



Lower vibrational transitions of the ${}^3\text{He}{}^4\text{He}^+$ ion calculated without the Born–Oppenheimer approximation and with leading relativistic corrections

Sergiy Bubin ^{a,*}, Monika Stanke ^b, Ludwik Adamowicz ^{c,d}

^a Department of Physics and Astronomy, Vanderbilt University, Nashville, TN 37235, USA

^b Department of Physics, Nicholas Copernicus University, ul. Grudzia, dzka 5, PL 87-100, Toruń, Poland

^c Department of Chemistry, University of Arizona, Tucson, AZ 85721, USA

^d Department of Physics, University of Arizona, Tucson, AZ 85721, USA

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ABSTRACT

Very accurate variational calculations of the five lowest vibrational states of the ${}^3\text{He}{}^4\text{He}^+$ ion are carried out within a framework that does not assume the Born–Oppenheimer (BO) approximation, i.e., treating the two nuclei and three electrons forming the system on an equal footing. The non-BO wave functions are expanded in terms of one-center explicitly correlated Gaussian functions multiplied by even powers of the internuclear distance. The wave functions are used to calculate the leading relativistic corrections. The approach reproduces the experimental ${}^3\text{He}{}^4\text{He}^+$ fundamental transition within 0.055 cm^{-1} and similar accuracy is expected for the higher yet unmeasured vibrational transitions determined in the present calculations.

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1. Introduction

Due to the slight asymmetry of the charge in the ${}^3\text{He}{}^4\text{He}^+$ ion that results from non-adiabatic interactions, the rovibrational spectrum of this system has more lines than of the parent fully symmetric ${}^4\text{He}{}^4\text{He}^+$ system. However even for ${}^3\text{He}{}^4\text{He}^+$, only the fundamental vibrational transition frequency is determined with very high accuracy of about 0.001 cm^{-1} [1]. In our recent calculations [2] we reproduced this transition within 0.06 cm^{-1} using an approach which combines a non-Born–Oppenheimer (non-BO) variational calculation of the nonrelativistic energy and a first-order perturbation-theory calculation of the leading relativistic corrections.

As the higher pure vibrational transitions of ${}^3\text{He}{}^4\text{He}^+$ are not experimentally determined, the theoretical calculations can provide predictions for those transitions that can guide an experimental attempt to measure them. This has motivated the present work where the non-BO approach combined with the perturbative determination of the relativistic effects is used in the calculations of the third, fourth and fifth pure vibrational levels of ${}^3\text{He}{}^4\text{He}^+$. Some small improvement was also made in the energies of the ground and first excited levels.

The non-BO calculations of molecular systems, such the ones featured in this work, are considerably more difficult than electronic structure calculations based on the BO approximation with

the nuclei placed in fixed positions. The first reason for this is the increased number of active particles, which now is the sum of the number of electrons and the number of nuclei. The second reason is that the use of a different type of basis functions for expanding the wave function is required, which results from equal treatment of electrons and nuclei. Due to the strong correlation of the motions of the nuclei and the electrons, this basis needs to explicitly depend on the electron–electron, electron–nucleus, and nucleus–nucleus distances. Also, as the Hamiltonian of both atomic or molecular systems (after separations of the center of mass motion) is spherically symmetric (isotropic; see the next section), the basis functions have to reflect this symmetry. In particular, in the calculations of pure vibrational states (i.e., states with zero angular momentum) of ${}^3\text{He}{}^4\text{He}^+$ the basis functions have to be rotationally invariant with respect to the center of the internal coordinate system, which in our approach is a Cartesian system centered at a selected particle (usually the heaviest nucleus).

In the last decade we have developed an approach for performing non-BO calculations of light atomic and molecular systems [3–8]. In these calculations we have used different types of explicitly correlated Gaussian basis functions for expanding the non-BO wave functions. As the correlated Gaussians explicitly depend on the interparticle distances, they can effectively describe the above mentioned correlation effects. In our diatomic non-BO calculations we have used explicitly correlated N -particle Gaussians multiplied by powers of the internuclear distance. The powers of the distance are needed to describe the strong nucleus–nucleus correlation effects. Unlike the electron correlation, which can be usually very effectively described by correlated

* Corresponding author.

E-mail address: sergiy.bubin@vanderbilt.edu (S. Bubin).

Gaussians where the inter-electron distances appear only in the Gaussian exponents, the correlation between the nuclei also requires the use of preexponential factors. The role of those factors is to help effectively describe the proper shape of the ‘vibrational’ part of the wave function, i.e., to reduce the probability of two nuclei to be found close to each other and to make the probability distribution reach its maximum at the points where the nuclei spent most of the time (for the ground vibrational states these are the points corresponding to the equilibrium bond lengths).

