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Lowest vibrational states of ^{4}He^{3}He$^+$: Non-Born-Oppenheimer calculations

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Very accurate quantum mechanical calculations of the first five vibrational states of the ^{4}He^{3}He$^+$ molecular ion are reported. The calculations have been performed explicitly including the coupling of the electronic and nuclear motions [i.e., without assuming the Born-Oppenheimer (BO) approximation]. The nonrelativistic non-BO wave functions were used to calculate the α^2 relativistic mass velocity, Darwin, and spin-spin interaction corrections. For the lowest vibrational transition, whose experimental energy is established with high precision, the calculated and the experimental results differ by only 0.16 cm^{-1}.

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I. INTRODUCTION

The one-electron (e.g., H_2^+) and two-electron (e.g., H_2) molecular systems have been used for the last four decades as models for comparing high accuracy quantum mechanical calculations with the most precise high-resolution spectroscopy experiments involving gas-phase measurements of such molecular quantities as rovibrational and electronic excitation energies, electron affinities, ionization potentials, bond dissociation, and atomization energies. These kinds of experiments have nowadays achieved the precision exceeding tenths or even hundredths of a wave number. In parallel to the advancements in the experimental techniques, the accuracy of theoretical quantum-mechanical calculations on molecular systems has also significantly increased. This not only applies to systems consisting of several atoms, but also to small diatomic two-electron systems. For those smaller systems, large scale calculations have led to improvements in the nonrelativistic energies and to the determination of relativistic and quantum-electrodynamic (QED) corrections [1–4]. Moreover, even for atomic and molecular systems with three and more electrons the calculated quantities have started to match very precisely the experimental measurements [5–10].

The recent works of our laboratory in the area of very accurate molecular calculations [2–4,11–18] have contributed to expanding the applicability of those calculations to atomic and molecular systems with more than two electrons and two nuclei. The approach we have used departs from the Born-Oppenheimer (BO) approximation and treats the nuclei and electrons on equal footing. The main part of the development has been the use of correlated Gaussian functions that depend explicitly on the distances between the particles (nuclei and electrons) forming the molecule in expanding the wave function. In the most recent works [2–4,9,10,18–20] we have also used the non-BO wave functions to determine relativistic corrections of the order of α^2, where $\alpha = e^2/(\hbar c)$ is the fine structure constant. In this work we describe the application of our non-BO relativistic approach to the ^{4}He^{3}He$^+$ molecular ion. There are several reasons for undertaking very precise calculations on this system. First, due to some slight charge asymmetry caused by a nonadiabatic interaction between the electrons and the two nuclei with different masses, this system is more likely to be observed in a spectroscopy experiment than its homonuclear counterpart ^{4}He^{4}He$^+$. Second, this system is one of the three-electron molecular models where the agreement between the theoretical calculations and very precise spectroscopic data can be tested. Third, the issue of the isotopically induced charge asymmetry is an interesting problem whose quantitative description can be obtained from calculations that are not based on the Born-Oppenheimer approximation as the ones performed in this work are.

The three-electron ^{4}He^{3}He$^+$ ion is similar to the two-electron ^{4}He^{1}He$^+$ ion, which we studied before with the non-BO approach before [2,4]. In both systems a neutral helium atom interacts with a positive ion. However, while in HeH$^+$ the electrons are strongly localized around the helium nucleus, in the ^{4}He^{4}He$^+$ ion they are almost evenly distributed among both nuclei. For the HeH$^+$ system, an excellent agreement with the experimental lowest vibrational transition energies required the inclusion of the mass-velocity and Darwin relativistic corrections to the non-BO energy [2]. We also calculate here these corrections for the lowest vibrational transitions of the ^{4}He^{3}He$^+$ ion.

The calculations presented in this work concern the five lowest bound states of the ^{4}He^{3}He$^+$ ion with zero total angular momentum. Such states are usually called "vibrational states" although, if the Born-Oppenheimer approximation is not invoked, the vibrational motion of the nuclei is coupled with the electronic motion and, strictly speaking, the vibrational quantum number, v, is not a good quantum number.

Some highly precise measurements of the vibration-rotational and pure rotational gas phase spectral lines of ^{4}He^{3}He$^+$ have been performed [21–23]. In this work we use those measurements to estimate the ground-state pure vibra-

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tional transition. This is the only transition that can be determined with a satisfactory accuracy based on the available experimental data. The experimental ground-state transition is compared with the result of the calculations.

