corrected (approximately) if we apply the mean excitation energy approximation [31] to the isotropic dispersion coefficient C_6^{000} as well as to the anisotropy factors γ_6^{200} and γ_6^{220} :

$$C_6^{000} = -\frac{3}{4} \bar{\Delta} \bar{\alpha}^2, \tag{10}$$

and:

$$\gamma_6^{200} = \frac{1}{9} \left[\frac{\Delta_{\parallel} \alpha_{\parallel}^2 - 2\Delta_{\perp} \alpha_{\perp}^2 + 2\Delta_{\parallel} \Delta_{\perp} \alpha_{\parallel} \alpha_{\perp} / (\Delta_{\parallel} + \Delta_{\perp})}{\bar{\Delta} \bar{\alpha}^2} \right], \tag{11 a}$$

$$\gamma_6^{220} = \frac{1}{3} \left[\frac{\Delta_{\parallel} \alpha_{\parallel}^2 + \Delta_{\perp} \alpha_{\perp}^2 - 4\Delta_{\parallel} \Delta_{\perp} \alpha_{\parallel} \alpha_{\perp} / (\Delta_{\parallel} + \Delta_{\perp})}{\bar{\Delta} \bar{\alpha}^2} \right] \tag{11 b}$$

($\gamma_6^{221} = -\frac{2}{3}\gamma_6^{220}$; $\gamma_6^{222} = \frac{1}{3}\gamma_6^{220}$ (see [30, 76])). For convenience we have introduced the following notations: $\alpha_{\parallel} \equiv \alpha_{110}$; $\alpha_{\perp} \equiv \alpha_{111}$; $\bar{\alpha} \equiv \bar{\alpha}_1$; similar definitions apply to the mean excitation energies Δ , which are defined as $\Delta = 2 \text{ STM}/\alpha$, isotropically as well as componentwise (see formulae (2) and (3)). If the mean excitation energy is assumed to be isotropic ($\Delta_{\parallel} = \Delta_{\perp} = \bar{\Delta}$), it can be eliminated from expressions (11 *a*) and (11 *b*), yielding the simple approximate relations:

$$\gamma_6^{200} = \frac{\alpha_{\parallel} - \alpha_{\perp}}{3\bar{\alpha}} = \kappa, \quad (12 \text{ a})$$

$$\gamma_6^{220} = \frac{(\alpha_{\parallel} - \alpha_{\perp})^2}{3\bar{\alpha}^2} = 3\kappa^2. \quad (12 \text{ b})$$

The expressions (10) and (11), although in a slightly different notation are due to London [77, 78]. (Similarly orientation dependent formulae have been derived for some specific higher dispersion coefficients of linear molecules (which are increasingly unwieldy though): ($l_A l'_A$; $l_B l'_B$) = (11; 22), (22; 22) and (11; 33) by Van der Merwe [79, 80]; (11; 13) by Koide and Kihara [27]. Koide has derived closed expressions for all the anisotropic long range interactions [81], which are very similar to ours [30], both being general and much more convenient than the earlier formulae.)

The isotropic C_6 dispersion coefficient which we have calculated is 25 per cent larger than the accurate semi-empirical value [72], in spite of the fact that our calculated isotropic dipole polarizability is smaller than the experimental value by 6 per cent. Apparently, according to formula (10), our calculated mean excitation energy $\bar{\Delta}$ is much too large. Indeed this is the reason why the orbital energy differences method has been reported to yield too small polarizabilities for a number of molecules [30, 31, 57, 58]. The good agreement for our calculated $\bar{\alpha}_1$ for N_2 with the experimental value should therefore be ascribed to an approximately equal overestimate of both the excitation energies in the denominator and the transition multipoles in the numerator of the sum-over-states expression (2) for α .

