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Citation: *J. Chem. Phys.* **122**, 084313 (2005); doi: 10.1063/1.1850096

View online: <http://dx.doi.org/10.1063/1.1850096>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v122/i8>

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A complete configurational study for the bound states of Ne trimers

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(Received 8 October 2004; accepted 29 November 2004; published online 17 February 2005)

The structural properties and the energetics of the ground and the excited bound states of Ne₃ for zero total angular momentum are examined using different modelings for the two-body interactions. We employ a method consisting of a variational approach with a distributed Gaussian functions (DGF) basis set expansion. We discuss at length the advantages and possible limitations of such an approach, comparing it to other methods which have been applied in the literature to the same system. The DGF method turns out to be very accurate in giving us the bound states energetics and also provides in a natural way a convincing pictorial description of all the states, including those with dominant linear configurations. Additional bound states are found for the Ne₃ system with respect to those indicated in previous works and we suggest a "stabilization" procedure that can be used to assess the truly bound nature of a state. Some considerations on the relative reliability of the examined two-body interactions are also reported. © 2005 American Institute of Physics.
[DOI: 10.1063/1.1850096]

I. INTRODUCTION

In the last 20 years several papers have sought to describe the ground and excited states of bosonic van der Waals clusters because of the many reasons which motivate this research. For example, the evaluation of theoretical spectra of polyatomic molecules and clusters (including highly excited vibrational states), once compared with the experiment, leads to a rich amount of information on the molecular properties of the systems. Furthermore, the study of clusters of increasing size may help our understanding of how bulk properties of a material (such as the superfluidity of ⁴He clusters, the phase transitions in finite droplets, etc.) arise from properties of finite systems made up of the same components.^{1,2}

In the case of van der Waals aggregates, and most especially of their excited states, the problem requires an accurate quantum-mechanical description because of the strong anharmonicity and nonseparability of the molecular vibrations, and of the even larger amplitude motions occurring at higher energies. In general, such systems are characterized by a marked "floppiness," that is to say by very delocalized nuclear positions and by strong coupling amongst the various degrees of freedom.

In this work we focus our attention on a typical rare-gas trimer, Ne₃, aiming at calculating the energies of its bound states (for a nonrotating complex) and at further providing a satisfactory pictorial analysis of their structural features. A number of recent papers have been devoted to such systems

(e.g., see Refs. 3–7 and references therein), all of them trying to apply to this kind of problem a variety of numerical methods.

The one we employ here is a variational approach, which uses atom pair coordinates and a distributed Gaussian function (DGF) basis set.^{5,8} The method has already been shown to provide an accurate, alternative treatment to the study of the bound states of triatomic systems^{5,9} and a numerically robust method that is able to confirm the findings of, e.g., classical optimization and diffusion Monte Carlo (DMC) calculations.^{10–12} Our goal here is to test the capability of the DGF method not only for the ground state but also for the excited states of such weakly bound identical partners, including those with predominant collinear shapes that have been suggested to be better described by other methods.^{7,13}

II. THE INTERACTION FORCES

The potential energy surface for Ne₃ is described as the simple addition of accurate atom-atom interactions.^{10–12} In order to properly compare our results with some of the previously published data,^{3,5–7} we employ three different pair potentials.

(1) The Lennard-Jones (LJ) potential

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

whose parameters were taken from Ref. 3.

(2) The Morse potential [coming from a numerical fitting, in the region of the well, of the potentials given by Aziz and Slaman for Ne–Ne (Ref. 14)]

$$V_{\text{Ne-Ne}}(R) = D[e^{-2\alpha(R-R_e)} - 2e^{-\alpha(R-R_e)}], \quad (2)$$

the above parameters were previously obtained in Ref. 15.

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

Ne ₂					
PECs parameters			Bound states		
			(cm ⁻¹)	Units of ϵ	
LJ	ϵ	35.6 K	-14.0245	-0.5668	$k=0$
	σ	5.195 a.u.	-2.6834	-0.1085	$k=1$
	m_{Ne}	20.18 amu	-0.0298	-0.0012	$k=2$
Morse	D	29.36 cm ⁻¹	-16.5572		$k=0$
	α	2.088 Å ⁻¹	-1.8774		$k=1$
	R_e	3.091 Å			
	m_{Ne}	20.00 amu			
	α	0.5872 a.u. ⁻¹	-16.1758		$k=0$
CCSD(T)	c_1	-1.767 K	-2.7476		$k=1$
	c_2	-16.52 K	-0.0074		$k=2$
	c_3	-16.41 K			
	c_4	47.35 K			
	R_e	5.86 a.u.			
	C_6	6.447 (hartree)×(bohr ⁶)			
	m_{Ne}	20.18 amu			

(3) One recent two-body (2B) coupled-clusters-single-and-double(triple) [CCSD(T)] potential fit by a four-term Morse-type function (Ref. 16)

$$V_{\text{Ne-Ne}}(R) = \sum_{j=1}^4 c_j e^{-j\alpha(R-R_e)} + \frac{C_6}{R^6}, \quad (3)$$

where the term C_6/R^6 is added by the authors to have the correct long-range behavior and the C_6 coefficient is taken from the semiempirical HFD-B potential of Aziz and Slaman.^{14,17}

For the reader's convenience we report in Table I all the parameters used in the calculations, along with the resulting bound states for the dimers calculated via a direct diagonalization in a discrete variable representation (DVR).¹⁸ It is clear from the above comparison that the differences in the number and positions of the dimer's bound states reflect the

different shapes of the potential energy curves (PECs) in the three adopted models (see Fig. 1). In the case of the Morse potential we get the most strongly bound ground state [reflecting its deeper well depth with respect to the LJ and CCSD(T) potentials], while it supports two bound states only because of its poorer description of the dispersion tail. On the other hand, both LJ and CCSD(T) potentials support three bound states, and while the deeper well depth of the CCSD(T) potential leads to a more stable ground state ($k=0$), the slightly stronger dispersion tail of the LJ potential lowers its second excited state, $k=2$ (see also Fig. 1).

In Table I we further report (for the LJ case) the energies of the bound states in units of ϵ in order to compare our results with those of Leitner and co-workers (see Table III of Ref. 3) who employed the same LJ potential. We also employed their same atomic mass ($m_{\text{Ne}}=20.18$ amu) in order to yield fully comparable energies. They found the ground state for Ne₂ to be at -0.5668ϵ , the $k=1$ at -0.1084ϵ , and $k=2$ at -0.0168ϵ . While the first two states are in excellent agreement with our results, their third state is one order of magnitude lower. We carefully checked our convergence with respect to the extension of the spatial grid (up to $R_{\text{max}}=1200$ a.u.) and the number of DVR points (up to 6000 points for the most extended grid, leading to a very dense grid with respect to the de Broglie wavelength associated to the three states,^{18,19} to confirm the accuracy of our results.

We notice here that in the Morse case, again to yield fully comparable energies, we employed the same mass used by Roy⁷ ($m_{\text{Ne}}=36458m_e=20.00$ amu, having taken $m_e=0.000\,548\,579\,911$ amu). In the CCSD(T) case we decided to use the same mass as in Ref. 3.