As mentioned, the isotopic asymmetry of the ^{4}He^{3}He$^+$ ion makes this system an interesting case for a non-BO calculation. Unlike ^{4}He^{3}He$^+$, its homonuclear counterpart ^{4}He^{4}He$^+$ contains an additional permutational symmetry that the wave function for each state has to possess. Since in ^{4}He^{4}He$^+$ both nuclei are bosons, the total wave function has to be symmetric with respect to interchanging them. Thus, in a non-BO calculation of ^{4}He^{4}He$^+$ the total non-BO wave function has to be fully symmetrized with respect to the nuclei permutation. The total non-BO wave function explicitly and simultaneously depends on the coordinates of both the electrons and the nuclei. For ^{4}He^{4}He$^+$ in the $^2\Sigma_u$ ground electronic state, the electronic part of the wave function is antisymmetric with respect to the nuclei permutation. Therefore, in order to make the whole wave function fully symmetric with respect to that permutation, the nuclear part has to be antisymmetric. Only then does the superposition of the antisymmetric electronic component and the antisymmetric nuclear component give the fully symmetric total wave function. This means that in the ground electronic state ^{4}He^{4}He$^+$ can only exist in rotational states corresponding to odd rotational quantum numbers (those states have antisymmetric nuclear wave functions). For the mixed nuclei system, ^{4}He^{3}He$^+$, rotational states with both odd and even rotational quantum numbers should exist. In this case, no nuclear symmetry needs to be implemented in the wave function in a non-BO calculation. This is how the present calculations have been performed. However, since we have only used basis functions that are fully symmetric with respect to rotations of the internal coordinate system in the calculations, the states we described correspond to the ground rotational state.

For several decades the most frequently used two-electron model system for testing the accuracy of high level quantum mechanical molecular calculations has been the hydrogen molecule. For a three electron system, the helium dimer cation can become such a model. Our present non-BO calculations concern only the first five lowest pure vibrational excitations of this system. Even for these few excitations the calculations have taken almost a year to complete and the results are not as well converged as those obtained before for the hydrogen molecule or for the HeH$^+$ ion [2]. This is because with one extra electron ^{4}He^{3}He$^+$ is a much more complicated problem than H$_2$.

We should add that ^{4}He^{3}He$^+$ is also a "work in progress" on the experimental site. Only a limited number of rovibrational transitions have been assigned, and no pure vibrational transitions have been measured. In this work we show how well the experimental and theoretical investigations are converging in determining the transition energies between the rotationless vibrational levels.

II. METHOD USED IN THE CALCULATIONS

The total nonrelativistic Hamiltonian for ^{4}He^{3}He$^+$ in the laboratory Cartesian coordinate system has the following form:

$$\hat{H}_{\mathrm{tot}} = -\sum_{i=1}^{5} \frac{1}{2M_i}\nabla^2_{\mathbf{R}_i} + \sum_{i=1}^{4}\sum_{j>i}^{5} \frac{Q_i Q_j}{R_{ij}}, \tag{1}$$

where the masses, charges, and positions of the five particles forming ^{4}He^{3}He$^+$ are denoted as M_i, Q_i, and $\mathbf{R}_i$, respectively. The first two particles are the ^{4}He and ^{3}He nuclei, and the last three are the electrons. The masses of the nuclei, according to Ref. [24], are $M_{^4\mathrm{He}}=7294.2995363M_e$ and $M_{^3\mathrm{He}}=5495.885269M_e$ (M_e is the electron mass).

At the first stage we transform the Hamiltonian (1) by separating the center-of-mass motion. In this transformation it is convenient to change the laboratory coordinate system to a system whose first three coordinates are the laboratory coordinates of the center of mass $\mathbf{r}_0$ and the remaining coordinates are Cartesian coordinates $\mathbf{r}_i$ ($\mathbf{r}_i=\mathbf{R}_{i+1}-\mathbf{R}_1$), that described the positions of particles 2 to 5 with respect to particle 1, which is called the reference particle. In the calculations on ^{4}He^{3}He$^+$ the reference particle was the ^{4}He nucleus. After the coordinate transformation the internal Hamiltonian $\hat{H}$ is

$$\hat{H} = -\frac{1}{2}\left(\sum_{i}^{4} \frac{1}{m_i}\nabla^2_{\mathbf{r}_i} + \sum_{i\neq j}^{4} \frac{1}{M_1}\nabla'_{\mathbf{r}_i}\nabla_{\mathbf{r}_j}\right) + \sum_{i=1}^{4} \frac{q_0 q_i}{r_i} + \sum_{i<j}^{4} \frac{q_i q_j}{r_{ij}}, \tag{2}$$

where $r_i=|\mathbf{r}_i|$, $r_{ij}=|\mathbf{R}_{j+1}-\mathbf{R}_{i+1}|=|\mathbf{r}_j-\mathbf{r}_i|$, and where a prime denotes vector transposition. The separation of the internal Hamiltonian and the Hamiltonian of the motion of the center of mass is exact. The internal Hamiltonian (2) describes four pseudoparticles with charges $q_i=Q_{i+1}$ and reduced masses $m_i=M_1M_{i+1}/(M_1+M_{i+1})$ moving in the central potential of the charge of the reference particle.