In table 5 we show some results for N_2 and H_2 , obtained with the different expressions for the anisotropic interactions (7), (11) and (12). Approximation (11) yields anisotropy factors which are hardly different from the full double sum-over-states results (expression (7)). (This result also confirms the usefulness of the Unsöld method in relatively small AO basis sets for estimating the anisotropic second-order interactions, by analogy with the calculation of the polarizabilities (table 3). We have obtained results in the Unsöld approach with different AO basis sets, which are very close to our best results (basis G'); the Unsöld anisotropy factors especially are remarkably constant. The Unsöld method has a great computational advantage over the sum-over-states method, since the double summations over all the excited states are avoided. As a consequence the CPU time (on an IBM 370/158) required for the computation of all the long range interaction coefficients C_6 – C_{10} in one particular orientation of the molecules is reduced from 2400 s (sum-over-states, basis G') to 1.5 s (Unsöld.) Approximation (12), which has been used frequently [1, 23, 25, 27, 28, 34, 82, 83] because of the lack of information on the anisotropy of the mean excitation energy, deviates significantly, however (larger by 17–52 per cent than the results of expression (7)). Indeed the assumption of an isotropic mean

Table 5. The anisotropy factors for the dispersion coefficients C_6 of H_2 and N_2 , calculated with different approximations (a).

	H_2			N_2		
	$-C_6^{000}/E_H a_0^6$	γ_6^{200}	γ_6^{220}	$-C_6^{000}/E_H a_0^6$	γ_6^{200}	γ_6^{220}
(I) Expressions (7), (9) (b)	14.18	0.120	0.044	92.66	0.165	0.087
(II) Approx. (10), (11)	14.74	0.117	0.042	99.40	0.163	0.086
(III) Approx. (10), (12)	14.74	0.140	0.058	99.40	0.210	0.132
(IV) (12) with expt. α (c)	—	0.128	0.049	—	0.124	0.046
(V) Corrected	12.14	0.107	0.036	73.39	0.096	0.030
(VI) Literature (d)	12.14	0.105	0.035	73.39	<0.106	<0.036
		(0.112)	(0.039)			

(a) The first three lines contain our results according to the exact formula (I), the approximative expressions (10) for C_6^{000} and (11) for the anisotropy factors (II), and the approximative expressions (10), and (12) for the anisotropy factors (III). In line IV the experimental $\bar{\alpha}$, α_{\parallel} and α_{\perp} have been used in approximation (12). The corrected results, listed in line V, have been obtained according to the procedure described in the text (part (ii)).

(b) Results for H_2 from [30].

(c) Experimental α s from [76] (for H_2) and [61] (for N_2).

(d) For H_2 : Meyer's theoretical results [76] (in parentheses the semi-empirical estimates of [74]). For N_2 : C_6^{000} estimated by Zeiss and Meath [72]. The γ_6 are those of [74], which also contains values in approximation (12): $\gamma_6^{200}=0.131$, $\gamma_6^{220}=0.051$; the corresponding results of line IV are slightly smaller than the latter since the recently remeasured static dipole polarizability anisotropy is slightly smaller than the value used in [74]. As a consequence the results in line VI for N_2 are probably too large; another argument, underlining this statement, is that the H_2 results of [74], without approximation (12), are larger already than the accurate values of Meyer.

excitation energy is not valid. For H_2 our calculated Δ s are $0.56 E_H$ (parallel) and $0.63 E_H$ (perpendicular), whereas from the data presented in [76] the following results are obtained: 0.52 and $0.61 E_H$. Our corresponding results for N_2 , 0.94 and $1.20 E_H$, are much larger (partly due to the method used), but also the anisotropy is larger than for H_2 . Nevertheless the approximate relations (12) are useful as a first approximation and show in a simple way how a large relative anisotropy of the dipole polarizability generates large anisotropy factors γ_6 .

In order to improve our *ab initio* results we should include the effects of electron correlation in the sum-over-states (7), both in the wavefunctions $|k\rangle$ and in the energies E^k . This is not easily done, since the use of (7) requires the knowledge of a very large number of excited states and their energies. Instead we have adopted another approach for the present, because it will be useful to have the best estimates for the higher dispersion coefficients and their anisotropy factors. These estimates have been obtained in a way which is suggested by the results of table 5 and described as follows.

