



Research paper

D_{3h} symmetry adapted correlated three center wave functions of the ground and the first five excited states of H_3^+

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HIGHLIGHTS

- Three-center basis for the D_{3h} symmetry of the H_3^+ studied here with electronic correlation.

ARTICLE INFO

Keywords:

Electronic structure of equilateral triangular H_3^+ molecule
Three center wave functions
 D_{3h} symmetry

ABSTRACT

The $^1A_1'$, $^3E'$, $^1E'$, $^3A_1'$, $^1A_2'$, $^3A_2'$ representing the ground and the five excited states, which have the common character of being symmetrical with respect to reflection on the plane of the equilateral triangular H_3^+ molecule, are determined by an original three center wave function constructed by the use of the irreducible representations of the D_{3h} point group. In contrast to past large one center or linear combinations of atomic orbitals functions, our model has the advantage of being well adapted to all internuclear distances, with limited number of basis functions including the electron-electron term. Our functions satisfy, by their nature, the triangular geometry of the molecule and thus permit the study the asymptotic behavior of the potential energy curves of the fundamental and excited levels for which, new experimental and theoretical results are needed to confirm astronomical observations. The results of this work and the implementation of the computational techniques employed opens the way to further studies on complex three center systems.

1. Introduction

H_3^+ is the simplest existing polyatomic molecule, which provokes interest in different fields of chemistry and astronomy. It is most stable in the equilateral triangular configuration [1]. It has the particularity of dissociating both when an electron is attached or detached from it. It is the subject of many studies concerning specially the dissociative recombination with electrons [2,3], or the observations of its vibration-rotation band [4]. It plays also an important role in the domain of the study of magnetic and ionospheric properties of planets [5,6].

It is evident that, like helium and H_2 the smallest two electron systems, for which electron-electron correlation can be evaluated and understood both theoretically and experimentally (e.g. in the determination of the cross sections of the double ionization [7–9], the study of

the electronic structure of H_3^+ is one of the fundamental challenges of molecular physics. As the smallest three center molecule existing naturally, it has been largely studied in the past [10–16]. These calculations employ wave functions constructed by linear combinations of atomic orbitals (LCAO), Gaussians, or one center basis functions and do not include, in contrast to the present work, the electron-electron correlation term separately. We can mention here the original model presented in [17,18] in which the singlet and triplet excited states of H_3^+ are studied by the application of the “diatomic in molecules” method, employing a product of diatomic and atomic orbitals. Although these different types of orbitals succeed in producing comparable results for intermediate internuclear distances by employing very large Gaussian basis functions [16], still some disagreements exist between them and verified potential energy curves are needed specially for large

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<https://doi.org/10.1016/j.cplett.2020.137304>

Received 9 January 2020; Received in revised form 1 March 2020; Accepted 2 March 2020

Available online 05 March 2020

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internuclear distances.

In recent years, Berencz type functions [19] have shown their efficiency in the treatment of many center electronic structures [20,21]. In this method, the LCAO applied to the diatomic cases, is replaced by a products of atomic orbitals centered on each nucleus. For the three center case, this model was successfully applied to the fundamental electronic level of H_3^+ [22]. Recently, we have introduced, for the three center two electron case, the electron-electron correlation to this type of functions and applied it to the determination of the multiply differential cross section of the simple ionization of H_3^+ by electron impact [23].

The aim of the present paper is to show that, the above mentioned three center model, which contains, by its nature, the equilateral triangular symmetry, presents many advantages, as it permits the application of the group theoretical irreducible representation of the D_{3h} point group to the construction of the wave functions of the first five excited states of H_3^+ , which are symmetrical with respect to reflection on the plane of the molecule, and permits to identify the dissociation limits of each level, and produces, with a small basis, compared to that applied in [16] for example, quite good accuracy for the energy values of the different levels. We believe also, that this wave functions will bring as in [23] theoretical support in the determination of cross sections in electronic excitation and ionization experiments. From a more practical point of view, we can say that the tackling of the analytic and numerical computational difficulties related to the two-electron three center problem in this work, opens the way to further developments in more complex three center systems, that we intend to study.

2. Theory

The Hamiltonian, which describes, for fixed nuclei, the two electrons of the H_3^+ ion (see Fig. 1) is written in atomic units as follows

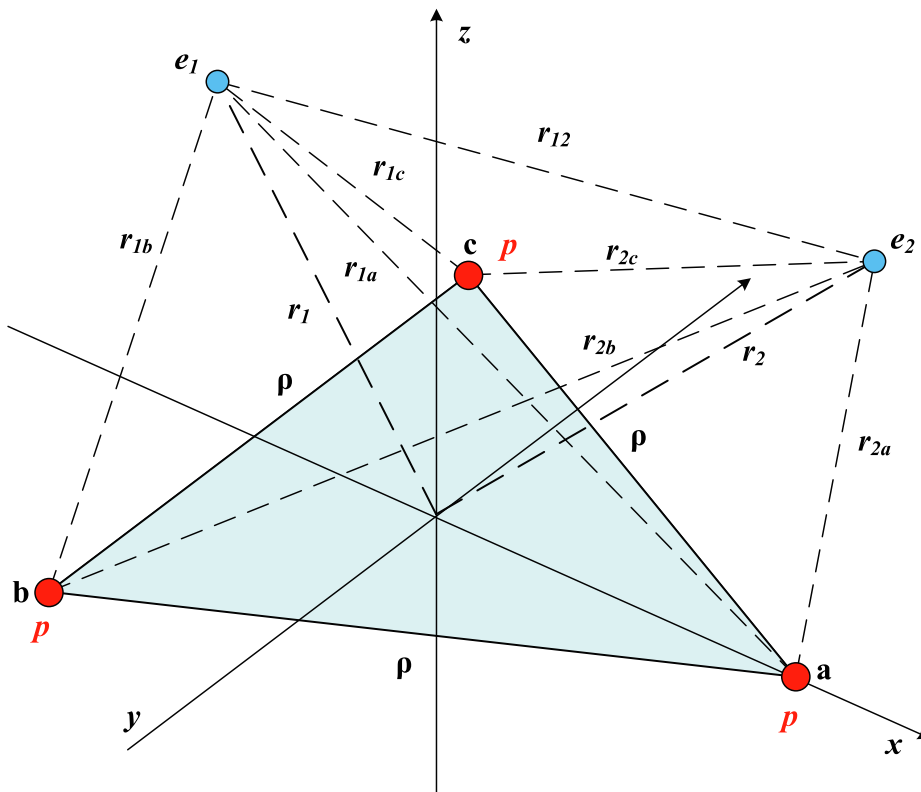


Fig. 1. The positions of the three fixed protons a , b , c and the two electrons e_1 , e_2 in a body fixed frame (x, y, z) with the origin on the barycenter of the equilateral triangle, and the z axis perpendicular to plane of the molecule H_3^+ .

