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Fundamental vibrational transitions of the ^{3}He ^{4}He$^+$ and ^{7}LiH$^+$ ions calculated without assuming the Born-Oppenheimer approximation and with including leading relativistic corrections

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Very accurate variational calculations of the fundamental pure vibrational transitions of the ^{3}He ^{4}He$^+$ and ^{7}LiH$^+$ ions are performed within the framework that does not assume the Born-Oppenheimer (BO) approximation. The non-BO wave functions expanded in terms of one-center explicitly correlated Gaussian functions multiplied by even powers of the internuclear distance are used to calculate the leading relativistic corrections. Up to 10 000 Gaussian functions are used for each state. It is shown that the experimental ^{3}He ^{4}He$^+$ fundamental transitions is reproduced within 0.06 cm^{-1} by the calculations. A similar precision is expected for the calculated, but still unmeasured, fundamental transition of ^{7}LiH$^+$. Thus, three-electron diatomic systems are calculated with a similar accuracy as two-electron systems.

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The lithium hydride molecule and the lithium hydride cation have been frequently studied models in theoretical calculations. Literature search reveals numerous theoretical papers devoted to the calculations of LiH and LiH$^+$ [1]. With only a few exceptions [2–5] those calculations have been performed within the Born-Oppenheimer (BO) approximation that assumes separability of the electronic and nuclear motions. Non-BO calculations of molecular systems are considerably more difficult than electronic structure calculations based on the BO approximation with the nuclei placed in fixed positions. The coupled electron-nuclear motion that needs to be described in the non-BO calculations requires the use of unconventional basis functions in the wave-function expansion not typically used in the electronic calculations. Due to the strong correlation of the motions of the nuclei and the electrons these basis functions need to explicitly depend on the electron-electron, electron-nucleus, and nucleus-nucleus distances.

In the last decade we have been developing methods for performing non-BO calculations of light atomic and molecular systems [6–11]. The key feature of these methods has been the use of different types of explicitly correlated Gaussian basis functions for expanding the non-BO wave functions. The correlated Gaussians explicitly depend on the interparticle distances and can very effectively describe the above-mentioned interparticle correlation effects. As the Hamiltonian of a system consisting of nuclei and electrons after separation of the center-of-mass motion is rotationally invariant (see the next section), its eigenfunctions have to reflect this symmetry. In calculating pure vibrational states with the zero angular momentum, as we do in this work, the wave functions representing these states have to be spherically symmetric. In our diatomic non-BO calculations this is achieved by expanding the wave functions in terms of correlated N-particle Gaussians multiplied by powers of the internuclear distance. The powers of the distance is needed to describe the nuclei avoiding each other in their relative motion and to generate radial nodes in wave functions representing excited vibrational states. We showed that this type of basis very effectively describes the interparticle correlation effects in diatomic molecules with σ electrons. Examples of such systems are the ^{3}He ^{4}He$^+$ and ^{7}LiH$^+$ ions considered in this work.

The goal of this work is to demonstrate that very accurate quantum-mechanical molecular non-BO calculations of molecular systems can now be extended from two-electron diatomic molecules to molecules with three electrons. For over two decades the two-electron diatomics have served as models for which various theoretical methods have been tested against the most accurate experimental measurements. The seminal works by Kolos and Wolniewicz [12] and by Wolniewicz [13] concerning transition energies for the H_2 molecule set standards for such testing. Now, with the implementation of methods for non-BO calculations of molecular systems with more than two electrons employing explicitly correlated Gaussians and with a multifold increase in the computational power brought by the development of massive parallel computer systems the rigorous testing of the high-accuracy theoretical calculations can be expanded to diatomics with three electrons. In this work we show that the accuracy of a few hundreds of a wave number in the transition energy calculations previously only possible for two-electron diatomic systems is now also possible for diatomics with three electrons. With that, the "reference standards" for the experimental-theoretical interaction in verifying the most accurate models for molecular calculations now also include three-electron systems.

As in other advancements in quantum-mechanical calculations, the present work would not be possible without a combination of efforts that include the derivation of algorithms, the development of efficient computational strategies, and their implementation that optimizes the use of computational resources offered by the parallel computational environment. Even with all that involved the present calculations have taken several months of continuous computations.