Due to a strong coupling of the motions of the pseudoparticles through the two-particle mass polarization term $\sum_{i\neq j}^{4}\frac{1}{M_1}\nabla'_{\mathbf{r}_i}\nabla_{\mathbf{r}_j}$ and through the Coulombic interactions, the correlation effects can be expected to be significant. This reflects on the choice of the basis functions for the calculations.

In order to compare the results obtained in calculations with highly accurate spectrocsopic data it is not sufficient to only compute the eigenvalues of the nonrelativistic Hamiltonian. Accounting for relativistic corrections is often desirable or even necessary. In this work, in addition to accurate evaluation of nonrelativistic energies, we also compute mass-velocity (MV), Darwin (D), and spin-spin (SS) interaction corrections using Breit-Pauli formalism.

After the transformation to the internal coordinate system the operators representing the MV, D, and SS interaction in the Breit-Pauli equation (in the relativistic limit we do not neglect the contributions from the anomalous magnetic moments of the particles [25]) have the following form [26]:

$$\hat{H}_{\mathrm{D}} = -\alpha^2\frac{\pi}{2}\sum_{i=1}^{4}\left[\frac{q_0 q_i(1+2\kappa_i)}{M_{i+1}^2}\delta^3(r_i) + \sum_{j\neq i}^{4}\frac{q_i q_j(1+2\kappa_i)}{M_{i+1}^2}\delta^3(r_{ij})\right], \tag{3}$$

$$\hat{H}_{\rm MV} = -\alpha^2 \frac{1}{8}\left[\frac{1}{M_1^3}\left(\sum_{i=1}^{4} \nabla_{\mathbf{r}_i}\right)^4 + \sum_{i=1}^{4} \frac{1}{M_{i+1}^3}\boldsymbol{\nabla}^4_{\mathbf{r}_i}\right], \tag{4}$$

$$\hat{H}_{\rm SS} = -\alpha^2\frac{8}{3}\pi\sum_{j=1}^{4}\sum_{i>j}^{4} \frac{q_iq_j(1+\kappa_i)(1+\kappa_j)}{M_{i+1}M_{j+1}}\delta^3(r_{ij})(\mathbf{S}_i\cdot\mathbf{S}_j), \tag{5}$$

where $\mathbf{r}=\{\mathbf{r}_1',\mathbf{r}_2',\mathbf{r}_3'\}'$ and $\kappa_1=1.12749772$ is the anomalous magnetic moment of the ^{3}He nucleus [27] and $\kappa_2=\kappa_3=\kappa_4=0.0011596521811$ are the anomalous magnetic moments of the electrons [24]. In general, the relation of the anomalous magnetic moment of the nucleus with the charge Ze and mass M to its magnetic moment $\boldsymbol{\mu}$ is $\boldsymbol{\mu}=(1+\kappa)Ze\mathbf{S}/M$, where $\mathbf{S}=\boldsymbol{\sigma}/2$ is the spin operator.

It should be noted that only fermions contribute (in the order of α^2) to the D correction and the ^{4}He nucleus (zero spin) should be excluded from the sums in Eq. (3). Also, the ^{4}He nucleus does not contribute to the spin-spin interaction (5) because of its zero spin.

TABLE I. Dunham's spectral parameters (in cm^{-1}) fitted to the ^{4}He^{3}He$^+$ vibration-rotational spectrum for $v=0\rightarrow1$ and $J=1-12$.

Y_{ij}	Fit 1	Fit 2	Fit 3
Y_{10}	1750.5574(37)	1750.55538(88)	1750.55687(98)
Y_{11}	−0.2832(13)	−0.28391(15)	−0.28337(20)
Y_{01}	8.3927(32)	8.39446(47)	8.39314(59)
$Y_{02}\times10^{-4}$	−7.43(69)	−7.033(28)	−7.322(58)
$Y_{03}\times10^{-8}$	−1.2(7.4)	3.07(36)	
$Y_{12}\times10^{-6}$	0.9(1.6)		6.61(73)
$\hat{\sigma}$	0.2564	0.2340	0.2230
σ	0.00015	0.00014	0.00013
$\nu_{0\rightarrow1}$	1750.5574(37)	1750.55538(88)	1750.55687(98)

The calculation of the relativistic correction for the system was done separately for each state as the expectation value of the Hamiltonian representing the mass-velocity, Darwin, and the spin-spin interaction contributions

$$\hat{H}' = \hat{H}_{\rm MV} + \hat{H}_{\rm D} + \hat{H}_{\rm SS}, \tag{6}$$

with the non-BO wave function.