$$\mathcal{H} = \sum_{j=1}^2 \left(-\frac{1}{2} \Delta_{\mathbf{r}_j} - \frac{1}{r_{ja}} - \frac{1}{r_{jb}} - \frac{1}{r_{jc}} \right) + \frac{1}{r_{12}} + \frac{3}{\rho}, \quad (1)$$

with $\mathbf{r}_{ja} = \mathbf{r}_j - \mathbf{a}$, $\mathbf{r}_{jb} = \mathbf{r}_j - \mathbf{b}$, $\mathbf{r}_{jc} = \mathbf{r}_j - \mathbf{c}$, $r_{12} = r_1 - r_2$. Here \mathbf{r}_j gives the position of the j -th electron, and \mathbf{a} , \mathbf{b} , \mathbf{c} the position vectors of the three protons in a body fixed system of reference with the following coordinates:

$$\begin{aligned} \mathbf{a} &= \frac{\rho}{\sqrt{3}}(1, 0, 0), \\ \mathbf{b} &= \frac{\rho}{\sqrt{3}}\left(-\frac{1}{2}, -\frac{\sqrt{3}}{2}, 0\right), \\ \mathbf{c} &= \frac{\rho}{\sqrt{3}}\left(-\frac{1}{2}, \frac{\sqrt{3}}{2}, 0\right), \end{aligned} \quad (2)$$

with ρ representing the mutual internuclear distance between the three nuclei.

The computational schemes, which will deliver the wave functions and the energy values of the desired levels are based on the Rayleigh-Ritz variational functional with the electronic energy given by

$$\varepsilon_Q = \frac{\langle \Psi_Q(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_1, \mathbf{r}_2) | \mathcal{H} | \Psi_Q(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_1, \mathbf{r}_2) \rangle}{\langle \Psi_Q(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_1, \mathbf{r}_2) | \Psi_Q(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_1, \mathbf{r}_2) \rangle}, \quad (3)$$

where Q represents the energy levels ${}^1A_1'$, ${}^1E'$, ${}^3E'$, ${}^3A_1'$, ${}^1A_2'$, ${}^3A_2'$ under consideration and $\Psi_Q(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_1, \mathbf{r}_2)$ the corresponding trial wave function. We admit that these functions must be orthogonal

$$\langle \Psi_Q(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_1, \mathbf{r}_2) | \Psi_{Q'}(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_1, \mathbf{r}_2) \rangle = \delta_{QQ'}, \quad (4)$$

and satisfy the symmetry properties of the D_{3h} group.

2.1. The seven-parametric basis functions

Let us first form the bi-electronic correlated basis functions, with which we will construct the variational wave function $\Psi_Q(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_1, \mathbf{r}_2)$

of Eq. (3) for the different levels. We consider, as in [22], a combination of functions constructed by a product of two Berencz type [19] mono-electronic functions, adapted each to the equilateral triangular system and an electron-electron correlation term which fits in very elegantly. This forms the following seven-parametric function

$$\chi(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_1, \mathbf{r}_2) = \exp(-\alpha_1 r_{1a} - \alpha_2 r_{1b} - \alpha_3 r_{1c} - \alpha_4 r_{2a} - \alpha_5 r_{2b} - \alpha_6 r_{2c} - \alpha_7 r_{12}). \quad (5)$$

Here the nonlinear α_i parameters will be determined by the variational method described below. The wave function of a given state $\Psi_Q(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_1, \mathbf{r}_2)$ of Eq. (3) must include all the permutations with respect to the three centers $\mathbf{a}, \mathbf{b}, \mathbf{c}$, and between electrons 1 and 2, (see Fig. 1). We will thus consider the following twelve functions, which have the structure of the one given in (5) representing all the permutation cases:

$$\begin{aligned} \chi_1 &= \chi(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_1, \mathbf{r}_2), & \chi_2 &= \chi(\mathbf{a}, \mathbf{c}, \mathbf{b}, \mathbf{r}_1, \mathbf{r}_2), \\ \chi_3 &= \chi(\mathbf{c}, \mathbf{a}, \mathbf{b}, \mathbf{r}_1, \mathbf{r}_2), & \chi_4 &= \chi(\mathbf{b}, \mathbf{a}, \mathbf{c}, \mathbf{r}_1, \mathbf{r}_2), \\ \chi_5 &= \chi(\mathbf{b}, \mathbf{c}, \mathbf{a}, \mathbf{r}_1, \mathbf{r}_2), & \chi_6 &= \chi(\mathbf{c}, \mathbf{b}, \mathbf{a}, \mathbf{r}_1, \mathbf{r}_2), \end{aligned} \quad (6)$$

$$\begin{aligned} \chi_7 &= \chi(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_2, \mathbf{r}_1), & \chi_8 &= \chi(\mathbf{a}, \mathbf{c}, \mathbf{b}, \mathbf{r}_2, \mathbf{r}_1), \\ \chi_9 &= \chi(\mathbf{c}, \mathbf{a}, \mathbf{b}, \mathbf{r}_2, \mathbf{r}_1), & \chi_{10} &= \chi(\mathbf{b}, \mathbf{a}, \mathbf{c}, \mathbf{r}_2, \mathbf{r}_1), \\ \chi_{11} &= \chi(\mathbf{b}, \mathbf{c}, \mathbf{a}, \mathbf{r}_2, \mathbf{r}_1), & \chi_{12} &= \chi(\mathbf{c}, \mathbf{b}, \mathbf{a}, \mathbf{r}_2, \mathbf{r}_1). \end{aligned}$$

Our task will be to find the appropriate combinations of these twelve functions for each of the states ${}^1A'_1, {}^3E', {}^1E', {}^3A'_1, {}^1A'_2, {}^3A'_2$ defined by the irreducible representations of the D_{3h} point group.

2.2. Method of construction of the ground and excited state wave functions

The spin part of the two electron wave function being eliminated, the space wave functions of the singlet states such as ${}^1A'_1, {}^1A'_2$, etc. must be symmetrical with respect to exchange of electrons. Those of the triplet states, such as ${}^3A'_1, {}^3A'_2$, etc. must be antisymmetrical with respect to this exchange. So we can write the general conditions for the permutation of the two electrons:

$$\Psi_{1Q}(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_1, \mathbf{r}_2) = +\Psi_{1Q}(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_2, \mathbf{r}_1), \quad (7)$$

$$\Psi_{3Q}(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_1, \mathbf{r}_2) = -\Psi_{3Q}(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_2, \mathbf{r}_1). \quad (8)$$

Let us define two constants

$$\sigma_1 = \begin{cases} 0; & \text{for even states,} \\ 1; & \text{for odd states,} \end{cases} \quad (9)$$

which will characterize symmetry with respect to exchange of any two centers, and

$$\sigma_2 = \begin{cases} 0; & \text{singlet states,} \\ 1; & \text{triplet states,} \end{cases} \quad (10)$$

which will characterize the spin state.