In the first part of this work we describe the method used

in the calculations. The results and their discussion is presented in the second part.

This work focuses on the fundamental pure vibrational transitions in the ^{3}He ^{4}He$^+$ and ^{7}LiH$^+$ ions. While for the former system the experimental transition energy is very well established [14], for the latter system no experimental value has been determined yet. As it is shown, the calculations performed in this work reproduce the experimental ^{3}He ^{4}He$^+$ transition energy within 0.06 cm^{-1} and a similar accuracy can be expected for the calculated ^{7}LiH$^+$ transition as the procedure applied in the calculations for both systems has been identical. The present calculations are performed with the variational method applied separately to the ground and first-excited vibrational states of each system. The state energy is determined as the expectation value of the internal Hamiltonian, $\hat{H}_{\text{nonrel}}$, obtained from the "laboratory-frame" Hamiltonian by separating out the center-of-mass motion. Using an internal Cartesian coordinate system with the center placed at the heaviest nucleus (the ^{4}He nucleus for ^{3}He ^{4}He$^+$ and the ^{7}Li nucleus for ^{7}LiH$^+$) $\hat{H}_{\text{nonrel}}$ has the following form:

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

In Eq. (1) q_0 and q_1 are the charges of the nuclei and $q_2 = q_3 = -1$ are the electron charges, $\mathbf{r}_i$, $i=1,2,3,4$, are the position vectors of the lighter nucleus and the three electrons with respect to the heavier nucleus (called the "reference particle"), r_i are their lengths, $r_{ij}=|\mathbf{r}_j-\mathbf{r}_i|$, m_0 is the mass of the heavies nucleus (7294.299 536 $3m_e$ for the ^{4}He nucleus and 12 786.3933m_e for the ^{7}Li nucleus, where $m_e=1$ is the electron mass), and $\mu_i = m_0 m_i/(m_0+m_i)$ is the reduced mass of particle i (in that we used 5495.885 $269m_e$ for the mass of the ^{3}He nucleus, and 1836.152 672 $61m_e$ for the hydrogen nucleus mass [15]). More information on the center-of-mass separation and the form of internal Hamiltonian (1) can be found elsewhere [16,17].

In the calculations, the spatial parts of the non-BO wave functions of the lowest two vibrational states of the ^{3}He ^{4}He$^+$ and ^{7}LiH$^+$ ions 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 [8–11],

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

where $\mathbf{r}=\{\mathbf{r}_1',\mathbf{r}_2',\mathbf{r}_3'\}'$ and $'$ denotes the vector (matrix) transposition, $\otimes$ denotes the Kronecker product, and I_3 is a 3×3 unit matrix. The $r_1^{m_k}$ factors in functions (2) generate radial nodes in the wave function when the molecule becomes vibrationally excited. As we showed before [8,9], limiting the powers of m_k in basis functions (2) to only even values has very little effect on the energy, but significantly speeds up the calculations, as the algorithms for calculating the Hamiltonian matrix elements are less complicated. A_k in Eq. (2) is a matrix of exponential coefficients which has to be positive definite in order for the ϕ_k basis function to be square integrable. To avoid imposing restrictions on the elements of A_k's in the calculation, which would lead to an inefficient algorithm, we used 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). With the Cholesky-factored representation of A_k, this matrix is automatically positive definite for any real values of the L_k matrix elements. In the calculations the L_k matrix elements are the variables which are optimized. In the optimization we use the standard variational method involving minimization of the Rayleigh quotient with respect to the linear-expansion coefficients, $\{c_k\}$, the Gaussian exponential parameters, $\{L_k\}$, and the pre-exponential powers, $\{m_k\}$,

$$E = \min\frac{c'H(\{m_k\},\{L_k\})c}{c'S(\{m_k\},\{L_k\})c}, \tag{3}$$

where $H(\{m_k\},\{L_k\})$ and $S(\{m_k\},\{L_k\})$ are the Hamiltonian and overlap matrices, respectively. In our approach we used the analytical energy gradient calculated with respect to the Gaussian exponential parameters, L_k, in the minimization of Rayleigh quotient (3). This greatly accelerates the optimization process. The pre-exponential powers, m_k, in the present calculations range from 0 to 250, and each power is optimized when the functions containing that power is first added to the basis set.

