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On the many-body contributions to the interaction polarisability and hyperpolarisability of He_n

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The many-body contributions to the interaction polarisability and hyperpolarisability of He_n ($n = 3, 4, 5$), for various configurations and distances have been determined and analysed. Several cases have been found where the three-body terms contribute more than 20% to $\Delta\alpha$ or $\Delta\gamma$ of He_n. The remarkable dependence of the above interaction properties on the internuclear distances and the shape of the cluster has been demonstrated. The interaction hyperpolarisabilities are shown to be uniquely sensitive probes of the electronic structure changes induced by variation of the cluster configuration. The results were computed by employing a computational procedure which relies on an *ab initio* wave function, McWeeny's et al. coupled Hartree-Fock perturbation theory and an efficient algorithm for the determination of hyperpolarisabilities starting from a non-orthogonal basis set. The function counterpoise method has been used to reduce the basis set superposition error.

Key words: Polarisability — Hyperpolarisability — Perturbation theory — Helium

1. Introduction

The polarisability, α, of atoms or molecules and the second hyperpolarisability, γ, determine the distortion of the species by electric fields [1]. Both properties are essential for the understanding of the induced moments of atoms and molecules, the determination and analysis of which is the major goal of our studies. The second hyperpolarisability is associated with various processes (e.g.

the Kerr effect, induced second harmonic generation, the third harmonic generation, four wave mixing [2]) and it has been instrumental in the understanding of chemical reactivity, intermolecular forces, etc. [1]. Further, it provides a stringent criterion to test the quality of a wave function and especially the description of the outer regions of the charge cloud. Thus, the second hyperpolarisability, due to its many applications and the fundamental interest it presents, is the subject of intensive current research [2–5].

The objective of this communication is to report and analyse the interaction polarisability, $\Delta\alpha$, and hyperpolarisability, $\Delta\gamma$, of some helium clusters He_n ($n=3,4,5$) and in particular to discuss the many-body contributions to these (that is the two-, three-, four-, and five-body terms) and their dependence on geometry elements (form of the cluster and internuclear distances). The helium clusters have often been considered as a prototype system for the study of many-body effects [6–8]. More specifically we consider:

(a) The two- and three-body contributions to $\Delta\alpha$ and $\Delta\gamma$ of He_3 and the variation of these terms with interatomic distance (Fig. 1). The change of the above contributions with the angle Θ (Fig. 1) is also discussed.

(b) The effect of basis set variation on the two- and three-body contributions to $\Delta\alpha$ and $\Delta\gamma$ of He_3. This effect is also examined as a function of the internuclear distance.

(c) The various many-body contributions to $\Delta\alpha$ and $\Delta\gamma$ of He_n ($n=4,5$). It is added that for He_4 we employ two configurations (linear and tetrahedral) and each of these is examined by using two interatomic distances (4.0 and 6.0 a.u.).

(d) The effect of increasing the number of atoms in helium clusters on $\Delta\alpha$ and $\Delta\gamma$.

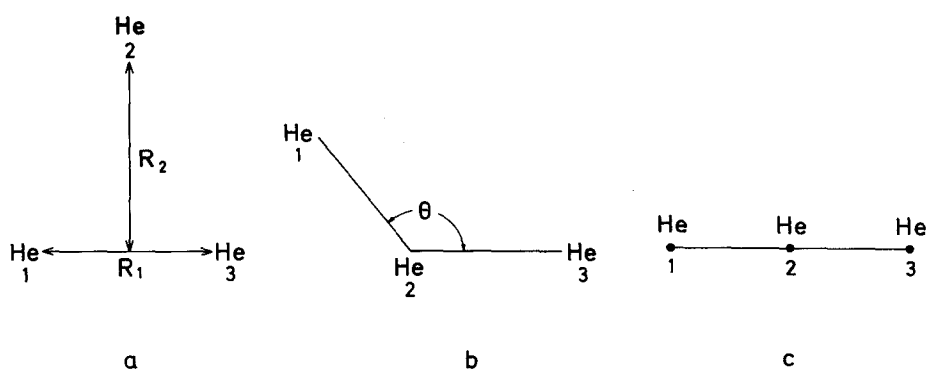

Fig. 1. Configurations of He_3 and the definition of R_1, R_2 and the angle Θ

The many-body contributions to the total interaction energy of clusters have been the subject of several theoretical studies [6, 8, 9], because these effects are likely to be significant in the study of properties of all states of matter. For example the three-body potential has been suggested to be of importance in determining the properties of rare gas solids [6b, 10]. [11] reports several reviews which discuss the importance of the many-body effects. However, the information concerning the many-body contributions to the electric properties (both linear and non-linear) of clusters is very limited. The results reported here are complementary to previous studies of many-body effects and they are considered as a starting point for more refined calculations.

