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Anisotropy of long range interactions between linear molecules: H_2-H_2 and H_2-He^\dagger

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We derive a closed expression for the orientation dependence of the long range interaction coefficients of Σ state linear molecules and then calculate the dispersion and induction multipole interaction coefficients for the systems H_2-H_2 and H_2-He up to R^{-10} terms inclusive. The monomer states are described by SCF-LCAO wave functions with polarization functions optimized with respect to the different multipole polarizabilities. The anisotropy factors γ_8 and γ_{10} , describing the orientation dependence of the R^{-8} and R^{-10} terms, are approximately equal and much larger than γ_6 , due to the occurrence of the (completely anisotropic) mixed-pole terms.

1. INTRODUCTION

For a relatively long time the attempts to determine accurate van der Waals interaction potentials were mainly concentrated on rare gas atoms [1], but now the interest of both theorists and experimentalists is being focused on (small) molecules. Of particular interest is the anisotropy in the interaction potential between molecules, which leads, for instance, to rotational energy transfer in gas phase collisions and to the occurrence of librational phonon modes in molecular solids. Although experiments are being performed [2-5] which probe this anisotropy rather sensitively, the extraction of potential parameters from these measurements is only possible at the expense of using simplified model potentials. Therefore, it is useful that for very small molecules the van der Waals potentials, and also their anisotropy, can be obtained from *ab initio* calculations. For somewhat larger molecules, where the *ab initio* calculation of the complete potential energy surface is not yet practical, the theoretical information can still be used to improve the (semi-empirical) model potentials. For example, the determination of the isotropic and anisotropic long range part of some recently proposed, rather sophisticated, model potentials [5-10] depends on the availability of theoretically calculated multipole interaction coefficients.

As the simplest systems in which anisotropic interactions are present, much attention is focused on the dimers H_2-He and H_2-H_2 . *Ab initio* calculations of the entire van der Waals potentials for H_2-He were performed by Tsapline and

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Kutzelnigg [11], by Geurts *et al.* [12] and by Hariharan and Kutzelnigg [13], for H₂-H₂ by Kochanski [14] and by Gallup [15]. Meyer [16] has computed the isotropic long range dispersion interaction coefficients C_6 , C_8 and C_{10} and the anisotropy factors γ_6 and γ_8 in He-He, H₂-He and H₂-H₂. In contrast with the calculations of the complete H₂-H₂ potential [14, 15] which use only s and p type functions in the basis set, and with the older H₂-He and H₂-H₂ long range calculations [17-20], Meyer's computation yields accurate values for C_8 and C_{10} . The calculated γ_8 , however, is much too small, because the so-called cross (or mixed-pole) terms, which have a drastic effect on the anisotropy of the interaction of molecules [21, 22] were omitted. Thakkar [23] has shown by an approximate calculation that the inclusion of cross terms increases γ_8 for H₂-He by a factor of about 3.3, and a similar result was found by us on the basis of a non-empirical Unsöld computation [24].

Therefore, we present here for H₂-He and H₂-H₂ the complete set of anisotropy factors γ_6 , γ_8 and γ_{10} , originating from dispersion and induction interactions. These are obtained from *ab initio* computations by three different perturbation methods with a basis of monomer Hartree-Fock wave functions using optimized atomic orbitals. For H₂-H₂, where the information about the long range interactions (and their anisotropy) is also important for crystal lattice dynamics [25-27], we have compared the second-order anisotropic coefficients with the first-order electrostatic interaction coefficients C_5 , C_7 and C_9 .

2. THEORY : ORIENTATIONAL DEPENDENCE OF THE INTERACTION ENERGY BETWEEN LINEAR MOLECULES

In the Born-Oppenheimer approximation, with or without averaging over the molecular vibrations, the anisotropy of the interaction energy between two linear molecules A and B, in a Σ state can be expressed in the following very general way. Let $\hat{r}_A = (\theta_A, \phi_A)$ and $\hat{r}_B = (\theta_B, \phi_B)$ define the orientations of the molecular axes and $\mathbf{R} = (R, \theta, \phi)$ the vector which connects the molecular centres of mass (pointing from A to B). All variables are measured relative to the same arbitrary coordinate system. Because the interaction energy is invariant under rotations of this coordinate system, it can be expanded in terms of a complete set of scalar-valued angular dependent functions :

$$\Delta E(\hat{r}_A, \hat{r}_B, \mathbf{R}) = \sum_{L_A, L_B, L} \Delta E_{L_A L_B L}(R) A_{L_A L_B L}(\hat{r}_A, \hat{r}_B, \hat{R}), \quad (1)$$

with

$$A_{L_A L_B L}(\hat{r}_A, \hat{r}_B, \hat{R}) = \sum_{M_A, M_B, M} (-1)^M (L_A, M_A; L_B, M_B | L, M) \times C_{L_A, M_A}(\hat{r}_A) C_{L_B, M_B}(\hat{r}_B) C_{L, -M}(\hat{R}), \quad (2)$$

where $(L_A, M_A; L_B, M_B | L, M)$ is a Clebsch-Gordan coefficient and $C_{l,m}(\hat{r})$ is a Racah spherical harmonic [28],

$$C_{l,m}(\hat{r}) = \left(\frac{4\pi}{2l+1} \right)^{1/2} Y_{l,m}(\hat{r}).$$

In general the expansion coefficients $\Delta E_{L_A L_B L}(R)$ are very hard to calculate, but for large distances R it is possible to expand the interaction operator V^{AB} in a multipole series and one can use this operator in first- and second-order

perturbation theory. If the multipole expansion is written in terms of spherical tensors [28, 29], the derivation of the first-order anisotropic interaction coefficients is straightforward for Σ state linear molecules, because the multipole operators $Q_{l,m} = \sum_i z_i r_i^l C_{l,m}(\hat{r}_i)$ have non-zero expectation values for $m=0$ only (along the molecular axis). Therefore, the general rotation matrices $D_{m,m'}^l(\omega)$ occurring in the formula for arbitrary molecules (formula (5) of [30]) can be replaced by spherical harmonics and, by equating this formula to formula (1), we arrive directly at the result† :

$$\Delta E_{L_A L_B L}^{(1)}(R) = \delta_{L_A + L_B, L} (-1)^{L_B} \left(\frac{2L_A + 2L_B}{2L_A} \right)^{1/2} R^{-L_A - L_B - 1} \\ \times \langle 0_A | Q_{L_A, 0} | 0_A \rangle \langle 0_B | Q_{L_B, 0} | 0_B \rangle. \quad (3)$$

The second-order energy is more complicated, but again we can derive a closed formula rather easily for the anisotropic multipole interaction coefficients for linear molecules of the form of formula (1). This result is actually achieved because in the derivation of the general expression [29, 30], which we apply to linear molecules in this paper, a recoupling scheme has been used: the original $(l_A l_B)$ and $(l_A' l_B')$ coupling between the transition moments on the molecules A and B via the multipole interaction tensors is replaced by a scheme which first couples the transition moments within the same molecule :

$$T_{(l_A l_A') L_A, M_A}^{0_A k_A} = \sum_{m_A, m_A'} \langle 0_A | Q_{l_A, m_A} | k_A \rangle \langle k_A | Q_{l_A', m_A'} | 0_A \rangle (l_A, m_A; l_A', m_A' | L_A, M_A)$$

with

$$L_A = |l_A - l_A'|, |l_A - l_A'| + 2, \dots, l_A + l_A'. \quad (4)$$

The labels 0_A and k_A denote ground and excited states of A with energy differences $\Delta E^{0_A k_A}$; an analogous formula holds for B. These coupled transition moments $T_{L_A, M_A}^{0_A k_A}$ and $T_{L_B, M_B}^{0_B k_B}$ have only non-zero components for $M_A = 0$ and $M_B = 0$ ($m_A' = -m_A$ and $m_B' = -m_B$), just as the permanent moments $\langle Q_{L_A, M_A} \rangle$ and $\langle Q_{L_B, M_B} \rangle$, and they transform in the same way as the latter under rotations. Using these results the general formula (formula (8) of [30]) yields, for linear molecules

$$\Delta E_{L_A L_B L}^{(2)}(R) = \sum_{l_A, l_A', l_B, l_B'} \xi_{L_A L_B L}^{l_A l_A' l_B l_B'} R^{-l_A - l_A' - l_B - l_B' - 2} \\ \times \sum_{k_A, k_B}' (\Delta E^{0_A k_A} + \Delta E^{0_B k_B})^{-1} T_{(l_A l_A') L_A, 0}^{0_A k_A} T_{(l_B l_B') L_B, 0}^{0_B k_B}. \quad (5)$$

The coefficients $\xi_{L_A L_B L}^{l_A l_A' l_B l_B'}$ are purely algebraic; they are given by [29, 30]

$$\xi_{L_A L_B L}^{l_A l_A' l_B l_B'} = (-1)^{l_B + l_B'} \left[\frac{(2L_A + 1)(2L_B + 1)(2l_A + 2l_B + 1)!(2l_A' + 2l_B' + 1)!}{(2l_A)!(2l_B)!(2l_A')!(2l_B')!} \right]^{1/2} \\ \times (l_A + l_B, 0; l_A' + l_B', 0 | L, 0) \begin{Bmatrix} l_A & l_A' & L_A \\ l_B & l_B' & L_B \\ l_A + l_B & l_A' + l_B' & L \end{Bmatrix}, \quad (6)$$

† Atomic units are used throughout this paper: 1 a.u. of length (bohr) = $a_0 \simeq 5.29177 \times 10^{-11}$ m. 1 a.u. of energy = $E_H \simeq 4.3598 \times 10^{-18}$ J $\simeq 2.6255 \times 10^6$ J/mol $^{-1}$. 1 a.u. of electric charge = $e \simeq 1.60219 \times 10^{-19}$ C. 1 a.u. of quadrupole moment = $ea_0^2 \simeq 4.48658 \times 10^{-40}$ C m 2 . 1 a.u. of dipole polarizability = $4\pi\epsilon_0 a_0^3 \simeq 1.64878 \times 10^{-41}$ C 2 m 2 J $^{-1}$.

where the expression between curly brackets is a Wigner 9- j symbol [28]. In principle, the summations over l_A, l_A', l_B, l_B' run independently from zero to infinity, but because of the presence of the Clebsch–Gordan coefficients and the 9- j symbol in (6) a number of triangular conditions must be satisfied.