- (i) All the isotropic dispersion coefficients (which can be represented by expressions similar to (10)) are reduced by a factor $73.39/92.66$, the ratio of the accurate semi-empirical C_6^{000} and our calculated C_6^{000} . The underlying assumptions are that $\bar{\alpha}_1$, $\bar{\alpha}_2$ and $\bar{\alpha}_3$ are equally underestimated and that $\bar{\Delta}_1$, $\bar{\Delta}_2$ and $\bar{\Delta}_3$ are equally too large.

- (ii) The anisotropy factors for C_6 are obtained by multiplying $\gamma_{6,IV}$ (see table 5) with the corresponding ratios $\gamma_{6,II}/\gamma_{6,III}$. Hence we assume that the corrections to expression (12) for the anisotropy in the excitation energies are the same for the γ s resulting from the experimental polarizabilities and for those from our calculated polarizabilities. For H_2 as well as for N_2 this gives quite good agreement with the available semi-empirical and *ab initio* data (table 5, note caption (d)).
- (iii) For the higher multipole dispersion anisotropy factors, γ_n^{200} and $\gamma_n^{22,1}$ we probably cannot do much better than multiply our sum-over-states results (table 4) with the same correction factors as for C_6 : $\gamma_{6,V}/\gamma_{6,I}$. For H_2 the resulting anisotropy factors, γ_8 and γ_{10} , are slightly smaller now than the results of Meyer including electron correlation [75] (compare, for instance, the corrected γ_8^{200} , $\gamma_{10}^{200}=0.223$, 0.240 with Meyer's values: 0.264 , 0.294). In following this procedure we suppose the deviations in the anisotropies of all the higher multipole polarizabilities, for which no experimental information is available, to be the same as for the dipole polarizability.

Table 6. Anisotropic long range interaction coefficients (a).

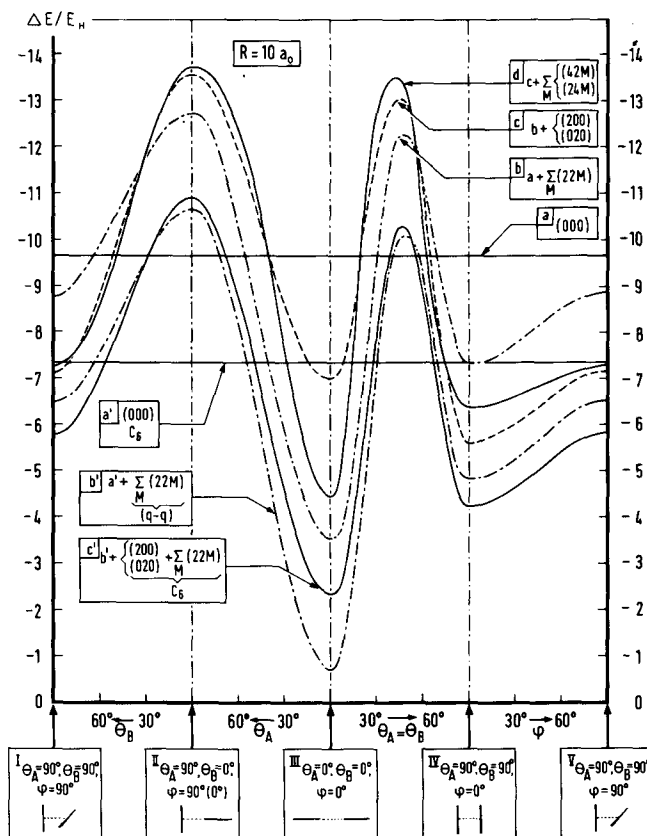
$L_A L_B M$	$C_{5,\text{elst}}/E_H a_0^5$ (b)	$C_{6,\text{disp}}/E_H a_0^6$ (c)	$C_{7,\text{elst}}/E_H a_0^7$ (b)	$C_{8,\text{disp}}/E_H a_0^8$ (c)	$C_{9,\text{elst}}/E_H a_0^9$ (b)	$C_{10,\text{disp}}/E_H a_0^{10}$ (c)
000	—	-73.39	—	-1825	—	-49538
200	—	-7.04	—	-731	—	-29555
220	6.623	-2.20	—	-135	—	-12969
221	-1.472	0.489	—	18.7	—	1413
222	0.0920	-0.061	—	-0.81	—	-45.4
400	—	—	—	Negl.	—	Negl.
420	—	—	122.64	Negl.	—	Negl.
421	—	—	-16.35	Negl.	—	Negl.
422	—	—	0.681	Negl.	—	Negl.
440	—	—	—	—	4239	Negl.
441	—	—	—	—	-339.2	Negl.
442	—	—	—	—	9.42	Negl.
443	—	—	—	—	-0.192	Negl.
444	—	—	—	—	0.0030	Negl.
600	—	—	—	—	—	Negl.
620	—	—	—	—	503.3	Negl.
621	—	—	—	—	-47.93	Negl.
622	—	—	—	—	1.498	Negl.