In our previous works involving non-BO calculations on small diatomic molecular systems [11–14,18] we have

TABLE II. Nonrelativistic non-BO energies ($E_{\rm nonrel}$), relativistic corrections ($\alpha^2E_{\rm MV}$, $\alpha^2E_{\rm D}$, $\alpha^2E_{\rm SS}$) and their sum ($\alpha^2E_{\rm rel}$), and the total energies ($E_{\rm nonrel}+\alpha^2E_{\rm rel}$) for lowest vibrational states of ^{4}He^{3}He$^+$ with zero angular momentum computed with different number of basis functions. All values are in a.u.

v	basis size	$E_{\rm nonrel}$	$\alpha^2E_{\rm MV}$	$\alpha^2E_{\rm D}$	$\alpha^2E_{\rm SS}$	$\alpha^2E_{\rm rel}$	$E_{\rm nonrel}+\alpha^2E_{\rm rel}$
0	4500	−4.98971892	-1.26532×10^{-3}	1.02646×10^{-3}	3.859×10^{-5}	-2.0026×10^{-4}	−4.98991918
	5000	−4.98971910	-1.26540×10^{-3}	1.02655×10^{-3}	3.858×10^{-5}	-2.0027×10^{-4}	−4.98991936
	5500	−4.98971924	-1.26569×10^{-3}	1.02684×10^{-3}	3.858×10^{-5}	-2.0028×10^{-4}	−4.98991952
	6000	−4.98971935	-1.26585×10^{-3}	1.02699×10^{-3}	3.857×10^{-5}	-2.0029×10^{-4}	−4.98991963
	6500	−4.98971943	-1.26598×10^{-3}	1.02712×10^{-3}	3.857×10^{-5}	-2.0029×10^{-4}	−4.98991972
1	4500	−4.98174074	-1.26145×10^{-3}	1.02298×10^{-3}	3.829×10^{-5}	-2.0018×10^{-4}	−4.98194092
	5000	−4.98174140	-1.26169×10^{-3}	1.02321×10^{-3}	3.828×10^{-5}	-2.0019×10^{-4}	−4.98194159
	5500	−4.98174195	-1.26212×10^{-3}	1.02364×10^{-3}	3.827×10^{-5}	-2.0022×10^{-4}	−4.98194216
	6000	−4.98174235	-1.26266×10^{-3}	1.02415×10^{-3}	3.826×10^{-5}	-2.0024×10^{-4}	−4.98194259
	6500	−4.98174262	-1.26324×10^{-3}	1.02474×10^{-3}	3.824×10^{-5}	-2.0025×10^{-4}	−4.98194287
2	4500	−4.97413380	-1.25908×10^{-3}	1.02096×10^{-3}	3.802×10^{-5}	-2.0010×10^{-4}	−4.97433390
	5000	−4.97413545	-1.25946×10^{-3}	1.02133×10^{-3}	3.800×10^{-5}	-2.0012×10^{-4}	−4.97433557
	5500	−4.97413649	-1.25977×10^{-3}	1.02165×10^{-3}	3.799×10^{-5}	-2.0013×10^{-4}	−4.97433661
	6000	−4.97413721	-1.26011×10^{-3}	1.02196×10^{-3}	3.798×10^{-5}	-2.0017×10^{-4}	−4.97433738
	6500	−4.97413773	-1.26037×10^{-3}	1.02222×10^{-3}	3.797×10^{-5}	-2.0018×10^{-4}	−4.97433791
3	4500	−4.96689762	-1.25616×10^{-3}	1.01819×10^{-3}	3.781×10^{-5}	-2.0016×10^{-4}	−4.96709778
	5000	−4.96690134	-1.25683×10^{-3}	1.01897×10^{-3}	3.776×10^{-5}	-2.0011×10^{-4}	−4.96710145
	5500	−4.96690338	-1.25801×10^{-3}	1.02004×10^{-3}	3.773×10^{-5}	-2.0024×10^{-4}	−4.96710362
	6000	−4.96690466	-1.25828×10^{-3}	1.02032×10^{-3}	3.771×10^{-5}	-2.0025×10^{-4}	−4.96710491
	6500	−4.96690556	-1.25861×10^{-3}	1.02067×10^{-3}	3.769×10^{-5}	-2.0025×10^{-4}	−4.96710581
4	4500	−4.96003213	-1.25200×10^{-3}	1.01453×10^{-3}	3.757×10^{-5}	-1.9991×10^{-4}	−4.96023203
	5000	−4.96003768	-1.25341×10^{-3}	1.01584×10^{-3}	3.753×10^{-5}	-2.0004×10^{-4}	−4.96023772
	5500	−4.96004114	-1.25414×10^{-3}	1.01654×10^{-3}	3.750×10^{-5}	-2.0010×10^{-4}	−4.96024124
	6000	−4.96004356	-1.25495×10^{-3}	1.01735×10^{-3}	3.749×10^{-5}	-2.0010×10^{-4}	−4.96024366
	6500	−4.96004526	-1.25517×10^{-3}	1.01757×10^{-3}	3.748×10^{-5}	-2.0011×10^{-4}	−4.96024537