In actual calculations the use of an arbitrary space-fixed coordinate system is usually not very convenient. A simplification of the formulae can be accomplished by choosing the z -axis to coincide with R . In such a system the angular dependent functions defined in (2) reduce to

$$A_{L_A L_B L}(\hat{r}_A, \hat{r}_B, \hat{R}) = \sum_{M=0}^{\min(L_A, L_B)} \eta_{L_A L_B L}^M P_{L_A}^M(\cos \theta_A) P_{L_B}^M(\cos \theta_B) \times \cos M(\phi_A - \phi_B), \quad (7)$$

with

$$\eta_{L_A L_B L}^M = (-1)^M (2 - \delta_{M,0}) (L_A, M; L_B, -M | L, 0) \times \left[\frac{(L_A - M)!(L_B - M)!}{(L_A + M)!(L_B + M)!} \right]^{1/2}. \quad (8)$$

The functions $P_L^M(\cos \theta)$ are associated Legendre functions [28]. Inserting this special formula into expression (1), we find for the first- and second-order energies

$$\Delta E^{(1,2)}(R, \theta_A, \phi_A, \theta_B, \phi_B) = \sum_{L_A, L_B} \sum_{M=0}^{\min(L_A, L_B)} \epsilon_{L_A L_B M}^{(1,2)}(R) \times P_{L_A}^M(\cos \theta_A) P_{L_B}^M(\cos \theta_B) \cos M(\phi_A - \phi_B), \quad (9)$$

where

$$\epsilon_{L_A L_B M}^{(1)}(R) = C_{L_A + L_B + 1}^{L_A L_B M} R^{-L_A - L_B - 1}, \quad (10 a)$$

with

$$C_{L_A + L_B + 1}^{L_A L_B M} = (-1)^{L_B + M} (2 - \delta_{M,0}) \frac{(L_A + L_B)!}{(L_A + M)!(L_B + M)!} \times \langle 0_A | Q_{L_A, 0} | 0_A \rangle \langle 0_B | Q_{L_B, 0} | 0_B \rangle, \quad (10 b)$$

and

$$\epsilon_{L_A L_B M}^{(2)}(R) = - \sum_{l_A, l_A', l_B, l_B'} C_{l_A + l_A' + l_B + l_B' + 2}^{l_A l_A' L_A; l_B l_B' L_B; M} R^{-l_A - l_A' - l_B - l_B' - 2}, \quad (11 a)$$

with

$$C_{l_A + l_A' + l_B + l_B' + 2}^{l_A l_A' L_A; l_B l_B' L_B; M} = - \zeta_{L_A L_B M}^{l_A l_A' l_B l_B'} \sum_{k_A, k_B} (\Delta E^{0_A k_A} + \Delta E^{0_B k_B})^{-1} \times T_{(l_A l_A') L_A, 0}^{0_A k_A} T_{(l_B l_B') L_B, 0}^{0_B k_B}. \quad (11 b)$$

The coefficients $\zeta_{L_A L_B M}^{l_A l_A' l_B l_B'}$, which contain the algebraic coefficients (6) and (8)

$$\zeta_{L_A L_B M}^{l_A l_A' l_B l_B'} = \sum_L \zeta_{L_A L_B L}^{l_A l_A' l_B l_B'} \eta_{L_A L_B L}^M, \quad (12)$$

have been calculated for all combinations (l_A, l_A', l_B, l_B') occurring in the multipole expansion of $\Delta E^{(2)}$ to R^{-10} terms inclusive, using a computer program for the calculation of the Wigner 3- j and 9- j symbols [31]. The results are collected in Appendix A1.

Since the 'dynamical' factor in expression (11) does not contain M , the ratios between the terms in $\epsilon_{L_A L_B M}^{(2)}$ with the same L_A , L_B , l_A , l_A' , l_B , l_B' but different M are system independent. These ratios can be obtained directly from Appendix A1; they have been calculated by Meyer [16] already for the quadratic C_6 and C_8 terms. For comparison with experiment, it is convenient to collect all terms in (11) with the same R -dependence, i.e. $l_A + l_A' + l_B + l_B' + 2 = n$. Moreover, it is customary to express the anisotropic contributions in the series

$$\epsilon_{L_A L_B M}^{(2)}(R) = - \sum_n C_n^{L_A L_B M} R^{-n}, \quad (13)$$

as fractions of the isotropic coefficients (anisotropy factors):

$$\gamma_n^{L_A L_B M} = C_n^{L_A L_B M} / C_n^{000}. \quad (14)$$

The angular dependent formula for the first-order energy (10) is equivalent to the expression derived by Ng, Alnatt and Meath [32]. The second-order result (11) is a generalization of Meyer's [16] formula (4). This generalization is non-trivial since the inclusion of the mixed-pole terms, i.e. the terms with $l_A \neq l_A'$ or $l_B \neq l_B'$, necessitates a more complicated vector coupling scheme. Actually, the recoupling of the transition moments in the second-order energy expression could be performed by Meyer in an *ad hoc* way by his transformation (7).

Obviously, if one of the interacting systems (say A) is an S -state atom or a molecule in a $J=0$ state for which we average over the molecular rotations, the only non-zero terms in (10) and (11) are those with $L_A = M = 0$.

3. OPTIMIZATION OF THE AO BASIS SETS; POLARIZABILITIES

The AO basis sets for He and H_2 which were used to compute the dispersion interaction coefficients have been determined by maximization of the quadratic polarizabilities defined as

$$\alpha_{ll'm} = 2 \sum_k \langle 0 | Q_{l,m} | k \rangle \langle k | Q_{l',-m} | 0 \rangle (E^k - E^0)^{-1}, \quad (15)$$

with $l=l'$. The ground state wave function $|0\rangle$ was fixed by first performing a Hartree-Fock calculation. For the excited states $|k\rangle$ and the corresponding energies E^k , occurring in the perturbation expression (15) we have chosen:

I. the (singly-excited) eigenvectors and eigenvalues of the Hartree-Fock hamiltonian, which are obtained directly from the Hartree-Fock calculation on the ground state $|0\rangle$ (This method is equivalent to the Hartree-Fock partitioning method of [14], and method c of [33].);

II. the eigenvectors and eigenvalues of the matrix of the total hamiltonian over the ground state $|0\rangle$ and all singly-excited configurations; and

III. the eigenvectors of the Hartree-Fock hamiltonian and the corresponding expectation values of the total hamiltonian (This method is equivalent to the Epstein-Nesbet partitioning method of [14], and similar to method b of [33].).

For the methods I and II one can prove by using the Hylleraas variation principle [34], that the best $\alpha_{ll'm}$ can indeed be obtained by a maximization of (15) when varying the excited state functions $|k\rangle$. In method III the expression (15) is not strictly bound, but in a number of calculations this method has been found to give results which are rather close to the experimental values, in contrast with method I [14, 21, 33].

As variation parameters for the excited state functions $|k\rangle$, which are built up from LCAO's, we have used the scale factors ζ of the various p, d and f sets of gaussian type atomic polarization functions†. So, the ratios of the different GTO exponents within a particular set are fixed [35], by fitting the GTO's to a single STO. The results of these STO-GTO expansions obtained with the criterion of maximum overlap [36] are listed in Appendix A2. This criterion is slightly preferable to the atomic energy criterion [35, 37] for determining the optimal GTO exponents of polarization functions, since we found the resulting SCF energy to be slightly lower for H_2 and for N_2 [38]. The polarization GTO's are not contracted in the calculations of the polarizabilities and the van der Waals coefficients.

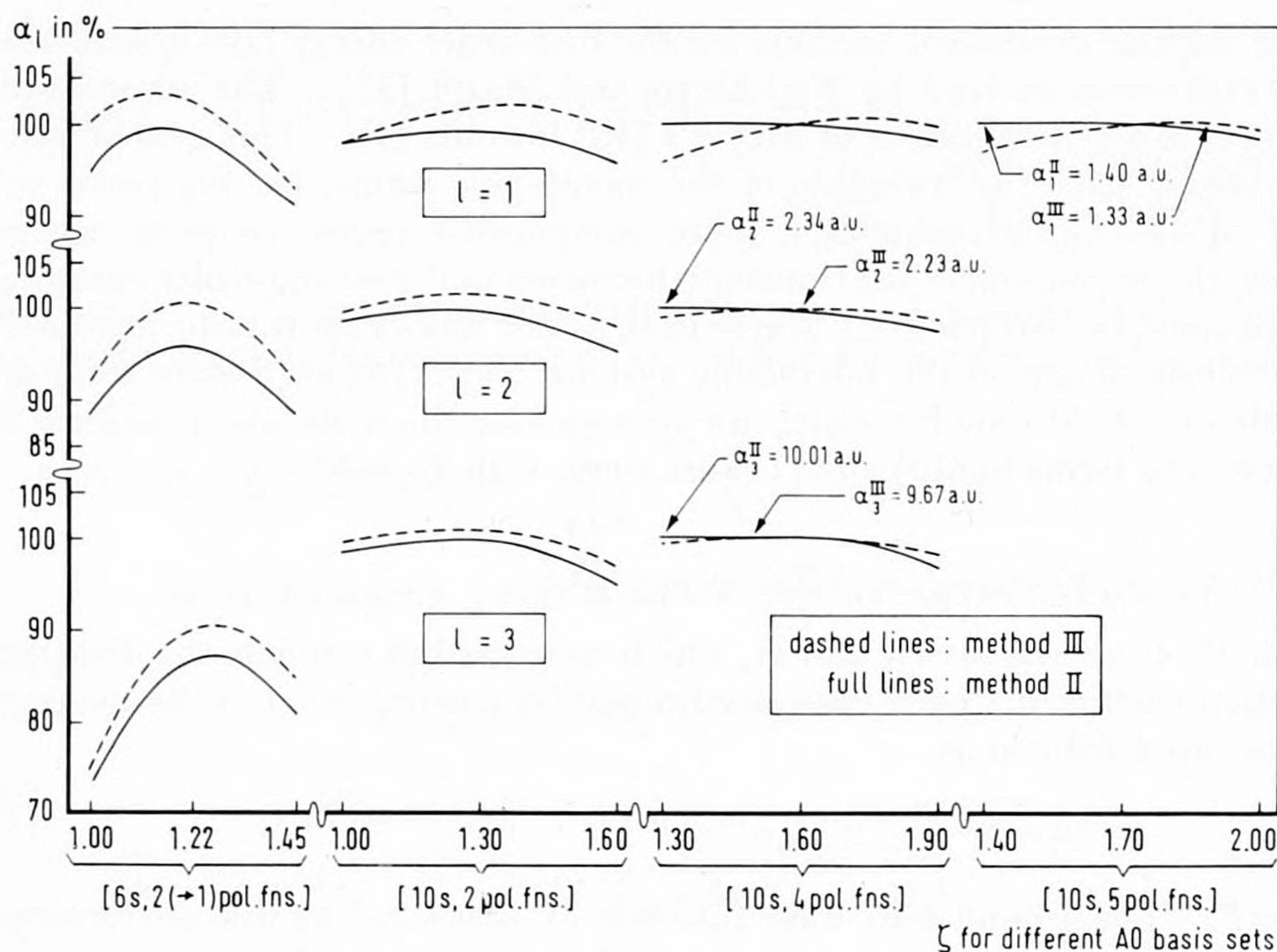


Figure 1. Optimization of the AO basis set for He (maximization of the polarizability, equation (15)). Pol. fns. stands for: polarization functions (p for dipole, d for quadrupole, and f for octupole transitions). The 100 per cent levels on the vertical scale correspond with the final optimal polarizabilities for the two methods II and III (description, see § 3), which are indicated in the figure.

