Bound-state energies in argon trimers via a variational expansion: The effects from many-body corrections

I. Baccarelli, F. A. Gianturco, T. González-Lezana, G. Delgado-Barrio, S. Miret-Artés et al.

Citation: *J. Chem. Phys.* **122**, 144319 (2005); doi: 10.1063/1.1879972

View online: <http://dx.doi.org/10.1063/1.1879972>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v122/i14>

Published by the [American Institute of Physics](#).

Additional information on *J. Chem. Phys.*

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT

**ALL THE PHYSICS
OUTSIDE OF
YOUR JOURNALS.**

physics
today

www.physicstoday.org

Bound-state energies in argon trimers via a variational expansion: The effects from many-body corrections

I. Baccarelli and F. A. Gianturco^{a)}

*Department of Chemistry and Istituto Nazionale di fisica Nucleare (INFN),
University of Rome La Sapienza, 00185 Rome, Italy*

T. González-Lezana, G. Delgado-Barrio, S. Miret-Artés, and P. Villarreal

*Instituto de Matematicas y Fisica Fundamental, Consejo Superior de Investigaciones Cientificas, Serrano,
123, 28006 Madrid, Spain*

(Received 20 January 2005; accepted 2 February 2005; published online 13 April 2005)

In this paper we study the bound-state energies and geometries of Ar_3 for $J=0$, using the distributed Gaussian functions method that provides a configurational description of the different structures contributing to these states. Atom-atom potentials are employed and three-body long-range effects are also included in the computational treatment by adding to the sum of potentials the Axilrod–Teller triple-dipole correction for the whole rotationless energy spectrum. An estimate of the total number of bound states for the Ar trimer is given. With respect to previous calculations, limited to the lower-lying states, our results show slightly larger nonadditive effects and are further able to predict the full range of the bound spectrum. Changes on the geometries of a large part of the vibrationally excited states of Ar_3 when the Axilrod–Teller term is included in the molecular potential are found by the present study. © 2005 American Institute of Physics. [DOI: 10.1063/1.1879972]

I. INTRODUCTION

To attain accurate descriptions of their properties and an understanding of the nanoscopic behavior of atomic and molecular aggregates (and, ultimately, of the condensed phase of materials) requires a correspondingly accurate and realistic knowledge of their intermolecular forces. In particular, ensembles of variable size which are made up of fairly simple components, such as the neutral, identical rare gases (Rg's), have been for a long time the preferred testing ground for a broad variety of theoretical and computational analysis of such intermolecular forces.¹ In many of these studies the modeling of the relevant forces within the familiar approximation of a sum of potentials, i.e., the use of pairwise additivity to provide the full interaction, has been known to describe many phenomena reasonably well, although the marked improvement of experimental techniques has made apparent in several instances that the above scheme could not explain some of the observations.^{2–4} The earliest attempts at explaining the discrepancies involved the inclusion of the leading component of the multipolar expansion of the third-order dispersion energy in order to approximate the three-body (3B) nonadditivity effects over the two-body (2B) model implicit within the sum-of-potentials approximations: it led to the now well-known Axilrod–Teller (AT) terms in the long-range region of the interaction.^{5,6}

The success which may come from adding such corrections to the overall behavior of the interaction in a large aggregate of even simple, neutral Rg atoms is of course related to our capability of setting up a sort of zeroth-order

description of the clusters by selecting first reliable forms of the underlying 2B forces within the aggregate. They would in turn control our capability of generating a high-quality description of the spectral structure of the system, i.e., an acceptable initial approximation to the number and location of its bound states.

The study of the effect of the 3B terms in the intermolecular potential of complexes with Rg atoms has been the subject of a great number of previous works. In particular, the inclusion of nonadditive exchange corrections was found to be needed to understand the preferred crystal structure of solid argon.⁷ Theoretical calculations with the AT term added to the molecular potential explained the experimentally observed occurrence of the so-called “magic numbers” in the distribution of masses of Xe clusters.⁸ In their studies of the Ar_nBr^- ,⁹ Ar_nI^- ,⁹ and Xe_nI^- (Ref. 10) clusters, Neumark and co-workers found that it was necessary to include various nonadditive terms to bring the theoretical results for electron affinities and binding energies closer to the experimental observations. Furthermore, conclusive evidence on the need of 3B corrections to reproduce experimental results were found in a large series of recent simulations of thermodynamical properties in liquid Ar,^{11–14} Xe,^{13–15} Ne,¹⁶ and Kr.^{14,16–18}

Besides the correction to the binding energies introduced by the 3B terms, one of the issues of interest is the possible influence of such terms on the structure and geometry of the Rg complexes. The largest changes with respect to the geometries which are produced by using only 2B interactions have been reported for fluids or liquids. Thus, the radial distribution function for liquid Ar (Ref. 11) and the pair-correlation function for fluid Xe (Ref. 15) and fluid Kr (Ref. 17) were found to suffer significant alterations when the AT

^{a)}Author to whom correspondence should be addressed. FAX: +39-06-49913305. Electronic mail: fa.gianturco@caspur.it

term was included in the overall interatomic potential. These effects, however, are expected to be more important at intermediate densities where the three-atom encounters are not negligible anymore (as it happens at low densities) but the liquid structure is not as yet dominated by close-packing effects as it occurs for high densities.^{11,12} For the clusters, on the other hand, the situation seems to differ somehow and the 3B effects on the global structure of the complex are not that significant. Xu and Jager¹⁹ attributed the lengthening of the Ne–Ne bond in the Ne₂OCS cluster in comparison with the Ne₂ molecule to the 3B nonadditive interaction. The inclusion of the AT term to study the clusters which result from the combination of several Ar atoms with SF₆ (Ref. 20) and HF (Ref. 21) subunits did not yield relevant structural changes. For Ar trimer, the subject of the present study, information regarding the effects of 3B terms on the geometry of the system is limited to a few studies which mainly deal with either the vibrational ground state or the equilibrium configuration associated with the minimum of the potential-energy surface (PES). Chalasinski *et al.*,²² in their *ab initio* study of the many-body dispersion interactions for Rg complexes, predicted that the 3B effect in the equilibrium equilateral triangle would lengthen the interatomic equilibrium distance in Ar₃. Hutson and co-workers^{23,24} found only small differences between the rotational constants of the ground state for a purely 2B molecular interaction and those for a potential which also included nonadditive forces. In this sense, the effect of the AT term on the analytical expression of the centrifugal displacements for a rotating Ar₃ was considered not large enough to be taken into account when dealing with bigger Ar clusters.²⁵ Interestingly enough, an artificial increase of the AT term has been associated with an earlier appearance of the Ar₃ lowest-energy linear bound state.²⁶ An analysis of the possible influence of the AT term on the geometries associated with a broader number of vibrational bound states beyond just simply the ground state therefore constitutes an interesting task.

The aims of the present study are therefore the following: (i) to employ the argon trimer Ar₃ as a test system in order to generate its $J=0$ (rotationless) bound-state structures within a 2B sum-of-potentials modeling of the overall interaction, (ii) to select among the most recent pair potentials the one for which the highest level of accuracy in describing the dimer could be attained, and (iii) to show what sort of changes to the bound-state spectrum, with regard to both energies and structural configurations, are caused by the addition of 3B forces along the lines mentioned above.

The accurate evaluation of the bound states for a simple trimer cluster involving such many-electron atomic partners is, in fact, already a challenging problem in itself and therefore, in the present study, we intend to address it by employing a variational approach that uses expansions over Gaussian-type functions, the distributed Gaussian functions (DGF) approach, which has been introduced by us a while ago (e.g., see Refs. 27–29). We shall thus show in the following that, once a judicious check of the relative importance of possible linear configurations is included within the variational study, one can indeed attain rather high accuracy

in reproducing the full spectrum and in deciding on a reliable way for correctly finding all the numerically converged bound states provided by the calculations.