The computation of the polarisability and hyperpolarisability components [12] has been performed using an *ab initio* wave function [4] and McWeeny's et al. [13] coupled Hartree–Fock perturbation theory. The function counterpoise approach has been used to reduce the basis set superposition error [8, 14].

2. Method

The properties have been computed by employing a method which relies on:

(a) An *ab initio* wave function determined by using a modified version of POLYATOM II (QCPE 238 and [4]).

(b) McWeeny's et al. coupled Hartree–Fock perturbation theory [13].

(c) An algorithm for the efficient determination of hyperpolarisability components starting from a non-orthogonal basis set [4].

(d) The function counterpoise method [14]. This procedure reduces [15] the basis set superposition error (BSSE), which results from the effective expansion of the size of the basis set when the atoms interact [16]. It is noted that although the function counterpoise method [14] is considered to be helpful [16], there is still some controversy connected with it [16, 17]. In this work we employ a generalization of the Boys and Bernardi approach [14], introduced by Wells and Wilson [8] for the case of many-body clusters. This generalization is called by the authors [8] the "site-site function counterpoise" (SSFC) method. The total interaction property, ΔP, is given by:

$$\Delta P = \frac{1}{2!}\sum_{ij}{}' P_{ij} + \frac{1}{3!}\sum_{ijk}{}' P_{ijk} + \cdots$$

where P_{ij}, $P_{ijk}\ldots$ in the SSFC approximation are given by [8]:

$$P_{ij} = P(ijG_{klm}\ldots) - P(iG_{jkl}\ldots) - P(jG_{ikl}\ldots)$$

$$P_{ijk} = P(ijkG_{lmn}\ldots) - P_{ij} - P_{jk} - P_{kl} - P(iG_{jkl}\ldots) - P(jG_{ikl}\ldots) - P(kG_{ijl}\ldots)$$

$G_{ijk}\ldots$ is a "ghost" center [5, 18].

For completeness we note that $G_{ij}\ldots$ practically means that in the computations, we use the full set of orbitals which correspond to atoms $i, j\ldots$ while the nuclear

charge and the number of electrons which belong to $i, j \ldots$ have been set to zero. It is noted that in most cases the BSSE has a considerable effect. Thus for example for He_4 ($R = 4.0$ a.u., Fig. 5) the corrected for BSSE and the non corrected $\Delta\gamma$ values are -22.6 a.u. and -45.8 a.u. respectively.

(e) A basis set optimised with respect to the polarisability and hyperpolarisability of He. Extensive experimentation, involving several standard basis sets, extension with polarisation functions and a wide variety of exponents has been performed. The primary aim was to derive basis sets which should be compact (thus computationally, relatively, economic) and which would allow the physically correct description of the interaction properties (which are of interest in this work). Analysis of the calculations led to the following choice for the basis set [5]:

$$31G[19]+p(0.59)p(0.1)d(0.1)$$

The computed polarisability and hyperpolarisability values, using this basis set, together with the experimentally determined ones, are presented in Table 1. The experimental γ values with respect to which the optimization has been carried out is 53.6 a.u. [20], because this value is considered accurate to better than ±10% [21]. Other experimental values are also given in Table 1. For completeness it is added that there are several high quality theoretical results for the second hyperpolarisability of He [22-24].

It has been shown that employing the above basis set, the determined $\Delta\alpha(R)$ of He_2[5] is in reasonably good agreement with other theoretical results and in particular those determined by the spectral model of Proffitt, Keto and Frommhold, which are expected to approximate $\Delta\alpha(R)$ of He_2 to within ±20%, on average for 3.6 a.u. $< R <$ 5.0 a.u. [25a]. These observations allow some optimism concerning the adequacy of the employed wave function to approximate the interaction properties of the considered helium clusters.

The effect of changes in the basis set (and the exponents in particular) on α and γ of He together with the resulting changes in ΔP (P in the present work stands for either α or γ) of He_2 has been commented on in [5].

Table 1. The polarisability and second hyperpolarisability of He by employing the basis set: $31G[16]+p(0.59)p(0.1)d(0.1)$

α(a.u.)[a]		γ(a.u.)[a]	
Calculated	Experimental	Calculated	Experimental
1.26[5]	1.38[26]	52.3[5]	53.6±4[20] 45.3[21][b] 51.6±7.9[27]

[a] 1 a.u. of polarisability $\simeq 0.148176 \times 10^{-24}$ esu $\simeq 0.164867 \times 10^{-40}$ C^2 m^2 J^{-1}. 1 a.u. of second hyperpolarisability $\simeq 0.503717 \times 10^{-39}$ esu $\simeq 0.623597 \times 10^{-64}$ C^4 m^4 J^{-3}

[b] This value is associated with an estimated factor-of-three uncertainty [21]

It is demonstrated (Table 2) that ΔP_{ij} and ΔP_{123} of He_3 have a remarkable dependence on the basis set. Further, this dependence is a function of the distance between the interacting atoms.