The calculations presented here are a continuation of our work on extending the very accurate quantum mechanical treatment to molecular systems with more than two electrons. For over two decades the hydrogen molecule and its isotopologues described by seminal works by Kolos and Wolniewicz [9] and by Wolniewicz [10] have served as models on which various theoretical methods have been tested against the most accurate experimental measurements. Now, thanks to the development of methods that utilize explicitly correlated Gaussians and advances in computer hardware, the models, where the highly accurate theoretical calculations can be tested against the experiment, have extended to three- and four-electron molecular systems. The present work contributes to extending this fruitful interaction between theory and experiment.

In the next part of this Letter we describe the method used in the calculations. The results and their discussion is presented in the second part.

2. The method

The internal nonrelativistic all-particle Hamiltonian, \hat{H}_{nonrel} , used in the present calculations is obtained from the ‘laboratory frame’ Hamiltonian by separating the center-of-mass motion. In this an internal Cartesian coordinate system is used with the center placed at the heaviest nucleus (the ^4He nucleus). \hat{H}_{nonrel} has the following form:

$$\hat{H}_{\text{nonrel}} = -\frac{1}{2} \left(\sum_{i=1}^4 \frac{1}{\mu_i} \nabla_{\mathbf{r}_i}^2 + \sum_{i=1}^4 \sum_{j \neq i}^4 \frac{1}{m_0} \nabla_{\mathbf{r}_i} \cdot \nabla_{\mathbf{r}_j} \right) + \sum_{i=1}^4 \frac{q_0 q_i}{r_i} + \sum_{i < j}^4 \frac{q_i q_j}{r_{ij}}. \quad (1)$$

In (1) $q_0 = q_1 = 2$ are the charges of the nuclei and $q_2 = q_3 = q_4 = -1$ are the electron charges, \mathbf{r}_i , $i = 1, 2, 3, 4$, are the position vectors of the ^3He nucleus and the three electrons with respect to the ^4He nucleus (called the ‘reference particle’), r_i are their lengths, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, $m_0 = 7294.2995363m_e$ and $m_1 = 5495.885269m_e$ are the masses of the ^4He and ^3He nuclei [11], $m_e = 1$ is the electron mass, and $\mu_i = m_0 m_i / (m_0 + m_i)$ is the reduced mass of particle i . More information on the center-of-mass separation and the form of the internal Hamiltonian (1) can be found elsewhere [12,13].

In the calculations, the spatial parts of the non-BO wave functions of the vibrational states of the $^3\text{He}^4\text{He}^+$ ion are expanded in terms of the following one-center, spherically symmetric, explicitly correlated Gaussian functions multiplied by even powers (m_k) of the internuclear distance, r_1 [5–8]:

$$\phi_k = r_1^{m_k} \exp[-\mathbf{r}'(A_k \otimes I_3)\mathbf{r}], \quad (2)$$

where $\mathbf{r} = \{\mathbf{r}'_1, \mathbf{r}'_2, \mathbf{r}'_3, \mathbf{r}'_4\}'$ and $'$ denotes the vector (matrix) transposition, \otimes denotes the Kronecker product, and I_3 is a 3×3 unit matrix. Values in the range of 0–250 are used for m_k and they are optimized for each basis function just after the function is added to the basis set. Limiting the powers of m_k in basis functions (2) to only even values has very little effect on the energy [5,6], but significantly speeds up the calculations, as the algorithms for calculating the Hamiltonian matrix elements are less complicated.

The matrix of exponential coefficients, A_k , for each basis function (2) has to be positive definite in order for the ϕ_k basis function

to be square integrable. Imposing restrictions on the elements of A_k 's that would make the matrix positive definite is not optimal from the computational point of view. A more efficient way to deal with this issue is to use the Cholesky-factored form of A_k , $A_k \equiv L_k L_k'$, where L_k is a lower triangular matrix (all elements above the diagonal are zero). As the $L_k L_k'$ product is automatically positive definite for any values of the L_k matrix elements, no restrictions need to be imposed on those elements in the variational energy minimization. Using L_k matrix elements as the variational parameters considerably simplifies the minimization of the energy, which is computed as the solution of the secular equation

$$Hc = ES c, \quad (3)$$

where $H(\{m_k\}, \{L_k\})$ and $S(\{m_k\}, \{L_k\})$ are $K \times K$ Hamiltonian and overlap matrices (K is the size of the basis) and c is the vector of linear expansion coefficients. The minimization of the energy, E , with respect to $\{L_k\}$ in our approach involves the analytical first derivatives of the energy with respect to those parameters (i.e., the energy gradient). The use of the energy gradient considerably accelerates the energy minimization.