Using these constants, let us associate the twelve basis functions χ_j , which have in common the exchange between the centers and \mathbf{c} . This will give us the following set of three new functions:

$$\begin{aligned} \psi_1 &= \chi_1 + (-1)^{\sigma_1} \chi_2 + (-1)^{\sigma_2} [\chi_7 + (-1)^{\sigma_1} \chi_8], \\ \psi_2 &= \chi_3 + (-1)^{\sigma_1} \chi_4 + (-1)^{\sigma_2} [\chi_9 + (-1)^{\sigma_1} \chi_{10}], \\ \psi_3 &= \chi_5 + (-1)^{\sigma_1} \chi_6 + (-1)^{\sigma_2} [\chi_{11} + (-1)^{\sigma_1} \chi_{12}]. \end{aligned} \quad (11)$$

We can now define the wave function for a given state Q in the following form

$$\Psi_Q(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_1, \mathbf{r}_2) = c_{1Q} \psi_1 + c_{2Q} \psi_2 + c_{3Q} \psi_3. \quad (12)$$

Here c_{iQ} -s correspond to the coefficient of ψ_i for the state Q .

Let us apply the circular permutation $(\mathbf{a}, \mathbf{b}, \mathbf{c}) \rightarrow (\mathbf{b}, \mathbf{c}, \mathbf{a})$ to Eq. (12). We will then obtain a new combination for the same c_{iQ} s

$$\Psi_Q(\mathbf{b}, \mathbf{c}, \mathbf{a}, \mathbf{r}_1, \mathbf{r}_2) = c_{1Q} \tilde{\psi}_1 + c_{2Q} \tilde{\psi}_2 + c_{3Q} \tilde{\psi}_3, \quad (13)$$

where the $\tilde{\psi}_i$ correspond to the association of the twelve basis functions having in common the exchange between \mathbf{a} and \mathbf{c} such that

$$\begin{aligned} \tilde{\psi}_1 &= \chi_5 + (-1)^{\sigma_1} \chi_4 + (-1)^{\sigma_2} [\chi_{11} + (-1)^{\sigma_1} \chi_{10}], \\ \tilde{\psi}_2 &= \chi_1 + (-1)^{\sigma_1} \chi_6 + (-1)^{\sigma_2} [\chi_7 + (-1)^{\sigma_1} \chi_{12}], \\ \tilde{\psi}_3 &= \chi_3 + (-1)^{\sigma_1} \chi_2 + (-1)^{\sigma_2} [\chi_9 + (-1)^{\sigma_1} \chi_8]. \end{aligned} \quad (14)$$

Finally a third circular permutation is possible $(\mathbf{a}, \mathbf{b}, \mathbf{c}) \rightarrow (\mathbf{c}, \mathbf{a}, \mathbf{b})$, which will result into

$$\Psi_Q(\mathbf{c}, \mathbf{a}, \mathbf{b}, \mathbf{r}_1, \mathbf{r}_2) = c_{1Q} \hat{\psi}_1 + c_{2Q} \hat{\psi}_2 + c_{3Q} \hat{\psi}_3, \quad (15)$$

with

$$\begin{aligned} \hat{\psi}_1 &= \chi_3 + (-1)^{\sigma_1} \chi_6 + (-1)^{\sigma_2} [\chi_9 + (-1)^{\sigma_1} \chi_{12}], \\ \hat{\psi}_2 &= \chi_5 + (-1)^{\sigma_1} \chi_2 + (-1)^{\sigma_2} [\chi_{11} + (-1)^{\sigma_1} \chi_8], \\ \hat{\psi}_3 &= \chi_1 + (-1)^{\sigma_1} \chi_4 + (-1)^{\sigma_2} [\chi_7 + (-1)^{\sigma_1} \chi_{10}], \end{aligned} \quad (16)$$

where the exchange is between \mathbf{a} and \mathbf{b} .

By adding the three functions of the Eq. (12), (13) and (15), we obtain the following relation

$$\begin{aligned} \Xi_Q &= \Psi_Q(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_1, \mathbf{r}_2) + \Psi_Q(\mathbf{b}, \mathbf{c}, \mathbf{a}, \mathbf{r}_1, \mathbf{r}_2) + \Psi_Q(\mathbf{c}, \mathbf{a}, \mathbf{b}, \mathbf{r}_1, \mathbf{r}_2) \\ &= (c_{1Q} + c_{2Q} + c_{3Q}) \\ &\times \sum_{k=0}^2 \{ \chi_{1+2k} + (-1)^{\sigma_1} \chi_{2+2k} + (-1)^{\sigma_2} [\chi_{7+2k} + (-1)^{\sigma_1} \chi_{8+2k}] \} \\ &= (c_{1Q} + c_{2Q} + c_{3Q}) (\psi_1 + \psi_2 + \psi_3). \end{aligned} \quad (17)$$

This is a general relation valid to all the levels. Our aim during the minimization process is to determine the coefficients c_{iQ} and the parameters α_i for each level Q defined above. Before passing to the variational determination, let us first exploit the symmetry properties of equilateral triangular system to simplify the relations between the coefficients c_{iQ} of each state.

2.3. The symmetry properties of the ground and excited states

Let us begin with the A'_1 states, for which any permutation of the centers should leave the wave function invariable, such that

$$\begin{aligned} \Psi_{A'_1}(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_1, \mathbf{r}_2) &= \text{perm}_{(\mathbf{a}, \mathbf{b}, \mathbf{c})} \Psi_{A'_1}(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_1, \mathbf{r}_2) \\ &= \frac{1}{3} \Xi_{A'_1} = c_{1A'_1} \psi_1 + c_{2A'_1} \psi_2 + c_{3A'_1} \psi_3. \end{aligned} \quad (18)$$

Here $\text{perm}_{(\mathbf{a}, \mathbf{b}, \mathbf{c})}$ is the permutation operator for the three nuclei ($\mathbf{a} \leftrightarrow \mathbf{b} \leftrightarrow \mathbf{c}$). Introducing this relation in Eq. (17) we can show that the coefficients of the ${}^1A'_1$ and ${}^3A'_1$ states (i.e. for $\sigma_1 = 0$ in Eq. (11)) must satisfy the condition

$$c_{1A'_1} = c_{2A'_1} = c_{3A'_1}. \quad (19)$$

For the A'_2 states, the wave functions are antisymmetric with respect to exchange of the two nuclei, such that

$$\begin{aligned} \Psi_{A'_2}(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_1, \mathbf{r}_2) &= -\Psi_{A'_2}(\mathbf{a}, \mathbf{c}, \mathbf{b}, \mathbf{r}_1, \mathbf{r}_2) = \Psi_{A'_2}(\mathbf{c}, \mathbf{a}, \mathbf{b}, \mathbf{r}_2, \mathbf{r}_1) \\ &= -\Psi_{A'_2}(\mathbf{c}, \mathbf{b}, \mathbf{a}, \mathbf{r}_1, \mathbf{r}_2) = \Psi_{A'_2}(\mathbf{b}, \mathbf{c}, \mathbf{a}, \mathbf{r}_1, \mathbf{r}_2) = -\Psi_{A'_2}(\mathbf{b}, \mathbf{a}, \mathbf{c}, \mathbf{r}_1, \mathbf{r}_2). \end{aligned} \quad (20)$$