(a) Defined according to the formulae (5) for $C_{n,\text{elst}}$ (electrostatic) and (6) and (7) for $C_{n,\text{disp}}$ (dispersion); the induction terms have been omitted from the table since they can be neglected with respect to the dispersion interactions (see table 4).

(b) Calculated with the $\langle Q_{l,0} \rangle$ results for basis set G (table 1).

(c) Estimated from the *ab initio* results of table 4, which have been corrected according to the procedure described in the text. The higher ($L_A L_B M$) anisotropic interactions can be neglected both with respect to the lower ($L_A L_B M$) terms and the corresponding ($L_A L_B M$) electrostatic interactions. For instance, C_8^{420} is not larger than $20.3 E_H a_0^8$, and C_{10}^{440} and C_{10}^{620} are as small as -331 and $69 E_H a_0^{10}$ respectively (applying the same correction factor used for the (22M) terms).

Since the higher ($L_A L_B M$) dispersion anisotropy factors as well as the complete induction interaction may be neglected and the electrostatic interactions do not require a correction (the calculated permanent multipoles are close to the available experimental data) we arrive finally at table 6, which contains our best estimates for the main contributions to the anisotropic long range interactions. The estimates for the anisotropic dispersion interaction coefficients are believed to be low.



Anisotropic long range interaction energy ΔE (equation (4)) at $R=10 a_0$. The different contributions to the energy are indicated in the figure by ($L_A L_B M$). The a' , b' and c' curves refer to calculations including only the C_6 dispersion and the C_5 quadrupole-quadrupole ($q-q$) interactions. For the a , b , c and d curves we have used the C_6 , C_8 and C_{10} dispersion and the C_5 and C_7 electrostatic interactions. The anisotropic interaction coefficients $C_n^{L_A L_B M}$ are those of table 6.

The anisotropic interaction coefficients of table 6 have been used to study a number of relative molecular orientations at $R=10 a_0$ (the figure). At this distance charge penetration effects, which strongly modify the orientation dependence at short range, can safely be neglected [48, 59]. Even at this relatively large distance (compare the distance of the isotropic minimum: $7.8-8.0 a_0$ [25]) we observe from the figure a rather strong deviation from the pure quadrupole-quadrupole ($q-q$) anisotropy. The modifications mainly arise

from the (200) dispersion anisotropy, especially if the higher dispersion terms are included (compare the curves b' and c' , and b and c respectively). Furthermore the (22*M*) dispersion anisotropy reduces the (22*M*) (q - q) interaction, although to a rather small extent only (at $R=10 a_0$ the total (220) dispersion contribution is -8 per cent of the (220) (q - q) interaction). For N_2 , contrary to H_2 [30], the higher electrostatic multipole terms cannot generally be ignored (compare the curves c and d). All these effects support the suggestions made by Cheung and Powles [20], that the remaining discrepancies in their calculated thermodynamic data should be corrected either by using a quadrupole moment slightly smaller than the experimental value or by adding the dispersion anisotropy to the pure (q - q) anisotropy.