The structure of the present paper will be the following: in Sec. II we will describe the different pairwise potentials we employed in the present work and we will briefly recall the outline of the DGF method, while Sec. III will present our results obtained first by using just the 2B forces and then by adding the 3B correction. A detailed analysis of our findings will also be given in that section, while Sec. IV will finally present our conclusions.

II. THEORETICAL APPROACH

A. The interaction forces

The PES for Ar₃ is usually described via the addition of three identical atom-atom interactions. The many-body dispersion interactions in Ar₃ have been studied, e.g., in Ref. 22 by means of a supermolecular approach; the total 3B term in the van der Waals region, when the interatomic separation is that of the equilibrium separation of the related dimer, proved to be repulsive. This meant that the 3B effect would lengthen the equilibrium distance in the ground-state equilateral trimer, but the relative magnitude of the total 3B effect versus 2B effect was limited to -3.7% . Horn *et al.*³⁰ and Cooper *et al.*²³ calculated the shifts in the vibrational frequencies due to the nonadditive interactions; their results are qualitatively in agreement with each other, although the frequencies themselves are not. They estimate the redshifts due to nonadditive dispersion forces to be between 0.3 and 0.6 cm⁻¹.

In order to properly compare our results with some of the previously published data,^{23,28,30–33} we employ in the present study various different pair potentials:

- (1) The Lennard-Jones (LJ) potential,

$$V_{\text{Ar-Ar}}(R) = 4\epsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right], \quad (1)$$

whose parameters were taken from Ref. 31.

- (2) The Morse potential [coming from a numerical fitting, in the region of the well, of the potential given by Aziz and Slaman for Ar–Ar (Ref. 34)],

$$V_{\text{Ar-Ar}}(R) = D \left[e^{-2\alpha(R-R_e)} - 2e^{-\alpha(R-R_e)} \right]. \quad (2)$$

The above parameters were previously obtained in Ref. 35.

- (3) One more recent 2B potential based on the Tang–Toennies (TT) model (Ref. 36),

$$V_{\text{Ar-Ar}}(R) = Ae^{-bR} - \sum_{n=3}^5 f_{2n}(bR) \frac{C_{2n}}{R^{2n}}, \quad (3)$$

whose parameters have been calculated in Ref. 37.

We already employed the TT potential in our previous work on H⁻-doped Ar clusters.³⁸ The equilibrium distance and the well depth obtained by describing the Ar–Ar interaction with such a potential are in excellent agreement with the accurate

TABLE I. Parameters used to describe Ar–Ar interaction with three different models [Eqs. (1)–(3)], and corresponding dimer’s bound states. See main text for references.

Ar ₂					
PECs parameters			cm ^{−1}	Bound states units of ϵ	v
LJ	ϵ	119.4 K	−70.4491	−0.8489	0
			−49.2065	−0.5929	1
	σ	6.434 a.u.	−32.5700	−0.3925	2
			−20.0649	−0.2418	3
			−11.1779	−0.1347	4
			−5.3535	−0.0645	5
			−1.9909	−0.0240	6
			−0.4423	−0.0053	7
Morse	D	99.00 cm ^{−1}	−0.0170	−0.0002	8
			−83.9300		0
			−57.5206		1
			−36.0857		2
			−19.6253		3
			−8.1393		4
			−1.6278		5
			−84.4418		0
TT	b	2.031 a.u. ^{−1}	−58.1931		1
			−37.5348		2
	C_6	64.30 hartrees × (bohr ⁶)	−22.1280		3
	C_8	1623 hartrees × (bohr ⁸)	−11.4789		4
	C_{10}	49060 hartrees × (bohr ¹⁰)	−4.8941		5
			−1.4766		6
			−0.1966		7

ab initio calculations in Ref. 39 and with the semiempirical results of Aziz.⁴⁰

In Ref. 30 the Aziz–Slaman potential³⁴ was also used together with the LJ one, and in Ref. 23 the authors repeated the calculations with the LJ, the Aziz–Slaman³⁴ (denoted by them as HFD-B2) and the Aziz–Chen potential⁴¹ (denoted as HFD-C). These last two potentials have similar functional form with respect to the one based on the TT model; the differences lie in the form of the intermediate range damping function, which does not depend on the dispersion term in both the HFD-B2 and HFD-C potentials, and in the repulsive component, which shows an additional parameter β in the HFD-B2 model ($Ae^{-\alpha x+\beta x^2}$) and an additional term $x^\gamma(Ax^\gamma e^{-\alpha x})$ (as suggested by Gilbert *et al.*⁴²) in the HFD-C model. Therefore, in order to compare our estimate of the 3B dispersion forces with the results found by Refs. 30 and 23, we also carried out the calculation of the lowest-lying states of Ar₃ with the HFD-B2 and the HFD-C potentials.

We report in Table I all the parameters used in the cal-

culations, along with the resulting bound states for the dimer calculated via a direct diagonalization in a discrete variable representation⁴³ (DVR) (for the parameters used with the HFD-B2 and HFD-C models see Ref. 23). In order to yield fully comparable energies with the previously published data, in the calculations with the LJ potential we used for the Ar mass the value given in Ref. 31 ($m_{\text{Ar}}=39.95$ amu), and we also report the bound-state energies of Ar₂ in units of ϵ for an easier comparison with the values in Table III of Ref. 31. When using the Morse potential we adopted instead the mass given in Ref. 33 ($m_{\text{Ar}}=728.47$ and $m_e=39.962\,334\,41$ amu, having taken the electronic mass $m_e=0.000\,548\,579\,911$ amu). We checked, however, that the change in the value of the mass affects the bound-state energies by less than 0.05%. In the TT calculations we used the value of the Ar mass averaged over all stable isotopes (with weights corresponding to their relative abundance), i.e., $m_{\text{Ar}}=39.948$ amu.

The differences in the number and positions of the

FIG. 1. Ground-state potential energy curves for Ar₂. (a) Reference 31. (b) Reference 35. (c) Reference 37.

TABLE II. Comparison of theoretical (LJ, Morse, and TT) and experimental dissociation energies and vibrational spacings for Ar₂. All values are given in cm⁻¹.

D_0	LJ	Morse	TT	HFD-C	HFD-B2	Expt. Ref. 44
	70.45	83.93	84.44	84.70	84.73	84.47
Transition						
0 → 1	21.24	26.41	26.25	25.67	25.66	25.69 ± 0.01
1 → 2	16.64	21.43	20.66	20.46	20.50	20.58 ± 0.02
2 → 3	12.51	16.46	15.41	15.51	15.49	15.58 ± 0.02
3 → 4	8.89	11.49	10.65	10.93	10.94	10.91 ± 0.03
4 → 5	5.82	6.51	6.58	6.86	6.84	6.84 ± 0.07

dimer's bound states reflect the different shapes of the potential-energy curves (PECs) in the three adopted models (see Fig. 1). The Morse potential supports fewer bound states (a total of six) with respect to the LJ and the TT potentials. Furthermore, comparing these last two potentials, we notice that the more markedly strong dispersion contributions of the LJ potential allow the appearance of one more bound state with respect to the TT model, although the deeper well depth of the latter now lowers the location of the first four bound states.

We remark here that we find an additional bound state ($v=8$) for Ar₂ with respect to Ref. 31 when using the LJ PEC, while the first eight states are in very good agreement with the latter work. The absence of the highest bound state in Ref. 31 might be due to their not having used a large enough radial grid: we, in fact, verified that in order to get the present highest bound state ($v=8$) it was necessary to extend the radial grid to nearly 40 a.u. as the last point of the integration field. However, the authors of Ref. 31 did not report the parameters used in their two-dimensional (2D) DVR calculations.