This means that

$$\begin{aligned} \Psi_{A'_2}(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_1, \mathbf{r}_2) &= \Psi_{A'_2}(\mathbf{b}, \mathbf{c}, \mathbf{a}, \mathbf{r}_1, \mathbf{r}_2) = \Psi_{A'_2}(\mathbf{c}, \mathbf{a}, \mathbf{b}, \mathbf{r}_1, \mathbf{r}_2) \\ &= \frac{1}{3} \Xi_{A'_2} = c_{1A'_2} \psi_1 + c_{2A'_2} \psi_2 + c_{3A'_2} \psi_3. \end{aligned} \quad (21)$$

Comparing with Eq. (17) corresponding to ${}^1A'_2$ and ${}^3A'_2$ (i.e. for $\sigma_1 = 1$ in Eq. (11)) we can find that

$$c_{1A'_2} = c_{2A'_2} = c_{3A'_2}. \quad (22)$$

Let us pass to the E' states. The singlet ${}^1E'$ and the triplet ${}^3E'$ states are doubly degenerate, such that they are symmetric or antisymmetric

with respect to the exchange of any two nuclei. We will designate these states by $e^{1E'}$ and $e^{3E'}$ for the symmetrical (even) cases, and by $o^{1E'}$ and $o^{3E'}$ for the antisymmetrical (odd) cases, such that:

$$\Psi_{e^{1E'}}(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_1, \mathbf{r}_2) = +\Psi_{e^{1E'}}(\mathbf{a}, \mathbf{c}, \mathbf{b}, \mathbf{r}_1, \mathbf{r}_2) = +\Psi_{e^{1E'}}(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_2, \mathbf{r}_1), \quad (23)$$

$$\Psi_{o^{1E'}}(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_1, \mathbf{r}_2) = -\Psi_{o^{1E'}}(\mathbf{a}, \mathbf{c}, \mathbf{b}, \mathbf{r}_1, \mathbf{r}_2) = +\Psi_{o^{1E'}}(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_2, \mathbf{r}_1), \quad (24)$$

$$\Psi_{e^{3E'}}(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_1, \mathbf{r}_2) = +\Psi_{e^{3E'}}(\mathbf{a}, \mathbf{c}, \mathbf{b}, \mathbf{r}_1, \mathbf{r}_2) = -\Psi_{e^{3E'}}(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_2, \mathbf{r}_1), \quad (25)$$

$$\Psi_{o^{3E'}}(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_1, \mathbf{r}_2) = -\Psi_{o^{3E'}}(\mathbf{a}, \mathbf{c}, \mathbf{b}, \mathbf{r}_1, \mathbf{r}_2) = -\Psi_{o^{3E'}}(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_2, \mathbf{r}_1). \quad (26)$$

We have demonstrated in the A (Eqs. (A.9), (A.13)) that

$$\Xi_{E'} = \Psi_{E'}(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_1, \mathbf{r}_2) + \Psi_{E'}(\mathbf{b}, \mathbf{c}, \mathbf{a}, \mathbf{r}_1, \mathbf{r}_2) + \Psi_{E'}(\mathbf{c}, \mathbf{a}, \mathbf{b}, \mathbf{r}_1, \mathbf{r}_2) = 0. \quad (27)$$

Using Eq. (17) we can write

$$\Xi_{E'} = (c_{1E'} + c_{2E'} + c_{3E'}) (\psi_1 + \psi_2 + \psi_3) = 0, \quad (28)$$

which imposes the condition

$$c_{1E'} + c_{2E'} + c_{3E'} = 0. \quad (29)$$

Till now, we have studied the case, where we had a basis function with 7 parameters Eq. (5). We will now extend our choice to additional 7 nonlinear parameters α_i , with indices $i = 8, \dots, 14$. This will create twelve additional functions χ_j with $j = 13, \dots, 24$, thus three more functions like in Eq. (11)

$$\begin{aligned} \psi_4 &= \chi_{13} + (-1)^{\sigma_1} \chi_{14} + (-1)^{\sigma_2} [\chi_{19} + (-1)^{\sigma_1} \chi_{20}], \\ \psi_5 &= \chi_{15} + (-1)^{\sigma_1} \chi_{16} + (-1)^{\sigma_2} [\chi_{21} + (-1)^{\sigma_1} \chi_{22}], \\ \psi_6 &= \chi_{17} + (-1)^{\sigma_1} \chi_{18} + (-1)^{\sigma_2} [\chi_{23} + (-1)^{\sigma_1} \chi_{24}], \end{aligned} \quad (30)$$

with which we can define our extended wave function for a given state Q in the following form

$$\Psi_Q(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_1, \mathbf{r}_2) = \sum_{i=1}^6 c_{iQ} \psi_i. \quad (31)$$

Applying the symmetry conditions to the new function we can show for the complete set of coefficients we must impose the following conditions

$$\begin{aligned} c_{1A_1'} &= c_{2A_1'} = c_{3A_1'}, & c_{4A_1'} &= c_{5A_1'} = c_{6A_1'}, \\ c_{1A_2'} &= c_{2A_2'} = c_{3A_2'}, & c_{4A_2'} &= c_{5A_2'} = c_{6A_2'}, \\ c_{1E'} + c_{2E'} + c_{3E'} &= 0, \\ c_{4E'} + c_{5E'} + c_{6E'} &= 0. \end{aligned} \quad (32)$$

Table 1

The energies values (in au) of the ground $^1A_1'$ and excited $^3E'$, $^1E'$, $^3A_1'$, $^1A_2'$ and $^3A_2'$ states of H_3^+ for internuclear distance $\rho = 1.65$ au. The second row corresponds to results obtained with seven-parameter functions and the third row to those obtained by fourteen-parameter functions. The lower rows show existing results from the references [12,15,16,22,23] (where [12] at $\rho = 1.63332$ au and [23] with 6 parameters function at $\alpha_7 = 0$).