The figure shows two competitive dimer geometries, which have a large long range attraction peak, a T -shaped one (geometry II) and a shifted parallel one (between the geometries III and IV with $\theta_A = \theta_B \simeq 45^\circ$). Similar results were obtained for other quadrupole molecules [27-30, 84], including N_2 [28]. The latter, semi-empirical, whole range potential calculations and those of [27], which differ in their choice of the molecular shape occurring in the Kihara core model potential, yield considerable differences for the N_2 dimer; in [27] two comparable minima occur for the T and X geometries (our geometries II and I), while in [28] this happens for the same two geometries, which peak in the figure. (In both references the dispersion anisotropy is taken into account according to approximation (12); the resulting γ_6 values are substantially too large (e.g. $\gamma_6^{200} = 0.176$). Moreover, the extra anisotropy due to the (11; 13) mixed-pole dispersion term (which is called octopolar induction in [27, 28]) is included in a very inventive but rather approximate way; in particular the assumption, that their model parameters l_{\parallel} and l_{\perp} , which determine the ratios of α_{13m} and α_{11m} , are equal, is not confirmed by our results, neither for H_2 [30] nor for N_2 (where we find $l_{\parallel} = 1.37 a_0^2$ and $l_{\perp} = 2.25 a_0^2$). As a consequence, their estimates for $\alpha_{130} = 36.4 e^2 a_0^4 E_H^{-1}$ and $\alpha_{131} = 16.6 e^2 a_0^4 E_H^{-1}$ [27] differ significantly from our calculated results (table 2).) The recent paper by MacRury *et al.* [26] also contains curves for some geometries (I, II and IV), but since the dispersion anisotropy has not been included explicitly in any of their model potentials, the latter show an orientation dependence which is too small, at least at long range. Raich and Gillis [25] have obtained the following order of geometries with increasing long range attraction at $R=10 a_0$: IV, I, III, II, which differs from ours by the interchange of I and III. This seems to be mainly due to the quadrupole-hexadecapole interaction, which has been included in our calculations (see the figure, the difference between the curves c and d); furthermore the $C_8^{000} (= 547 E_H a_0^8)$ and $C_{10}^{000} (= 2116 E_H a_0^{10})$ adopted in [25] according to the old calculations by Margenau [85] are probably much too small and the dispersion anisotropy was taken into account in [25] by following the approach of Koide and Kihara [27], which is subject to some uncertainties as we have noted. Although, of course, our own results are not free of uncertainties either, the electrostatic and the C_6 dispersion interactions especially are probably rather accurate. From the experimental side the equilibrium geometry of the $(N_2)_2$ van der Waals dimer has not yet been established satisfactorily [86-88]. Long *et al.* [86] could not provide direct evidence from their analysis of the I.R. spectrum of the $(N_2)_2$ dimer, but stated that other considerations favour the T shaped geometry. The molecular beam electric deflection

experiments of Novick *et al.* [87] predict a non-polar $(N_2)_2$ geometry (which would point to the shifted parallel geometry), but probably the experiments are not sensitive enough to detect the dipole of the $(N_2)_2$ dimer in any geometry [87, 88].

The R dependence of the long range interaction in the two geometries under consideration is given in table 7. Our earlier conclusion that the anisotropic

Table 7. Long range interaction energies (in $10^{-6} E_H$) in the T -shaped and shifted parallel geometries (a), calculated with the anisotropic interaction coefficients of table 6.