The maximum number of basis functions used for each state is 10 000. To get to this number of functions the basis set is grown from a small randomly selected set of a few dozen functions using a procedure involving successive additions of small groups of functions and optimizing them using the gradient-based minimization approach. When the number of functions is less than 400 all functions are optimized simultaneously. After passing 400 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 10 000 basis set is constructed for each state additional 50–100 cyclic optimizations of all basis functions are performed.

After completing the variational calculations the non-BO wave functions are used to determine the leading relativistic corrections of the order α^2, where α is the fine-structure parameter ($\alpha=\frac{1}{c}$). The corrections include the mass-velocity (MV), Darwin (D), spin-spin (SS), and orbit-orbit (OO) contributions. In the internal coordinate frame the contributions are represented by the following operators [18]:

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

$$\hat{H}_{\text{D}} = -\frac{\pi}{2}\sum_{i=1}^{4}\left(\frac{1}{m_0^2}+\frac{1}{m_i^2}\right)q_0 q_i\delta^3(r_i) - \frac{\pi}{2}\sum_{i=1}^{4}\sum_{j\neq i}^{4}\frac{1}{m_i^2}q_i q_j\delta^3(r_{ij}), \tag{5}$$

TABLE I. The convergence of the total nonrelativistic non-BO energies (E_{NR}) and the total energies that include the MV, D, SS, and OO relativistic corrections of two lowest vibrational states of the ^{3}He ^{4}He$^+$ and ^{7}LiH$^+$ ions with the number of basis functions (in hartrees).

	^{3}He ^{4}He$^+$		^{7}LiH$^+$	
No. of basis functions	E_{NR}	E_{REL}	E_{NR}	E_{REL}
		$v=0$		
6000	−4.989719347857	−4.989926273607	−7.783246935297	−7.783882660878
7000	−4.989719480152	−4.989926454867	−7.783246969703	−7.783882701889
8000	−4.989719567399	−4.989926567912	−7.783246990309	−7.783882721531
9000	−4.989719606165	−4.989926610971	−7.783247002698	−7.783882728599
10000	−4.989719632360	−4.989926639746	−7.783247011621	−7.783882742863
10000[a]	−4.989719650441	−4.989926664113	−7.783247012198	−7.783882743422
		$v=1$		
6000	−4.981742345259	−4.981949320180	−7.781628943481	−7.782264607518
7000	−4.981742799734	−4.981949811664	−7.781629146155	−7.782264789843
8000	−4.981742994516	−4.981950001652	−7.781629259299	−7.782264895674
9000	−4.981743113128	−4.981950152555	−7.781629361067	−7.782264989061
10000	−4.981743188790	−4.981950227126	−7.781629442910	−7.782265073442
10000[a]	−4.981743229732	−4.981950271325	−7.781629450577	−7.782265080769

[a]Results obtained by performing several additional cyclic optimizations of the nonlinear parameters.

$$\hat{H}_{SS} = 2\pi \sum_{i=2}^{4} \sum_{j>i}^{4} \frac{q_i q_j}{m_i m_j} \delta^3(r_{ij}) + 2\pi \frac{q_0 q_1}{m_0 m_1} \delta^3(r_1), \tag{6}$$

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

The total α^2 relativistic correction was calculated for each state as the expectation value of the relativistic Hamiltonian, $\hat{H}^{rel} = \hat{H}_{MV} + \hat{H}_D + \hat{H}_{SS} + \hat{H}_{OO}$, with the non-BO wave function. One should note that the spin-orbit interaction is zero for the states considered in this work as the wave functions are spherically symmetric.