In Table II we compare the vibrational spacings for the lowest levels, obtained with the three potential models we employed, with the available experimental data.⁴⁴ Even though the agreement is not of the order of the spectroscopic accuracy, Table II clearly shows that a markedly better description of the Ar–Ar interaction is given by the TT model with respect to the LJ and the Morse potentials. The HFD-C and HFD-B2 potentials yield an even better agreement between the calculated spacings and the experimental data, but a worse agreement on the value of the dissociation energy from the ground vibrational state (with zero angular momentum). As we already pointed out in our work on the excited states of Ne₃,⁴⁵ it is crucial to use accurate pair potentials whenever the excited states of a system (and not only the properties of its ground state) are sought.

As for the role of the 3B forces, the best-known contribution to them is given by the long-range AT potential,²⁶ which represents the triple-induced-dipole forces among the three atoms,⁴⁶

$$U_{DDD}(1,2,3) = \frac{3C_{DDD}}{R_1^3 R_2^3 R_3^3} (1 + 3 \cos \phi_1 \cos \phi_2 \cos \phi_3), \quad (4)$$

which can be written solely in terms of atom-atom distances by using the relation

$$\cos \phi_l = \frac{R_m^2 + R_n^2 - R_l^2}{2R_m R_n}. \quad (5)$$

The factor C_{DDD} is a constant, and we employed for the Ar₃ system the value given in Ref. 46 ($C_{DDD}=176.7$ hartrees $\times$ bohr⁹), as used in Ref. 23. In Ref. 30 the authors used the average value between the upper and lower bounds for C_{DDD} , as calculated in Ref. 47, which gives the very similar value of 176 hartrees $\times$ bohr⁹. The inclusion of higher-order 3B interactions³⁰ produces frequency shifts of the bound states of the Ar₃ of the order of 0.03 cm⁻¹,³⁰ namely, one order of magnitude less than the shifts produced by the AT interaction. Hence, we decided to limit our analysis of the effects of the 3B forces to the AT term.

B. The distributed Gaussian functions approach

In this section we briefly review the DGF method, which was introduced by us as an alternative variational treatment to study boson triatomic systems and has been discussed at length in our previous publications.^{27–29,45}

Once the Hamiltonian for the system of three identical particles is expressed in terms of atom-atom coordinates,²⁷ the total wave function is expanded in terms of products, properly symmetrized, of monodimensional DGF defined along each atom-atom coordinate,

$$\Phi_k(R_1, R_2, R_3) = \sum_j a_j^{(k)} \phi_j(R_1, R_2, R_3), \quad (6)$$

with

$$\phi_j(R_1, R_2, R_3) = N_{lmn}^{-1/2} \sum_{P \in S_3} P[\varphi_l(R_1) \varphi_m(R_2) \varphi_n(R_3)]. \quad (7)$$

Here, j denotes a collective index such as $j=(l \leq m \leq n)$, for the three identical particles and N_{lmn} is a normalization factor.²⁷ Each one-dimensional function φ_p is chosen to be a Gaussian function⁴⁸ centered at the R_p position,

$$\varphi_p(R_i) = \sqrt{\frac{2A_p}{\pi}} e^{-A_p(R_i - R_p)^2}, \quad (8)$$

where A_p is a parameter defining the width of φ_p (Ref. 48) which inversely depends on the distance between two neighboring Gaussian functions and on an empirical parameter β which we took to be near to 1 ($\beta=1.05$). Basically, each $\phi_j(R_1, R_2, R_3)$ function describes a triangular configuration in such a way that it represents all the possible triangular arrangements (according to the exchange of the identical par-

ticles) formed when the R_1 , R_2 , and R_3 sides are equal to the centers of the Gaussian functions R_l , R_m , and R_n , respectively.

Besides formulating the problem Hamiltonian in its exact form, the use of pair coordinates allows us to obtain several indicators on the spatial behavior of the bound states of the systems (see again, e.g., Refs. 27–29 and 45 for a detailed discussion of the capabilities of the method). Moreover, it is also possible to assess which are the dominant triangular structures and what is their relative importance in the description of each bound state, thereby providing a useful pictorial description of the latter as we shall illustrate below. Such configurational analysis is carried out, for each bound state k , by means of the pseudoweights (PWs) P_j^k of each basis function ϕ_j ,^{28,45}

$$P_j^k = a_j^k \langle \Phi_k | \phi_j \rangle. \quad (9)$$

As discussed at length in the previous papers^{28,45} the trimer's bound states can be analyzed in terms of triangular configurations by means of the DGF method. In particular, the functions $\phi_j(R_1, R_2, R_3)$ [Eq. (7)] in the expansion of the total wave function of each bound state k can, in fact, be associated with a particular triangular arrangement which has a PW P_j^k [see Eq. (9)]. The total number of “triangular” functions generated by our basis set can be divided into five families: “flat” isosceles (where the two equal distances are shorter than the third one), “tall” isosceles (with the two equal distances greater than the third one), collinear, equilateral, and scalene. The corresponding classification of the different basis functions into each triangular category is done by allowing for a small variation of the length of the sides of the triangles, variation which takes into account the finite width of the Gaussian functions and is chosen to be given by the step Δ between two neighboring Gaussian functions. The Δ value of our final basis set is equal to $0.23a_0$, and with this step we find that 6.6% of the basis functions describe a flat isosceles configuration, 8.9% tall isosceles, 1.3% collinear, 0.4% equilateral, and finally 82.8% correspond to a scalene arrangement.

Furthermore, the expectation values of different observables can be calculated via the PWs, resorting to the mean value theorem,

$$\langle x \rangle_k = \sum_j a_j^k \langle \Phi_k | x | \phi_j \rangle \approx \sum_j P_j^k x_j, \quad (10)$$

where in the integrations involved we have assumed that the magnitude x , depending on the three pair coordinates, has been replaced by a mean value corresponding to the triangular configuration described by the ϕ_j functions.

It has been remarked earlier^{33,49} that this kind of approach might become problematic for states near the isomerization barrier to linearity (which corresponds to the energy required to break one of the dimer bonds and can be easily estimated knowing the dimer's ground-state energy), because the corresponding eigenfunction amplitudes would be non-zero at the triangle inequality boundaries controlled by the following triangle's inequality relation (TIR):

$$|R_l - R_m| \leq R_n \leq R_l + R_m. \quad (11)$$

We have shown⁴⁵ that, by using a more restrictive inequality between the DGF centers, such that only the functions $\phi_j(R_1, R_2, R_3)$ in Eq. (7) with $|R_l - R_m| < R_n < R_l + R_m$ will belong to the basis set, and with a proper choice of the location of the centers, our approach based on atom-pair coordinates is perfectly capable of accurately describing all the bound states of the trimers, even those lying over the isomerization barrier.

In Ref. 45 we provided a relationship that yields the optimal location of the centers along each atom-atom distance for each given step Δ (defining the distance between two neighboring Gaussian functions). According to that formula, by locating the DGF centers at integer multiples of Δ it is possible to render negligible the deviation from the triangle's inequality requirement. In other words, we can choose the 1D Gaussian basis set in Eq. (8) such that it minimizes the nonphysical nonzero amplitude of the total wave function at the triangle's inequality boundaries.