Experimental information on Ne₂ is extremely scarce not only because of the absence of a permanent electric dipole moment in the ground state prevents investigation by microwave and infrared spectroscopy but also because the lowest optically accessible electronic state of Ne₂ is located more than 16.5 eV above the ground neutral state and is thus not easy to study by high-resolution spectroscopy. However, Wüest and Merkt²⁰ have recently succeeded in mapping the rovibrational structure of the ground state of the dimer by

FIG. 1. Ground state potential energy curves for Ne₂. (a) Reference 3. (b) Reference 15. (c) Reference 16.

excitation of the $\Pi 0_u^+ \leftarrow X 0_g^+$ transition at 16.8 eV using a high-resolution vacuum ultraviolet laser technique. Based on their rovibrational analysis of the above transition they deduce the energy difference between the lowest two rotationless vibrational levels of the ground state ($k=0$ and $k=1$ in Table I) to be $13.76 \pm 0.14 \text{ cm}^{-1}$. The corresponding energy differences calculated from the LJ, Morse, and CCSD(T) potentials (see Table I) are 11.34, 14.68, and 13.43 cm^{-1} , respectively. Due to the position of the dimer's bound states, the first vibrational spacing is mapping an extended spatial region of the interaction potential. Therefore it is clear that the CCSD(T) potential gives a better description of the Ne-Ne interaction not only in the well region but also in the long-range part. This is obviously important when diffused van der Waals systems are studied, and even more if their excited states are sought.

In the following part of the paper we will see how the accuracy of the potential employed influences the properties of the trimer that we shall compute with our method.

III. THE DISTRIBUTED GAUSSIAN FUNCTION METHOD

We review here and further optimize the DGF method which was introduced earlier on by us as an alternative variational treatment to study boson triatomic systems with a zero total angular momentum ($J=0$).^{5,8} The procedure uses atom pair coordinates and a basis set formed by properly symmetrized products of monodimensional DGFs defined along each atom-atom coordinate.

This choice of coordinates provides a suitable way to tackle configurational studies since the method directly allows the analysis of the structural features of the trimers' bound states in terms of the probability densities, transparently expressed using the *physical* atom-atom coordinates. Moreover, it is possible to assess which are the predominant triangular structures and their relative importance in the description of each bound state, thereby providing a useful pictorial description of the bound states, as we shall illustrate below. For a trimer with three identical particles, the Hamiltonian for zero total angular momentum, using atom-atom pair coordinates R_1 , R_2 , and R_3 , can be straightforwardly derived to be⁸

$$H = \sum_{i=1}^3 \left\{ \frac{-\hbar^2}{m_A} \left[\frac{1}{R_i^2} \frac{\partial}{\partial R_i} R_i^2 \frac{\partial}{\partial R_i} + \frac{R_j^2 + R_k^2 - R_i^2}{2R_j R_k} \frac{\partial^2}{\partial R_j \partial R_k} \right] + V(R_i) \right\}, \quad (4)$$

where $i \neq j \neq k$. In these coordinates, the phase space volume element is

$$d\tau = R_1 R_2 R_3 \quad dR_1 dR_2 dR_3. \quad (5)$$

If Ψ is one of the eigenstates of the Hamiltonian given in Eq. (4), the transformation

$$\Phi = \sqrt{R_1 R_2 R_3} \quad \Psi \quad (6)$$

leads to the standard normalization condition⁸ and Φ can then be obtained as an eigenfunction of the following Hamiltonian:

$$H = \sum_{i=1}^3 \left\{ \frac{-\hbar^2}{m_A} \left[\frac{\partial^2}{\partial R_i^2} + t_i \right] + V(R_i) \right\}, \quad (7)$$

where $V(R_i)$ is the atom-atom interaction potential and the t_i operators have been given before.^{5,8} Notice that the Hamiltonian of Eq. (7) is totally symmetric under the change of any pair of particles. By excluding the t_i operators, this Hamiltonian would strictly correspond to the sum of three 2B Hamiltonians.

The total wave function is then expanded in terms of symmetrized basis functions

$$\Phi_k(R_1, R_2, R_3) = \sum_j a_j^{(k)} \phi_j(R_1, R_2, R_3), \quad (8)$$

with

$$\phi_j(R_1, R_2, R_3) = N_{lmn}^{-1/2} \sum_{P \in S_3} P[\varphi_l(R_1) \phi_m(R_2) \phi_n(R_3)]. \quad (9)$$

Here, j denotes a collective index such as $j = (l \leq m \leq n)$ for three identical particles and N_{lmn} are normalization factors.⁵ Each one-dimensional function φ_p is chosen to be a normalized Gaussian function²¹ centered at the R_p position

$$\varphi_p(R_i) = \sqrt{\frac{2A_p}{\pi}} e^{-A_p(R_i - R_p)^2}, \quad (10)$$

where A_p is a parameter defining the width of φ_p (Ref. 21) which inversely depends on the distance between two neighboring Gaussian functions and on an empirical parameter β which we took near to 1 ($\beta = 1.05$),

$$A_p = \frac{4\beta}{(R_{p+1} - R_{p-1})^2}, \quad A_1 = \frac{\beta}{(R_2 - R_1)^2}, \quad (11)$$

$$A_M = \frac{\beta}{(R_M - R_{M-1})^2},$$

where A_1 defines the first DGF and A_M the last Mth DGF. Hence, the larger the step between two neighboring Gaussians, the more extended the Gaussians are. 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 particles) 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.

In practice, in order to set up the basis set we have only to define the location of the monodimensional Gaussians along each atom-atom coordinate (for homonuclear systems the three distances are equivalent), namely, for an equidistant set we define the constant step Δ , the center R_p of the first DGF, and the total number M of DGFs. We obtain in this way a set $\{R_p\}$, with the centers of the M monodimensional DGFs or, equivalently, a set $\{\varphi_p(R_i)\}$ of M DGFs. From this set we build, according to Eq. (9), the three-dimensional ba-

sis functions. However, not all the products of three DGFs, whose centers belong to the chosen set, are acceptable. In fact, in order to fulfill the triangle's inequality requirement (TIR), the product $\varphi_l \varphi_m \varphi_n$ shall belong to the chosen basis if the corresponding DGF centers verify the inequality

$$|R_l - R_m| < R_n < R_l + R_m. \quad (12)$$

Note that Eq. (12) corresponds to a more restrictive inequality (instead of the classical triangular inequality requirement $|R_l - R_m| \leq R_n \leq R_l + R_m$ to avoid unphysical behavior of the total wave functions at the triangle's inequality boundaries, see the following section for a lengthy discussion of the procedure we adopted).

Since the basis functions ϕ_j are not orthogonal, we have to finally solve the generalized matrix eigenproblem,

$$\mathcal{H}\Phi = \mathcal{S}\Phi\mathcal{E}, \quad (13)$$

where $\mathcal{S}$ is the overlap matrix in the $\{\phi_j\}$ basis set.