The polarisability and hyperpolarisability components for the linear clusters, obey the following relationships:

$$\alpha_{xx} = \alpha_{yy},$$

$$\gamma_{xxxx} = \gamma_{yyyy} = 3\gamma_{xxyy},$$

$$\gamma_{xxzz} = \gamma_{yyzz},$$

where the cluster lies on the z axis. The same symmetry relationships are also obeyed for He_3, when the nuclei are placed at the corners of an equilateral triangle.

For the tetrahedral cluster (T_d symmetry group), we have:

$$\alpha_{xx} = \alpha_{yy} = \alpha_{zz},$$

$$\gamma_{xxxx} = \gamma_{yyyy} = \gamma_{zzzz},$$

$$\gamma_{xxyy} = \gamma_{xxzz} = \gamma_{yyzz}.$$

Thus for the linear ($D_{\infty v}$) and the tetrahedral (T_d) clusters we have determined 3 and 2 hyperpolarisability components, respectively. For the remaining configurations all 6 components of γ were calculated, and in all cases the average property values were given by [12]. All the polarisability and hyperpolarisability components employed in this study are available on request.

The convergence criteria adopted for the self-consistent computation of the density matrices [13] are:

$$|{}^kR^n_{ij} - {}^{k-i}R^n_{ij}| < 10^{-6}$$

for every ijth element of the nth order correction to the density matrix, ${}^kR^n_{ij}$, at the kth cycle. The SCF was performed wholly in double precision as were the calculations of all sums and inner products for the perturbed density matrices. However, the intermediate results occurring in the latter case were stored in single precision.

Table 2. The effect of the basis set variation on some properties of He_3[a,b]

Basis set	R	$\alpha_{12}(=\alpha_{13}=\alpha_{23})$	α_{123}	$\gamma_{12}(=\gamma_{13}=\gamma_{23})$	γ_{123}
A[c]	4.5	−0.016	0.003	−3.990	1.410
	6.5	0.0[d]	0.0[d]	−0.413	0.009
B[e]	4.5	−0.015	0.003	−3.070	1.262
	6.5	0.0[d]	0.0[d]	−0.238	0.006

[a] The results are in atomic units

[b] The nuclei of He_3 form an equilateral triangle of side R (Fig. 1a)

[c] 31G[19]+$p(0.59)p(0.1)d(0.1)$

[d] The property value is approximated to 0.0 because its absolute value is less than 10^{-3}

[e] 31G[19]+$p(0.8)p(0.09)d(0.15)$

The properties are reported in atomic units. Conversion factors to other units are given in footnote a of Table 1.

The calculations presented here were performed on a 32-bit computer (3240 Perkin-Elmer) with a 2-Mbyte core.

3. Results and discussion

From the results of Table 3 we observe that the contribution of P_{123} to ΔP for He_3 (Fig. 1c) is rather small, except at 6.0 a.u., where α_{123} contributes 20.2% to $|\Delta\alpha|$.

We have taken He_3 as a model system and considered in detail how $\Delta\gamma$, γ_{12}, γ_{13} and γ_{123} vary as a function of R_1 or R_2 (Fig. 1a). It is observed (Fig. 2) that as R_1 increases, $\Delta\gamma$, γ_{12}, γ_{13} tend to zero from negative values, while γ_{123} from positive. It is also seen that the variation of γ_{13} is not affected (to a good approximation) by increasing the distance of He_1 from He_2 and He_3. This shows

Table 3. The interaction polarisabilities and hyperpolarisabilities, as well as the various contributions to them of He_n ($n = 3, 4, 5$). The results are in atomic units

Species	Interaction polarisabilities	R[a]		Interaction hyperpolarisabilities	R[a]	
		4.0	6.0		4.0	6.0
He_3[b]	$\Sigma\alpha_{ij}$	−0.066	−0.001	$\Sigma\gamma_{ij}$	−14.462	−1.792
	α_{123}	−0.002	0.0[c]	γ_{123}	−0.222	0.032
	$\Delta\alpha$	−0.068	−0.001	$\Delta\gamma$	−14.684	−1.760
He_4[d]	$\Sigma\alpha_{ij}$	−0.10	−0.002	$\Sigma\gamma_{ij}$	−22.215	−2.742
	$\Sigma\alpha_{ijk}$	0.001	0.0[c]	$\Sigma\gamma_{ijk}$	−0.355	0.071
	α_{1234}	0.0[c]	0.0	γ_{1234}	−0.074	0.002
	$\Delta\alpha$	−0.099	−0.002	$\Delta\gamma$	−22.644	−2.669
He_4[e]	$\Sigma\alpha_{ij}$	−0.221	−0.005	$\Sigma\gamma_{ij}$	−35.179	−4.124
	$\Sigma\alpha_{ijk}$	0.047	0.0[c]	$\Sigma\gamma_{ijk}$	13.832	0.178
	α_{1234}	−0.004	0.0[c]	γ_{1234}	−1.749	−0.001
	$\Delta\alpha$	−0.178	−0.005	$\Delta\gamma$	−23.096	−3.947
He_5[f]	$\Sigma\alpha_{ij}$	−0.138		$\Sigma\gamma_{ij}$	−29.737	
	$\Sigma\alpha_{ijk}$	0.002		$\Sigma\gamma_{ijk}$	−0.677	
	$\Sigma\alpha_{ijkl}$	0.001		$\Sigma\gamma_{ijkl}$	−0.233	
	α_{12345}	0.0[c]		γ_{12345}	0.150	
	$\Delta\alpha$	−0.135		$\Delta\gamma$	−30.497	