The optimization for He is shown in figure 1; method I is not included, because the curves for methods I and II appear to be parallel. Method III behaves differently and we observe clearly that the polarizability is not bound in this method, so that extension of the virtual orbital set does not necessarily cause an increase of the polarizability; even for the largest basis sets used, this method is still sensitive to the scale parameter ζ in contrast with the other two methods. Using the dispersion interaction coefficients for the optimization

† For the calculation of $\alpha_{ll'}^{\sigma} = \alpha_{ll'0}$ of H_2 these polarization functions slightly mix into the ground state wave function. The Hylleraas variation principle does not exactly hold then, but in practice this did not affect our calculations.

rather than the polarizabilities, we have found an increase of the optimal ζ for the smallest basis set by about 10 per cent, while for the largest basis sets no significant change could be observed. Finally, figure 1 shows the increasing need for a high-quality ground state when calculating higher transition multipoles; the reason is that the higher multipole moments are giving more weight to the outer region of the ground state wave function.

For H_2 we first optimized the ground state wave function by minimizing the SCF energy in a (10s, 3p, 1d) AO basis. The excited states of the different symmetries of interest were optimized by maximizing the quadratic polarizabilities $\alpha_{111} = \alpha_{11}^\pi$, $\alpha_{222} = \alpha_{22}^\delta$ and $\alpha_{333} = \alpha_{33}^\phi$ in AO basis sets of $(3p)_\pi$, $(2d)_\delta$ and $(2f)_\phi$ respectively. Extending the $(3p)_\pi$ to a $(4p)_\pi$ basis set increased the optimal α_{11}^π by only 0.1 per cent, whereas α_{22}^δ improved by not more than 0.5 per cent when adding one extra d function. So these quadratic polarizabilities are sufficiently well described by these basis sets, which is confirmed

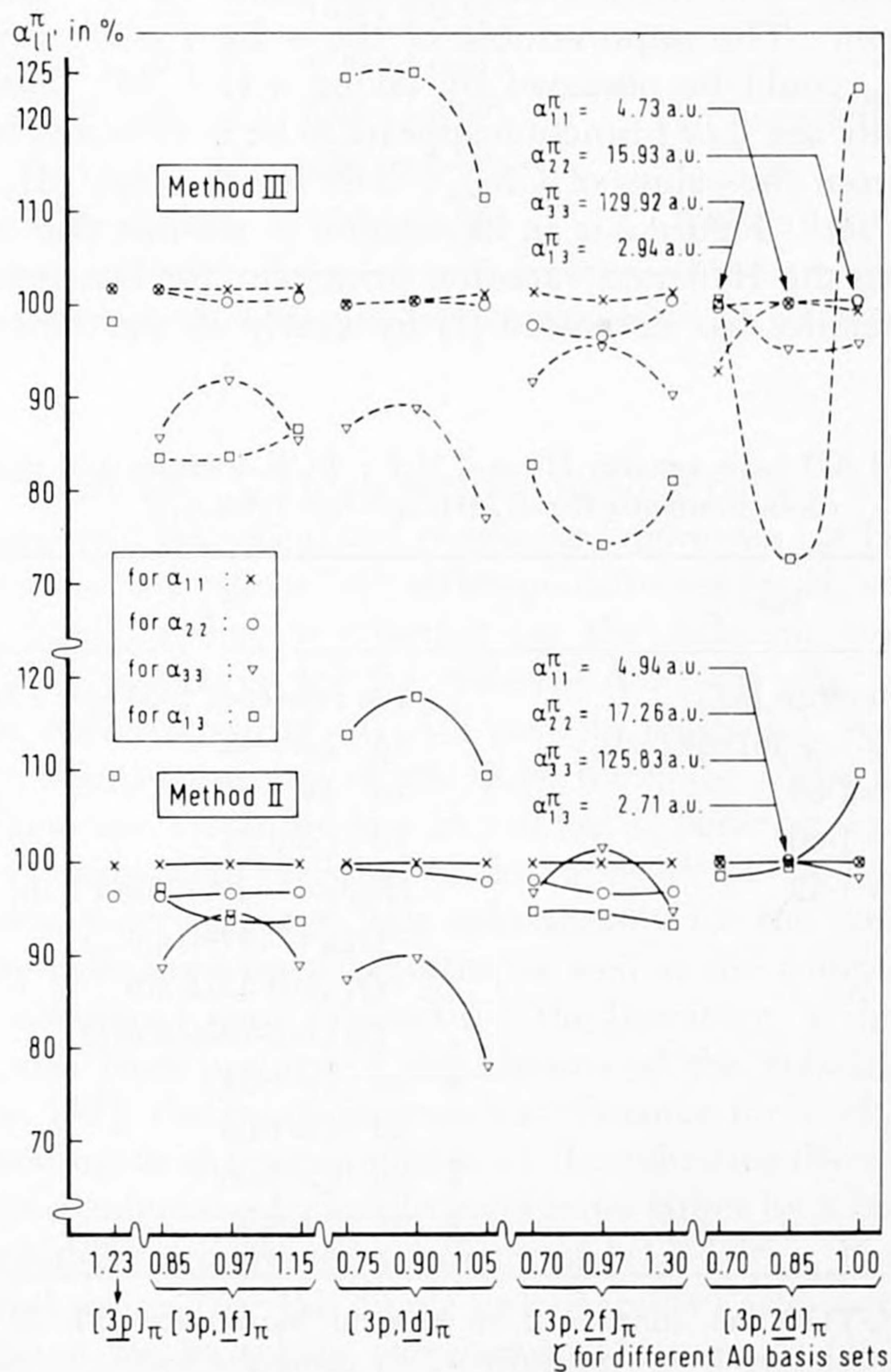


Figure 2. Optimization of the π AO basis set for H_2 (see also caption figure 1). The σ AO basis is fixed: (10s, 3p, 1d) \rightarrow [4s, 3p, 1d]. The ζ scale applies to the underlined p, d or f functions. Note that the optimal value for α_{33}^π is slightly larger in the $[3p, 2f]_\pi$ basis than in the $[3p, 2d]_\pi$ basis, which we have used, but the latter basis yields a better result for α_{22}^π (in method II).

by the value of 1.00 of the completeness ratios (CR) for the corresponding multipole operators. The completeness ratio is defined by [21]

$$\text{CR}_{l'l'm} = \text{STM}_{l'l'm} / \text{CM}_{l'l'm}, \quad (16)$$

where

$$\text{STM}_{l'l'm} = \sum'_k \langle 0 | Q_{l,m} | k \rangle \langle k | Q_{l',-m} | 0 \rangle, \quad (16 a)$$

(STM \equiv sum over transition moments)

$$\text{CM}_{l'l'm} = \langle 0 | Q_{l,m} Q_{l',-m} | 0 \rangle - \langle 0 | Q_{l,m} | 0 \rangle \langle 0 | Q_{l',-m} | 0 \rangle, \quad (16 b)$$

(CM \equiv closure moment).

For a complete basis this ratio equals 1, or, in other words, the sum rule for $S_{l,l',m}(-1)$ is obeyed [34]. Because the completeness ratios CR_{220} , CR_{221} , CR_{330} and CR_{331} were still deviating too strongly from 1, we extended the σ and π AO basis sets. For the σ basis this was achieved by adding one extra (diffuse) d function. The improvement of the π basis necessary to calculate good α_{22}^π and α_{33}^π could be obtained by taking a $(3p, 2d)_\pi$ basis (figure 2). The addition of only one d or f function appears to be insufficient for $\alpha_{331} = \alpha_{33}^\pi$; this also follows from the values of CR_{331} : 0.89 for the $(3p, 1d)_\pi$ and 0.93 for the $(3p, 1f)_\pi$ basis set. Figure 2 is an illustration of the fact that method III is not strictly obeying the Hylleraas variation principle; for instance, for $\zeta_d = 0.70$ the dipole polarizability has decreased (!) by nearly 10 per cent as compared

Table 1. Optimized AO basis sets for He and H_2^\dagger ; SCF energies and permanent multipole moments for H_2 ($r_{\text{H-H}} = r_e = 1.4$ a.u.).

He		H ₂	
10s reference [35]		σ	10s reference [35] ($\zeta = 1.20$) \ddagger
($E_{\text{SCF}} = -2.8616692$ a.u.)			3p $\zeta = 1.48$
5p $\zeta = 1.88$			1d $\zeta = 3.61$
4d $\zeta = 1.60$			1d' $\zeta = 0.85$
4f $\zeta = 1.49$			($E_{\text{SCF}} = -1.1335949$ a.u.,
			$Q_{2,0} = 0.4940$ a.u.,
			$Q_{4,0} = 0.3218$ a.u.,
			$Q_{6,0} = 0.1849$ a.u.) \S
		π	3p $\zeta = 1.23$
			2d $\zeta = 1.00$
		δ	2d $\zeta = 1.06$
		ϕ	2f $\zeta = 0.97$

\dagger All cartesian GTO's are contracted to tesseral harmonics [39, 21]. The GTO exponents α_i can be obtained from Appendix A2 by using the scaling relation [35]: $\alpha_i = \zeta^2 \chi_i$.