As we have discussed at length before^{5,8,22} the use of pair coordinates, besides formulating the Hamiltonian problem in its exact form, allows us to obtain several indicators on the spatial behavior of the bound states of the systems. In particular, one can associate to the large number of triangular configurations which make up expansion (8) various statistical quantities such as the root mean value of the square area of the triangle (S) through the use of Heron's formula, the average of the cosine value (and the various moments) of any angle in each triangular structure through the use of the cosine theorem and others (e.g., see Ref. 9). We can also derive several distribution functions, e.g., the pair-distribution (PD) functions

$$D^{(k)}(R_1) = \int \int |\Phi_k(R_1, R_2, R_3)|^2 dR_2 dR_3. \quad (14)$$

A further useful tool for the analysis of the trimers' geometrical features is provided by the definition of "pseudoweights" P_j^k (Ref. 8) associated to each triangular configuration ϕ_j [Eq. (9)] in the expansion of the total wave function for the k th bound state [Eq. (8)]. These quantities naturally arise from the normalization condition of the wave functions:

$$1 = \langle \Phi_k | \Phi_k \rangle = \sum_j a_j^k \langle \Phi_k | \phi_j \rangle = \sum_j P_j^k. \quad (15)$$

One must keep in mind that, although the sum of the quantities P_j^k is effectively equal to one, their values (not always positive) prevent them from being considered proper statistical weights. This is a consequence of the nonorthogonality of the basis functions ϕ_j ,

$$P_j^k = a_j^k \langle \Phi_k | \phi_j \rangle \neq |a_j^k|^2. \quad (16)$$

Despite this drawback, the above quantities still enable us to assess the importance of the different triangular configurations (linear, isosceles, equilateral, and scalene) which are present in a classical description of the triatomic system and, thus, give us the dominant geometrical structure of each bound state. Moreover the expectation values of different observables can be calculated via the pseudoweights, resorting to the mean value theorem,

FIG. 2. A pictorial example of the triangle's inequality for requirement for "collinear" configurations, which are not finally included in our basis set. See text for details.

$$\langle x \rangle_k = \sum_j a_j^k \langle \Phi_k | x | \phi_j \rangle \approx \sum_j P_j^k x_j, \quad (17)$$

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. We can thus further characterize the bound states of the trimer by evaluating, for instance, the average values of the interatomic distances in the dominant structures, thereby gaining some insight on the nuclear motion in the ground and excited states.

A. Optimizing of the DGF basis set expansion

The DGF procedure would provide exact results in the limit of using an infinite number of δ functions as selected basis functions.²¹ In practice, however, one has to deal with a finite number of Gaussian functions of nonzero width.

Let us indicate by $\varphi_l^j(R_1)$, $\varphi_m^j(R_2)$, and $\varphi_n^j(R_3)$ the DGFs constituting the generic basis function $\phi_j(R_1, R_2, R_3)$ according to Eq. (9), and by R_1 , R_2 , and R_3 the integration grid values along the three atom-atom distances (see Fig. 2). The width of the chosen DGFs (which depends on the step between two neighboring Gaussians and on the empirical parameter A_p , see Eq. (10) will determine the radial domain in the R_1 , R_2 , and R_3 coordinates where ϕ_j is appreciably nonzero. Now, even when the three centers satisfy the TIR, it may exist a subdomain in the space of the coordinates in which one of the distances is greater than the sum of the other two ($P[R_3^* > R_1^* + R_2^*]$, $P \in S_3$, see Fig. 2), causing the corresponding ϕ_j to have in such subdomain nonzero amplitude at the triangle's inequality boundaries which is clearly an unphysical feature. The basis functions mostly affected by this unphysical behavior correspond to the permutational products of DGFs whose centers describe a collinear geometry, i.e., $R_n \sim R_l + R_m$. When this is the case, as in the example shown in Fig. 2 for $R_l = 4.4a_0$, $R_m = 6.4a_0$, and $R_n = 10.8a_0$, respectively, we find values for R_1^* , R_2^* , and R_3^* which do not satisfy the triangular requirement. For instance, the three possible values shown in the figure with vertical

dashed lines are far to verify that $R_3^* \leq R_1^* + R_2^*$. In fact one should notice that for those particular values of R_1^* and R_2^* in Fig. 6, the first nonacceptable value for R_3^* is reached even before the center of the third Gaussian function, $R_m = 10.8a_0$. Consequently, this problem will largely affect only the vibrational states with non-negligible contributions of collinear configurations i.e., all the excited states with energy higher than the barrier to linearity, given by the energy of the ground vibrational state of the dimer).

First of all, we wish to point out that reducing the value of Δ is in itself an improvement, since the Gaussian functions will have a smaller width and the subdomain where the TIR is not satisfied will be automatically smaller. We are obviously looking for a more general recipe to obtain reliable results without choosing too small values of Δ , which would heavily increase the number of basis functions, especially if extended grids are needed, thereby increasing computational costs.

Furthermore, and as mentioned in the preceding section, we restrict the accepted basis functions according to Eq. (12), thus discarding from the basis set those with $R_n = R_l + R_m$, which would be classically allowed. This choice reduces the subdomain where the total wave function behaves pathologically, without affecting appreciably the description of the linear configurations.

In order to quantify, for a given basis set, the relevance of the subdomain where the total wave function for each vibrational bound state is unphysically nonzero, we introduced an operator $\mathcal{W}$ which we called the “badness” operator and which “measures” the deviation from the TIR (Refs. 5 and 8):

$$\mathcal{W}(R_1, R_2, R_3) = \begin{cases} 0, & |R_1 - R_2| \leq R_3 \leq R_1 + R_2 \text{ holds} \\ 1, & \text{otherwise.} \end{cases} \quad (18)$$

This operator can be easily represented in terms of DGFs as $\mathcal{I}(ll', mm', nn')$

$$\begin{aligned} &= \langle \varphi_l(R_1) \varphi_m(R_2) \varphi_n(R_3) | \mathcal{W} | \varphi_{l'}(R_1) \varphi_{m'}(R_2) \varphi_{n'}(R_3) \rangle \\ &= \frac{1}{2} s_{nn'} \int_0^\infty \int_0^\infty dR_1 dR_2 \varphi_l(R_1) \varphi_{l'}(R_1) \varphi_m(R_2) \varphi_{m'}(R_2) \\ &\quad \times \{ 2 + \operatorname{erf}[\sqrt{A_{nn'}}(|R_1 - R_2| - R_{nn'}^*)] \\ &\quad - \operatorname{erf}[\sqrt{A_{nn'}}(R_1 + R_2 - R_{nn'}^\dagger)] \}, \end{aligned} \quad (19)$$

where $s_{nn'}$ is the overlap of two Gaussian functions centered at R_n and $R_{n'}$, $\operatorname{erf}(x)$ is the error function and, finally, $A_{nn'}$ 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. (9). In practice, the remaining integrals are numerically computed by resorting to the mean value theorem:

$$\begin{aligned} \mathcal{I}(ll', mm', nn') &\approx \frac{1}{2} s_{ll'} s_{mm'} s_{nn'} \{ 2 + \operatorname{erf}[\sqrt{A_{nn'}}(|R_{ll'}^\dagger \\ &\quad - R_{mm'}^\dagger| - R_{nn'}^\dagger)] - \operatorname{erf}[\sqrt{A_{nn'}}(R_{ll'}^\dagger \\ &\quad + R_{mm'}^\dagger - R_{nn'}^\dagger)] \}. \end{aligned} \quad (20)$$

This expression, together with the coefficients of the total wave function in the chosen basis set, $\{\phi_j(R_1, R_2, R_3), j = (l \leq m \leq n) \text{ [Eq. (9)] [i.e., the eigenfunctions of the Hamiltonian of Eq. (7)]}$, is used to estimate, through the average value $\langle \mathcal{W} \rangle$, how much the norm of the wave function integrated over the entire space (equal to unity) differs from the norm, which we call the TIR norm, integrated only in the domain (the TIR domain) where the TIR is satisfied. With a well-behaving basis set, the TIR norm should be equal to one as well. However, the smallest $\langle \mathcal{W} \rangle$, the better the corresponding basis set will reproduce the bound states.