	$^1A_1'$	$^3E'$	$^1E'$	$^3A_1'$	$^1A_2'$	$^3A_2'$
with 7-parameters	-1.340 352	-0.775 600	-0.609 823	-0.498 901	-0.186 083	-0.028 621
with 14-parameters	-1.342 520	-0.792 082	-0.626 730	-0.510 758	-0.209 148	-0.035 843
[12]		-0.776 695	-0.622 277	-0.496 986		
[15]	-1.342 230		-0.632 050			
[16]	-1.343 835		-0.633 512	-0.511 569		
[22]	-1.340 345					
[23]	-1.331 48					

3. Numerical methods

After substituting the expansion Eq. (12) for the simpler seven-parameter case, or Eq. (31) for the extended case into the variational functional Eq. (3) and minimizing, we obtain the generalized eigenvalue problem

$$\mathbf{A}_Q \mathbf{c}_Q = \varepsilon_Q \mathbf{B}_Q \mathbf{c}_Q, \quad \mathbf{c}_Q^T \mathbf{B}_Q \mathbf{c}_Q = 1. \quad (33)$$

Here \mathbf{A}_Q and \mathbf{B}_Q represent symmetric matrices with matrix elements respectively

$$A_{ij} = \langle \psi_i | \mathcal{H} | \psi_j \rangle, \quad B_{ij} = \langle \psi_i | \psi_j \rangle, \quad (34)$$

$\mathbf{c}_Q = (c_{1Q}, c_{2Q}, c_{3Q})^T$ (or $\mathbf{c}_Q = (c_{1Q}, c_{2Q}, c_{3Q}, c_{4Q}, c_{5Q}, c_{6Q})^T$ for the extended case) represent the eigenvectors. Using for each state Q the conditions of Eqs. (19), (22) and (29) (or (32) and applying linear transformation of the Eq. (33), we reduce the matrices and obtain the following problem

$$\tilde{\mathbf{A}}_Q \tilde{\mathbf{c}}_Q = \varepsilon_Q \tilde{\mathbf{B}}_Q \tilde{\mathbf{c}}_Q, \quad \tilde{\mathbf{c}}_Q^T \tilde{\mathbf{B}}_Q \tilde{\mathbf{c}}_Q = 1, \quad (35)$$

with $\tilde{\mathbf{c}}_Q = (c_{1Q})^T$ (or $\tilde{\mathbf{c}}_Q = (c_{1Q}, c_{4Q})^T$) for A' states, and $\tilde{\mathbf{c}}_Q = (c_{1Q}, c_{2Q})^T$ (or $\tilde{\mathbf{c}}_Q = (c_{1Q}, c_{2Q}, c_{4Q}, c_{5Q})^T$) for E' states.

To minimize the energy ε_Q with the variation of the parameters α_i , we have used a sequential quadratic programming method for several variables [24–26] and the code E04UCF from NAG Library [27] with additional constraints on the parameters:

$$\begin{aligned} \alpha_1 + \alpha_2 + \alpha_3 + \alpha_7 &> 0, \\ \alpha_4 + \alpha_5 + \alpha_6 + \alpha_7 &> 0, \\ \alpha_8 + \alpha_9 + \alpha_{10} + \alpha_{14} &> 0, \\ \alpha_{11} + \alpha_{12} + \alpha_{13} + \alpha_{14} &> 0. \end{aligned} \quad (36)$$

We have also performed the optimization as in our previous paper [23], where we have studied only the fundamental state, by calculating the first derivatives with the parameters of the energy:

$$\frac{\partial \varepsilon_Q}{\partial \alpha_i} = \tilde{\mathbf{c}}_Q^T \left(\frac{\partial \tilde{\mathbf{A}}_Q}{\partial \alpha_i} - \varepsilon_Q \frac{\partial \tilde{\mathbf{B}}_Q}{\partial \alpha_i} \right) \tilde{\mathbf{c}}_Q. \quad (37)$$

All 6D integrals, which appear in the functional of the energy were calculated numerically using a globally adaptive subdivision scheme [28–30] and a code Cuhre [31]. All numerical integrations were done with an absolute accuracy $10^{-6} - 10^{-7}$.

4. Results and discussion

As we mentioned above, the aim of our present work is, among others, to implement the application of a new three center two electron correlated wave function, described above, for the triangular equilateral case represented by the H_3^+ system. The motivations for such a work are multiple. These are, for instance, the need for observation of

Table 2Optimal seven-variational parameters $\alpha_1, \dots, \alpha_7$ for the ground $^1A'_1$ and excited $^3E', ^1E', ^3A'_1, ^1A'_2$ and $^3A'_2$ states of H_3^+ for $\rho = 1.65$ au.

	$^1A'_1$	$^3E'$	$^1E'$	$^3A'_1$	$^1A'_2$	$^3A'_2$
α_1	-0.026 442	0.240 329	0.535 125	0.080 623	-2.028 037	0.436 381
α_2	0.211 880	0.504 412	0.137 175	-0.270 522	1.024 753	-0.229 632
α_3	1.409 787	0.689 107	0.994 871	0.794 331	1.136 674	0.858 861
α_4	1.068 443	0.241 417	0.901 676	1.181 098	0.561 273	0.990 903
α_5	0.122 722	0.773 526	-0.044 017	0.099 545	0.552 654	0.157 249
α_6	0.603 098	0.459 867	0.042 509	0.369 651	0.552 356	-0.193 064
α_7	-0.212 311	-0.249 522	-0.166 339	-0.088 500	-0.014 324	-0.084 081

Table 3The coefficients c_1, c_2 and c_3 corresponding to each energy level.

	c_1	c_2	c_3
$^1A'_1$	0.220 519	c_1	c_1
even $^3E'$	15.23 642	-5.857 385	$-c_1 - c_2$
odd $^3E'$	2.036 528	-14.29 091	$-c_1 - c_2$
even $^1E'$	0.376 844	-0.209 584	$-c_1 - c_2$
odd $^1E'$	0.024 434	0.314 108	$-c_1 - c_2$
$^3A'_1$	0.061 310	c_1	c_1
$^1A'_2$	0.078 908	c_1	c_1
$^3A'_2$	0.170 436	c_1	c_1

electronic transitions in interstellar media, where this ion is present abundantly, more, the fact that, like atomic helium and diatomic H_2 , triatomic H_3^+ is a two electron system in which, electron–electron correlation is identifiable, because it is the principal cause of many photo-excitation effects such as the photo-double-ionization of this type of targets. Our work is also motivated by the possibility that these three center calculations develop benchmark procedures extendable to more complex three center molecules. We seek also to verify our variational procedure and the numerical calculations of six order integrals involving the two bound electrons in the triangular coulomb field.