[a] In the linear clusters, R is the distance between two successive helium atoms (Figs. 1c and 5), while in the tetrahedral cluster, R is the distance of two helium atoms lying on a diagonal of the faces of the cube (Fig. 6)

[b] Linear cluster, Fig. 1c

[c] The property value is approximated to 0.0 because its absolute value is less than 10^{-3}

[d] Linear cluster, Fig. 5

[e] Tetrahedral cluster, Fig. 6

[f] Linear cluster, Fig. 5

how a two-body interaction is affected by a third body (Fig. 2). The change of $\Delta\gamma$, γ_{12} and γ_{123} with R_2 (R_1 being kept constant) obeys the above defined trends (Fig. 3). Furthermore, it is observed again that a two-body interaction is not practically affected by changing the distance of a third body (Fig. 3). It is noted that this remark is verified by the results of Fig. 4.

The above defined trends for the variation of $\Delta\gamma$, γ_{12}, γ_{13} and γ_{123} as a function of R_1 or R_2 are followed by the change of $\Delta\alpha$, α_{12}, α_{13} and α_{123} of He_3 as a function of either at the above distances or the angle Θ.

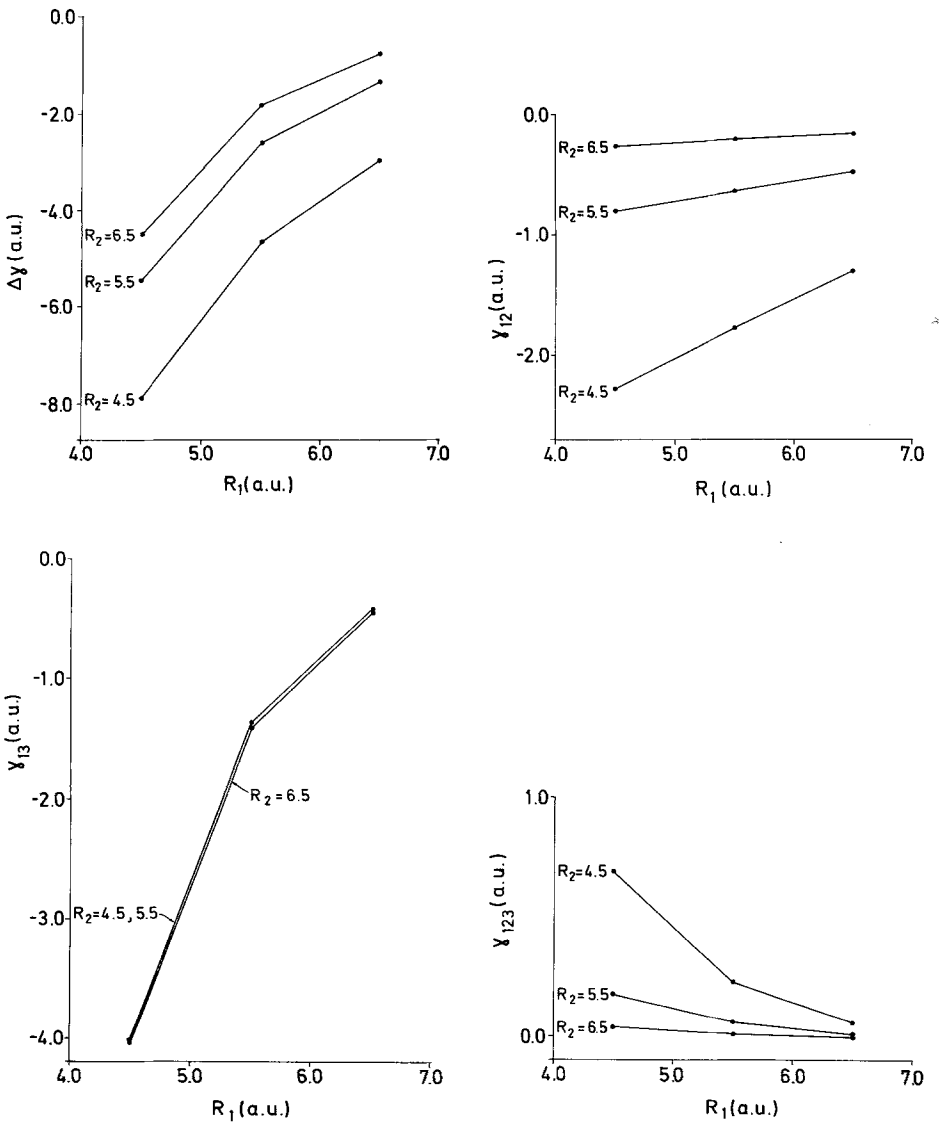

Fig. 2. Variation of $\Delta\gamma$, γ_{12}, γ_{13} and γ_{123} of He_3 with R_1

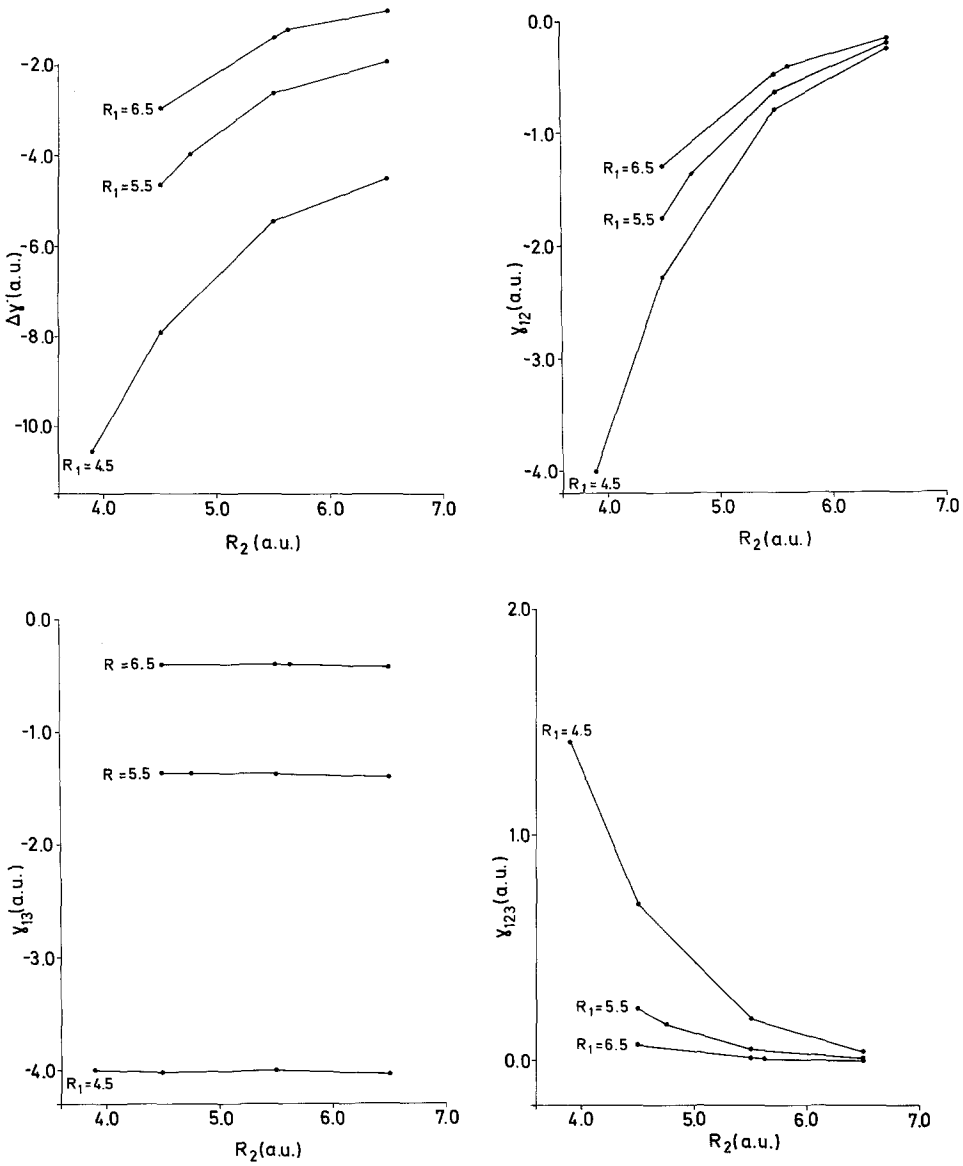

Fig. 3. Variation of $\Delta\gamma$, γ_{12}, γ_{13} and γ_{123} of He_3 with R_2

Table 3 shows that the contribution of ΣP_{ijk} to ΔP for He_4 (linear, Fig. 5), similar to He_3, is very small, except for $\Sigma\alpha_{ijk}$, at 6.0 a.u., where its contribution to $|\Delta\alpha|$ is 31.3%. In the other cases the contribution of $|\Sigma P_{ij}|$ to $|\Delta P|$ is more than an order of magnitude greater than that of $|\Delta P_{ijk}|$. The four-body contribution to both $\Delta\alpha$ and $\Delta\gamma$ is negligibly small (Table 3).