The largest basis set we use in the present work is given by 73 Gaussian functions, equidistantly located from $5.52a_0$ to $22.08a_0$ with a step of $0.23a_0$. Such a basis set leads to 56 867 symmetrized basis functions [see Eq. (6)] and is able to describe the trimer's bound states over the entire spectral range, with the exclusion of those states k which lay very near the dissociation threshold (with $E_{\text{threshold}} - E_k < 2 \text{ cm}^{-1}$) which are diffuse over nearly $30a_0$ and thus require a larger and denser DGF basis set, as we shall further discuss below. We notice here that, if all the possible combinations of three Gaussians out of the chosen 73 were allowed, the appropriate binomial coefficient would produce 67 525 symmetrized basis functions. However, the triangle's inequality requirement of Eq. (11) discards all the triplets not satisfying the triangular constraint, thus reducing the total number of acceptable basis functions to 56 867. As a control of the triangular requirement constraint, we employed the following operator to estimate the basis set “badness”:⁴⁵

$$\mathcal{W}(R_1, R_2, R_3) = \begin{cases} 0, & |R_1 - R_2| \leq R_3 \leq R_1 + R_2 \text{ holds,} \\ 1, & \text{otherwise.} \end{cases} \quad (12)$$

This operator can be easily represented in terms of DGF as

$$\begin{aligned} \mathcal{I}(ll', mm', nn') &= \langle \varphi_l(R_1) \varphi_m(R_2) \varphi_n(R_3) | \mathcal{W} | \varphi_{l'}(R_1) \varphi_{m'}(R_2) \varphi_{n'}(R_3) \rangle \\ &= \frac{1}{2} s_{mm'} \int_0^\infty \int_0^\infty dR_1 dR_2 \varphi_l(R_1) \varphi_{l'}(R_1) \varphi_m(R_2) \varphi_{m'}(R_2) \\ &\quad \times \{ 2 + \text{erf}[\sqrt{A_{mm'}}(|R_1 - R_2| - R_{nn'}^\dagger)] \\ &\quad - \text{erf}[\sqrt{A_{mm'}}(R_1 + R_2 - R_{nn'}^\dagger)] \}, \end{aligned} \quad (13)$$

where $s_{mm'}$ is the overlap of two Gaussian functions centered at R_n and $R_{n'}$, $\text{erf}(x)$ is the error function and, finally, $A_{mm'}$ and $R_{nn'}^\dagger$ are the width and center, respectively, of the product of two Gaussian functions $\varphi_n \varphi_{n'}$. This integral must be evaluated for each pair of basis functions built as in Eq. (7).

TABLE III. Comparison of the energetics in Ar_3 for $J=0$ ground and some excited states using different pairwise interactions (see Table I) and methods. See main text for a full explanation of the symbols. All energies are in cm^{-1} .

k	LJ					Morse	
	BO-hs ^a	Adiab-hs ^a	CAC-hs ^a	DVR-DT ^b	DGF ^c	Lanczos ^d	DGF ^c
0	-212.12	-211.45	-211.78	-211.87	-211.89	-252.45	-252.45
1	-185.87	-183.84	-186.61	-186.72	-186.74	-220.94	-220.94
2	-179.12	-174.01	-176.14	-176.43	-176.46	-208.24	-208.24
3	-164.19	-156.83	-165.22	-165.64	-165.68	-193.75	-193.74
4	-160.70	-150.27	-160.96	-161.58	-161.55	-189.07	-189.06
5	-159.35	-147.44	-154.44	-155.77	-155.78	-181.41	-181.40
6	-152.21	-143.17	...	-152.28	-152.25	-177.28	-177.27
7	-150.30	-137.61	...	-148.46	-148.46	-171.72	-171.72
8	-144.66	-128.65	...	-145.31	-145.31	-168.90	-168.90
9	-144.15	-123.67	...	-144.73	-144.72	-168.00	-168.00
10	-140.58	-120.45	...	-143.49	-143.49	-167.34	-167.33
11	-138.23	-119.75	...	-141.66	-141.70	-165.53	-165.48
12	-135.19	-115.83	...	-140.25	-140.25	-163.16	-163.04
13	-133.69	-112.42	...	-138.67	-138.54	-161.83	-161.68
14	-130.13	-111.33	...	-135.85	-135.76	-159.16	-158.63
15	-127.80	-104.55	...	-135.52	-135.24	-156.16	-156.08
16	-123.51	-101.55	...	-132.61	-132.17	-155.41	-154.51
17	-120.90	-94.15	...	-130.79	-130.27	-151.96	-151.10
18	-120.10	-93.64	...	-128.38	-128.03	-149.67	-148.64
19	-111.21	-87.41	...	-127.30	-127.28	-148.29	-148.05

^aBlume *et al.* (Ref. 32). Hyperspherical coordinates at different levels of approximation, LJ potential.

^bD. Leitner *et al.* (Ref. 31). DVR with diagonalization-truncation, LJ potential.

^cDGF (present work).

^dRoy (Ref. 33). Symmetry-adapted Lanczos approach with Pekeris coordinates in DVR, Morse potential.

This expression, together with the coefficients of the total wave function in the chosen basis set, is used to estimate, through the average value $\langle \mathcal{W} \rangle$, how much the norm (equal to unity) of the wave function integrated over the entire space differs from the norm, which we call the TIR norm, integrated only over the domain where the TIR is satisfied: with a well-behaving basis set, the TIR norm should be equal to one as well. Furthermore, the smaller $\langle \mathcal{W} \rangle$ the better the corresponding basis set will reproduce the bound states. For the present system that index never went below 0.98, thus providing a clear assessment of the “goodness” level of the present basis set choice.

III. RESULTS AND DISCUSSION

A. The bound states of Ar_3 with model 2B potentials

In Table III we report the energies of the first 20 bound states of the Ar_3 trimer, calculated with the DGF method and the first two atom-atom potentials discussed in Sec. II A, LJ and Morse, compared with some previously published results.

The first three sets of data are the results of Blume *et al.*,³² who used the hyperspherical coordinates at different levels of approximation and the LJ potential given in Ref. 31. In the first column (BO-hs) we report their Born–Oppenheimer energies, in the second column (Adiab-hs) their adiabatic energies and in the third one (CAC-hs) their coupled-adiabatic channel results which include three channels. The next set of data (DVR-DT) comes from Leitner *et*

al.,³¹ who used a DVR with diagonalization-truncation method and the LJ potential (notice that the authors expressed their results in unit of $\epsilon=119.4$ K; in Table III we converted the energies into cm^{-1} , using $0.695\,039\,\text{cm}^{-1}/\text{K}$ as the conversion factor from K to cm^{-1}). To complete the calculations obtained with a LJ PEC we also report in the fifth column our present results for the same potential: the agreement with the results of Ref. 31 is very good. In the sixth column of Table III (labeled Lanczos) we report the results of Ref. 33 which used Pekeris coordinates⁵⁰ and a symmetry-adapted Lanczos approach with a Morse potential (the author also employs a LJ potential, but we only consider here the results he obtained with the Morse potential). In Ref. 33 the findings on Ne_3 and Ar_3 described by sums of the LJ potentials are compared with those of Ref. 51, while in the Morse case they are compared with our results of Ref. 28 and to those of Ref. 49. We report next to it our present DGF results obtained with the same Morse potential and, again, we find a very good agreement between the two sets of data.

It is worth noting that such a good accord found for all the reported states with the two potentials also includes those states lying above the isomerization barrier to linearity. By characterizing the bound states obtained for the LJ potential in terms of the triangular arrangements contributing to their description [see Eq. (9) and the relative discussion in the text] we find that the collinear arrangements are absent in the first eight states (up to $k=7$), acquire some importance in the next bound states, and become the dominant arrangement in the state $k=10$.

FIG. 2. Convergence analysis of different regions of the energy spectrum of Ar_3 modeled by additive LJ potential.