We begin by presenting, on Table 1, the energy values of the ground $^1A'_1$ and excited $^3E', ^1E', ^3A'_1, ^1A'_2$ and $^3A'_2$ states of H_3^+ for the ground state equilibrium internuclear distance $\rho = 1.65$ au. On this Table the second row shows the results obtained by the wave function of Eq. (12) having seven-parameters, while the third row shows the results obtained by the expression of Eq. (31) having fourteen-parameter functions. We observe that the extended fourteen-parameter (Eq. (31)) wave function improves the results. These $^1A'_1, ^3E', ^1E'$ and $^3A'_1$ are in good agreement (up to three digits after the decimal point) with the results of [12,15,16,22]. The influence of the electron–electron correlation term can be seen by the comparison of the energy values of $^1A'_1$, level of this table with those

Table 4Optimal fourteen-variational parameters $\alpha_1, \dots, \alpha_{14}$ for the ground $^1A'_1$ and excited $^3E', ^1E', ^3A'_1, ^1A'_2$ and $^3A'_2$ states energies of H_3^+ at the for $\rho = 1.65$ au.

	$^1A'_1$	$^3E'$	$^1E'$	$^3A'_1$	$^1A'_2$	$^3A'_2$
α_1	0.115 567	0.083 428	0.208 380	1.260 608	1.091 554	0.210 296
α_2	0.136 146	-0.009 707	0.223 048	0.233 957	-0.906 230	1.241 690
α_3	1.499 119	0.975 277	1.280 699	0.215 901	0.142 430	0.317 057
α_4	1.124 039	0.200 127	0.869 745	0.262 064	0.558 355	0.739 985
α_5	0.093 855	1.216 321	0.042 846	0.509 664	0.550 752	0.372 041
α_6	0.587 165	0.248 488	-0.023 289	0.053 417	0.554 221	0.041 675
α_7	-0.467 799	-0.103 159	-0.117 594	-0.026 991	-0.018 901	-0.057 578
α_8	0.595 668	1.239 064	0.297 544	0.243 724	0.557 903	0.441 187
α_9	0.084 919	0.209 395	0.098 634	0.207 222	0.551 828	-0.065 797
α_{10}	1.142 581	0.298 909	1.314 096	1.251 002	0.554 588	0.808 231
α_{11}	1.507 875	0.606 583	0.619 055	0.538 336	1.063 816	1.0302191
α_{12}	0.126 634	0.645 124	-0.359 666	0.102 680	-0.889 231	0.165 134
α_{13}	0.136 727	-0.167 738	0.659 638	0.311 287	0.130 554	-0.032 221
α_{14}	-0.511 026	-0.084 233	-0.214 367	-0.013 325	-0.019 960	-0.087 467

given on the last row in [23] for $\alpha_7 = 0$.

Now in the aim of verifying the process of convergence and trying to approach the results of [16] which uses a very large basis we additionally calculated the ground state $^1A'_1$, level the energy $\epsilon_{^1A'_1}$ with twenty-one-parameters and obtained $\epsilon_{^1A'_1} = -1.343 083$ au. This shows that our procedure converges and brings the agreement up to four digits. Using the extrapolation formula given in [32]

$$\epsilon_{^1A'_1}^{qs} = \epsilon_{^1A'_1}(N) + \frac{C}{N^\beta}, \quad (38)$$

we will define the convergence rate β with respect to the number of the basis set N . Here $\epsilon_{^1A'_1}^{qs}$ is the extrapolated value of the energy, i.e. $N \rightarrow \infty$, $\epsilon_{^1A'_1}(N)$ is the energy for a given N basis set, and C is the constant. We have for $N = 1$ the result of the seven-parameter case with 12 basis functions, for $N = 2$ that of fourteen-parameter case with 24 basis functions and $N = 3$ that of twenty-one-parameter case with 36 basis functions. $\epsilon_{^1A'_1}^{qs}$, β and C are obtained from the system of nonlinear problem (38) at $N = 1 - 3$:

$$\epsilon_{^1A'_1}^{qs} = -1.343 796 \text{ au}, \quad \beta = 1.429876, \quad C = -0.003447. \quad (39)$$

One can see that the extrapolated value of the energy is very close to the result of [16].

In Tables 2 and 3, respectively, we display the optimal seven-variational parameters $\alpha_i, i = 1, \dots, 7$ for the ground and excited states energies under consideration, and the corresponding coefficients $c_{iQ}, i = 1, \dots, 3$ including odd and even excited states of $^3E', ^1E'$. In Tables 4 and 5, we display the same cases as in Tables 2 and 3, but for the optimal fourteen-variational parameters $\alpha_i, i = 1, \dots, 14$ and corresponding coefficients $c_{iQ}, i = 1, \dots, 6$. We must mention here that some parameters α_i in Tables 2 and 4 have negative values. This is quite normal, as long as the conditions of Eq. (36) are satisfied. The negative values α_7 and α_{14} can be particularly reasonable as the distribution of the two electrons must have relatively higher density for large r_{12} , such that they have higher probability to be apart, because of the two electron repulsion potential $1/r_{12}$.

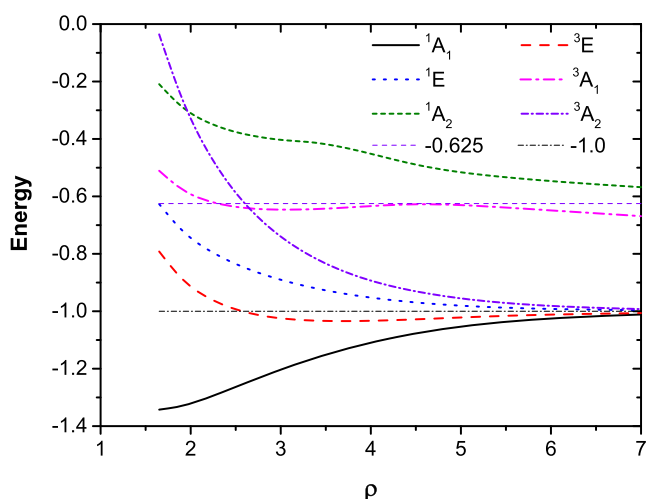
To compare further our results with existing ones. We consider

Table 5The coefficients c_1, c_2, c_3, c_4, c_5 and c_6 corresponding to each energy level (see the Table 4).

	c_1	c_2	c_3	c_4	c_5	c_6
$^1A'_1$	1.274 131	c_1	c_1	-1.069 841	c_4	c_4
even $^3E'$	0.060 304	0.273 509	$-c_1 - c_2$	0.410 264	-0.035 898	$-c_4 - c_5$
odd $^3E'$	0.349 790	-0.228 055	$-c_1 - c_2$	0.196 415	-0.451 523	$-c_4 - c_5$
even $^1E'$	-0.289 907	0.073 125	$-c_1 - c_2$	0.023 981	0.125 188	$-c_4 - c_5$
odd $^1E'$	0.082 955	-0.292 542	$-c_1 - c_2$	-0.158 406	0.099 972	$-c_4 - c_5$
$^3A'_1$	0.829 633	c_1	c_1	-1.052 157	c_4	c_4
$^1A'_2$	-2.149 799	c_1	c_1	2.236 809	c_4	c_4
$^3A'_2$	1.064 310	c_1	c_1	0.719 721	c_4	c_4

Table 6The ground $^1A'_1$ and excited $^3E', ^1E', ^3A'_1, ^1A'_2$ and $^3A'_2$ states energies (in au) of H_3^+ versus the internuclear distance ρ .