It is seen (Table 3) that $\Sigma\gamma_{ijk}$ of He_4 (tetrahedral, Fig. 6) has a remarkable contribution to $|\Delta\gamma|$, at 4.0 a.u. (59.9%). Similarly a high contribution to $|\Delta\alpha|$ of

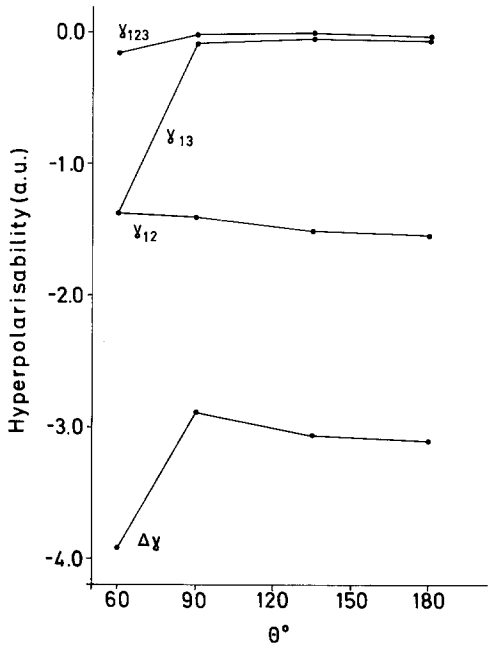

Fig. 4. Variation of $\Delta\gamma$, γ_{12}, γ_{13} and γ_{123} of He_3 with the angle Θ

He_4 (tetrahedral, 4.0 a.u.) is also made by $\Sigma\alpha_{ijk}$ (26.2%). A noticeable contribution (7.6%) is also made by γ_{1234} (at 4.0 a.u.). Further it is seen that $|\Sigma P_{ij}| > |\Delta P|$ (Table 3).

We observe that $|\Delta P|$ is larger in the tetrahedral cluster, than in the linear, as one could have expected, due to all interactions being nearest neighbour in the former configuration. The difference is more pronounced in $\Delta\alpha$ than $\Delta\gamma$, which is unexpected as generally γ is by far the more sensitive property (Table 3). In particular we note the difference in magnitude and sometimes in sign, which is observed in the two- three- and four-body contributions to $\Delta\alpha$ and $\Delta\gamma$ for the two configurations (linear and tetrahedral). This emphasizes the need for a detailed study of the many-body effects on the electric linearities and non-linearities of clusters.

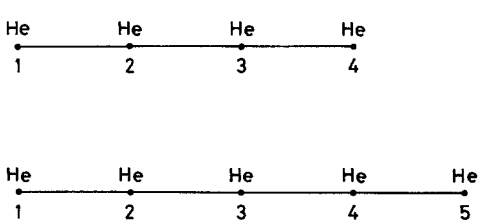

Fig. 5. The linear He_4 and He_5 clusters

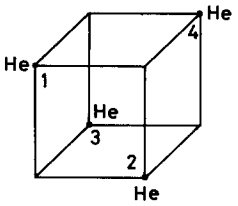

Fig. 6. The tetrahedral cluster He_4

The major contribution to ΔP of He_5 (Fig. 6) comes from ΣP_{ij} (Table 3). The other terms contribute very little to ΔP and this contribution becomes less, in percentage terms as m increases (where m refers to the m-body term).

From the present rather limited number of data (Table 4), it is seen that on increasing the number of helium atoms in the linear cluster, the quantity $|\Delta P_{n+1} - \Delta P_n|$ passes through a maximum (the exact meaning of this difference is given in footnote b of Table 4).

It is also observed (Table 4) that if we consider the linear cluster He_n as $n-1$ interacting dimers (we only take into account the dimers formed by successive helium atoms), then the approximated interaction polarisability, $\Delta\alpha'$ (footnote c of Table 4) has an average difference, with respect to $\Delta\alpha$, of 7.1%. The approximated interaction hyperpolarisability, $\Delta\gamma'$, has an average difference, with respect to $\Delta\gamma$, of 9.7%. It is noted that the individual differences in $\Delta\gamma'$ (7.7%, 10.3% and 11.2%) tend to increase with n (where n is the number of helium atoms). The results of Table 5 show that, in general, the absolute value of the average n-body contribution to $\Delta\alpha$ of He_n reduces with n (one exception has been observed).