shown that the explicitly correlated Gaussians (ECGs) involving functions with preexponential multipliers consisting of the internuclear distance $\mathbf{r}_1$ raised to a nonnegative even power p_k:

$$\phi_k = r_1^{p_k} \exp[-\mathbf{r}'(A_k \otimes I_3)\mathbf{r}], \tag{7}$$

where $\mathbf{r}=\{\mathbf{r}_1', \mathbf{r}_2', \mathbf{r}_3'\}'$, are very effective in describing nonadiabatic, zero angular momentum states of diatomic systems with σ electrons. These are the functions used in the present calculations. The reader can obtain more information on the Hamiltonian transformation and the selection of the basis functions for diatomic calculations from our recent reviews [16,17]. The details of the evaluation of matrix elements with the D, MV, and SS operators can be found in Ref. [18].

As in our previous works, also here the wave function for each state of $^4\mathrm{He}^3\mathrm{He}^+$ has been obtained by minimizing the total non-BO energy of the system with respect to the expansion coefficients in terms of the basis functions, c_k, the basis-function exponential parameters $\{A_k\}$ and the preexponential powers $\{p_k\}$. The optimization was done separately for each state and using an algorithm based on analytical derivatives of the energy with respect to $\{A_k\}$. To achieve high accuracy we used 6500 basis functions for each state. We believe that with this many functions in the basis the nonrelativistic energies were converged to the sixth or seventh decimal figure, depending on the state (the accuracy decreases with the excitation level, as the corresponding wave functions have progressively more complicated structure). The range of the preexponential powers, $\{p_k\}$, used was from 0 to 250, and all the powers were partially optimized for each state.

After the wave functions for the lowest five vibrational states were generated, we calculated the expectation values of the relativistic Hamiltonian (6) for each state and added them to the variational energies of the corresponding states. Those values were used to calculate the transition energies.

III. ESTIMATION OF THE PURE VIBRATIONAL TRANSITION 0→1 OF $^4\mathrm{He}^3\mathrm{He}^+$ FROM IR SPECTRA

The frequency of the pure vibrational transition $J=0 \rightarrow 1$ of $^4\mathrm{He}^3\mathrm{He}^+$ has been estimated by fitting the line positions of the rotation-vibrational transitions obtained by Yu and Wing [21] to the Dunham's energy formula [22]

$$E_{vJ} = \sum_{i,j} Y_{ij}\left(v + \frac{1}{2}\right)^i [J(J+1)]^j, \tag{8}$$

where $v=0,1,2,\ldots$ and $J=0,1,2,\ldots$ denote the vibrational and rotational quantum numbers, respectively. In this approach the frequency of the $0 \rightarrow 1$ vibrational transition is directly obtained from the relationship

$$\nu_{0\rightarrow 1} = Y_{10}\ \mathrm{cm}^{-1}. \tag{9}$$

We assume that the higher order vibrational parameters, Y_{20}, Y_{30}, etc., can be neglected.

In the work of Yu and Wing [21], the Dunham's parameters Y_{12}, Y_{02}, and Y_{03} evaluated from the IR spectra of $^4\mathrm{He}^3\mathrm{He}^+$ had large standard errors. The authors also used the constrained parameter $Y_{20}=-41.1\ \mathrm{cm}^{-1}$ taken from Ref. [23] in the fit. We decided to revise the results of Yu's and Wing's calculations to get a more accurate value of the $\nu_{0\rightarrow 1}$ transition frequency. By making some preliminary fits, we discovered that the presence of the constrained parameter Y_{20} in the fit influences very little the accuracy of the spectral reproduction. Hence, we removed it from the set of the fitted parameters. Additionally, removing the parameters Y_{12} or Y_{03} improves the statistical criteria associated with the quality of the fit. A detailed analysis of the results presented in Table I reveals that the most reliable parameters Y_{ij} are obtained from Fit 3. Hence, the most precise value of the $0 \rightarrow 1$ transition frequency is $\nu_{0\rightarrow 1}=1750.55687(98)\ \mathrm{cm}^{-1}$. The uncertainty values shown in the parenthesis in Table I are estimated standard deviations in units of the last quoted digit of the values of the fitted Dunham's constants.