A complete calculation of the total number of $J=0$ bound states N_{tot} , together with a full characterization of the most excited states, for a system, such as Ar_3 , are not affordable tasks with our computational resources. However, we tried to give an estimate of the degree of convergence of our results and of the expected number of rotationless bound states of Ar_3 , as illustrated in Fig. 2. In the three panels we report how the energies of different regions of the spectrum vary when the step Δ between two neighboring Gaussian functions of the basis set is reduced. The energies here refer to the 2B dissociation threshold (corresponding to the loss of one Ar atom and given by the ground-state energy of Ar_2) taken as the zero of energy. On the left panel of that figure we report the energies for the states from $k=15$ to $k=20$; on the bottom right panel we report the states from $k=20$ to $k=80$ (selecting, for the sake of clarity, only the states whose k value is a multiple of 10) and, finally, on the top right panel of Fig. 2 we report the states with $k > 70$. In this last panel we coarsely fitted the energy values with a quadratic function, which gives the general behavior of the high-energy spectrum of the system for each chosen step Δ : this is the expected behavior due to the presence of anharmonicity.⁵²

We clearly see, therefore, that Fig. 2 shows how we have reached a high degree of convergence over the whole spectral region: the smallest step Δ we used, namely, $0.23a_0$, guarantees an expansion of three to four Gaussian functions for the shortest de Broglie wavelength, in accord with the

standard study on bound-state convergence behavior.⁴³ This could help us to obtain an estimate of N_{tot} of the present system as a function of Δ by using a quartic regression, as plotted in Fig. 3. Extrapolating to the Dirac δ function limit ($\Delta=0$), we indeed find a plateau which finally suggests a maximum number of 127 for N_{tot} in the LJ case. This seems to us a useful piece of information never, to our knowledge, provided before for this trimer. Moreover, by limiting the fitting with the quartic regression to the points corresponding to the largest four steps Δ (from 0.5 to $0.35a_0$), we find a very similar function which extrapolates N_{tot} to the same value (namely, 127 bound states) in the Dirac δ function limit. Hence, with a moderate computational effort we can give an estimate of the total number of bound states (for $J=0$) supported by the ground PES, at the price of reducing the degree of accuracy attained for the energy values. In any event, by choosing the step $\Delta=0.35a_0$ the convergence of the numerical values of the energy is ensured within 0.1 cm^{-1} for the first ten values, within 1 cm^{-1} up to $k=30$ and is kept below 2 cm^{-1} for the highest bound states.

B. Improved bound states of Ar_3 and the role of the 3B forces

In Table IV we report the results relative to the first 60 vibrational energy levels of Ar_3 (at zero angular momentum) which we obtain using the more accurate TT model to de-

FIG. 3. Extrapolation to the Dirac δ function limit for the basis Gaussian function widths (i.e., null separation between consecutive Gaussian functions, $\Delta=0$ limit) of the number of $J=0$ bound states of Ar_3 modelled by additive LJ potential. The fitting function is $y(x)=a_0+a_2x^2+a_4x^4$, with $a_0=127.044$, $a_2=-57.6408$, and $a_4=-123.58$.

TABLE IV. Effects of AT nonadditive dispersion forces on the energies of the first 60 states of Ar₃. E_k^{TT} : energies obtained when Ar₃ is described by a sum of pairwise TT potential (see text). $E_k^{\text{TT+pert}}$: energies obtained calculating the value of the AT term by using the zeroth-order wave-function eigenstates of the Hamiltonian matrix which does not include the AT term. $E_k^{\text{TT+AT}}$: energies obtained when the AT triple-dipole interaction is included in the potential. All values are in cm⁻¹.

k	E_k^{TT}	$E_k^{\text{TT+pert}}$	$E_k^{\text{TT+AT}}$	k	E_k^{TT}	$E_k^{\text{TT+pert}}$	$E_k^{\text{TT+AT}}$
0	-253.976	-250.965	-250.983	30	-136.141	-135.624	-135.629
1	-222.819	-220.136	-220.155	31	-133.996	-132.925	-132.973
2	-210.153	-207.801	-207.817	32	-132.564	-132.667	-132.760
3	-196.696	-194.620	-194.650	33	-132.091	-131.218	-131.139
4	-191.647	-189.445	-189.455	34	-131.350	-130.673	-130.740
5	-184.693	-183.050	-183.089	35	-130.614	-129.822	-129.754
6	-180.400	-178.630	-178.665	36	-129.690	-129.221	-129.351
7	-176.011	-174.996	-175.029	37	-128.705	-128.510	-128.371
8	-172.529	-172.171	-172.318	38	-127.754	-127.214	-127.265
9	-171.165	-170.534	-171.043	39	-125.767	-125.070	-125.086
10	-170.681	-169.724	-169.301	40	-124.821	-124.320	-124.345
11	-168.929	-168.682	-168.544	41	-124.369	-123.674	-123.632
12	-166.333	-165.633	-165.803	42	-123.811	-123.082	-123.064
13	-164.941	-163.600	-163.450	43	-122.406	-121.602	-121.644
14	-162.177	-161.685	-161.634	44	-121.024	-120.134	-120.526
15	-159.749	-158.160	-158.189	45	-120.923	-120.514	-120.123
16	-158.106	-157.513	-157.525	46	-118.960	-118.254	-118.264
17	-154.909	-153.803	-153.821	47	-117.833	-117.373	-117.550
18	-152.460	-151.805	-151.808	48	-117.040	-116.581	-116.672
19	-150.972	-151.186	-151.259	49	-116.618	-116.321	-116.172
20	-150.112	-149.630	-149.610	50	-116.230	-115.648	-115.667
21	-148.775	-148.649	-148.641	51	-115.819	-115.421	-115.345
22	-146.668	-146.091	-146.208	52	-115.285	-114.828	-114.818
23	-145.982	-145.423	-145.511	53	-113.648	-112.983	-113.013
24	-145.669	-144.381	-144.191	54	-113.321	-112.904	-112.939
25	-143.808	-142.368	-142.473	55	-112.484	-112.022	-112.223
26	-142.809	-142.354	-142.256	56	-111.948	-112.030	-111.814
27	-140.766	-140.290	-140.275	57	-111.532	-111.055	-111.073
28	-138.386	-137.607	-137.643	58	-110.947	-110.610	-110.579
29	-137.858	-136.585	-136.586	59	-109.943	-109.125	-109.386

scribe the pairwise-additive potential. Such a potential has never been previously used for the calculation of the bound states of Ar₃. By using the extrapolation procedure suggested in Sec. III A (see Fig. 3 and the related text) we find a total number of 128 bound states when the TT potential is used.

Besides the energy obtained with the additive 2B PES (E_k^{TT}), for each state k we report the energy $E_k^{\text{TT+pert}}$ obtained with the addition of the AT contribution as a perturbation to the zeroth-order energy as follows:

$$E_k^{\text{TT+pert}} = E_k^{\text{TT}} + \langle \Psi_k^{\text{TT}} | U_{\text{DDD}}(1,2,3) | \Psi_k^{\text{TT}} \rangle. \quad (14)$$

Finally, the energies which are instead obtained when the 3B AT term is included in the potential ($E_k^{\text{TT+AT}}$) are shown in the fourth and in the last columns of Table IV. All these energies are in cm⁻¹. Both approaches to include the 3B effect, perturbation and direct inclusion in the total Hamiltonian, reveal that the AT effect never shifts the energy E_k^{TT} by more than 1.3%. The largest effect is found for the lower bound states ($k=0-6$) which are expected to be those where the interparticle distances remain smaller. The AT term seems to noticeably decrease for the next states, falling down to the 0.1% of the corresponding E_k^{TT} for $k=8$ and to even less for $k=9$. The net effect is always repulsive, thus increasing the

energy, with the exception of the states $k=19, 32$ and, within the perturbation scheme, of $k=56$.