Table 4. The effect of increasing the number of atoms in helium clusters[a] on $\Delta\alpha$ and $\Delta\gamma$

Linear cluster	$\Delta\alpha$	$\Delta\alpha_{n+1} - \Delta\alpha_n$[b]	$\Delta\alpha'$[c]	$\Delta\gamma$	$\Delta\gamma_{n+1} - \Delta\gamma_n$[b]	$\Delta\gamma'$[c]
He_2	−0.037 [5]			−6.773 [5]		
		−0.031			−7.910	
He_3	−0.068		−0.074(8.8%)[d]	−14.683		−13.546(7.7%)[d]
		−0.035			−7.961	
He_4	−0.103		−0.111(7.8%)[d]	−22.644		−20.320(10.3%)[d]
		−0.033			−7.853	
He_5	−0.136		−0.148(8.8%)[d]	−30.497		−27.093(11.2%)[d]

[a] Footnote a of Table 3. In this case $R = 4.0$ a.u.

[b] The difference $\Delta P_{n+1} - \Delta P_n$ is defined by subtracting the interaction property which corresponds to He_n from that of He_{n+1}

[c] $\Delta P'(\Delta\alpha'$ or $\Delta\gamma')$ of He_n is formed by multiplying ΔP of He_2 with $n-1$

[d] The percents in parentheses denote the error of $\Delta P'$ with respect to ΔP

Table 5. The average[a] n-body contributions to the interaction polarisability and hyperpolarisability of He_n $(n = 3, 4, 5)$[b]

Average contribution	He_2	He_3	He_4	He_5	Average contribution	He_2	He_3	He_4	He_5
$\overline{\Sigma\alpha_{ij}}$	(-0.037)[c]	-0.022	-0.017	-0.014	$\overline{\Sigma\gamma_{ij}}$	(-6.773)[c]	-4.821	-3.702	-2.974
$\overline{\Sigma\alpha_{ijk}}$		(-0.002)	0.0[d]	0.0[d]	$\overline{\Sigma\gamma_{ijk}}$		(-0.222)	-0.089	-0.068
$\overline{\Sigma\alpha_{ijkl}}$			(0.0)[d]	0.0[d]	$\overline{\Sigma\gamma_{ijkl}}$			(-0.074)	-0.047

[a] $\overline{\Sigma P_{ij}}$ is given by $\Sigma P_{ij}/m$, where m is the number of the 2-body interactions in the cluster. $\overline{\Sigma P_{ijk}}$ and $\overline{\Sigma P_{ijkl}}$ are defined similarly. In parentheses are the values for which $m = 1$

[b] The distance between two successive helium atoms is $R = 4.0$ a.u.

[c] The value is from [5]

[d] The property value is approximated to 0.0 because its absolute value is less than 10^{-3}

4. Concluding remarks

The choice of the right basis set for polarisability and in particular hyperpolarisability calculations is of crucial importance. Our experience which relies on a large number of computations shows that a basis set optimized with respect to α and γ of a model compound is a reasonable choice for computations (of these properties) on other similar systems. Thus we have optimized the basis set (with which we have performed the computations for He_n) with respect to the experimental α and γ of He. Further it has been demonstrated [5] that this basis set has given $\Delta\alpha$ of He_2 in reasonably good agreement with the best reported results. This point combined with the fact that the leading contribution to $\Delta\alpha$ comes from the sum of the two-body terms, indicates that $\Delta\alpha$ for He_n ($n=3, 4, 5$) is in general well represented (at the Hartree–Fock level of approximation).

The above observations and indications allow some optimism concerning the quality of the hyperpolarisability results, although their accuracy is more hard to appraise. However, the pair $\Delta\alpha$ and $\Delta\gamma$, through their similarities and differences establishes certain general trends concerning the change of polarisation properties of He_n with various parameters (e.g. geometry and size of cluster). Specifically the present calculations have shown:

(a) $|\Delta\alpha|$ decreases much more rapidly than $|\Delta\gamma|$ with increasing internuclear distance.

(b) In all the considered cases the main contribution to $\Delta\alpha$ and $\Delta\gamma$ is from the sum of the two-body terms.

(c) There are some cases (and most notably in the tetrahedral cluster) where the three-body terms have a large contribution.

(d) $\Sigma P_{ij} > \Sigma P_{ijk} > \Sigma P_{ijkl}$.

(e) The term γ_{1234}, in the tetrahedral cluster (at 4.0 a.u.), makes a relatively large contribution. This observation underlines the necessity for a careful study of the n-body terms (where $n>3$), as a function of size and configuration, because in medium (and even more in large) clusters these terms are likely to have a considerable contribution, especially in favourable configurations (like the tetrahedron).