Contribution $L_A L_B M$	$C_n^{L_A L_B M}$ n	Distance/ a_0							
		8 (c)	9 (c)	10	12	15	19	25	
000	6	-280.0	-138.1	-73.39	-24.58	-6.44	-1.56	-0.301	
	8	-108.8	-42.4	-18.25	-4.24	-0.71	-0.11	-0.012	
	10	-46.1	-14.2	-4.95	-0.80	-0.09	-0.01	-0.000	
200	6	-13.4	-6.6	-3.52	-1.18	-0.31	-0.07	-0.014	
	8	-21.8	-8.5	-3.66	-0.85	-0.14	-0.02	-0.002	
	10	-13.8	-4.2	-1.48	-0.24	-0.03	-0.00	-0.000	
T-shaped geometry									
22M	6	4.2	2.1	1.10	0.37	0.10	0.02	0.005	
	8	4.0	1.6	0.68	0.16	0.03	0.00	0.000	
	10	6.0	1.9	0.65	0.10	0.01	0.00	0.000	
Disp (total)		-469.7	-208.4	-102.82	-31.26	-7.58	-1.75	-0.324	
22M	5	-101.1	-56.1	-33.12	-13.31	-4.36	-1.34	-0.339	
42M	7	-7.3	-3.2	-1.53	-0.43	-0.09	-0.02	-0.003	
44M	9	11.8	4.1	1.59	0.31	0.04	0.00	0.000	
62M	9	-3.0	-1.1	-0.41	-0.08	-0.01	-0.00	-0.000	
Elst (total)		-99.6	-56.3	-33.47	-13.51	-4.42	-1.36	-0.342	
Disp + Elst		-569.3	-264.7	-136.29	-44.77	-12.00	-3.11	-0.666	
Shifted parallel geometry									
22M	6	3.1	1.6	0.83	0.28	0.07	0.02	0.003	
	8	1.9	0.8	0.32	0.07	0.01	0.00	0.000	
	10	2.1	0.7	0.23	0.04	0.00	0.00	0.000	
Disp (total)		-476.8	-210.9	-103.87	-31.50	-7.64	-1.75	-0.326	
22M	5	-82.1	-45.6	-26.91	-10.81	-3.54	-1.09	-0.276	
42M	7	-17.4	-7.6	-3.64	-1.02	-0.21	-0.04	-0.005	
44M	9	9.4	3.3	1.26	0.25	0.03	0.00	0.000	
62M	9	2.2	0.8	0.30	0.06	0.01	0.00	0.000	
Elst (total)		-87.9	-49.1	-28.99	-11.52	-3.71	-1.13	-0.281	
Disp + Elst		-564.7	-260.0	-132.86	-43.02	-11.35	-2.88	-0.607	

(a) The T -shaped geometry is geometry II of the figure; the shifted parallel geometry is that with $\theta_A = \theta_B = 45^\circ$, between the geometries III and IV.

(b) The (000) and (200) contributions are equal for both geometries. If M is not specified in the label ($L_A L_B M$), all different M terms have been added; if $L_A (=L_1) \neq L_B (=L_2)$ the total result for $(L_1 L_2 M)$ plus $(L_2 L_1 M)$ is given.

(c) At these distances the influence of charge penetration is already rather large [48]: for instance, there are (000) and (200) electrostatic contributions of -57.3 and -37.0 $10^{-6} E_H$, at $R=8 a_0$, and -6.49 and -4.22 $10^{-6} E_H$ at $R=9 a_0$; these contributions have decreased at $R=10 a_0$ to -0.70 and -0.48 $10^{-6} E_H$ [48].