\ddagger The primitive (10s) basis has been contracted to [4s] via a $\langle 5, 2, 2, 1 \rangle$ scheme; the contraction coefficients were taken from the SCF result for the optimized uncontracted (10s, 3p) $_\sigma$ AO basis set.

\S The best values for $Q_{2,0}$ and $Q_{4,0}$, obtained with correlated wave functions, are: 0.4574 and 0.2826 a.u. [40].

with the value for the $(3p)_\pi$ basis set. The cross polarizabilities, of which α_{13}^{π} is plotted in figure 2, are not bound in any method and show a much larger sensitivity to the variation parameters than the quadratic polarizabilities. It appears that a calculation of the cross polarizabilities at the same level of accuracy as the quadratic polarizabilities would require a still larger AO basis set.

Table 2. Average ratios $\alpha_{ll'm}^I/\alpha_{ll'm}^{II}$ and $\alpha_{ll'm}^{III}/\alpha_{ll'm}^{II}$ and their deviations (in parentheses), estimated from the results for the different AO basis sets used in this paper.

$ll'm^\dagger$	H_2		He	
	α^I/α^{II}	α^{III}/α^{II}	α^I/α^{II}	α^{III}/α^{II}
11m	0.66 (± 0.00)	0.94 (± 0.02)	0.71 (± 0.00)	0.94 (± 0.02)
13m	0.68 (± 0.00)	1.06 (± 0.16)	—	—
15m	0.71 (± 0.01)	1.20 (± 0.37)	—	—
22m	0.72 (± 0.00)	0.95 (± 0.02)	0.77 (± 0.00)	0.95 (± 0.02)
24m	0.72 (± 0.01)	0.95 (± 0.02)	—	—
33m	0.78 (± 0.00)	0.99 (± 0.02)	0.82 (± 0.00)	0.97 (± 0.01)

\dagger The dependence on m has also been considered in the resulting deviations.

The final 'optimum' AO basis sets are listed in table 1, which also contains the SCF energies and the calculated permanent moments for H_2 . From table 2 one can observe that the ratio α^I/α^{II} , although different for H_2 and He and for the different (ll') combinations, is constant for the different m -components of a particular $\alpha_{ll'}$ and, moreover, for the different AO basis sets. So, it is justified to perform the optimization of the AO basis in method I, which is by far the least computer time consuming of the three methods. The absolute values of the polarizabilities are much too low in method I, however, in comparison with experimental values. The variation in the ratios α^{III}/α^{II} is larger, only slightly for the quadratic polarizabilities, but substantially for the cross polarizabilities (table 2). The calculated polarizabilities as well as the completeness ratios are collected and compared with values from the literature, as far as available, in table 3. We also have performed calculations of the polarizability at $r_{H-H} = \langle r \rangle = 1.449$ a.u. [43], the mean internuclear distance for $\nu=0$, which is a very good approximation to the computation of the vibrationally averaged polarizability [16]: the quadratic polarizabilities become larger by a factor of 1.04–1.09, the cross polarizabilities increase by a factor of 1.12–1.16. The deviations from the experimental values (for the dipole polarizability) also increase then, which must be corrected for by taking correlation into account [16]. Although the best agreement with the experimental dipole polarizability is obtained for method III, in general we prefer the results of method II, because of its better theoretical basis and because in practice this method appears clearly to be more stable. The results of both methods do not differ drastically, except for the calculated cross polarizabilities, which are probably better in method II.

Table 3. Polarizabilities (in a.u.) and completeness ratios for He and H₂ ($r_{\text{H-H}} = r_e = 1.4$ a.u.).

$l'm$	CR†	$\alpha^{\text{II}\ddagger}$	$\alpha^{\text{III}\ddagger}$	α (Meyer)§
H ₂				
110(σ)	1.00	7.33	6.76	6.44
111(π)	1.00	4.93	4.70	4.57
11, isotr.		5.73	5.39	5.19
130(σ)	1.00	3.93	3.53	—
131(π)	1.03	2.88	3.53	—
150(σ)	1.14	1.49	1.24	—
151(π)	1.19	1.59	2.49	—
220(σ)	0.99	17.99	17.08	17.78
221(π)	1.00	17.13	15.87	16.97
222(δ)	1.00	14.33	13.86	13.85
22, isotr.		16.18	15.31	15.90
240(σ)	0.91	19.45	18.78	—
241(π)	1.05	18.89	17.59	—
242(δ)	1.24	12.69	12.21	—
330(σ)	0.98	125.50	123.88	115.8
331(π)	0.98	121.29	122.06	119.9
332(δ)	0.99	113.69	111.72	113.0
333(ϕ)	0.99	103.86	100.94	93.7
33, isotr.		114.74	113.33	109.8
He				
11(p)	1.00	1.38	1.33	1.38
22(d)	1.00	2.34	2.23	2.41
33(f)	1.00	10.01	9.66	10.09

† CR is the completeness ratio as defined by (16).

‡ Methods II and III are described in the text (paragraph 3).

§ Reference [16]. These values are obtained with correlated wavefunctions in slightly less-quality AO basis sets. Meyer has also presented the vibrationally averaged values, which are systematically larger: $\bar{\alpha}_{11} = 5.43$ a.u., $\bar{\alpha}_{22} = 17.06$ a.u., $\bar{\alpha}_{33} = 120.1$ a.u. [16]. This improves the agreement with the experimental α_{11} . Our corresponding results are: $\bar{\alpha}_{11} = 6.00$ a.u., $\bar{\alpha}_{22} = 17.24$ a.u., $\bar{\alpha}_{33} = 125.0$ a.u. The experimental values for the dipole polarizability are: H₂: $\bar{\alpha}_{11} = 5.44$ a.u.; $\alpha_{110} = 6.94$ a.u.; $\alpha_{111} = 4.82$ a.u., measured at a wavelength of 6328 Å [41]; He: $\alpha_{11} = 1.38$ a.u., from refractive index data [42].

4. LONG RANGE INTERACTION COEFFICIENTS

The calculated isotropic dispersion and induction interaction coefficients and their anisotropy factors are listed for method II in table 4. The results for method I are essentially the same for the anisotropy factors, while the isotropic dispersion interaction coefficients are smaller by factors of 0.70 (C_6), 0.72 (C_8), and 0.75 (C_{10}) for H₂-He; 0.67 (C_6), 0.70 (C_8), and 0.73 (C_{10}) for H₂-H₂ (a similar result has been found for the polarizabilities, table 2). Fractions of about 0.7 have also been found for the ethylene dimer [21]. The anisotropy factors up to L_A, L_B values of 2 inclusive, computed with method III, are also very close to the tabulated results, whereas for higher L values deviations occur,

Table 4. The isotropic dispersion and induction interaction coefficients (in a.u.) and their anisotropy factors, calculated with method II ($r_{H-H} = r_e = 1.4$ a.u.).

Calculated quantity†	C_6		C_8		C_{10}	
	Dispersion‡	Dispersion‡	Induction	Dispersion‡	Induction	
He-He						
C_n (isotropic)	1.541	14.06	—	177.3	—	
H_2-He						
C_n^0 (isotropic)	4.464	56.39	0.506 §	988.9	3.990	
γ_n^2	0.114	0.286	1.143 §	0.306	1.414	
γ_n^4	—	0.0058	0.857 §	0.0075	0.809	
γ_n^6	—	—	—	-0.000019	0.175	
H_2-H_2						
C_n^{000} (isotropic)	14.18	223.9	4.194	4799.0	55.29	
γ_n^{200}	0.120	0.250	0.627	0.269	0.832	
γ_n^{220}	0.044	0.051	0.200	0.075	0.506	
γ_n^{221}	-0.0099	-0.0069	-0.040	-0.0081	-0.052	
γ_n^{222}	0.0012	0.00012	0.010	0.00013	-0.0013	
γ_n^{400}	—	0.0046	0.429	0.0068	0.355	
γ_n^{420}	—	0.0021	0.263	0.0019	0.214	
γ_n^{421}	—	-0.00027	-0.036	-0.00017	-0.021	
γ_n^{422}	—	0.13×10^{-4}	0.0020	0.26×10^{-6}	0.00057	
γ_n^{600}	—	—	—	-0.55×10^{-4}	0.052	
γ_n^{620}	—	—	—	-0.85×10^{-5}	0.040	
γ_n^{621}	—	—	—	-0.04×10^{-6}	-0.0038	
γ_n^{622}	—	—	—	0.09×10^{-6}	0.00014	
γ_n^{440}	—	—	—	0.00014	0.037	
γ_n^{441}	—	—	—	-0.11×10^{-4}	-0.0030	
γ_n^{442}	—	—	—	0.03×10^{-5}	0.83×10^{-4}	
γ_n^{443}	—	—	—	-0.01×10^{-6}	-0.15×10^{-5}	
γ_n^{444}	—	—	—	$< 10^{-8}$	-0.01×10^{-6}	

† Defined in equations (13) and (14).

‡ Isotropic results for $r = r_e$, obtained by Meyer [16]: He-He: $C_n = 1.456, 13.90, 175.4$ a.u., H_2-He : $C_n^0 = 3.904, 53.12, 940.5$ a.u., H_2-H_2 : $C_n^{000} = 11.40, 196.7, 4303.0$ a.u. ($n = 6, 8, 10$). Our values for $r_{H-H} = \langle r \rangle$ are: H_2-He : $C_n^0 = 4.613, 59.02, 1051.6$ a.u., H_2-H_2 : $C_n^{000} = 15.24, 245.0, 5365.0$ a.u., which can be compared with Meyer's vibrationally averaged analogues [16]: H_2-He : $C_n^0 = 4.016, 55.65, 1001.1$ a.u., H_2-H_2 : $C_n^{000} = 12.14, 215.2, 4813.9$ a.u.