Even though the 3B effects are very small, the action of the AT operator cannot be fully treated as a perturbation for all the states, as can be seen comparing the third with the fourth column and the seventh with the last column of Table IV. Differences between energies from a zeroth-order perturbation theory and those obtained from the diagonalization of the Hamiltonian with the TT potential and the AT term are always smaller than 0.5 cm⁻¹ but there seems to be no rule for predicting whether or not $E_k^{\text{TT+pert}}$ is smaller or larger than $E_k^{\text{TT+AT}}$. Given the different origin of these two energies, one possible reason for the discrepancy between $E_k^{\text{TT+pert}}$ and $E_k^{\text{TT+AT}}$ may be the different geometrical nature of the wave functions Ψ_k^{TT} and $\Psi_k^{\text{TT+AT}}$, respectively, associated with them: the validity of the perturbative approach is clearly based on the assumption that the perturber does not change significantly the zeroth-order wave functions Ψ_k^{TT} .

To show this in a simple way we estimated the AT contribution due to each single triangular basis function $(U_{\text{DDD}})_j = \langle \phi_j | U_{\text{DDD}} | \phi_j \rangle$. We depict in Fig. 4 the computed values of $(U_{\text{DDD}})_j$ ordered according to the shape of the corresponding triangular basis function and not to the position

FIG. 4. Calculated AT term, $(U_{DDD})_j$, for all the elements of the basis set classified according to the possible triangular family.

that the particular ϕ_j occupies within the basis set: as an example, the first basis function in the collinear family is the 24th of the 56 867 functions constituting our final basis set. The number of the basis functions, N_{type} , which fall within each type of triangular configuration is reported in the corresponding panel. While the tall isosceles and the equilateral basis functions always produce a positive AT term, we see that the collinear arrangements yield a negative AT contribution, usually smaller than the previous ones, while the last two families (flat isosceles and scalene) show both negative and positive values, with the positive terms larger than the negative ones. For all of the triangular arrangements the values of $(U_{DDD})_j$ quickly go to zero for the more extended basis functions, corresponding to high values of the interatomic distances. From a qualitative point of view, this behavior can be explained by looking at the particular triangular geometry and the functional form of the AT operator

[which depends, in the Ar_3 case, on a positive factor C_{DDD} , see Eq. (4)]. For instance, in the equilateral and the tall isosceles triangles, the cosines of the three internal angles are always positive; the associated, positive AT terms therefore decrease as the triangle's sides increase. In the collinear arrangement, on the other hand, the product of the three cosines will be negative and classically equal to -1 (in the DGF case, since the triangle's sides are described by the Gaussian functions, there is some flexibility which causes the product of the three cosines not to be equal to unity but only close to it). It follows that the AT term will always be negative and its magnitude will depend on the values of the interatomic distances.

It appears now more clearly that, if the perturber changes the geometry in a not negligible way by modifying either the relative percentage contributions of the triangular families or the “size” i.e., the radial averages) of a bound state, we can-

FIG. 5. PWs of the different triangular families some Ar_3 bound states for the TT potential when no AT term is included in the Hamiltonian, $[P_j^{(k)}]^{TT}$, on the left side and when the AT term is included $[P_j^{(k)}]^{TT+AT}$, on the right side. In both cases PWs are expressed in percentage.

FIG. 6. Percentage PWs of the different triangular families for the ground state $k=0$ of Ar_3 (top panel) and corresponding PDF (bottom panel) for the TT potential as only molecular interaction.

not expect the perturbative approach to be in good accord with the results obtained by diagonalizing the full Hamiltonian concerning that state. We have calculated the composition in terms of triangular families of the bound states of the Ar_3 trimer by employing the PWs obtained when the AT term is included or not, $(P_j^k)^{\text{TT+AT}}$ and $(P_j^k)^{\text{TT}}$, respectively. The examples of this structural analysis for some of the states which show a large difference between $E_k^{\text{TT+pert}}$ and $E_k^{\text{TT+AT}}$ values are shown in Fig. 5. The percentage of the different PWs to make up Ψ_k^{TT} for $k=8, 9, 11, 32, 47$, and 56 are presented on the left column of Fig. 5, whereas on the right column the same analysis is carried out for $(P_j^k)^{\text{TT+AT}}$. The change of the weights from collinear structures when the 3B correction is added to the interatomic potential is clearly noticeable in all states presented in the figure, especially for $k=9$ and 47 , where the presence of collinear arrangements increases around 30% in comparison with the rest of the triangular families, whose populations instead decrease. The opposite effect is found for the states $k=11, 32$, and 56 , where the inclusion of the AT term yields a marked reduction of the importance of collinear triangles.

More in general, we verified that the discrepancies between the perturbative and the variational approaches are al-

ways associated with structural changes in the corresponding wave functions either in the population of the triangular families and/or in the radial averages. On the other hand, for some states, whose geometry is sensibly altered by the AT term, the two approaches give very similar energies: even though Ψ_k^{TT} and $\Psi_k^{\text{TT+AT}}$ are quite different, the contributions to the AT term of the individual basis functions sum up to nearly the same quantity. We cannot hence establish a general rule to predict the effect of the AT term on a particular state simply based on the structure of the zeroth-order wave function.

As mentioned before, the perturbative approach seems to work reasonably well for the first seven bound states. Despite the fact that the AT term plays a major role in varying their binding energy obtained with purely 2B interactions, the populations of the different triangular families for such states (not shown in Fig. 5, but see the upper panel of Fig. 6 for the ground state) hardly change with the inclusion of the 3B correction. Therefore, marginal modifications of their rotational constants should be expected when the AT term is included, also as previously predicted for the ground state.^{23,24} For that state the geometrical configuration, reported on the top panel of Fig. 6, does not show any collinear contribution while the other triangular configurations are present with fairly similar weights which leave the equilateral arrangement to be the dominant one: due to the quasi-classical nature of the heavy masses of this system, we might expect the Ar_3 ground state to present a dominance of its equilateral configuration. As already mentioned in the Sec. II B, our classification of the basis functions in terms of the triangular families is done by allowing for a small variation of the length of the triangle's sides, variation which depends on the step Δ between two neighboring Gaussian functions. Only if the three sides do not differ by more than Δ (here taken as equal to $0.23a_0$) the corresponding basis function is classified as equilateral, and only 0.4% of the basis functions fall into the equilateral family. Even so, the 217 equilateral basis functions contribute to the ground state by more than 25%. Although the Ar_3 system behaves somewhat more classically than, e.g., the Ne_3 ,⁴⁵ it nevertheless still shows floppiness associated with its zero point-energy (which is around 15% of the well depth). Accordingly, the radial pair distribution function (PDF) spreads over a few atomic units, as

TABLE V. Energy levels without AT term (second, third, and fourth columns) and frequencies ($E_k - E_0$) with respect to the ground state with and without the AT term (the last four columns): comparison between the results given in Ref. 23 using two different approaches (HHCC and Jacobi) and the present results. 2B: frequencies obtained with the sum of pairwise HFD-C potentials (see text). 3B: frequencies obtained including the AT triple-dipole effect. All values are given in cm^{-1} .

k	E_k^{2B}			$E_k - E_0$			
	Ref. 23		This work DGF	Ref. 23 (Jacobi)		This work (DGF)	
	HHCC	Jacobi		2B	3B	2B	3B
0	-254.733	-254.736	-254.728				
1	-224.215	-224.187	-224.199	30.549	30.242	30.529	30.216
2	-211.846	-211.518	-211.832	43.218	42.620	42.896	42.254
3	-198.282	-196.350	-198.266	58.386	57.804	56.462	55.557
4	-193.523	-191.667	-193.497	63.069	62.302	61.231	60.453

TABLE VI. Energy levels referred to the potential minimum (second and third columns) and frequencies ($E_k - E_0$): comparison between the results found in Ref. 30 (with a vibrational SCF-CI approach) and the present results. 2B: results obtained using a sum of pairwise HFD-B2 potentials (see text). 3B: results obtained by including the AT triple-dipole effect. All values are given in cm^{-1} .

k	E_k^{2B}		$E_k - E_0$			
	Ref. 30	This work	Ref. 30		This work (DGF)	
	SCF-CI	DGF	2B	3B	2B	3B
0	43.72	43.82				
1	76.64	74.36	32.92	32.68	30.54	30.23
2	88.90	86.72	45.18	44.56	42.90	42.25
4	106.49	100.35	62.77	61.87	56.52	55.61
5	108.56	105.09	64.84	64.02	61.26	60.48

shown by the bottom panel of Fig. 6. Such range of definition of the PDF for $k=0$ involves the need of other arrangements besides the equilateral to properly describe that state. This might appear at odds with the results of our previous work²⁸ where a population of more than 70% of equilateral configurations for the ground state of Ar_3 was reported. Note, however, that the DGF classification into different families strongly depends on the Δ value used: the value of $\sim 0.38a_0$ in Ref. 28 enabled a larger amount of arrangements to be counted as equilateral triangles. It also depends on the adopted criterium for the triangle inequality which is taken to be stricter in the present work [see Eq. (11)]. Furthermore, the average values of the three atom-atom distances for this state, estimated by means of the PW for each contributing family, show differences among them which are not larger than $0.7a_0$ whatever family is considered. This finding is thus fully consistent with an overall equilateral geometry for the Ar_3 ground state.