higher dispersion terms start to become important already at larger distances than the isotropic higher dispersion terms [30], is confirmed. This is more noticeable for N_2 than for H_2 and it arises from the larger ratios γ_8/γ_6 and γ_{10}/γ_6 : for instance, for γ^{200} these ratios are 4.18 and 6.22 for N_2 (see table 6) and 2.08 and 2.24 for H_2 [30]. For a geometry such as III the relatively larger importance of the higher dispersion terms when considering the anisotropy is even more apparent, since the anisotropic contribution is then a maximum: the ratios $C_6R^{-6} : C_8R^{-8} : C_{10}R^{-10}$ (at $R=10 a_0$) change from 1 : 0.25 : 0.07 to 1 : 0.38 : 0.14 when adding the (200) and (220) terms to the isotropic interactions. The observation from table 7 that the higher electrostatic terms are not important (small and largely cancelling) is somewhat misleading, since this is not true for all orientations; for example, for geometry III at $R=10 a_0$ the different contributions are 6.62, 2.45 and $0.52 \times 10^{-6} E_H$, arising from C_5 , C_7 and C_9 respectively.

4. CONCLUSIONS

For an adequate description of the long range anisotropy of the N_2 pair potential down to the minimum, higher terms in the multipole series usually applied must be included (cf. the figure and tables 6 and 7). Close to the minimum the applicability of the multipole expansion becomes questionable, not only because of charge penetration [48], but also since the anisotropic terms in the dispersion energy series, C_nR^{-n} , apparently do not converge with respect to n (tables 6 and 7). This is contrary to the isotropic dispersion energy, for which the successive C_nR^{-n} contributions decrease by a factor as large as 2.4, even at the minimum (table 7). It is caused by the higher dispersion anisotropy factors which are much larger than those for R^{-6} : for instance, $\gamma_{10}^{200} = 0.597 > \gamma_8^{200} = 0.401 \gg \gamma_6^{200} = 0.096$ (table 6). The mixed-pole terms, which are responsible for this effect, strongly affect the induction anisotropy too, but the complete induction energy appears to be negligible relative to the dispersion energy (table 4). The $(L_A L_B M)$ anisotropic dispersion terms, which can safely be limited to L_A, L_B values not larger than 2, substantially modify the pure (22M) quadrupole-quadrupole anisotropy; to a smaller extent also the higher $(L_A L_B M)$ electrostatic terms change the orientational dependence of the interaction energy (cf. the figure).

The figure and table 7 support the recent result of Sakai, Koide and Kihara [28], that probably two competitive geometries exist for the $(N_2)_2$ van der Waals molecule, a T-shaped and a shifted parallel one (rotation angles $\theta_A = \theta_B \simeq 45^\circ$). Since the experimental geometry of the $(N_2)_2$ dimer seems not yet to have been established [86-88], it is worth focusing future studies of the $(N_2)_2$ dimer on these two geometries.

In the first instance, the anisotropic N_2-N_2 long range interactions have been calculated *ab initio*. The anisotropy of the dipole polarizability and the dispersion coefficient C_6 turned out to be significantly too large however, due to our use of SCF wavefunctions, despite the rather large and optimized AO basis set (tables 2 and 3). Therefore we have applied a correction procedure for the (an)isotropic C_6, C_8 and C_{10} , which relies on the use of two approximate expressions for the R^{-6} anisotropy factors (formulae (11) and (12)) and the availability of accurate (semi)-empirical values for C_6 and the dipole polarizability;

the approximate formula (12), which is frequently used, appears to be rather crude (table 5). The results obtained via the non-empirical Unsöld approach (tables 3 and 5) confirm the earlier reported [29, 31] usefulness of this method for calculations of multipole polarizabilities and dispersion interaction coefficients in limited AO basis sets.

Preliminary results from intermediate range calculations [89] which use the exact interaction operator instead of its multipole expansion, indicate that charge penetration effects are surprisingly small for the second-order dispersion energy, even for distances inside the van der Waals minimum. In the first-order energy, where such effects are indeed large [48, 89] the extra attraction resulting from charge penetration is dominated by the exchange repulsion which in absolute value is 5 to 10 times larger [89]. Altogether, the orientational dependence of the first-order long range (multipole) interaction energy is considerably modified in the shorter range, whereas the second-order multipole result is only slightly affected by charge penetration.

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