We first describe the results for the ^{3}He ^{4}He$^+$ ion. Our previous calculations of this ion [14] performed with 6500 Gaussians and without accounting for the orbit-orbit relativistic interaction yielded a value of the fundamental transition being off from the experimental value by 0.15 cm^{-1}. The present calculations are significantly more accurate and should provide a much better value. The total non-BO nonrelativistic energies and total energies that include the MV, D, SS, and OO relativistic corrections for the $v=0$ and $v=1$ states are shown in Table I for different numbers of basis functions. As one can see, for both states the energies are converged to within eight significant figures or better. The transition energy calculated as the difference between the $v=0$ and $v=1$ energies for the different basis set sizes are shown in Table II. As one can see, the transition energy value

TABLE II. The convergence of the fundamental pure vibrational transition energies of the ^{3}He ^{4}He$^+$ and ^{7}LiH$^+$ ions determined with and without the MV, D, SS, and OO relativistic corrections with the number of basis functions (in cm^{-1}).

	^{3}He ^{4}He$^+$		^{7}LiH$^+$	
No. of basis functions	$E_{NR}^{v=1}-E_{NR}^{v=0}$	$E_{REL}^{v=1}-E_{REL}^{v=0}$	$E_{NR}^{v=1}-E_{NR}^{v=0}$	$E_{REL}^{v=1}-E_{REL}^{v=0}$
6000	1750.7497	1750.7389	355.1082	355.1217
7000	1750.6790	1750.6708	355.0712	355.0906
8000	1750.6554	1750.6539	355.0509	355.0717
9000	1750.6379	1750.6303	355.0313	355.0528
10000	1750.6270	1750.6202	355.0153	355.0374
10000[a]	1750.6220	1750.6159	355.0137	355.0359

[a]Results obtained by performing several additional cyclic optimizations of the nonlinear parameters.

is converged to about 0.01 cm^{-1}. Our best result obtained with 10 000 basis functions and with the inclusion of the relativistic corrections of 1750.6159 cm^{-1} overestimates the experimental transition of 1750.556 87(98) cm^{-1} [14] by only about 0.06 cm^{-1}. In our view higher order relativistic effects and quantum electrodynamics (QED) effects are likely to be responsible for the overestimation. For H_2 the fundamental vibrational transition was overestimated by 0.02 cm^{-1} by our calculations performed with a similar accuracy and with the same approach as used here [18]. The consistency of the two results seems to confirm our conclusion concerning the source of the experimental-theoretical discrepancy.

The $^7LiH^+$ ion is isoelectronic with $^3He\ ^4He^+$. Thus it is reasonable to assume that, if the method used to calculate the two systems is the same, similar accuracy in the determination of the fundamental transition should be achieved. As this transition has not been measured yet [1], very accurate calculations can contribute to its experimental determination. Three previous calculations performed within the Born-Oppenheimer approximation resulted in the following results: 351.6 [19], 357.4 [20], and 353.9 cm^{-1} [1]. Clearly those are far less accurate than the results of the present calculations. Our previous calculations of the pure vibrational transitions of $^7LiH^+$ [2] performed with 5600 correlated Gaussians and without relativistic corrections yielded 355.125 cm^{-1} for the fundamental transition. The present calculations should significantly improve this value.

The total energies of $^7LiH^+$ calculated with the number of basis functions ranging from 6000 to 10 000 are presented in Table I. These energies show similar convergence patterns as for $^3He\ ^4He^+$. In Table II we show the convergence of the fundamental $^7LiH^+$ transition energy calculated with and without the relativistic corrections included in the total energies of the $v=0$ and $v=1$ states. As one can see the precision of the calculations is close to 0.01 cm^{-1} and it is similar to that achieved for $^3He\ ^4He^+$. Our best value for the fundamental pure vibrational transition of $^7LiH^+$ is 355.0359 cm^{-1} and it is expected to be off from the real transition frequency by a value comparable in magnitude to 0.06 cm^{-1} off from the real value.

In conclusion, this work shows that three-electron diatomic systems can now be calculated with a similar accuracy as achieved for two electron systems. The strategy for the variational optimization of the wave function expanded in terms of explicitly correlated Gaussian functions developed in this work facilitated such high-accuracy calculations. It is the first time an accuracy higher than 0.1 cm^{-1} was achieved in the calculations of fundamental vibrational transition energies of three-electron molecular systems.

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