§ Comparative results, obtained by Thakkar [23] using Meyer's results: $C_{8,ind}^0 = 0.483$ a.u.; $\gamma_{8,ind}^2$ and $\gamma_{8,ind}^4$ are exactly the same as our values, because they are purely algebraic, just as the quadratic part of $\gamma_{10,ind}$.

which in some cases are very drastic (even changes of sign); the ratios of the isotropic interaction coefficients for methods III and II are: 0.95 (C_6, C_8) and 0.96 (C_{10}) for H_2-He , and 0.94 (C_6, C_8) and 0.96 (C_{10}) for H_2-H_2 . Calculations at $r_{H-H} = \langle r \rangle$ instead of r_e enlarge all results by 5-10 per cent.

Table 5 shows the relative contributions of the different quadratic and cross terms to the anisotropy factors for the dispersion energy up to L_A, L_B values of 2

Table 5. Relative contributions of the different multipole terms to the lowest L dispersion anisotropy factors, calculated with method II for $r_{H-H}=r_e$ (notation: (22; 11) stands for the sum of the (1_A1_A, 2_B2_B) and the (2_A2_A, 1_B1_B) contributions, etc.).

	C_6^\dagger	C_8^\dagger		C_{10}		
H_2-He γ_n^2	0.114	0.286		0.306		
	(0.093)					
		(22; 11)	(13, 11)	(33; 11)	(22, 22)	'quadr.'
		'quadr.'	'cross'	0.052	0.024	0.076
		0.089	0.197	(13, 22)	(24, 11)	'cross'
	(0.091)		0.084	0.146	0.230	
H_2-H_2 γ_n^{200}	0.120	0.250		0.269		
	(0.100)					
		(22; 11)	(13; 11)	(33; 11)	(22, 22)	'quadr.'
		'quadr.'	'cross'	0.051	0.027	0.078
		0.091	0.159	(13; 22)	(24; 11)	'cross'
	(0.089)		0.097	0.094	0.191	
γ_n^{220}	0.044	0.051		0.075		
	(0.031)					
		(22; 11)	(13; 11)	(33; 11)	(22, 22)	'quadr.'
		'quadr.'	'cross'	0.006	0.003	0.009
		0.013	0.038	(13, 13)	(13, 31)	
	(0.012)		0.023	0.008		
			(13; 22)	(24; 11)	'cross'	
			0.017	0.018	0.066	

† The values in parentheses, which describe the quadratic anisotropy only, are obtained by Meyer [16] (see also note ‡ table 4).

inclusive. The anisotropy factors arising from the quadratic terms are in good agreement with Meyer's results. The contributions of the cross terms are very pronounced (65–90 per cent). For the induction energy coefficients the mixed-pole contributions to C_{10} vary from 28 per cent (γ_{10}^2 , H_2-He) to 100 per cent (γ_{10}^6 , H_2-He). The assumption of Tang and Toennies [5] that $\gamma_8^2 = \gamma_{10}^2$ for H_2-He , which was based on our preliminary results, appears to be justified, also for H_2-H_2 . Our calculated values ($\gamma_8^2 = 0.29$, $\gamma_{10}^2 = 0.31$) are close to the value $\gamma_8^2 = 0.33$ [23, 44], which has been used with success by Tang and Toennies

[5] in their model potential for interpreting the measurements of Zandee and Reuss [3, 4]. These latter authors have measured the orientation dependence of the total cross section for a beam of state selected H_2 molecules in collisions with He and other rare gas atoms. Our isotropic dispersion interaction coefficients differ slightly from Meyer's coefficients, which is partly due to the different quality of the AO basis sets (in particular for H_2 ours seems to be slightly better). The main source of this difference is the electron correlation, which has been taken into account by Meyer and therefore his isotropic coefficients should be preferred. Moreover, his calculated C_6 for H_2-He and H_2-H_2 are closer to the empirical values [17, 18] which can be determined rather accurately from spectroscopic data.

The convergence of $\gamma^{L_A L_B M}$ is very fast for the dispersion energy (table 5), so that the (L_A, L_B, M) series for the anisotropic interaction can be truncated safely at $L_A = L_B = 2$. This is a fortunate circumstance, because the higher L anisotropy factors are less accurate. The induction anisotropy factors converge more slowly, but the induction energy in these systems can be neglected in comparison with the dispersion energy.

From figure 3 one can get an impression of the convergence of the $C_n R^{-n}$ series for H_2-He . In the isotropic van der Waals minimum ($R \simeq 6.5$ a.u. [12, 5]), the isotropic long range interaction increases by 43 per cent by adding $(C_8^0 R^{-8} + C_{10}^0 R^{-10})$ to $C_6^0 R^{-6}$. For the anisotropic $L_A = 2$ contribution this increase is much larger: 112 per cent, which of course is due to the anisotropy of C_8 and C_{10} being substantially larger than the anisotropy of C_6 . This modification of the convergence behaviour by the anisotropic contributions is shown in figure 3.

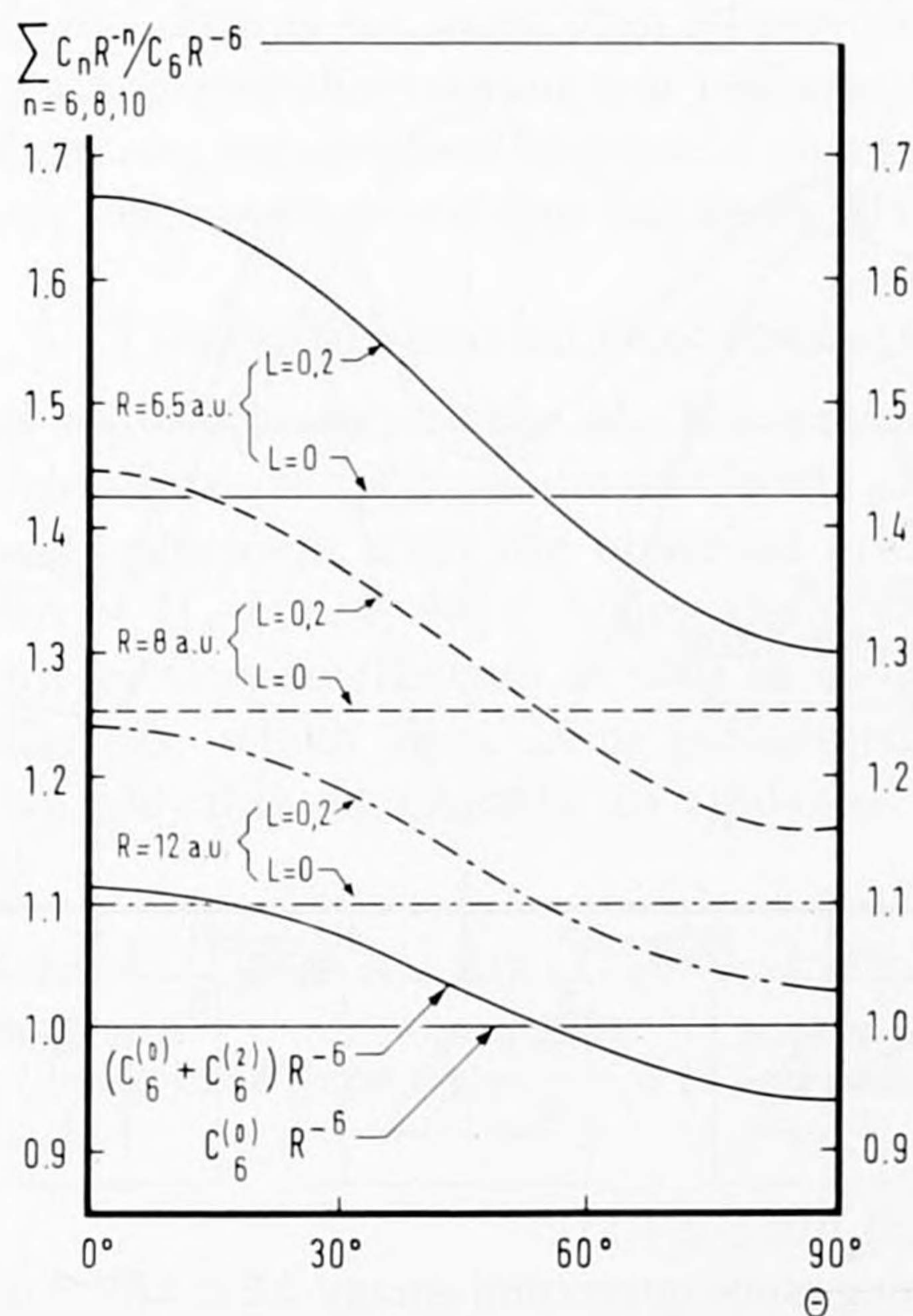


Figure 3. Convergence of the multipole expanded dispersion energy for H_2-He , both isotropic ($L = L_A = 0$) and including anisotropic terms ($L = L_A = 0, 2$).

We have also calculated the dispersion interaction coefficients in the AO basis which was used in [12] for the calculation of the complete van der Waals potential for H_2 -He by the multi-structure valence bond method. The results: $C_6^0 = 4.34$ a.u., $\gamma_6^2 = 0.115$, $C_8^0 = 52.38$ a.u., $\gamma_8^2 = 0.323$, give rise to the same conclusions. Therefore, contrary to some criticism [16], the original conclusion of [12] that γ_8 is substantially larger than γ_6 is certainly valid. It must be stressed, however, that the values of C_6^0 , C_8^0 , γ_6^2 and γ_8^2 presented in [12], which seem to disagree with the present results at first sight, were not obtained from a direct computation using perturbation theory but rather by fitting the valence bond (VB) results for large distances. The isotropic coefficients are essentially the same, but γ_6^2 , obtained by fitting the VB results, is larger, because it necessarily contains the contributions of higher multipole cross terms, e.g. the (strongly anisotropic) C_8 (13 ; 11). Similarly γ_8^2 is smaller because it lacks this contribution C_8 (13 ; 11); on the other hand it contains the contributions of the higher multipole cross terms C_{10} (13 ; 22) and C_{10} (24 ; 11), thus yielding a γ_8^2 which is still larger than the value arising from C_8 (11 ; 22) alone.