The maximum number of basis functions used for each of the five vibrational states considered in the calculations is 10000. In the process of generating this number of functions we start with a small randomly selected basis set of a few dozen functions. Next the basis set is grown by successive additions of small groups of functions which, after the inclusion in the basis set, are optimized using the gradient-based energy minimization approach. When the number of functions is less than 1000 all functions are optimized simultaneously. After passing 1000 functions the optimization is done by adjusting the parameters of only one function at a time and cycling over all functions in the basis set. After a 10000 basis set is constructed for each state several additional optimization cycles of all basis functions are performed.

In the next step the non-BO wave functions are used to determine the leading relativistic corrections of the order α^2 (α is the fine structure constant; in atomic units $\alpha = 1/c$, where c is the speed of light in vacuum). The mass-velocity (MV), Darwin (D), spin-spin (SS), and orbit-orbit (OO) corrections are determined using first-order perturbation theory. The corrections are represented by the following operators in the internal coordinate frame:

$$\hat{H}_{\text{MV}} = -\frac{1}{8} \left[\frac{1}{m_0^3} \left(\sum_{i=1}^4 \nabla_{\mathbf{r}_i} \right)^4 + \sum_{i=1}^4 \frac{1}{m_i^3} \nabla_{\mathbf{r}_i}^4 \right], \quad (4)$$

$$\hat{H}_{\text{D}} = -\frac{\pi}{2} \sum_{i=2}^4 \frac{q_0 q_i}{m_i^2} \delta(\mathbf{r}_i) - \frac{\pi}{2} \sum_{i=1}^4 \sum_{j \neq i}^4 \frac{q_i q_j}{m_i^2} \delta(\mathbf{r}_{ij}), \quad (5)$$

$$\hat{H}_{\text{SS}} = 2\pi \sum_{i=2}^4 \sum_{j > i}^4 \frac{q_i q_j}{m_i m_j} \delta(\mathbf{r}_{ij}), \quad (6)$$

$$\hat{H}_{\text{OO}} = -\frac{1}{2} \sum_{i=1}^4 \sum_{j=1}^4 \frac{q_0 q_j}{m_0 m_j} \left[\frac{1}{r_j} \nabla_{\mathbf{r}_i} \cdot \nabla_{\mathbf{r}_j} + \frac{1}{r_j^3} \mathbf{r}_j \cdot (\mathbf{r}_j \cdot \nabla_{\mathbf{r}_i}) \nabla_{\mathbf{r}_j} \right] + \frac{1}{2} \sum_{i=1}^4 \sum_{j > i}^4 \frac{q_i q_j}{m_i m_j} \left[\frac{1}{r_{ij}} \nabla_{\mathbf{r}_i} \cdot \nabla_{\mathbf{r}_j} + \frac{1}{r_{ij}^3} \mathbf{r}_{ij} \cdot (\mathbf{r}_{ij} \cdot \nabla_{\mathbf{r}_i}) \nabla_{\mathbf{r}_j} \right]. \quad (7)$$

We should mention that the spin-orbit interaction is zero for the states considered in this work as the non-BO wave functions are spherically symmetric. The total relativistic correction is the sum of the MV, D, SS, and OO corrections. Taking into account the indistinguishability of electrons the expectation values of \hat{H}_{D} and \hat{H}_{SS} reduce to:

$$\langle \hat{H}_{\text{D}} \rangle = 3\pi[\delta(\mathbf{r}_2) + \delta(\mathbf{r}_{12}) - \delta(\mathbf{r}_{23})], \quad \langle \hat{H}_{\text{SS}} \rangle = 6\pi\delta(\mathbf{r}_{23}). \quad (8)$$

Table 1

The convergence of the total nonrelativistic non-BO energies (E_{NR}) and the relativistically corrected energies (E_{REL}) for low-lying vibrational states of the $^3\text{He}^4\text{He}^+$ ion. The values in parentheses are estimated theoretical uncertainties due to the finite size of the basis used. All values are in hartrees.

| ν | Basis | E_{NR} | E_{REL} |
|-------|--------------------|--------------------|--------------------|
| 0 | 10000 ^a | −4.989719657(30) | −4.989926676(30) |
| 1 | 10000 ^a | −4.981743256(80) | −4.981950301(80) |
| 2 | 6000 | −4.974137214 | −4.974344203 |
| | 7000 | −4.974138191 | −4.974345236 |
| | 8000 | −4.974138670 | −4.974345736 |
| | 9000 | −4.974138951 | −4.974346032 |
| | 10000 | −4.974139132 | −4.974346207 |
| | 10000 ^a | −4.974139290(250) | −4.974346391(250) |
| 3 | 6000 | −4.966904665 | −4.967111834 |
| | 7000 | −4.966906214 | −4.967113384 |
| | 8000 | −4.966907070 | −4.967114273 |
| | 9000 | −4.966907673 | −4.967114884 |
| | 10000 | −4.966907994 | −4.967115195 |
| | 10000 ^a | −4.966908238(2000) | −4.967115441(2000) |
| 4 | 6000 | −4.960043560 | −4.960250681 |
| | 7000 | −4.960046529 | −4.960253651 |
| | 8000 | −4.960048178 | −4.960255289 |
| | 9000 | −4.960049158 | −4.960256291 |
| | 10000 | −4.960049834 | −4.960257023 |
| | 10000 ^a | −4.960050253(2500) | −4.960257477(2500) |