It is, however, evident that this procedure is somewhat impractical since it always requires to get the solution of the variational problem for each given basis set, even for those that will be rejected. However, the unphysical behavior originates in the choice of the basis set as it depends on the number of basis functions $\varphi_l(R_1) \varphi_m(R_2) \varphi_n(R_3)$ (with correct permutation) which do not satisfy the TIR somewhere over their definition space and on the extent of the radial subdomain where the requirement is not satisfied. This ill behavior is obviously amplified for those eigenstates which present non-negligible contributions from the pathological basis functions, but the best-behaving basis set will provide the closest to one TIR norms for all the bound states, since it structurally ensures the extent of the unphysical domain to be as small as possible. It then becomes more reasonable to select the optimal basis set before solving the eigenvalue problem, i.e., to evaluate Eq. (20) for each pair of basis functions (l, m, n) ; (l', m', n') and then to sum over all of them after taking into account the permutation symmetry. If we now divide the result by the number of basis functions in that particular basis set, we produce a “normalized” indicator $\langle \mathcal{W} \rangle_{\text{basis}}$, which only depends on the location of the basis functions and not anymore on the dimension of the basis set. This procedure is equivalent to evaluating the expectation value $\langle \mathcal{W} \rangle_{\text{basis}}$ of $\mathcal{W}$ for a “democratic” wave function with equal weights,

$$\Phi(R_1, R_2, R_3) = \sum_j \phi_j(R_1, R_2, R_3), \quad (21)$$

where $\phi_j(R_1, R_2, R_3)$ has the same meaning as in Eq. (9).

The practical scheme that we followed for a uniform DGF grid requires the following steps.

(i) Set up the initial basis set by (a) choosing the constant step Δ ; (b) selecting the center of the first DGF and the number of the monodimensional Gaussian functions that will constitute the basis set.

(ii) Set up the “sibling” basis set by rigidly shifting all the centers of the DGFs of the starting basis set by an amount $d\Delta$, $\Delta/d\Delta$ times (so that, at the end, the first DGF is brought to coincide with the second DGF of the starting basis set).

(iii) Now select the optimal basis set by evaluating the $\langle \mathcal{W} \rangle_{\text{basis}}$ for the entire family of basis sets with the given step Δ , thereby finding the one set with the minimal badness, as defined before.

The scheme was then repeated for a set of smaller values

TABLE II. Basis badness indicator $\langle \mathcal{W} \rangle_{\text{basis}}$ for a family of basis sets differing only by the location of the DGFs, with corresponding norms $\langle \Phi_k | \Phi_k \rangle^{\text{TIR}}$ integrated in the domain where the TIR is satisfied, and energies (in cm^{-1}) for some selected bound states ($k=1, 2, 3, 6$) of Ne_3 .

First DGF	$\langle \mathcal{W} \rangle_{\text{basis}}$	$k=1$		$k=2$		$k=3$		$k=6$	
		$\langle \Phi_k \Phi_k \rangle^{\text{TIR}}$	E_k	$\langle \Phi_k \Phi_k \rangle^{\text{TIR}}$	E_k	$\langle \Phi_k \Phi_k \rangle^{\text{TIR}}$	E_k	$\langle \Phi_k \Phi_k \rangle^{\text{TIR}}$	E_k
4.0	0.002 41	0.9999	−30.25	0.9999	−28.26	0.9999	−25.73	0.9997	−18.08
4.1	0.048 64	0.9890	−30.25	0.9950	−29.06	0.9966	−27.06	0.9292	−19.37
4.2	0.026 67	0.9934	−30.25	0.9968	−28.81	0.9984	−26.72	0.9637	−19.00
4.3	0.013 14	0.9970	−30.25	0.9982	−28.60	0.9992	−26.38	0.9847	−18.66
4.4	0.005 75	0.9989	−30.25	0.9991	−28.42	0.9996	−26.05	0.9939	−18.36
4.5	0.002 21	0.9997	−30.25	0.9996	−28.26	0.9998	−25.73	0.9978	−18.08

of Δ , thereby arriving at a formula which provides, for each Δ , the optimal location of the DGFs. If we denote by $\{R_i\}$ the DGF centers we find

$$R_i = (\Delta + n \cdot \Delta) + i \cdot \Delta, \quad i = 0, 1, 2, \dots, N-1, \quad (22)$$

where the value of n provides the correct multiples of Δ that radially locate the position of the first DGF of the expansion set. Since no specification about any particular trimer has been made so far, Eq. (22) is a system-independent formula which specifies, for each chosen Δ , the location of the basis Gaussian functions which ensures a negligible deviation from the TIR. Once repeated the calculation with two different values of Δ one can check the degree of accuracy of the results and eventually choose a smaller Δ . This can be necessary when the excited states of a system are sought, due to their smaller de Broglie wavelength in the well region. A few comments on the selection procedure and on the meaning of the formula are given below.

When selecting the starting basis set, for each given step Δ the number of DGFs must be sufficient to map the spatial extension of the most diffuse bound state which has to be described. A first, approximate value for R_{max} can be inferred from the 2B potentials. One then runs a full calculation (i.e., one obtains the eigenvalues and atom-atom pair distributions for the bound states) with $\Delta=0.5a_0$ and using a large R_{max} in order to better assess the spatial domain of the three interaction potentials used here to describe the trimer, i.e., the domain within which the radial distributions of all the found trimer's bound states are significantly nonzero.

As a choice of $d\Delta$ we took either $0.1a_0$ or $0.01a_0$, depending on the significative digits of the chosen Δ , to generate the family of “sibling” basis sets. The dimension of such a family is not a problem, since the calculation of $\langle \mathcal{W} \rangle_{\text{basis}}$ is very fast. For example, we could set up a starting basis set with a constant step $\Delta=0.5a_0$, the first DGF located at $4a_0$ and composed by 43 Gaussians (the last one being located at $25a_0$). The first sibling basis set was then obtained by rigidly shifting all the DGF centers by $0.1a_0$ (so that the first DGF is now located at $4.1a_0$ and the last one at $25.1a_0$), arriving to the fifth sibling ($\Delta/d\Delta=5$ in this case), for which the first DGF is at $4.5a_0$, thereby overlapping the initial basis set with the exclusion of its first DGF at $4a_0$ (now missing) and with an additional DGF at $25.5a_0$, the total number of DGFs being always kept the same.

Finally, Eq. (22) allows one, for each Δ value, to obtain the optimal location of the DGFs in order to make the sub-

domain of unphysical nonzero wave functions' amplitudes as negligible as possible. Computationally, this corresponds to make $\langle \mathcal{W} \rangle_{\text{basis}}$ as small as possible and, consequently, to have the norms of the wave functions for the bound states as close as possible to one when integrated in the TIR domain. The reason for this to be so relies on the existence of favorable geometrical relations between the DGF centers and, consequently, on a minor or major extension of the unphysical subdomain of definition.