For H_2 - H_2 the higher multipole dispersion terms are relatively more important than for H_2 -He. For example, in the isotropic van der Waals minimum ($R \simeq 6.5$ a.u. [46]) the ratios $(C_6^{000} R^{-6} + C_8^{000} R^{-8})/C_6^{000} R^{-6}$ and $(C_6^{000} R^{-6} + C_8^{000} R^{-8} + C_{10}^{000} R^{-10})/C_6^{000} R^{-6}$ are 1.37 and 1.56 respectively. This is even more striking for the corresponding anisotropic ratios, e.g. for $(L_A L_B M) = (200)$ the ratios are 1.78 and 2.20 respectively. This observation is of particular interest in relation to Gallup's calculation of the H_2 - H_2 complete potential [15]. The restriction of his CI calculations to an (s, p) AO basis set and a $(\sigma_g, \sigma_u, \pi_u)$

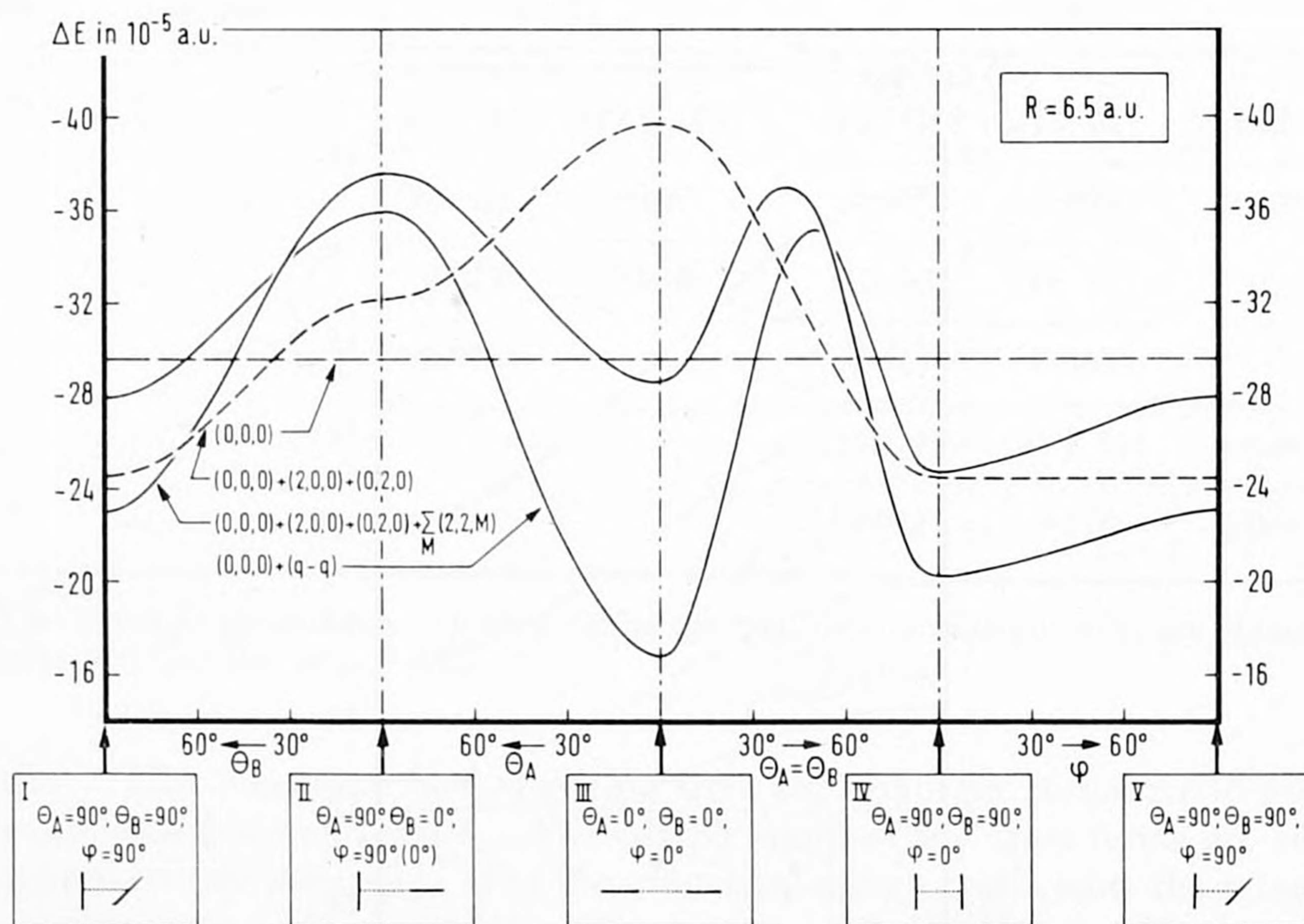


Figure 4. Anisotropic long range interaction energy $\Delta E \equiv \Delta E^{(1,2)}$ (equation (9)) for H_2 - H_2 at $R = 6.5$ a.u. The different contributions to the energy are indicated in the figure by (L_A, L_B, M) ; (q-q) denotes the pure quadrupole-quadrupole interaction $\epsilon_{220}^{(1)} + \epsilon_{221}^{(1)} + \epsilon_{222}^{(1)}$ (equation (10)).

MO basis set will cause a rather large underestimate of the C_8^{000} and C_{10}^{000} isotropic contributions, and, probably more pronounced even, of the C_8^{000} and C_{10}^{200} anisotropic contributions to the interaction energy. This applies equally to the perturbation type calculations of Kochanski *et al.* [14], which are also restricted to (s, p) AO basis sets. Gallup noticed that the (22M) anisotropic interaction is quite close to the electrostatic quadrupole–interaction over the whole range. This conclusion, which was also drawn by Ng *et al.* [32] in their elegant study of charge penetration in the H_2 dimer, is confirmed by our study since at $R=6.5$ a.u. the (220) C_6R^{-6} dispersion energy is smaller than the (220) electrostatic energy by a factor of 15.2. When adding the C_8 and C_{10} contribution to C_6R^{-6} , this factor decreases to 8.6. A much more pronounced modification of the anisotropic interaction arises, however, from the (200) dispersion terms. This is illustrated by figure 4 which shows the anisotropy of the first- and second-order interaction energy up to L_A, L_B values of 2 inclusive for $R=6.5$ a.u. (the higher L anisotropy has been omitted because it is not significant). The substantial difference between this curve and the curve composed of the isotropic dispersion energy and the (anisotropic) quadrupole–quadrupole interaction (figure 4) is reduced for larger distances, though. The apparent existence of two competitive stable dimer structures (perpendicular and shifted parallel), which we observe in figure 4, has been reported for similar quadrupole molecules [22, 46, 47], including H_2 [46]. Furthermore, it is interesting to note that the H_2 molecule can be considered as an ‘ideal point quadrupole’, which is illustrated by considering the multipole moments as dimensionless numbers:

$$\frac{Q_{2,0}}{r_{H-H}^2} = 0.252 \gg \frac{Q_{4,0}}{r_{H-H}^4} = 0.084 \gg \frac{Q_{6,0}}{r_{H-H}^6} = 0.025.$$

Consequently, the C_7R^{-7} term is not more than 50 per cent of the C_5R^{-5} term for orientation III, even at the very short distance of 1.80 a.u., where the multipole expansion result is, of course, meaningless because of charge penetration [32]. As stated before, this very fast convergence does not apply to the dispersion energy.

5. THE H_2-He INTERACTION POTENTIAL

A first analytical representation of the H_2-He interaction potential [12, 4], which was obtained as a fit to the VB results of Geurts *et al.* [12], was found by Zandee to be in good agreement with the observed orientation dependence of the total cross section of H_2-He [4, 48]. Using the presently calculated values for the long range interaction coefficients as well as some extra first-order [49] and VB [50] calculations, which have been performed for shorter distances ($R=3.0-4.5$ a.u.), we are able to provide an updated version of the H_2-He interaction potential

$$V(R, \theta) = 10^{-5}(1 + 0.277P_2(\cos \theta)) \exp(13.335 - 1.5643R - 0.051136R^2) \\ - \left[(1 + 0.114P_2(\cos \theta)) \frac{4.464}{R^6} + (1 + 0.286P_2(\cos \theta)) \frac{56.39}{R^8} \right. \\ \left. + (1 + 0.306P_2(\cos \theta)) \frac{988.9}{R^{10}} \right] F(R),$$

with

$$F(R) = 1 - \exp[-0.47(R - 2.97)] \quad \text{for } R \geq 2.97 \text{ a.u.} \\ = 0 \quad \text{for } R < 2.97 \text{ a.u.} \quad (17)$$

A preliminary version of the latter potential, which is slightly different only because its long range part is constructed from C_6 , γ_6 , C_8 and γ_8 calculated in the AO basis of [12], has been discussed and compared with other potentials [11, 13, 51] by Tang and Toennies [5] in relation to the experiment of Zandee [3, 48]. The damping function $F(R)$, which corrects the multipole expanded dispersion energy for penetration and exchange effects, has been obtained by comparing the present multipole results with the *ab initio* VB results for the second order energy.

6. CONCLUSIONS

For both systems, H_2 -He and H_2 - H_2 , we can draw the following conclusions :

- (a) the anisotropy of the dispersion (and of the induction) interaction is substantially increased by the mixed-pole or cross terms, yielding anisotropy factors γ_8 and γ_{10} which are definitely larger than γ_6 (tables 4 and 5). The assumption that $\gamma_8 \simeq \gamma_{10}$ [5] seems to be justified ;
- (b) the convergence of the anisotropy factors $\gamma^{L_A L_B M}$ with respect to L_A and L_B is very fast for the dispersion energy, but slow for the induction energy. The induction energy itself is negligible, however (table 4) ;
- (c) because of (b) and the fact that H_2 can be considered as an 'ideal point quadrupole', one can truncate the anisotropic interaction energy series (9) safely at L_A, L_B values of 2 (results : figures 3 and 4). The anisotropic dispersion interaction cannot be neglected in comparison with the (anisotropic) quadrupole-quadrupole interaction for H_2 - H_2 , at the van der Waals minimum (figure 4) ;
- (d) higher multipole dispersion terms cause a substantial lowering of the van der Waals minimum (figure 3) ;
- (e) Furthermore we mention the result that methods I, II and III show a similar behaviour under optimization of the polarizability, in particular methods I and II (table 2). Consequently, the cheaper method I, although it yields too small polarizabilities, can be used for optimizing the AO basis set. This optimized basis can then be employed for the final calculations with method II or III. The latter method has the theoretical and practical drawback that α is not strictly variationally bound (figures 1 and 2).

We thank Gerard van Dijk for his assistance with the calculation of the anisotropic induction energy and Rut Berns for his contribution to the determination of the analytical potential for H_2 -He (equation (17)).