^a Results obtained after performing additional optimization of the Gaussian nonlinear parameters.

3. The results

The total non-BO nonrelativistic energies and total energies that include the MV, D, SS, and OO relativistic corrections for the $\nu=0, 1, 2, 3,$ and 4 states are shown in Table 1 for different numbers of basis functions. As the results for the $\nu=0$ and 1 states were presented before [2], we only show the results obtained with different basis set sizes for the $\nu=2, 3, 4$ and 5 states. The energies shown in Table 1 for the $\nu=0$ and 1 are slightly improved with respect to the energies presented before [2]. The improvement was achieved by performing several additional optimization cycles of the nonlinear parameters of the Gaussians. That optimization, for example, lowered the total nonrelativistic energy of the $\nu=1$ state from -4.981743230 to -4.981743256 hartree.

As one can see in Table 1, for all four states considered in this work the energies (both nonrelativistic and those including relativistic corrections) are converged to within seven-eight significant figures. Such tight convergence was only possible because of extensive optimization of the nonlinear Gaussian parameters with the gradient-based procedure. As mentioned, when the basis set for each state reached 10000 functions several additional cyclic optimizations were performed. This further lowered the energy of each state by 1×10^{-7} – 5×10^{-7} hartree.

The transition energies, calculated as the difference between the total nonrelativistic and relativistic energies of the adjacent states, are shown for different basis set sizes in Table 2. As one can see, the transition energy values are converged to about 0.1 cm^{-1} . For the $0 \rightarrow 1$ transition the result obtained is this work is slightly improved with respect to the results obtained previously [2]. The $0 \rightarrow 1$ transition energy of $1750.612(60) \text{ cm}^{-1}$ obtained from the total energies that include the relativistic corrections is now off from the experimental value of $1750.55687(98) \text{ cm}^{-1}$ [1] by 0.055 cm^{-1} . For the other transition energies, i.e., the $1 \rightarrow 2$

Table 2

The convergence of vibrational transition energies of the $^3\text{He}^4\text{He}^+$ ion. All values are in cm^{-1} .

| Transition | Basis | NR | REL |
|-------------------|--------------------|---------------|---------------|
| $0 \rightarrow 1$ | 10000 ^a | 1750.618(60) | 1750.612(60) |
| $1 \rightarrow 2$ | 10000 ^a | 1668.878(130) | 1668.865(130) |
| $2 \rightarrow 3$ | 6000 | 1587.361 | 1587.321 |
| | 7000 | 1587.235 | 1587.208 |
| | 8000 | 1587.153 | 1587.123 |
| | 9000 | 1587.082 | 1587.054 |
| | 10000 | 1587.051 | 1587.024 |
| | 10000 ^a | 1587.033(200) | 1587.010(200) |
| $3 \rightarrow 4$ | 6000 | 1505.838 | 1505.849 |
| | 7000 | 1505.527 | 1505.537 |
| | 8000 | 1505.353 | 1505.373 |
| | 9000 | 1505.270 | 1505.287 |
| | 10000 | 1505.192 | 1505.195 |
| | 10000 ^a | 1505.154(400) | 1505.149(400) |

^a Results obtained after performing additional optimization of the Gaussian nonlinear parameters.

transition of $1668.865(130) \text{ cm}^{-1}$, the $2 \rightarrow 3$ transition of $1587.010(200)$, and the $3 \rightarrow 4$ transition of $1505.149(400)$, the expected accuracy is likely slightly lower, but still the results are very precise.

4. Summary

In this work we continue to show very accurate results obtained with our non-BO approach developed to study bound energy levels of diatomic systems. By using large sets of explicitly correlated Gaussian functions, variationally optimizing their nonlinear parameters with a gradient-based method, and including the leading relativistic corrections, we are able to generate pure vibrational transition energies of the three-electron $^3\text{He}^4\text{He}^+$ ion with an accuracy of the order of 0.1 cm^{-1} . Such an accuracy level is higher than ever achieved before for a three-electron diatomic system.

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