To better illustrate this feature we chose a family of basis sets, each made of 43 Gaussians distributed at the constant step $\Delta=0.5a_0$. We then calculated the normalized basis badness $\langle \mathcal{W} \rangle_{\text{basis}}$ to select the best basis set, and we nevertheless carried out the calculation of the bound states for all the sets to show the effects of the basis badness. The first basis set has the first Gaussian located at $4a_0$ (and the last one at $25a_0$). As explained above, choosing $d\Delta=0.1a_0$ we find five sibling basis sets, the last one having the first DGF located at $4.5a_0$ (and the last one at $25.5a_0$). In Table II we report for each basis set (identified by the location of its first DGF) the values of the corresponding $\langle \mathcal{W} \rangle_{\text{basis}}$, together with the TIR norms and the energies for some selected bound states. As already discussed (see Fig. 2 and related text) the pathological basis functions are those describing arrangements near to linearity and Eq. (22) provides the location of the DGFs which ensures the minimization of the unphysical deviation from the TIR. We expect the existence of ill-behaving basis functions, if any, to be evident for those states with a strong contribution from collinear arrangements in the state expansion, and to only slightly affect the states with other predominant structure. We will show in Sec. IV C that the collinear arrangements are barely describing the ground and first excited states of Ne_3 , while they give their greatest contribution to the states $k=2, 3$, and 6 . From Table II we see that the best basis sets are indeed those whose DGF centers are located at multiples of the corresponding Δ ($0.5a_0$ in this case) according to Eq. (22). The TIR norms of the bound states found with such basis sets are always closer to one with respect to using the other basis sets. Furthermore, we notice that while for the state $k=1$ (which has no significative contribution from collinear arrangements, see Sec. IV C) the energy is not affected by the choice of the basis set, for the other bound states the presence of ill-behaving basis functions artificially shifts the energy to lower values and moves the TIR norm away from one (or equivalently produces a more extended unphysical domain).

The formula is of general use and what really depends on the particular trimer under study is the choice of the locations of the first and the last DGF, since such selections obviously depend on the chosen potential function. This is indeed taken into account by Eq. (22) via the integer parameter “ n ,” which locates the first DGF, and the integer “ N ” which fixes the number of DGFs in order to map the requested radial grid, leading to N DGFs for each monodimensional radial grid. For the Ne_3 problem we took a grid which was extended from about $4.5a_0$ up to about $24a_0$ to properly describe the excited states supported by all the three different interaction potentials we use in the present study, even though the Morse potential could have allowed the choice of a smaller grid. In the case, for example, of $\Delta=0.5a_0$, we set $n=8$ and $N=42$.

The critical behavior of the wave functions at the triangle's inequality boundaries, when Gaussian functions along atom-atom coordinates are used, has been discussed earlier.^{7,13} In particular, the work of Ref. 7 shows that the triangle's inequality requirement is automatically satisfied when Pekeris coordinates^{23,24} are chosen, this feature being seen by the author as the advantage of using Pekeris coordinates with respect to the atom-atom ones distances.⁷

Our present results, reported in the following section, will however, show that a careful choice of the DGF basis set along the lines of our previous discussion, resulting in a practical and easy-to-use scheme, makes our approach based on pair coordinates perfectly capable of accurately describing not only the ground state but also the excited states of the trimer, even those lying well over the isomerization barrier.

Furthermore, the DGF method naturally allows a complete structural analysis of the bound states in terms of the radial distributions along the atom-atom coordinates, of the average values of distances and angles, and of the contribution of different configurations (equilateral, isosceles, and scalene) to each bound state.

IV. RESULTS AND DISCUSSION

Since our aim is to obtain a complete description of the ground and the excited bound states of the trimers with one single calculation, it implies the need of selecting both an extended spatial grid to describe the more diffuse excited states and a dense enough one to also accurately describe all the states, from those located more deeply down the attractive potential to those setting in the outer region and with the shortest associated wavelength. We find it necessary to stress here how important it is to carefully check the degree of convergence of the final results when the excited states are concerned. For example, a poor radial grid, both in its spatial extension and in the number of the basis functions or points (depending on the method), is obviously going to affect the excited states more than the ground state: since the latter is the most localized, and with the largest de Broglie wavelength in the well region, one can get away with a less dense grid than in the case of the states closer to the upper rim of the potential.

The problem of choosing an efficient distributed Gaussian basis for bound states has been the object of several

studies (see, e.g., Refs. 13 and 25, and references therein); for example, Garashchuk and Light¹³ showed that both the optimal widths and the density of Gaussians in their quasirandom distributed Gaussian basis are linear functions of the potential. Such an approach, or similar ones, helps in saving computational time while preserving the accuracy of the calculations. We proceeded in a systematic way to optimize the DGF set for the CCSD(T) potential and employing it also for the other two potential models (LJ and Morse), in order to focus only on the effects of changing the adopted pairwise potentials. We in fact expect (from the analysis of the PECs) that the basis set optimized for the CCSD(T) potential should also be realistic when using the other two PESs as well, even if reduced basis set choices could have been sufficient for achieving convergence in those cases.

After running the “light” calculation with step $\Delta=0.5a_0$ and the Gaussian functions distributed according to Eq. (22) we could define the extension of the radial grid necessary to describe all the produced bound states (from around $4.5a_0$ to $24a_0$, as already mentioned). We then progressively reduced the value of Δ , always locating the Gaussian functions according to Eq. (22). For $\Delta<0.3a_0$ the Gaussians become too many to cover the chosen radial domain, i.e., they lead to very large matrices which require a great amount of memory to be stored and also a great amount of CPU time to be solved. Since in the long range region it is unnecessary to use a very dense basis set, as also pointed out by¹³ we divided the radial domain into two parts, the first up to around $16a_0$ (the “well” region) where the Gaussian functions are equidistantly distributed with increasingly smaller Δ , and the second which maps the long range region, with the Gaussian functions distributed at the constant step of 2Δ (according to Eq. (22), in fact, taking the long range region step twice as big as the well region step ensures the best locations of the Gaussian functions in both regions).

The results we present in this work are obtained with a one-dimensional Gaussian basis set made up of 62 DGFs. The Gaussians are distributed with a constant step of $0.3a_0$ from $4.50a_0$ up to $22.80a_0$ leading to 32 197 symmetrized basis functions 9. Our integration grid on each of the three atom-atom coordinates is composed by 2000 points from $2.8a_0$ to $24.6a_0$. Such a basis set ensured converged results within 0.1 cm^{-1} for the upper states. A higher precision ($\leq 10^{-2} \text{ cm}^{-1}$) was attained for the lowest lying states.

A. The spectrum of the bound states

In Table III we report the energies of the bound states of Ne_3 trimer we calculated with the DGF method, using three different atom-atom potentials (see Sec. II and the caption to Table III) at $J=0$. The results are also compared with some previously published findings.

The first three sets of data are the results of Blume, Greene, and Esry,⁶ who used the hyperspherical coordinates at different levels of approximation and the LJ potential given in Ref. 3. 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

TABLE III. Comparison of the energetics in Ne_3 for $J=0$ ground and excited states using different pairwise interactions (see Table I) and methods. See main text for a full explanations of the symbols. All energies are in cm^{-1} .