Note added in proof : After submitting this article it came to our attention that the formulae (3) and (5), which we have derived as specializations of our results in reference [30], have been obtained directly in a recent paper by Koide [52].

Appendix A1. Table of the algebraic coefficients $\zeta_{L_A L_B M}^{l_A l'_A l_B l'_B}$ which occur in the second order energy expression (11); ζ is defined by the formulae (6), (8) and (12). The list is complete up to $N=10$ inclusive ($N=l_A+l'_A+l_B+l'_B+2$).

N	$l_A l'_A, l_B l'_B$	$L_A L_B M$								
		000	200	220	221	222				
6	11, 11	000	200	220	221	222				
		2	$-(2)^{\frac{1}{2}}$	3	$-\frac{2}{3}$	$\frac{1}{12}$				
7	21, 11	100	120	121	300	320	321	322		
		$3\left(\frac{6}{5}\right)^{\frac{1}{2}}$	$-3\left(\frac{3}{5}\right)^{\frac{1}{2}}$	$\frac{1}{2}\left(\frac{3}{5}\right)^{\frac{1}{2}}$	$-4\left(\frac{1}{5}\right)^{\frac{1}{2}}$	$7\left(\frac{2}{5}\right)^{\frac{1}{2}}$	$-\frac{7}{3}\left(\frac{1}{10}\right)^{\frac{1}{2}}$	$\frac{1}{6}\left(\frac{1}{10}\right)^{\frac{1}{2}}$		
8	22, 11	000	200	020	220	221	222	400	420	
		$-(15)^{\frac{1}{2}}$	$4\left(\frac{6}{7}\right)^{\frac{1}{2}}$	$2\left(\frac{6}{5}\right)^{\frac{1}{2}}$	$-5\left(\frac{3}{7}\right)^{\frac{1}{2}}$	$\left(\frac{3}{7}\right)^{\frac{1}{2}}$	$-\frac{1}{4}\left(\frac{3}{7}\right)^{\frac{1}{2}}$	$-(\frac{30}{7})^{\frac{1}{2}}$	$22\left(\frac{3}{35}\right)^{\frac{1}{2}}$	
		421	422							
		$-3\left(\frac{3}{35}\right)^{\frac{1}{2}}$	$\frac{1}{2}\left(\frac{1}{105}\right)^{\frac{1}{2}}$							
8	21, 21	110	111	310	311	330	331	332	333	
		$-\frac{36}{5}$	$\frac{18}{5}$	$\frac{8}{5}(6)^{\frac{1}{2}}$	$-\frac{3}{5}\left(\frac{3}{2}\right)^{\frac{1}{2}}$	$-\frac{44}{5}$	$\frac{101}{90}$	$-\frac{1}{18}$	$\frac{1}{360}$	
8	21, 12	110	111	310	311	330	331	332	333	
		$-\frac{27}{5}$	$-\frac{9}{5}$	$\frac{6}{5}(6)^{\frac{1}{2}}$	$-\frac{1}{5}\left(\frac{3}{2}\right)^{\frac{1}{2}}$	$-\frac{33}{5}$	$\frac{4}{5}$	$-\frac{1}{30}$	0	
8	31, 11	200	220	221	222	400	420	421	422	
		$12\left(\frac{1}{7}\right)^{\frac{1}{2}}$	$-6\left(\frac{2}{7}\right)^{\frac{1}{2}}$	$\frac{2}{3}\left(\frac{2}{7}\right)^{\frac{1}{2}}$	$\frac{1}{6}\left(\frac{1}{14}\right)^{\frac{1}{2}}$	$-10\left(\frac{1}{21}\right)^{\frac{1}{2}}$	$19\left(\frac{2}{21}\right)^{\frac{1}{2}}$	$-5\left(\frac{1}{42}\right)^{\frac{1}{2}}$	$\frac{1}{4}\left(\frac{1}{42}\right)^{\frac{1}{2}}$	
9	22, 21	010	210	211	030	230	231	232	410	
		$6(2)^{\frac{1}{2}}$	$-48\left(\frac{1}{35}\right)^{\frac{1}{2}}$	$6\left(\frac{1}{35}\right)^{\frac{1}{2}}$	$-(12)^{\frac{1}{2}}$	$2\left(\frac{42}{5}\right)^{\frac{1}{2}}$	$-13\left(\frac{1}{210}\right)^{\frac{1}{2}}$	$\frac{1}{2}\left(\frac{3}{70}\right)^{\frac{1}{2}}$	$12\left(\frac{1}{7}\right)^{\frac{1}{2}}$	
		411	430	431	432	433				
		$-\frac{3}{2}\left(\frac{1}{7}\right)^{\frac{1}{2}}$	$-2(42)^{\frac{1}{2}}$	$\frac{17}{2}\left(\frac{1}{42}\right)^{\frac{1}{2}}$	$-\frac{19}{60}\left(\frac{1}{42}\right)^{\frac{1}{2}}$	$\frac{1}{120}\left(\frac{1}{42}\right)^{\frac{1}{2}}$				

M.P.

1 M

Appendix A1 *continued*

N	$l_{A'}l'_A, l_{B'}l'_B$	$L_A L_B M$							
		100	120	121	300	320	321	322	500
9	32, 11	$-4 \left(\frac{15}{7}\right)^{\frac{1}{2}}$	$8 \left(\frac{6}{35}\right)^{\frac{1}{2}}$	$-\left(\frac{6}{35}\right)^{\frac{1}{2}}$	$2 (5)^{\frac{1}{2}}$	$-7 \left(\frac{2}{5}\right)^{\frac{1}{2}}$	$\frac{13}{6} \left(\frac{1}{10}\right)^{\frac{1}{2}}$	$-\frac{1}{4} \left(\frac{1}{10}\right)^{\frac{1}{2}}$	$-2 \left(\frac{10}{7}\right)^{\frac{1}{2}}$
		520	521	522					
		$10 \left(\frac{5}{7}\right)^{\frac{1}{2}}$	$-\frac{17}{3} \left(\frac{1}{35}\right)^{\frac{1}{2}}$	$\frac{1}{4} \left(\frac{1}{35}\right)^{\frac{1}{2}}$					
9	31, 21	210	211	230	231	232	410	411	430
		$-6 \left(\frac{30}{7}\right)^{\frac{1}{2}}$	$2 \left(\frac{30}{7}\right)^{\frac{1}{2}}$	$8 \left(\frac{5}{7}\right)^{\frac{1}{2}}$	$-\left(\frac{5}{7}\right)^{\frac{1}{2}}$	0	$5 \left(\frac{10}{7}\right)^{\frac{1}{2}}$	$-\frac{17}{2} \left(\frac{1}{70}\right)^{\frac{1}{2}}$	$-10 \left(\frac{15}{7}\right)^{\frac{1}{2}}$
		431	432	433					
		$\frac{61}{4} \left(\frac{1}{105}\right)^{\frac{1}{2}}$	$-\frac{1}{12} \left(\frac{7}{15}\right)^{\frac{1}{2}}$	$\frac{1}{48} \left(\frac{1}{105}\right)^{\frac{1}{2}}$					
9	31, 12	210	211	230	231	232	410	411	430
		$-18 \left(\frac{6}{35}\right)^{\frac{1}{2}}$	$-4 \left(\frac{6}{35}\right)^{\frac{1}{2}}$	$24 \left(\frac{1}{35}\right)^{\frac{1}{2}}$	$-\frac{4}{3} \left(\frac{1}{35}\right)^{\frac{1}{2}}$	$-\frac{1}{6} \left(\frac{1}{35}\right)^{\frac{1}{2}}$	$3 \left(\frac{10}{7}\right)^{\frac{1}{2}}$	$-\frac{3}{2} \left(\frac{1}{70}\right)^{\frac{1}{2}}$	$-6 \left(\frac{15}{7}\right)^{\frac{1}{2}}$
		431	432	433					
		$\frac{17}{2} \left(\frac{1}{105}\right)^{\frac{1}{2}}$	$-\frac{1}{4} \left(\frac{1}{105}\right)^{\frac{1}{2}}$	0					
9	41, 11	300	320	321	322	500	520	521	522
		$10 \left(\frac{1}{3}\right)^{\frac{1}{2}}$	$-5 \left(\frac{2}{3}\right)^{\frac{1}{2}}$	$\frac{5}{6} \left(\frac{1}{6}\right)^{\frac{1}{2}}$	$\frac{1}{12} \left(\frac{1}{6}\right)^{\frac{1}{2}}$	$-2 \left(\frac{5}{3}\right)^{\frac{1}{2}}$	$4 \left(\frac{10}{3}\right)^{\frac{1}{2}}$	$-\frac{13}{3} \left(\frac{1}{30}\right)^{\frac{1}{2}}$	$\frac{1}{6} \left(\frac{1}{30}\right)^{\frac{1}{2}}$
		000	200	220	221	222	400	420	421
10	22, 22	14	$-10 \left(\frac{10}{7}\right)^{\frac{1}{2}}$	$\frac{92}{7}$	$-\frac{16}{7}$	$\frac{6}{7}$	$9 \left(\frac{2}{7}\right)^{\frac{1}{2}}$	$-\frac{30}{7} (5)^{\frac{1}{2}}$	$\frac{4}{7} (5)^{\frac{1}{2}}$
		422	440	441	442	443	444		
		$-\frac{1}{21} (5)^{\frac{1}{2}}$	$\frac{181}{7}$	$-\frac{74}{35}$	$\frac{41}{630}$	$-\frac{1}{630}$	$\frac{1}{20160}$		