ρ	$^1A'_1$	$^3E'$	$^1E'$	$^3A'_1$	$^1A'_2$	$^3A'_2$
1.650	-1.342 520	-0.792 082	-0.626 730	-0.510 758	-0.209 149	-0.035 843
1.900	-1.329 584	-0.885 479	-0.716 543	-0.574 405	-0.287 441	-0.255 484
2.200	-1.299 819	-0.953 837	-0.787 186	-0.616 226	-0.343 498	-0.449 428
2.750	-1.232 880	-1.013 051	-0.865 638	-0.643 901	-0.392 400	-0.673 110
3.052	-1.197 553	-1.026 233	-0.894 834	-0.645 996	-0.404 557	-0.751 866
3.350	-1.165 897	-1.032 265	-0.917 646	-0.644 671	-0.412 183	-0.809 932
4.500	-1.077 293	-1.028 068	-0.969 321	-0.627 978	-0.489 352	-0.930 539
5.500	-1.036 820	-1.016 830	-0.987 624	-0.638 934	-0.533 256	-0.971 017
7.000	-1.011 227	-1.006 228	-0.997 107	-0.668 777	-0.567 851	-0.992 534

**Fig. 2.** Calculated potential-energy curves for the ground $^1A'_1$ and excited $^3E', ^1E', ^3A'_1, ^1A'_2$ and $^3A'_2$ states energies of H_3^+ versus the internuclear distance ρ .

particularly the results given in [15], which we think is the only reference that gives numerical results for singlet states of H_3^+ for different internuclear distances ρ . The comparison is made on Table 6. We observe that the singlet $^1A'_1, ^1E'$ states energies are in good agreement (up to three digits after the decimal point) with results of [15] (see their Table III, concerning the D_{3h} symmetry). What concerns the singlet $^1A'_2$ state energy for which we have some inconsistencies with [15] at $\rho \geq 2.75$ au, we will analyze the situation in more detail below. Also, we can observe that the minimum of the $^1E'$ state energy is comparable with the results of Alijah et al. [33].

Let us now pass to the potential-energy curves. We have two possible asymptotic limits for large ρ shown on Fig. 2. The lower one corresponds to the energy of a system constituted by two separate hydrogens having their electrons on the 1s level. The second higher level corresponds to the same system, but with one hydrogen on the 1s level

and the second on the 2s giving a total energy of $-0.5 - 0.125$ au. Now, we observe on Fig. 2 that the curves of the levels $^1A'_1, ^3E', ^1E'$ and $^3A'_2$, are consistent with the curves of [14] (see their Figures IV and V in [14]), and have a common asymptotic limit -1.0 au. This shows that at large ρ the wave functions of these states which have in our model conserved their D_{3h} character are still valid at the dissociation limit of $H(1s) + H(1s) + H^+$.

What concerns the state $^3A'_1$ which should normally dissociate into $H(1s) + H(2s) + H^+$ has a particular behavior above $\rho = 4$ au. It doesn't continue to the limit $-0.5 - 0.125$ au but it goes down (see please Fig. 2). In fact the potential curve is comparable to that of [12,14] which stops at the distance $\rho = 4$ au. We believe that in the equilateral triangular D_{3h} case, which we are adopting in our calculations even for large ρ , this state possesses two possible dissociation cases which could satisfy this configuration, one being the $H(1s) + H(2s) + H^+$ which could be the most probable, and the second the $H(1s) + H_2^+$ with large ρ , which has a lower energy limit than that of $H(1s) + H(2s) + H^+$ system. The existence of these two dissociation channels can explain the form of the potential energy curve of this level, which decreases after $\rho = 5$ au.

5. Conclusion

In this paper we construct original three center correlated wave functions necessary for the theoretical study of the electronic structure of the ground and the first five excited states of the equilateral triangular H_3^+ , which have the common character of being symmetrical with respect to reflection on the plane of the molecule. Our functions which possess by their nature the triangular symmetry, include electron-electron correlation and respect the irreducible representations of the D_{3h} point group. Our results concerning the electronic energy values of these levels, which are necessary to guide future experimental observations, confirm and complete the existing results which are obtained by large basis functions. Our functions permit also the determination of the asymptotic behavior of the potential energy curves, which show the possible dissociation fragments for this particular

equilateral symmetry. The three center two electron integrals are determined by applying new numerical and analytical approaches which open the way to further applications of this type of functions to more complex three center molecules.

CRedit authorship contribution statement

O. Chuluunbaatar: Methodology, Software. **S. Obeid:** Software. **B.B. Joulakian:** Conceptualization. **A.A. Gusev:** Conceptualization, Software. **P.M. Krassovitskiy:** Conceptualization, Software. **L.A. Sevastianov:** Formal analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial

Appendix A. Demonstration of the Eq. (27) for the E' states

We want to show that

$$\Psi(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_1, \mathbf{r}_2) + \Psi(\mathbf{c}, \mathbf{a}, \mathbf{b}, \mathbf{r}_1, \mathbf{r}_2) + \Psi(\mathbf{b}, \mathbf{c}, \mathbf{a}, \mathbf{r}_1, \mathbf{r}_2) = 0. \quad (\text{A.1})$$

For the sake of simplicity, let's represent the wave function of the two electron equilateral triangular system $\Psi(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_1, \mathbf{r}_2)$ in this form $\Psi(\mathbf{a}, \mathbf{b}, \mathbf{c}, \phi_1, \phi_2)$ where we show only the azimuthal angles of the two electrons. The three centers being given in Eq. (2). We can verify that for this equilateral triangular form

$$\begin{aligned} \Psi(\mathbf{c}, \mathbf{a}, \mathbf{b}, \phi_1, \phi_2) &= \Psi\left(\mathbf{a}, \mathbf{b}, \mathbf{c}, \phi_1 - \frac{2\pi}{3}, \phi_2 - \frac{2\pi}{3}\right), \\ \Psi(\mathbf{b}, \mathbf{c}, \mathbf{a}, \phi_1, \phi_2) &= \Psi\left(\mathbf{a}, \mathbf{b}, \mathbf{c}, \phi_1 + \frac{2\pi}{3}, \phi_2 + \frac{2\pi}{3}\right). \end{aligned} \quad (\text{A.2})$$

This permits us to write in Eq. (A.1) in the following more compact form

$$\sum_{s=-1} {}^1\Psi\left(\mathbf{a}, \mathbf{b}, \mathbf{c}, \phi_1 + s\frac{2\pi}{3}, \phi_2 + s\frac{2\pi}{3}\right) = 0. \quad (\text{A.3})$$