Regarding the possible influence of the AT term on the geometry of the Ar_3 bound states, our results seem to be consistent with the findings of Ref. 26. In that work Chakravarty *et al.* adjusted the strength of the AT potential by means of a single parameter and found that, by increasing such a parameter, they could actually lower the first Ar_3 bound state that shows a clear component of a linear geometry. In this sense, Fig. 5 shows here that the addition of the AT term makes the population of the collinear structures of the $k=8$ and 9 states to considerably increase. The global effect of this change is that the first bound state with a relevant collinear population once the AT term is included is now $k=8$ instead of $k=9$, as was the case when pure 2B interactions were considered. As mentioned before, for higher excited states the variation of the collinear populations as the 3B forces are added appears to exhibit a more erratic behavior and no simple rule was able to be found.

In Table V we finally compare our findings on the energy levels and frequencies with respect to the ground state ($k=0$) with those found in Ref. 23, where the authors used the HFD-C potential and two different approaches: the hyperspherical harmonic coupled channel (HHCC) and a basis set method in Jacobi coordinates. To properly compare the results we repeated the calculations with the HFD-C potential and we used a smaller basis set, since only the lowest bound states are needed for the comparison. As the authors noticed

in that paper,²³ the method based on the Jacobi coordinates, which was used to estimate the effect of AT term, is satisfactory at least for a few of the lower states. In fact, we also find fairly good agreement between the DGF energy values obtained without the inclusion of the AT term (shown in the fourth column) and the HHCC results (reported in the second column of Table V) while, with respect to those obtained with the Jacobi coordinates (in the third column), the accord begins to deteriorate starting from the $k=3$ state. From the fifth to the last columns we further compare the frequencies obtained with and without the inclusion of the AT term, in the columns labeled 3B and 2B, respectively. Since the ground state is the most affected by the 3B effect, all the frequencies appear redshifted once the AT term is included in the calculation. We always obtain a larger effect for the 3B correction than those listed in Ref. 23, that is to say, the shift towards the red of the DGF frequencies is bigger than found in Ref. 23.

In Table VI we further compare our results with those of Ref. 30, where the HFD-B2 potential and a vibrational SCF-CI approach are used. Whereas the energies already begin to differ from the first excited state, the 3B effect on the frequencies is described similarly by the two methods.

To conclude, we compare in Table VII the DGF results obtained with the three potentials TT, HFD-C, and HFD-B2. The last two potentials yield results which are in very good agreement, both for the frequency values and for the 3B corrections (the frequencies differ by less than 0.05 cm^{-1} and the corrections agree within 0.01 cm^{-1}). The TT potential produces slightly higher frequencies, but the net 3B corrections differ at most by 0.05 cm^{-1} with respect to what found with the two HFD PESs. Possible experimental measurements of such frequencies could be very useful to confirm the size of the AT effect (which we find to be somehow independent of the employed PES) and to select the most reliable description for the Ar-Ar interaction.

IV. CONCLUSIONS

In this work we employed the DGF method to study the bound states of the Ar_3 cluster for the zero total angular momentum configuration and to analyze the effect on the energy spectrum of the long-range 3B AT correction. In a previous paper⁴⁵ on the more weakly bound cluster Ne_3 we

TABLE VII. DGF calculated frequencies obtained by using different PESs with and without the inclusion of the AT term. The 3B effect is the frequency difference caused by the AT contribution for each PES. All values are in cm^{-1} .

k	$E_k^{2B} - E_0^{2B}$			$E_k^{3B} - E_0^{3B}$			3B effect		
	TT	HFD-B2	HFD-C	TT	HFD-B2	HFD-C	TT	HFD-B2	HFD-C
1	31.16	30.54	30.53	30.83	30.23	30.22	-0.33	-0.31	-0.31
2	43.82	42.89	42.90	43.17	42.25	42.25	-0.65	-0.64	-0.65
3	57.28	56.51	56.46	56.33	55.61	55.56	-0.95	-0.90	-0.90
4	62.33	61.25	61.23	61.53	60.48	60.45	-0.80	-0.77	-0.78

had already discussed at length a procedure which enabled us to choose an optimized DGF basis set and to avoid the pathological behavior that the wave functions can show at the triangle's inequality boundaries in the case of the important presence of collinear arrangements. In the present work we tested first the reliability of the DGF method, when using the above-mentioned procedure, by comparing our results with those already published on the same system and described by model pair potentials (LJ and Morse). A very good agreement was found for all the states, independent of their geometrical features. In particular, once an optimized DGF basis set is selected those states with predominant collinear configurations are also accurately described by our method.

We also suggest here a way to obtain an estimate of the total number of bound states (with $J=0$) for systems, such as Ar_3 , which support many vibrational levels and generally require a very dense and extended basis set to describe the states near the 2B dissociation threshold.

The description of the 2B interaction was improved by employing more accurate atom-atom potentials and by further including the triple-induced-dipole interaction in the potential: to the best of our knowledge, this is the first time that such an analysis is applied to the overall rotationless spectrum of Ar_3 . We found that, even though the inclusion of the AT term shifts the energy levels by no more than 1.3%, the AT effect cannot be treated for all the states as a first-order perturbation. The AT term contribution, with respect to the spectrum obtained when only purely 2B interactions are considered in the molecular potential, pushes up the energy of all levels (with the exception of two states) as a result of the chiefly repulsive nature of the AT forces in Ar_3 .

As a further effort to clarify the spectral behavior in Ar_3 we have qualitatively related the different AT effects on the various bound states of the system to the spatial features of the wave functions by using the pictorial description afforded by our triangular configurations and thus examining the changes in the geometrical structure induced by the 3B effects. We found that, despite the absence of a general rule to predict global effects, the evidence of the structural changes in the vibrationally excited spectrum of Ar_3 when the AT term is included is clearly manifested. The use of the PWs hence provides useful information to better understand for each bound state the contributions from the different triangular geometries to the global AT correction. Our structural analysis of the Ar trimer bound states is consistent with previous predictions of rather minor modifications of the rotational constants of the ground state^{23,24} and of a relationship between the AT contribution and the appearance of bound

states with linear geometries.²⁶ It would be interesting to further test whether the changes found in this work of the geometries in some of the excited states when the AT term is included could lead to relevant modifications in the overall rotational spectrum of Ar_3 .

In conclusion, the use of the DGF method for such a complex system (in terms of its large number of bound states) has been shown by the present work to provide a rather efficient and transparent way of describing the spatial features and energy distributions for the full bound spectrum of the Ar trimer when the 3B corrections are added to the more conventional sum of potentials employed to describe the intermolecular forces.