The calculations have been performed by making use of a weighted nonlinear least-square routine with weights taken as the inverse squares of the uncertainty $u_i=0.0006\ \mathrm{cm}^{-1}$ of the experimental data [21]. To obtain the best set of Dunham's constants Y_{ij} from fitting the spectra, we used the following criteria: the minimum number of the fitted parameters consistent with a minimum values of the normalized standard deviation $\hat{\sigma}$ and of the standard deviation σ, an optimal value of the estimated standard error σ_i of each fitted parameter i and of the correlation coefficient $CC(i,j)$ corresponding to the parameters i and j.

TABLE III. Nonrelativistic and relativistic transition energies for lowest vibrational states of $^4\mathrm{He}^3\mathrm{He}^+$. All values are in cm^{-1}.

$v \rightarrow v'$	Basis size	$\Delta E_{\mathrm{nonrel}}$	ΔE_{rel}
0→1	4500	1751.01	1751.03
	5000	1750.90	1750.92
	5500	1750.81	1750.83
	6000	1750.75	1750.76
	6500	1750.71	1750.71
1→2	4500	1669.53	1669.55
	5000	1669.31	1669.33
	5500	1669.21	1669.23
	6000	1669.13	1669.15
	6500	1669.08	1669.10
2→3	4500	1588.16	1588.14
	5000	1587.70	1587.71
	5500	1587.48	1587.46
	6000	1587.36	1587.34
	6500	1587.28	1587.26
3→4	4500	1506.80	1506.86
	5000	1506.40	1506.42
	5500	1506.09	1506.12
	6000	1505.84	1505.87
	6500	1505.66	1505.69

TABLE IV. Expectation values of ^{4}He^{3}He$^+$ computed with different basis sets. All quantities in a.u.

v	Basis size	$\langle r^{-1}_{^4\text{He-}^3\text{He}}\rangle$	$\langle r^{-1}_{^4\text{He-}e}\rangle$	$\langle r^{-1}_{^3\text{He-}e}\rangle$	$\langle r^{-1}_{e\text{-}e}\rangle$	$\langle r_{^4\text{He-}^3\text{He}}\rangle$	$\langle r_{^4\text{He-}e}\rangle$	$\langle r_{^3\text{He-}e}\rangle$	$\langle r_{e\text{-}e}\rangle$
0	4500	0.484420	1.155592	1.155498	0.649807	2.073844	1.511470	1.511559	1.994552
	5000	0.484420	1.155592	1.155498	0.649807	2.073844	1.511470	1.511559	1.994552
	5500	0.484420	1.155592	1.155498	0.649807	2.073844	1.511470	1.511559	1.994552
	6000	0.484420	1.155592	1.155498	0.649807	2.073844	1.511471	1.511560	1.994553
	6500	0.484420	1.155592	1.155498	0.649807	2.073845	1.511471	1.511560	1.994553
1	4500	0.473813	1.148678	1.148577	0.641600	2.139436	1.543778	1.543879	2.035189
	5000	0.473814	1.148678	1.148578	0.641600	2.139432	1.543776	1.543877	2.035188
	5500	0.473814	1.148678	1.148578	0.641600	2.139433	1.543777	1.543878	2.035188
	6000	0.473814	1.148678	1.148579	0.641600	2.139432	1.543777	1.543877	2.035188
	6500	0.473814	1.148678	1.148579	0.641600	2.139433	1.543778	1.543878	2.035189
2	4500	0.463006	1.141735	1.141626	0.633294	2.208802	1.577957	1.578075	2.078340
	5000	0.463009	1.141737	1.141629	0.633297	2.208783	1.577949	1.578066	2.078330
	5500	0.463010	1.141737	1.141630	0.633297	2.208782	1.577949	1.578065	2.078330
	6000	0.463010	1.141737	1.141631	0.633297	2.208779	1.577948	1.578063	2.078328
	6500	0.463010	1.141737	1.141631	0.633297	2.208780	1.577949	1.578064	2.078329
3	4500	0.451979	1.134756	1.134635	0.624883	2.282381	1.614226	1.614366	2.124294
	5000	0.451983	1.134758	1.134640	0.624885	2.282358	1.614217	1.614353	2.124281
	5500	0.451982	1.134757	1.134641	0.624884	2.282359	1.614219	1.614353	2.124283
	6000	0.451983	1.134757	1.134642	0.624885	2.282355	1.614218	1.614351	2.124281
	6500	0.451985	1.134758	1.134643	0.624886	2.282345	1.614214	1.614346	2.124276
4	4500	0.440707	1.127729	1.127592	0.616351	2.360722	1.652857	1.653027	2.173411
	5000	0.440720	1.127735	1.127603	0.616358	2.360650	1.652826	1.652990	2.173370
	5500	0.440725	1.127737	1.127608	0.616362	2.360620	1.652813	1.652974	2.173353
	6000	0.440723	1.127736	1.127608	0.616360	2.360625	1.652817	1.652976	2.173357
	6500	0.440722	1.127734	1.127608	0.616359	2.360627	1.652820	1.652976	2.173359