Appendix A1 *continued*

<i>N</i>	<i>l_Al'_A, l_Bl'_B</i>	<i>L_AL_BM</i>							
		000	200	020	220	221	222	400	420
10	33, 11	4 ($\frac{7}{3}$) ^½	- $\frac{50}{3}$ ($\frac{1}{7}$) ^½	-10 ($\frac{2}{21}$) ^½	$\frac{23}{3}$ ($\frac{2}{7}$) ^½	- $\frac{4}{3}$ ($\frac{2}{7}$) ^½	($\frac{1}{14}$) ^½	18 ($\frac{6}{77}$) ^½	-30 ($\frac{3}{77}$) ^½
		421	422	600	620	621	622		
		4 ($\frac{3}{77}$) ^½	-($\frac{1}{231}$) ^½	-($\frac{10}{3}$ ($\frac{7}{11}$)) ^½	$\frac{205}{3}$ ($\frac{2}{77}$) ^½	-($\frac{20}{3}$ ($\frac{2}{77}$)) ^½	$\frac{1}{2}$ ($\frac{1}{154}$) ^½		
10	31, 31	220	221	222	420	421	422	440	441
		$\frac{180}{7}$	-($\frac{40}{7}$)	$\frac{5}{14}$	-($\frac{50}{7}$ (3)) ^½	$\frac{17}{7}$ ($\frac{1}{3}$) ^½	-($\frac{1}{21}$ ($\frac{1}{3}$)) ^½	$\frac{205}{7}$	-($\frac{167}{70}$)
		442	443	444					
		$\frac{37}{504}$	-($\frac{1}{504}$)	$\frac{1}{20160}$					
10	31, 13	220	221	222	420	421	422	440	441
		$\frac{72}{7}$	$\frac{32}{21}$	$\frac{1}{42}$	-($\frac{20}{7}$ (3)) ^½	$\frac{2}{7}$ ($\frac{1}{3}$) ^½	$\frac{1}{28}$ ($\frac{1}{3}$) ^½	$\frac{82}{7}$	-($\frac{6}{7}$)
		442	443	444					
		$\frac{1}{56}$	0	0					
10	31, 22	200	220	221	222	400	420	421	422
		-10 ($\frac{15}{7}$) ^½	$\frac{40}{7}$ (6) ^½	-($\frac{10}{7}$ ($\frac{2}{3}$)) ^½	-($\frac{5}{14}$ ($\frac{2}{3}$)) ^½	6 ($\frac{5}{7}$) ^½	-($\frac{45}{7}$ (2)) ^½	$\frac{11}{7}$ ($\frac{1}{2}$) ^½	-($\frac{3}{28}$ ($\frac{1}{2}$)) ^½
		240	241	242	440	441	442	443	444
		-($\frac{10}{7}$ (30)) ^½	$\frac{5}{7}$ ($\frac{5}{6}$) ^½	$\frac{1}{84}$ ($\frac{5}{6}$) ^½	$\frac{48}{7}$ (10) ^½	-($\frac{153}{28}$ ($\frac{1}{10}$)) ^½	$\frac{13}{84}$ ($\frac{1}{10}$) ^½	-($\frac{1}{336}$ ($\frac{1}{10}$)) ^½	0
10	32, 21	110	111	310	311	130	131	330	331
		30 ($\frac{2}{7}$) ^½	-15 ($\frac{2}{7}$) ^½	-5 (6) ^½	5 ($\frac{1}{6}$) ^½	-10 ($\frac{3}{7}$) ^½	5 ($\frac{1}{21}$) ^½	10	-($\frac{5}{4}$)
		332	333	510	511	530	531	532	533
		$\frac{1}{12}$	-($\frac{1}{144}$)	10 ($\frac{3}{7}$) ^½	-($\frac{19}{5}$ ($\frac{1}{21}$)) ^½	-(40 ($\frac{2}{7}$)) ^½	$\frac{17}{5}$ ($\frac{2}{7}$) ^½	-($\frac{13}{60}$ ($\frac{1}{14}$)) ^½	$\frac{1}{180}$ ($\frac{1}{14}$) ^½

1 M 2

Anisotropic long range interactions H_2-H_2 , H_2-He

Appendix A1 *continued*

N	$l_{A'}l'_A, l_{B'}l'_B$	$L_A L_B M$							
		110	111	310	311	130	131	330	331
10	32, 12	24 $(\frac{2}{7})^{\frac{1}{2}}$	9 $(\frac{2}{7})^{\frac{1}{2}}$	-4 (6) $^{\frac{1}{2}}$	$(\frac{1}{6})^{\frac{1}{2}}$	-8 $(\frac{3}{7})^{\frac{1}{2}}$	$(\frac{1}{21})^{\frac{1}{2}}$	8	$-\frac{8}{9}$
		332	333	510	511	530	531	532	533
		$\frac{2}{45}$	$\frac{1}{360}$	8 $(\frac{3}{7})^{\frac{1}{2}}$	$-\frac{11}{5} (\frac{1}{21})^{\frac{1}{2}}$	$-32 (\frac{2}{7})^{\frac{1}{2}}$	$\frac{239}{45} (\frac{1}{14})^{\frac{1}{2}}$	$-\frac{1}{45} (\frac{7}{2})^{\frac{1}{2}}$	$\frac{1}{360} (\frac{1}{14})^{\frac{1}{2}}$
10	42, 11	200	220	221	222	400	420	421	422
		-25 $(\frac{2}{21})^{\frac{1}{2}}$	20 $(\frac{1}{21})^{\frac{1}{2}}$	$-\frac{5}{3} (\frac{1}{21})^{\frac{1}{2}}$	$-\frac{5}{12} (\frac{1}{21})^{\frac{1}{2}}$	12 $(\frac{15}{77})^{\frac{1}{2}}$	$-9 (\frac{30}{77})^{\frac{1}{2}}$	$(\frac{33}{70})^{\frac{1}{2}}$	$-\frac{3}{4} (\frac{3}{770})^{\frac{1}{2}}$
		600	620	621	622				
		-7 $(\frac{5}{33})^{\frac{1}{2}}$	19 $(\frac{10}{33})^{\frac{1}{2}}$	$-\frac{1}{3} (\frac{55}{6})^{\frac{1}{2}}$	$\frac{1}{3} (\frac{2}{165})^{\frac{1}{2}}$				
10	41, 21	310	311	330	331	332	333	510	511
		-6 (10) $^{\frac{1}{2}}$	3 $(\frac{5}{2})^{\frac{1}{2}}$	8 $(\frac{5}{3})^{\frac{1}{2}}$	$-\frac{1}{4} (15)^{\frac{1}{2}}$	0	$\frac{1}{144} (\frac{1}{15})^{\frac{1}{2}}$	6 (2) $^{\frac{1}{2}}$	$-\frac{9}{5} (\frac{1}{2})^{\frac{1}{2}}$
		530	531	532	533				
		-38 $(\frac{1}{3})^{\frac{1}{2}}$	$\frac{16}{5} (\frac{1}{3})^{\frac{1}{2}}$	$-\frac{1}{10} (\frac{1}{3})^{\frac{1}{2}}$	$\frac{1}{360} (\frac{1}{3})^{\frac{1}{2}}$				
10	41, 12	310	311	330	331	332	333	510	511
		-3 (10) $^{\frac{1}{2}}$	$-(\frac{5}{2})^{\frac{1}{2}}$	4 $(\frac{5}{3})^{\frac{1}{2}}$	$-\frac{1}{6} (\frac{5}{3})^{\frac{1}{2}}$	$-\frac{1}{12} (\frac{1}{15})^{\frac{1}{2}}$	0	3 (2) $^{\frac{1}{2}}$	$-\frac{1}{5} (\frac{1}{2})^{\frac{1}{2}}$
		530	531	532	533				
		-19 $(\frac{1}{3})^{\frac{1}{2}}$	$\frac{22}{15} (\frac{1}{3})^{\frac{1}{2}}$	$-\frac{1}{30} (\frac{1}{3})^{\frac{1}{2}}$	0				
10	51, 11	400	420	421	422	600	620	621	622
		6 $(\frac{15}{11})^{\frac{1}{2}}$	$-3 (\frac{30}{11})^{\frac{1}{2}}$	$(\frac{6}{55})^{\frac{1}{2}}$	$\frac{1}{2} (\frac{1}{330})^{\frac{1}{2}}$	$-7 (\frac{2}{11})^{\frac{1}{2}}$	29 $(\frac{1}{11})^{\frac{1}{2}}$	$-\frac{8}{3} (\frac{1}{11})^{\frac{1}{2}}$	$\frac{1}{12} (\frac{1}{11})^{\frac{1}{2}}$

Appendix A2. STO- n (GTO) expansions of 2p, 3d and 4f Slater functions with exponents $\zeta = 1.00^\dagger$.

No.	2p		3d		4f	
	Exponents	Coefficients	Exponents	Coefficients	Exponents	Coefficients
1	0.176068 ($S=0.975884$)	1.0	0.130272 ($S=0.974636$)	1.0	0.103388 ($S=0.973893$)	1.0
2	0.432603 0.106913 ($S=0.998453$)	0.452304 0.671384	0.278345 0.083484 ($S=0.998508$)	0.465498 0.665606	0.200666 0.068657 ($S=0.998556$)	0.476917 0.658743
3	0.917879 0.236956 0.080548 ($S=0.999866$)	0.161987 0.562813 0.425790	0.564903 0.176130 0.067659 ($S=0.999873$)	0.147163 0.558274 0.452630	0.348326 0.125124 0.053593 ($S=0.999900$)	0.173495 0.596123 0.394342
4	1.864486 0.481655 0.168824 0.066743 ($S=0.999985$)	0.053971 0.275794 0.551809 0.276269	0.926279 0.293518 0.118903 0.052757 ($S=0.999989$)	0.057171 0.303518 0.562625 0.242726	0.569633 0.207617 0.093042 0.044754 ($S=0.999992$)	0.058918 0.318839 0.564051 0.228825
5	3.653832 0.934948 0.326000 0.132100 0.057317 ($S=0.999998$)	0.017855 0.111998 0.355392 0.496813 0.177955	1.639533 0.523810 0.215016 0.098836 0.047291 ($S=0.999999$)	0.017712 0.118686 0.371455 0.493830 0.166067	0.901197 0.331898 0.151474 0.076163 0.039435 ($S=0.999999$)	0.019488 0.135647 0.402190 0.475243 0.139715

\dagger These expansions have been obtained with the aid of the computer program GTOFIT (Wachters, A. J. H., Van der Velde, G. A., 1968), using the criterion of maximum overlap [36]. In parentheses the values of the resulting overlap integrals S are given. The GTO exponents α_i for a Slater exponent ζ different from 1.00 can be obtained from the scaling relation [35]: $\alpha_i = \zeta^2 \chi_i$, where χ_i are the tabulated GTO exponents; the expansion coefficients C_i are the same as the tabulated ones. *Note added in proof.*—Similar expansions have been made earlier by Stewart [53].

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