Ne_3								
k	LJ					Morse		CCSD (T) DGF ^c
	BO-hs ^a	Adiab-hs ^a	CAC-hs ^a	DVR-DT ^b	DGF ^c	Lanczos ^d	DGF ^c	
0	-43.28	-41.67	-42.38	-42.51	-42.55	-50.09	-50.09	-49.21
1	-31.62	-26.60	-29.92	-30.19	-30.26	-34.21	-34.21	-34.65
2	-27.81	-22.53	-27.72	-28.16	-28.40	-32.57	-32.73	-32.74
3	-25.71	-18.46	-25.14	-25.61	-25.93	-29.71	-29.92	-30.19
4	-21.67	-16.72	-21.57	-22.22	-22.52	-25.95	-26.12	-26.57
5	-20.84	-14.89	-18.34	-19.23	-19.42	-21.74	-21.77	-22.56
6	-19.09	...	...	-18.21	-18.45	-20.26	-20.33	-21.17
7	-16.19	...	...	-17.44	-17.70	-19.27	-19.35	-20.68
8	-15.47	...	...	-15.24	-15.36	...	-16.74	-17.91
9	-14.54	...	...	-14.47	-14.53	...	...	-16.84
10	...	...	...	...	...	...	...	-16.50

^aBlume, Greene, and Esry (Ref. 6). Hyperspherical coordinates at different levels of approximation.

^bLeitner, Doll, and Whitnell (Ref. 3). DVR with diagonalization truncation.

^cDGF (present work).

^dRoy (Ref. 7). Symmetry-adapted Lanczos approach with Pekeris coordinates in DVR.

channels (notice that in this approach the authors find ten bound states, but they report in their paper only the first six).

The next set of data (DVR-DT) comes from Leitner, Doll, and Whitnell,³ who used a discrete variable representation with diagonalization-truncation method and the LJ potential. The authors expressed their results in unit of $\epsilon = 35.6$ K while in Table III we converted the energies into cm^{-1} , using $0.695\,039\,\text{cm}^{-1}/\text{K}$ as conversion factor from K to cm^{-1} . To complete the calculations obtained with a LJ PES we also report in the fifth column our present results for the same potential.

In the sixth column (labeled Lanczos) we report the results of Roy⁷ who used Pekeris coordinates and a symmetry-adapted Lanczos approach with a Morse potential¹⁵ (the author also employs a LJ potential, but we only consider here the results obtained with the Morse potential). In that paper the author compares his findings on Ne_3 and Ar_3 (using sums of LJ potentials) with Ref. 26, while in the Morse case he refers to our own work, Ref. 5, and to Ref. 13. Again, we report next to it our DGF results with the same Morse potential.

Finally, the last column contains the DGF results obtained with the CCSD(T) potential, which has never been previously used for the calculation of the bound states of Ne_3 .

With the largest basis set employed our DGF calculations found 10 bound states with the LJ potential, 9 states with the Morse potential, and 11 in the CCSD(T) case. Their energies are relative to the full fragmentation threshold (our zero of energy) but only the trimer's states which lie beneath the ground state energy of the dimer, which defines the 2B fragmentation threshold with the loss of one single atom, are actually bound (see Table I for the dimer's ground state energies in the three potential models). We further remark that the dimer's and the trimer's ground state energies are calculated using different methods (the DVR in the dimer's case

and the DGF method in the trimer's state). This could introduce some uncertainty regarding the highest bound states of the trimer which fall very near the 2B fragmentation threshold, because a change in the method could cause some numerical shifts in the energy values that, even if very small, can be comparable with the binding energy itself. However, the companion analysis of the geometrical properties of the bound states (as, e.g., the average values of distances or the distribution functions) helps in assessing the true bound nature of the highest trimer's states lying near the threshold and in finding it to be correctly so, as we shall further demonstrate below.

For the LJ potential, the agreement among the most accurate methods (CAC-hs, DVR-DT, and DGF) is quite good, even though the CAC-hs case seems to find increasingly poorer results starting from the last published state ($k=5$).

When using the Morse potential we found one more bound state with respect to Ref. 7, but the first eight states are in extremely good agreement. We also repeated the calculation using the greater mass employed in the LJ and CCSD(T) cases, but this does not change significantly the features of the spectrum and only slightly shifts all the energies at lower values (by at most $0.2\,\text{cm}^{-1}$) keeping the same number of bound states.

In Ref. 7, the author compares his results to those presented in Ref. 5, where the DGF method was applied for the first time to rare gas trimers, and a Morse-type potential was employed to model Ne-Ne and Ar-Ar interactions. Since our main interest there was on assessing the properties of the Rg_3 ground states, one should point out that 15 Gaussians were used to describe the Ne_3 system, distributed from 2.6 to 5.4 Å (i.e., from about 4.9 to 10.2 a.u.). As can be easily seen in Fig. 3, where the distribution functions for the first four states are reported (see the discussion in following section), such a spatial grid is sufficient to correctly describe the ground state, as was the main object of that work, but not to

FIG. 3. Distribution functions for the first four bound states of Ne_3 trimer.

accurately locate excited states. For the $k=1$ state, for instance, the grid must at least extend up to 14 a.u. and for $k=2$ up to 16 a.u.; consequently, the energies we found there were -50.23 , -33.81 , and -27.53 a.u., respectively, for $k=0,1,2$. This shows that we found there⁵ excited state energies that are too small compared to those from the present, more extended, study that specifically focuses on such excited states. We believe, in fact, that the present analysis demonstrates how any discrepancy seen in Ref. 5 was due to the fact that the quality of the basis set presented there was chiefly aimed at correctly reproducing the ground state energy but was not large enough for describing excited states. The analysis of the PD functions and of the relative importance of the different triangular families for each bound state (see Secs. IV B and IV C) further testifies to the ability of the DGF method to efficiently describe the bound states of a trimer even in the presence of predominant linear configurations.

Finally, our present results in Table III potential supports one additional bound state with respect to the LJ potential and two more with respect to the Morse potential. The absolute energy values obtained when using the LJ model differ markedly from those obtained using the CCSD(T) potential. However, the LJ good description of the dispersion tail partially compensates for its having a less deep well and the vibrational spacings reported in Table IV (simulating an hypothetical high-resolution spectrum) show for it to have similar features with respect to the CCSD(T) calculations: compare, for instance, the second, third, and fourth transitions as calculated here using LJ and CCSD(T) potentials and shown by the second and fifth columns. Moreover, if we express the zero point energy (ZPE) as a percentage of the classical well depth of the corresponding 3B potential (i.e., $D_e^{\text{Ne}_3} = 3 \times D_e^{\text{Ne}_2}$) we find in the CCSD(T) case a value of 42.46% while the LJ description yields $\text{ZPE} = 42.67\%$.

In the Morse case, due to the similar features between the new potential and the Morse one in the well region, we consequently find good agreement with the energy values of the lowest bound states of the trimer (up to $k=4$), which are supported by these two potentials. The largest dispersion tail

shown by the CCSD(T) potential is then responsible for the additional bound states which appear with it as opposed to the Morse calculations. As for the vibrational spacings, the use of the Morse potential generally shifts the transition energies towards the blue with the exception of the second and the last transitions. The ZPE in the Morse case is 42.96%, very similar to what we obtained using the other two potential functions.