v	Basis size	$\langle r^{2}_{^4\text{He-}^3\text{He}}\rangle$	$\langle r^{2}_{^4\text{He-}e}\rangle$	$\langle r^{2}_{^3\text{He-}e}\rangle$	$\langle r^{2}_{e\text{-}e}\rangle$	$\langle\delta(\mathbf{r}_{^4\text{He-}^3\text{He}})\rangle$	$\langle\delta(\mathbf{r}_{^4\text{He-}e})\rangle$	$\langle\delta(\mathbf{r}_{^3\text{He-}e})\rangle$	$\langle\delta(\mathbf{r}_{e\text{-}e})\rangle$
0	4500	4.320588	3.012967	3.013250	4.666898	3.41×10^{-11}	1.042650	1.036998	0.039161
	5000	4.320589	3.012969	3.013251	4.666900	2.17×10^{-11}	1.042656	1.037164	0.039152
	5500	4.320590	3.012969	3.013252	4.666901	1.50×10^{-11}	1.042681	1.037704	0.039145
	6000	4.320592	3.012971	3.013253	4.666903	1.39×10^{-11}	1.042793	1.037888	0.039141
	6500	4.320593	3.012972	3.013253	4.666903	1.22×10^{-11}	1.042803	1.038131	0.039139
1	4500	4.637416	3.172358	3.172691	4.878093	3.10×10^{-12}	1.040481	1.031950	0.038860
	5000	4.637400	3.172352	3.172685	4.878086	3.99×10^{-11}	1.040599	1.032285	0.038848
	5500	4.637403	3.172355	3.172687	4.878090	1.72×10^{-10}	1.040661	1.033058	0.038834
	6000	4.637400	3.172355	3.172686	4.878089	2.32×10^{-11}	1.040709	1.034018	0.038829
	6500	4.637407	3.172359	3.172689	4.878094	5.13×10^{-11}	1.040802	1.035077	0.038812
2	4500	4.981941	3.345678	3.346082	5.107980	3.28×10^{-10}	1.038110	1.030028	0.038587
	5000	4.981855	3.345640	3.346041	5.107929	3.63×10^{-10}	1.038184	1.030684	0.038571
	5500	4.981851	3.345641	3.346039	5.107930	2.94×10^{-10}	1.038217	1.031270	0.038562
	6000	4.981836	3.345636	3.346032	5.107922	1.64×10^{-10}	1.038609	1.031484	0.038547
	6500	4.981841	3.345640	3.346035	5.107927	1.71×10^{-10}	1.038826	1.031772	0.038540
3	4500	5.357991	3.534864	3.535360	5.359155	8.01×10^{-11}	1.035460	1.026959	0.038376
	5000	5.357878	3.534819	3.535301	5.359087	9.79×10^{-11}	1.035734	1.028188	0.038323
	5500	5.357875	3.534824	3.535302	5.359093	2.78×10^{-10}	1.036621	1.029409	0.038296
	6000	5.357858	3.534819	3.535295	5.359086	4.84×10^{-10}	1.036767	1.029787	0.038277
	6500	5.357811	3.534799	3.535273	5.359060	7.34×10^{-10}	1.036872	1.030370	0.038262
4	4500	5.770315	3.742310	3.742939	5.634841	2.81×10^{-10}	1.033512	1.021393	0.038128
	5000	5.769966	3.742154	3.742762	5.634622	2.37×10^{-10}	1.033655	1.023820	0.038091
	5500	5.769813	3.742091	3.742683	5.634531	2.34×10^{-10}	1.034504	1.024336	0.038063
	6000	5.769828	3.742105	3.742691	5.634546	9.78×10^{-11}	1.034639	1.025799	0.038056
	6500	5.769830	3.742113	3.742693	5.634554	6.32×10^{-11}	1.034710	1.026161	0.038047

IV. RESULTS AND DISCUSSION

The total energies for the five lowest vibrational states of ^{4}He^{3}He$^+$ with zero total angular momentum obtained in the calculations are presented in Table II. Both nonrelativistic results and results including the relativistic corrections are shown. As one can notice the energy convergence for the lowest state is noticeably faster than for the fifth state. While the total energy with the relativistic corrections for the $v=0$ state in going from 6000 to 6500 basis functions changes by only −0.00000008 a.u., the change is −0.00000171 a.u. for the fifth state. The increasingly less accurate energy results with the increasing vibrational quantum number affect the transition energies calculated as the difference of the energies of the consecutive states. The energy for the upper state being less tightly converged than the energy of the lower states will result in systematic overestimation of the transition energies. This point will be discussed next.