ACKNOWLEDGMENTS

The financial supports of the Ministry for University and Research (MUIR), of the University of Rome I Research Committee, of the Italy-Spain Integrated Action Programme No. HI02-74, DGICYT Spanish Grant with Ref. FIS2004-02461 and of the INFN institute, are gratefully acknowledged. One of the authors (T.G.L.) would also like to thank the support of the programa Ramón y Cajal. We also thank the 'Consorzio Universitario per le Applicazioni di Supercalcolo Per Università e Ricerca' (CASPUR) of Rome for supplying computational resources and advice.

¹Rare Gas Solids, edited by M. L. Klein and J. A. Venables (Academic, New York, 1976).

²J. Cuthbert, Trans. Faraday Soc. **54**, 617 (1958).

³A. J. Thakkar, H. Hettema, and P. E. S. Wormer, J. Chem. Phys. **97**, 3252 (1992).

⁴G. T. Fraser, A. S. Pine, W. J. Lafferty, and R. E. Miller, J. Chem. Phys. **77**, 1502 (1987).

⁵B. M. Axildrod and E. Teller, J. Chem. Phys. **11**, 299 (1943).

⁶B. M. Axildrod, J. Chem. Phys. **19**, 724 (1951).

⁷V. F. Lotrich and K. Szalewicz, Phys. Rev. Lett. **79**, 1301 (1997).

⁸E. E. Polymeropoulos and J. Brickmann, Chem. Phys. Lett. **92**, 59 (1982); **96**, 273 (1983).

⁹I. Yourshaw, Y. Zhao, and D. M. Neumark, J. Chem. Phys. **105**, 351 (1996).

¹⁰T. Lenzer, M. R. Furlanetto, N. L. Pivonka, and D. M. Neumark, J. Chem. Phys. **110**, 6714 (1999).

¹¹M. A. van der Hoef and P. A. Madden, J. Chem. Phys. **111**, 1520 (1999).

¹²R. Bukowski and K. Szalewicz, J. Chem. Phys. **114**, 9518 (2001).

¹³G. Marcelli and R. J. Sadus, J. Chem. Phys. **111**, 1533 (1999).

¹⁴A. Malijevský and A. Malijevský, Mol. Phys. **20**, 3335 (2003).

¹⁵J. M. Bommont and J. L. Bretonnet, Phys. Rev. B **65**, 224203 (2002).

¹⁶A. E. Nasrabadi, R. Laghaei, and U. K. Deiters, J. Chem. Phys. **121**, 6423 (2004).

¹⁷J. M. Bommont, N. Jakse, and J. L. Bretonnet, Phys. Rev. B **57**, 10217 (1998).

¹⁸N. Jakse, J. M. Bommont, I. Charpentier, and J. L. Bretonnet, Phys. Rev. B **62**, 3671 (2000).

- ¹⁹Y. Xu and W. Jäger, Phys. Chem. Chem. Phys. **2**, 3549 (2000).
- ²⁰D. J. Chartrand, R. J. Leroy, A. Kumar, and W. J. Meath, J. Chem. Phys. **98**, 5668 (1993).
- ²¹C. E. Dykstra, J. Chem. Phys. **108**, 6619 (1998).
- ²²G. Chalasinski, M. M. Szczęśniak, and R. A. Kendall, J. Chem. Phys. **101**, 8860 (1994).
- ²³A. R. Cooper, S. Jain, and J. M. Hutson, J. Chem. Phys. **98**, 2160 (1993).
- ²⁴A. Ernesti and J. M. Hutson, J. Chem. Phys. **103**, 3386 (1995).
- ²⁵L. L. Lohr, Int. J. Quantum Chem. **57**, 707 (1996).
- ²⁶C. Chakravarty, R. J. Hinde, D. M. Leitner, and D. J. Wales, Phys. Rev. E **56**, 363 (1997).
- ²⁷T. González-Lezana, J. Rubayo-Soneira, S. Miret-Artés, F. A. Gianturco, G. Delgado-Barrio, and P. Villarreal, Phys. Rev. Lett. **82**, 1648 (1999).
- ²⁸T. González-Lezana, J. Rubayo-Soneira, S. Miret-Artés, F. A. Gianturco, G. Delgado-Barrio, and P. Villarreal, J. Chem. Phys. **110**, 9000 (1999).
- ²⁹T. González-Lezana, S. Miret-Artés, G. Delgado-Barrio, P. Villarreal, J. Rubayo-Soneira, I. Baccarelli, F. Paesani, and F. A. Gianturco, Comput. Phys. Commun. **145**, 156 (2003).
- ³⁰T. R. Horn, R. B. Gerber, J. J. Valentini, and M. A. Ratner, J. Chem. Phys. **94**, 6728 (1991).
- ³¹D. M. Leitner, J. D. Doll, and R. M. Whitnell, J. Chem. Phys. **94**, 6644 (1991).
- ³²D. Blume, C. H. Greene, and B. D. Esry, J. Chem. Phys. **113**, 2145 (2000).
- ³³P. N. Roy, J. Chem. Phys. **119**, 5437 (2003).
- ³⁴R. A. Aziz and M. J. Slaman, Mol. Phys. **58**, 679 (1986); notice that in Ref. 23 the expression for the damping function $F(x)$ [their Eq. (3)] of the Aziz-Slaman and Aziz-Chen potentials is missing a minus sign in front of the argument of the exponential.
- ³⁵A. García-Vela, R. B. Gerber, and U. Buck, J. Phys. Chem. **98**, 3518 (1994).
- ³⁶K. T. Tang and J. P. Toennies, J. Chem. Phys. **80**, 3726 (1984).
- ³⁷K. T. Tang and J. P. Toennies, J. Chem. Phys. **118**, 4976 (2003).
- ³⁸F. Sebastianelli, I. Baccarelli, C. Di Paola, and F. A. Gianturco, J. Chem. Phys. **121**, 2094 (2004).
- ³⁹P. Slavíček, R. Kalus, P. Paška, I. Odvárková, P. Hobza, and A. Malijevský, J. Chem. Phys. **119**, 2102 (2003).
- ⁴⁰R. A. Aziz, J. Chem. Phys. **99**, 4518 (1993).
- ⁴¹R. A. Aziz and H. H. Chen, J. Chem. Phys. **67**, 5719 (1977).
- ⁴²T. L. Gilbert, O. C. Simpson, and M. A. Williamson, J. Chem. Phys. **63**, 4061 (1975).
- ⁴³D. T. Colbert and W. H. Miller, J. Chem. Phys. **96**, 1982 (1992).
- ⁴⁴P. R. Herman, P. E. LaRoque, and B. P. Stoicheff, J. Chem. Phys. **89**, 4535 (1988).
- ⁴⁵I. Baccarelli, F. A. Gianturco, T. González-Lezana, G. Delgado-Barrio, S. Miret-Artés, and P. Villarreal, J. Chem. Phys. **122**, 084313 (2005).
- ⁴⁶R. J. Bell and I. J. Zucker, in *Rare Gas Solids*, edited by M. L. Klein and J. A. Venables (Academic, London, 1976).
- ⁴⁷J. Standard and P. C. Certain, J. Chem. Phys. **83**, 3002 (1985).
- ⁴⁸J. P. Hamilton and J. C. Light, J. Chem. Phys. **84**, 306 (1986).
- ⁴⁹S. Garashchuk and J. C. Light, J. Chem. Phys. **114**, 3929 (2001).
- ⁵⁰C. L. Pekeris, Phys. Rev. **112**, 1649 (1958); E. R. Davidson, J. Am. Chem. Soc., **99**, 397 (1977).
- ⁵¹M. Nightingale and V. Melik-Alaverdian, Phys. Rev. Lett. **87**, 043401 (2001).
- ⁵²B. H. Bransden, and C. J. Joachain, *Physics of Atoms and Molecules* (Longmans, New York, 1992), p. 392.