The present work may be considered as a pilot study, which tries to answer the question: Do the many-body terms contribute significantly to $\Delta\alpha$ or $\Delta\gamma$ of small or medium size clusters? The present results involve several examples where the three-body terms contribute significantly (>20%) to $\Delta\alpha$ or $\Delta\gamma$ of He_n and therefore their automatic neglect should be avoided (unless there are arguments to support such a choice). Further the remarkable dependence of the relative contribution of these terms to $\Delta\alpha$ or $\Delta\gamma$ on the internuclear distance and the shape of the cluster has been shown. We believe that these findings are interesting enough to suggest a further, more extensive and refined, study on the efficient and economic ways to determine the polarisability and hyperpolarisability (which as fundamental constants provide valuable information about the electronic structure [1]) of clusters.

The structure and properties of small elemental clusters (and in particular their variation with cluster size) present great interest (they have been used as models for catalysis, chemisorption etc.) [25b]. The present work illuminates certain aspects of their induced moments, which besides their fundamental interest, are of importance because they modify the energy (and sometimes considerably) and therefore affect the stability of those clusters.

References and notes

1. Buckingham AD, Orr BJ (1967) Q Rev Chem Soc 21:195
2. Shelton DP (1986) J Chem Phys 85:4234
3. a. Pantinakis A, Dean KJ, Buckingham AD (1985) Chem Phys Lett 120:135
   b. Liu S-Y, Dykstra CE, Kolenbrander K, Lisy JM (1986) J Chem Phys 85:2077
   c. Sekino H, Bartlett RJ (1986) J Chem Phys 85:976
   d. Silverman JN, Bishop DM, Pipin J (1986) Phys Rev Lett 56:1358
4. Waite J, Papadopoulos MG (1986) J Chem Phys 85:2831
5. Papadopoulos MG, Waite J (1987) Chem Phys Lett 135:361
6. a. Novaro OA, Beltran-Lopez V (1972) J Chem Phys 56:815
   b. Bruch LW, Novaro O, Flores A (1977) J Chem Phys 67:2371
   c. Wells BH, Wilson S (1986) Mol Phys 57:421
   d. Wells BH, Wilson S (1985) Mol Phys 55:199
7. Pérez JJ, Clarke JHR, Hinchliffe A (1984) Chem Phys Lett 104:583
8. Wells BH, Wilson S (1983) Chem Phys Lett 101:429
9. Novaro O, Kołos W (1977) J Chem Phys 67:5066
10. Klein ML, Venables JA (1971) Rare gas solids. Wiley, New York
11. Meath WJ, Aziz RA (1984) Mol Phys 52:225
12. The average polarisability and second hyperpolarisability [1] are given by:

    $\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$

    $\gamma = \frac{1}{5}(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{xxzz} + 2\gamma_{yyzz})$

    where x, y and z denote Cartesian components
13. a. McWeeny R (1962) Phys Rev 126:1028
    b. Diercksen G, McWeeny R (1966) J Chem Phys 44:3554
    c. Dodds JL, McWeeney R, Raynes WT, Riley JP (1977) Mol Phys 33:611
    d. Dodds JL, McWeeney R, Sadlej AJ (1977) Mol Phys 34:1779
14. Boys SF, Bernardi F (1970) Mol Phys 19:553
15. Amorilli C, McWeeny R (1986) Chem Phys Lett 128:11
16. Buckingham AD (1987). In: Kilmister CW (ed) Schrödinger centenary celebration of a polymath, p 112. Cambridge University Press, Cambridge
17. a. Collins JR, Gallup GA (1986) Chem Phys Lett 129:329
    b. Gutowski M, van Duijneveldt FB, Chalasinski G, Piela L (1986) Chem Phys Lett 129:325
18. Ostlund NS, Merrifield DL (1976) Chem Phys Lett 39:612
19. Binkley JS, Whiteside RA, Hariharan PC, Seeger R, Pople JA, Hehre WJ, Newton MD (1978) Gaussian 76, QCPE 11:368
20. Buckingham AD, Dunmur DA (1968) Trans Farad Soc 64:1776
21. Finn RS, Ward JF (1971) Phys Rev Lett 26:285
22. Sitz P, Yaris R (1968) J Chem Phys 49:3546
23. Klingbeil R (1973) Phys Rev A7:48
24. Jaszunski M, Roos BO (1984) Mol Phys 52:1209
25. a. Proffitt MH, Ketto JW, Frommhold L (1981) Can J Phys 59:1459
    b. Harrison RJ, Handy NC (1986) Chem Phys Lett 123:321
26. Teachout RR, Pack RT (1971) At Data 3:195
27. Boyle LL, Buckingham AD, Disch RL, Dunmur DA (1966) J Chem Phys 45:1318