To conclude the analysis of the energetics of the trimer, we have shown that the simple descriptions of the Ne–Ne interaction given by the LJ and Morse models are able to well reproduce the effect of the quantum nuclear motion but they badly simulate (with the exception of some fortuitous compensations of the LJ potential) the rotationless vibrational spectrum of the trimer reported in Table IV.

B. The spatial distribution functions

The one-dimensional PD functions [Eq. (14)] are shown in Figs. 3–5 for the three potentials of the present study. For the CCSD(T) potential, we also report in Fig. 5 the PD functions obtained using a larger basis set for the last bound state

TABLE IV. Comparison of theoretical vibrational spacings for Ne_3 in the $J=0$ ground electronic state. All values are given in cm^{-1} .

	LJ		Morse		DCCSD(T) GF ^a
	DVR-DT ^a	DGF ^b	Lanczos ^c	DGF ^b	
0 $\rightarrow$ 1	12.32	12.29	15.88	15.88	14.56
1 $\rightarrow$ 2	2.03	1.86	1.64	1.64	1.89
2 $\rightarrow$ 3	2.55	2.47	2.86	2.81	2.54
3 $\rightarrow$ 4	3.39	3.41	3.76	3.80	3.59
4 $\rightarrow$ 5	2.99	3.10	4.21	4.35	3.99
5 $\rightarrow$ 6	1.02	0.98	1.48	1.44	1.39
6 $\rightarrow$ 7	0.77	0.74	0.99	0.98	0.56
7 $\rightarrow$ 8	2.20	2.35	...	2.61	2.69
8 $\rightarrow$ 9	0.77	0.82	...	...	1.10
9 $\rightarrow$ 10	...	...	...	...	0.44

^aLeitner, Doll, and Whitnell (Ref. 3).

^bRoy (Ref. 7).

^cDGF (present work).

FIG. 4. Distribution functions for the states from $k=4$ up to $k=7$ of Ne_3 trimer.

($k=10$, left bottom panel) and for the first state above threshold ($k=11$, right bottom panel). The distribution functions are normalized to unity and, because of the symmetry of the total wave function, they represent the average probability density along any of the three atom-atom distances.

Up to the state $k=9$ (the last bound state we found supported by the Morse potential) the Morse model and the CCSD(T) potential are seen to yield similar spatial shapes for their bound states, at least for their probability density values along any atom-atom coordinate. The LJ bound states show also very similar features with respect to the other two potentials, with the exception of the states labeled $k=5$, $k=7$, and $k=9$ (which is the last bound state for that potential).

The ground state PD function suggests a predominant equilateral structure with an expectation value for the atom-atom distance of 6.3 ± 0.6 a.u. (we already presented the results relative to the ground state in a previous work¹¹). This value is slightly larger than the classical value of 5.86 a.u. and it is in excellent agreement with the expectation value obtained by DMC calculations.¹¹ For the first excited state $k=1$, the PD function suggests a dominant isosceles configuration:

the probability density shows a maximum at around 6 a.u., and another local maximum at around $8.5a_0$. After integrating over the radial coordinate, about 2/3 of the density is found to lie before about $8a_0$, indicating that two of the three equivalent atom-atom distances have a probability maximum at $6a_0$ while the third one has a maximum at a larger distance, corresponding to a “flat” isosceles.

An interesting additional feature shows up for the present system starting from the state $k=2$ (see Fig. 3). The PD function exhibits a maximum at about $6.2a_0$ and another (local) maximum at about $12.6a_0$; furthermore, 2/3 of the density is clearly found before $10a_0$ and the remaining 1/3 after $10a_0$ (going through a region of nearly zero probability density): this suggests a dominant linear configuration.

The isomerization barrier to the linear configuration is given, with respect to the trimer’s ground state, by an amount of energy roughly equal to the ground state energy for the dimer Ne_2 : the effect of one of the Ne–Ne interactions is almost negligible in the linear arrangement, so twice the binding energy of one dimer gives the dominant contribution to the total binding. When using the LJ potential the ground

FIG. 5. Distribution functions for the states from $k=8$ up to $k=11$ of Ne_3 trimer.

state of Ne_2 is located at -14.02 cm^{-1} , so that we do not expect the system (whose ground state energy is -42.55 cm^{-1}) to assume a linear arrangement in its excited states at energies lower than $\sim -28.5 \text{ cm}^{-1}$. The energy of the LJ excited state which starts showing some appreciable contribution from the linear configuration, i.e., $k=2$, is located at -28.40 cm^{-1} , in accord with the above estimate. The first excited state ($k=1$) is instead at -30.26 cm^{-1} and its PD function is practically zero at around $12a_0$, where we would expect a non-negligible distribution in case of it having a linear arrangement.

The situation is very similar for the other two potentials. In the Morse case the dimer's ground state energy is -16.56 cm^{-1} and the trimer's ground state is -50.24 cm^{-1} , so that we expect some contribution from the linear arrangements for energies around (and above) -33.7 cm^{-1} . In the CCSD(T) case the isomerization barrier to linearity is 16.18 cm^{-1} and, the trimer's ground state energy being -49.21 cm^{-1} , we expect to find some contribution from the linear configurations at energies higher than -33 cm^{-1} . Again, the first excited state $k=1$ is for both these potentials too low in energy to go over the barrier, and the corresponding PD functions quickly die after $11a_0$. On the other hand, from the second excited state $k=2$ on, we expect that all the bound states will show a more or less important contribution from the linear configurations since they all lie above the isomerization barrier. Using the definition of pseudoweights [see Eq. (15)] we can therefore introduce a measure of the contribution from the linear (and other) configurations which are present in each bound state of the trimer, as we will describe below.

The analysis of the PD functions is thus seen to provide a rich amount of information. First of all, we notice that in spite of the important differences in the spectral features exhibited by the three potential models, it is surprising to find almost identical radial distribution functions (apart from some minor differences present in the LJ model). This shows that the energetics of the system is much more sensitive to the features of the potential than are the spatial descriptions of the corresponding wave functions.

Second, the above analysis provides the necessary tools for assessing the true bound nature of the calculated eigenstates, overcoming the uncertainty on the position of the 2B dissociation threshold with respect to the trimer's bound states (see Sec. IV A). We have therefore adopted here a stabilizationlike approach,²⁷ based on the different behavior shown by true bound states versus "scattering" states when the basis set is extended. In particular, we expect that if we add to the basis set some functions at a larger radial distance, the PD functions of the bound states will not change, while the scattering states will expand over the entire allowed physical space.