The transition energies calculated as the differences of the total energies of the consecutive states are shown in Table III. All transition energies corrected for the relativistic effects are marginally higher than their uncorrected counterparts. The largest shift is only 0.03 cm^{-1} (for the fifth state). Thus, one can conclude that the relativistic corrections are somewhat less important in this case than in the HeH$^+$ ion [2]. The comparison of the calculated transition frequency for the lowest transition where the experimental value is established with a very high precision (see the previous section) shows that this transition is not converged in the present calculation to the precision achieved by the experiment. Even though the transition frequency obtained with 6500 basis functions of 1750.71 cm^{-1} is only about 0.15 cm^{-1} off from the experimental frequency, this is, by far, more than the estimate experimental uncertainty of about 0.001 cm^{-1}. By analyzing the convergence pattern of the $0 \rightarrow 1$ frequency one can notice that with increasing the basis set size the frequency decreases. The increase of the basis size from 6000 functions to 6500 functions still produced a decrease of the transition energy by 0.05 cm^{-1}. Thus, a further increase of the number of functions is likely to bring the calculated result much closer to the experiment. However, it may require significantly more basis functions than was used in our calculations to approach the experimental accuracy. While such number of basis functions was not possible at present with our computational resources, it is certainly attainable in principle with the present-day computers.

As one can see from the results shown in Table III, the $1 \rightarrow 2$, $2 \rightarrow 3$, $3 \rightarrow 4$ transition frequencies are progressively less tightly converged with 6500 basis functions than the $0 \rightarrow 1$ transition. While the $0 \rightarrow 1$ frequency changes by only 0.05 cm^{-1} when the basis set is increased from 6000 to 6500, the change for the $3 \rightarrow 4$ frequency is 0.18 cm^{-1}. This is related to more complicated node structures of the higher excited states, whose description requires more functions in the basis set.

Lastly, the non-BO wave functions for the first vibrational states of ^{4}He^{3}He$^+$ calculated in this work have allowed us to calculate some expectation values. They are presented in Table IV. The convergence pattern here is similar to what it was for the total energies of the states. The expectation values are much better converged for the ground vibrational state than for the excited states. In calculating the expectation values we have been particularly interested in quantities showing the asymmetry of the electron charge distribution caused by the different masses of the two helium nuclei. One such quantity is the average electron-nucleus distance and, as expected, it is slightly shorter for the ^{4}He nucleus than for the ^{3}He nucleus. The electrons approach the heavier nucleus closer than the lighter one because the reduced ^{4}He-electron mass is larger than the reduced mass for the ^{3}He-electron pair. This results in the ^{4}He-electron energy levels being lower than the ^{3}He-electron levels and the average ^{4}He-electron radius being shorter. The difference between the average ^{4}He-electron and ^{3}He-electron distances increases with the excitation levels. For the ground state this difference is only 0.000089 a.u., but for the fifth state it is nearly two times larger and equal to 0.000156 a.u. The asymmetry of the electron charge distribution is also showing in the electron density at the nuclei [the $\langle \delta(\mathbf{r}_{^4\mathrm{He}} - e) \rangle$ and $\langle \delta(\mathbf{r}_{^3\mathrm{He}-e}) \rangle$ expectation values]. Here again, as expected, the electron density is slightly higher at ^{4}He than at ^{3}He, and the difference also increases with the electron excitation.

V. SUMMARY

In conclusion, it is clear from the results presented here that theoretical calculations performed on a three-electron diatomic system with an approach that does not assume the BO approximation and includes relativistic effects are capable of generating results whose accuracy can very closely approach the accuracy of the experimental measurements. However, as we showed, the basis set consisting of 6500 explicitly correlated Gaussian functions, while providing the $0 \rightarrow 1$ vibrational transition within 0.2 cm^{-1} to the experimental result, is still not large enough to bring the calculated results to accuracy comparable to the uncertainty range of the experiment.

In this work the vibrational transition energies have been calculated including some relativistic corrections of the order of α^2. The numerical results show that those corrections only marginally affect the transition energies in ^{4}He^{3}He$^+$. In continuing the work on the ^{4}He^{3}He$^+$ ion, we will make further improvements in the efficiency of our computer code for the optimization of the basis functions. These, and an access to a more powerful parallel computer system, will likely allow us to extend the basis set beyond 10 000 functions. We will also implement the algorithm to calculate orbit-orbit energy correction, which is the only remaining α^2 effect not included in the present calculations. We believe that with those improvements we will be able to further reduce the discrepancy between the experiment and the theory for the lowest transition energy.

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