Let us make use of the fact, that any square-integrable function $f(\theta_1, \phi_1, \theta_2, \phi_2)$ on the unit sphere, can be expressed as a linear combination of the product of the real spherical harmonic functions $Y_{l_1 m_1}(\theta_1, \phi_1)$ and $Y_{l_2 m_2}(\theta_2, \phi_2)$:

$$f(\theta_1, \phi_1, \theta_2, \phi_2) = \sum_{l_1, l_2=0}^{\infty} \sum_{m_1=-l_1}^{l_1} \sum_{m_2=-l_2}^{l_2} f_{l_1 m_1 l_2 m_2} Y_{l_1 m_1}(\theta_1, \phi_1) Y_{l_2 m_2}(\theta_2, \phi_2). \quad (\text{A.4})$$

This can also be written explicitly

$$\begin{aligned} &f(\theta_1, \phi_1, \theta_2, \phi_2) \\ &= \sum_{l_1, l_2=0}^{\infty} \sum_{m_1=-l_1}^{l_1} \sum_{m_2=-l_2}^{l_2} [\hat{f}_{l_1 m_1 l_2 m_2}(\theta_1, \theta_2) \cos(m_1 \phi_1 - m_2 \phi_2) + \hat{g}_{l_1 m_1 l_2 m_2}(\theta_1, \theta_2) \sin(m_1 \phi_1 - m_2 \phi_2)]. \end{aligned} \quad (\text{A.5})$$

A.1. The case of the even E' state wave function

Let us first consider the even E' state wave function. It should be symmetrical with respect to the following inversion of the signs of the azimuthal angles:

$$\Psi_e(\mathbf{a}, \mathbf{b}, \mathbf{c}, \phi_1, \phi_2) = \Psi_e(\mathbf{a}, \mathbf{b}, \mathbf{c}, -\phi_1, -\phi_2). \quad (\text{A.6})$$

Using the development of Eq. (A.5), we can express the wave function in the following form where the term with $[\sin(m_1 \phi_1 - m_2 \phi_2)]$ does not appear

$$\Psi_e(\mathbf{a}, \mathbf{b}, \mathbf{c}, \phi_1, \phi_2) = \sum_{l_1, l_2=0}^{\infty} \sum_{\substack{|m_1| \leq l_1, |m_2| \leq l_2, \\ \text{mod}(m_1 - m_2, 3) \neq 0}} \hat{f}_{l_1 m_1 l_2 m_2}(\theta_1, \theta_2) \cos(m_1 \phi_1 - m_2 \phi_2). \quad (\text{A.7})$$

In this decomposition terms with $\text{mod}(m_1 - m_2, 3) = 0$ should be excluded to insure the orthogonality of the wave functions $\Psi_e(\mathbf{a}, \mathbf{b}, \mathbf{c}, \phi_1, \phi_2)$ and $\Psi_{A'_1}(\mathbf{a}, \mathbf{b}, \mathbf{c}, \phi_1, \phi_2)$.

Now for the terms for which $\text{mod}(m_1 - m_2, 3) \neq 0$ we have the following relation.

$$\sum_{s=-1} \cos\left(m_1\left(\phi_1 + s\frac{2\pi}{3}\right) - m_2\left(\phi_2 + s\frac{2\pi}{3}\right)\right) = 0. \quad (\text{A.8})$$

From here, taking into account the symmetry conditions (A.2), we deduce the relation

interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the Hulubei-Meshcheryakov JINR-Romania program, RUDN University Program 5-100 and grant of Plenipotentiary of the Republic of Kazakhstan in JINR. Most of the calculations were performed on Central Information and Computer Complex, and heterogeneous computing platform HybriLIT through supercomputer "GOVORUN" of the Joint Institute for Nuclear Research.

$$\sum_{s=-1}^1 \Psi_e(\mathbf{a}, \mathbf{b}, \mathbf{c}, \phi_1 + s\frac{2\pi}{3}, \phi_2 + s\frac{2\pi}{3}) \equiv \Psi_e(\mathbf{a}, \mathbf{b}, \mathbf{c}, \phi_1, \phi_2) + \Psi_e(\mathbf{c}, \mathbf{a}, \mathbf{b}, \phi_1, \phi_2) + \Psi_e(\mathbf{b}, \mathbf{c}, \mathbf{a}, \phi_1, \phi_2) = 0. \quad (\text{A.9})$$

A.2. The odd E' type state wavefunction

Finally we consider the odd E' state wavefunction, antisymmetric with respect to the inversion of the sign of the two azimuthal angles

$$\Psi_o(\mathbf{a}, \mathbf{b}, \mathbf{c}, \phi_1, \phi_2) = -\Psi_o(\mathbf{a}, \mathbf{b}, \mathbf{c}, r, -\phi_1, -\phi_2). \quad (\text{A.10})$$

As in the even case, we can write the odd wavefunction in terms of the development of Eq. (A.5) including now the $\sin(m_1\phi_1 - m_2\phi_2)$ part

$$\Psi_o(\mathbf{a}, \mathbf{b}, \mathbf{c}, \phi_1, \phi_2) = \sum_{l_1, l_2=0}^{\infty} \sum_{\substack{|m_1| \leq l_1, |m_2| \leq l_2; \\ \text{mod}(m_1 - m_2, 3) \neq 0}} \hat{g}_{l_1 m_1 l_2 m_2}(r_1, r_2, \theta_1, \theta_2) \sin(m_1\phi_1 - m_2\phi_2). \quad (\text{A.11})$$

This decomposition also doesn't contain terms with $\text{mod}(m_1 - m_2, 3) = 0$, since the wavefunctions $\Psi_o(\mathbf{a}, \mathbf{b}, \mathbf{c}, \phi_1, \phi_2)$ and $\Psi_{A_2}(\mathbf{a}, \mathbf{b}, \mathbf{c}, \phi_1, \phi_2)$ are orthogonal. Now for $\text{mod}(m_1 - m_2, 3) \neq 0$ we should have

$$\sum_{s=-1}^1 \sin\left(m_1\left(\phi_1 + s\frac{2\pi}{3}\right) - m_2\left(\phi_2 + s\frac{2\pi}{3}\right)\right) = 0. \quad (\text{A.12})$$

From here, taking into account the symmetry conditions (A.2), we have relation

$$\sum_{s=-1}^1 \Psi_o(\mathbf{a}, \mathbf{b}, \mathbf{c}, \phi_1 + s\frac{2\pi}{3}, \phi_2 + s\frac{2\pi}{3}) \equiv \Psi_o(\mathbf{a}, \mathbf{b}, \mathbf{c}, \phi_1, \phi_2) + \Psi_o(\mathbf{c}, \mathbf{a}, \mathbf{b}, \phi_1, \phi_2) + \Psi_o(\mathbf{b}, \mathbf{c}, \mathbf{a}, \phi_1, \phi_2) = 0. \quad (\text{A.13})$$

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