This behavior is shown by the bottom panel of Fig. 5 for the CCSD(T) potential. We repeated (for all three of the potentials) the calculations with a Gaussian basis set extending up to more than twice the radial domain used to produce the results. Obviously enough, the step Δ in the calculations had to be larger ($0.5a_0$) and after $25a_0$ the Gaussians are distributed with increasingly larger step. While the $k=10$ state is

TABLE V. Structural properties for the first bound states $k=0-4$ of Ne_3 using the Morse potential (in angstroms).

k	Present work		Reference 7	
	$\langle R \rangle_k$	$\sqrt{\langle R^2 \rangle_k}$	$\langle R \rangle_k$	$\sqrt{\langle R^2 \rangle_k}$
0	3.31	3.32	3.31	3.32
1	3.78	3.87	3.77	3.86
2	4.16	4.37	4.14	4.34
3	4.01	4.18	4.01	4.18
4	3.96	4.12	3.97	4.13

stable after the enlargement of the basis set, the $k=11$ state ($k=10$ in LJ and $k=9$ in Morse, not reported here for sake of clarity) expands instead along the radial axis as much as is allowed by the maximum extension of the basis set, producing one peak around the equilibrium distance of the dimer and a second broad peak (after an intermediate zero-density region) at very large distances. Integrating the PD function along the radial axis, we find that $1/3$ of the density is reached after the first peak at around 8 a.u., then a plateau of zero density follows from 8 up to about 20 a.u. and finally the remaining $2/3$ of the density is spread out reaching the end of the grid. The behavior of the PD function is thus trying to describe, albeit within the limitation of a finite-basis-set expansion, the loss of one Ne atom from the trimer.

In conclusion, all the states we found lying below the 2B dissociation threshold result to be bound states. This means that whenever the 2B threshold is obtained by another method, it is also taken by the DGF method as the dissociation reference. It is thus essential to be able to discriminate among truly bound states and scattering ones between the states obtained by the present method for the trimer system.

Finally, it is worth nothing here that it would be very difficult to describe the vibrationally excited states of this very "floppy" system by using the conventional internal coordinates of the normal mode analysis:²⁸ above the $k=0$ state, in fact, all modes are always mixed by the all-important t_i operators of Eq. (7).

Another spatial indicator of the structural properties of the first few bound states is the value of $\langle R \rangle_k$ and $\sqrt{\langle R^2 \rangle_k}$ for each k state. In Table V the corresponding values for the first five ($k=0-4$) bound states of Ne_3 calculated using the Morse potential are shown in comparison with those from Ref. 7. The good agreement found between the two calculations reveals, as already mentioned in Sec. IV A, that a properly extended basis set directly guarantees a correct description of the excited states of Ne_3 by the DGF method, independently of the main triangular contributions being present.

C. A pictorial description of the bound states

We conclude the discussion of the bound states of Ne_3 by analyzing the weight that different triangular configurations have in the description of each state. We use here the definition of pseudoweights given before by Eq. (15) in Sec. III, where we showed that the functions ϕ_j in the expansion

FIG. 6. Composition in different triangular families (top left panel) and corresponding pseudoweights in percentage for the bound state $k=0-4$ of Ne_3 described by the CCSD(T) potential.

of the total wave function of each bound states k , can be associated to a particular triangular arrangement with a pseudoweight P_j^k , as discussed there.

The best basis set we employed generates, as already mentioned, an expansion of 32197 “triangular” functions which 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 with a certain minimum variation on the sides of the triangles. In the top left panel of Fig. 6 we report how many of the 32 197 generated basis functions fall within each type of triangular configuration and as a percentage fraction with respect to the number of total basis functions. Only 184 functions correspond to an equilateral arrangement (the 0.57% of the expansion basis) while nearly 79% of the basis functions describe a scalene triangle.

We could also define the weight of each type of triangular family for each bound state k by summing the pseudoweights P_j^{type} associated to each element of the family:

$$W_{\text{type}}^k = \sum_{j=1}^{N_{\text{type}}} P_j^{\text{type},k}. \quad (23)$$

This quantity is calculated for each bound state k and for the three potential models adopted in this work. We report here only the results for the eleven bound states found when using the CCSD(T) potential.

The state $k=0$ is described by a contribution of all the families with the exclusion collinear one. Now, the average Ne–Ne distance calculated from the PD function is $(6.3 \pm 0.6)a_0$. If we calculate the average distances within each family using the pseudoweights we find for the equilateral family $6.2a_0$ and, e.g., for the flat isosceles family two distances at around $6a_0$ and a third one equal to about $6.9a_0$. For the tall isosceles and scalene groups as well the distances are comprised between $5.8a_0$ and $6.9a_0$. These additional data give the quantum counterpart respect to the classical image of a rigid equilateral structure. However, we notice that the equilateral family contributes in a significative way only to the state $k=0$ while for all the other states its percentage weight is always less than 5%.

FIG. 7. Pseudoweights of the triangular families for the states $k=5-10$ of Ne_3 described by the CCSD(T) potential.

The findings for the first excited state, $k=1$, also confirm the description given by the PD function, as discussed in Sec. IV B: this state is mainly described by flat isosceles and scalene triangles. Finally, starting from the state $k=2$ we found that the collinear configurations always give important contributions to the description of the bound states.

The results obtained with the other two potentials, LJ and Morse, confirm what found in the analysis of the PD functions. From the state $k=0$ to the state $k=4$ the pseudo-weights for each family obtained with the three potentials are very similar (differing by at most 2%), presenting more marked differences for the states at higher energies. For example, for the state $k=5$, in the LJ case we always find the flat isosceles, the collinear and the scalene arrangements as the most important to describe the state but the weight of the flat isosceles structures is diminished in favor of the scalene ones. As in Ref. 7, a significant amplitude at linearity was found for the $k \geq 2$ excited states. (See Fig. 7.)

V. PRESENT CONCLUSIONS

In this work we studied the bound states of Ne_3 cluster at zero angular momentum using a method based on internuclear coordinates and a DGF basis set. We tried to elucidate in a systematic manner the difficulties arising with the description of vibrationally excited states which lie very close to the brim of a fairly shallow polyatomic potential well.

We found that it is crucial to ensure that the employed radial grid be sufficiently extended and that the function basis set is chosen to be dense enough in order to correctly reproduce the states closer to dissociation which are spread over a large spatial range and which have small de Broglie wavelengths within the well region. A stabilization procedure based on the analysis of the PD densities proved to be a very useful tool for identifying the true bound states produced by a given basis set.

With respect to the previously published data on the same system, and obtained with the same three potential models we have used here to describe Ne–Ne interaction, we found one additional bound state when the Morse potential is used. All our bound states have then been fully characterized in terms of their PD functions and of the importance of the different triangular configurations in the description of each state.

The use of simple models to describe the Ne–Ne interaction has a deep influence in the energetics and in the spectral features of the system, but does not seem to affect in a dramatic way the geometrical descriptions of the bound states.

The DGF method has been shown to be a robust procedure to study and to fully characterize the $J=0$ ground and excited states of a trimer, also those states above the isomerization barrier to linearity which present dominant linear configurations. Such conclusions bode well for the efficient use of the method to study a greater variety of identical trimer systems where deeper potential wells occur and where heavier partners are present in them. We are currently apply-

ing the DGF method to the next heavier Rg_3 cluster: the Ar_3 system. Furthermore, in relation to a very recent, accurate calculation²⁹ we intend to revisit the He_2H^- system studied by us before.³⁰

ACKNOWLEDGMENTS

The financial support 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, DGI, CYT Spanish Grant No. BFM2001-2179, and of the INFN institute are gratefully acknowledged. T.G.L. would also like to thank the support of the programa Ramón y Cajal. The authors also thank the “Consorzio Universitario per le Applicazioni di Supercalcolo Per Università e Ricerca” (CASPUR) of Rome for supplying computational resources and advice.

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