Vibrational transitions of the $^7LiH^+$ ion calculated without the Born–Oppenheimer approximation and with leading relativistic corrections

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We recently presented very accurate calculations of the fundamental vibrational frequency of the $^7LiH^+$ and $^3He^4He^+$ ions [Stanke *et al.,* Phys. Rev. A **79**, 060501(R) (2009)] performed without the Born–Oppenheimer approximation and included leading relativistic corrections. The accuracy of those calculations was estimated to be of the order of 0.06 cm^{-1}. In the present work we extend the calculations to the remaining pure vibrational states of $^7LiH^+$ and similarly accurate results are generated. They may lead to the experimental search for still unidentified lines corresponding to those transitions. © *2011 American Institute of Physics*. [doi:10.1063/1.3525679]

Pure vibrational transitions of a three-electron $^7LiH^+$ ion are still unknown experimentally even though it can be readily produced in experimental conditions by a photoinduced electron detachment. This makes the theoretical calculations of pure vibrational transitions an important prerequisite to any attempt to measure them. In a paper published four years ago[1] we described calculations of six pure vibrational states of $^7LiH^+$ performed at the nonrelativistic level without assuming the Born–Oppenheimer (BO) approximation. In the calculations we employed explicitly correlated Gaussian basis functions multipled by powers of the internuclear distance. In more recent work[2] we applied the non-BO approach to calculate the fundamental vibrational transitions of the $^3He^4He^+$ and $^7LiH^+$ ions. In the calculations we also included the leading relativistic corrections determined with the use of first-order perturbation theory with the non-BO wave function as the zero-order approximation. For $^3He^4He^+$ the calculations reproduced within 0.06 cm^{-1} the fundamental vibrational transition, which is known with very high accuracy of about 0.001 cm^{-1}.[3] In that work we also calculated the fundamental transition of $^7LiH^+$. As the approach used in the $^7LiH^+$ calculations was the same as used for $^3He^4He^+$, a similar accuracy was claimed for the $^7LiH^+$ transition. In the present work we use the approach to refine the theoretical predictions of the energies of higher pure vibrational transitions of $^7LiH^+$.

Nearly all quantum-mechanical molecular calculations are performed assuming the BO approximation with the nuclei placed at fixed positions. Well established procedures and functional basis sets have been developed for such calculations. The BO electronic calculations generate a potential energy surface (potential energy curve for a diatomic molecule) which is subsequently used to determine vibrational states of the molecule. When the electrons and the nuclei of the molecular system are treated on equal footing, as in the non-BO approach, unconventional basis functions for expanding the wave function need to be used. There are two major features which such basis functions need to describe. The first concerns the correlation effects of the coupled motions of the nuclei and the electrons and not just electrons as in the BO calculation. One way to effectively and accurately describe those effects is the use of basis functions that explicitly depend on the electron–electron, electron–nucleus, and nucleus–nucleus distances. The second feature concerns the symmetry of the non-BO state under consideration. As the molecular Hamiltonian obtained after separation of the system's center of mass motion is spherically symmetric (isotropic), the basis functions have to reflect this symmetry. In particular, in the calculations of pure vibrational states (more precisely, the states with zero total angular momentum) the basis functions have to be rotationally invariant.

The non-BO approach used here has been developed in our group over the last decade to study spectra of light molecular systems, particularly those with more than two electrons.[4–8] Our goal in that development has been to describe the rovibrational spectra of those systems with similar accuracy as had been achieved before for two-electron molecules[9–12] and as currently being achieved by the state-of-the-art experiments. The advances in computer hardware and software for numerical calculations make such calculations possible.

In the first part of this work we briefly describe the method used in the calculations (more details about the method can be found in Refs. 4–6). The results and their discussion are presented in the second part.

The internal nonrelativistic all-particle Hamiltonian, $\hat{H}_{\text{nonrel}}$, used in the present calculations is obtained from the "laboratory frame" Hamiltonian by separating out the center-of-mass motion. $\hat{H}_{\text{nonrel}}$ expressed using an internal Cartesian coordinate system with the center placed at the heaviest

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nucleus (the ^{7}Li nucleus). $\hat{H}_{\text{nonrel}}$ for $^7\text{LiH}^+$ has the following form in atomic units:

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

where $q_0 = 3$ and $q_1 = 1$ are the charges of the nuclei, $q_2 = q_3 = -1$ are the electron charges, $\mathbf{r}_i$ $(i = 1, 2, 3, 4)$ are the position vectors of the proton and the three electrons with respect to the ^{7}Li nucleus (called the "reference particle"), r_i are their lengths, $r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$, $m_0 = 12786.3933m_e$ and $m_1 = 1836.15267261m_e$ are the masses of the ^{7}Li and the proton, $m_e = 1$ 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.[5,6]

The following spherically symmetric Gaussian basis functions are used to expand the non-BO wave functions representing the pure vibrational states of $^7\text{LiH}^+$ in the present calculations:

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

where $\mathbf{r} = \{\mathbf{r}'_1, \mathbf{r}'_2, \mathbf{r}'_3, \mathbf{r}'_4\}'$ and $'$ symbol denotes the vector/matrix transposition, $\otimes$ denotes the Kronecker product, and I_3 stands for the 3×3 unit matrix. Even values in the range 0–250 are used for m_k and they are partially optimized for each basis function.

To make the basis function (2) square integrable the matrix of the Gaussian parameters, A_k, is represented in the Cholesky-factored form, $A_k \equiv L_k L'_k$, where L_k is a lower triangular matrix (all elements above the diagonal are zero). With that, for any real values of the L_k matrix elements, A_k is positive definite as is required for ϕ_k to be square integrable. The elements of matrices L_k are the variational parameters which we vary to lower the total energy. In this optimization process, the elements of L_k can vary in the range $[-\infty, \infty]$ without any restrictions.

In the calculations we use the standard variational method involving minimization of the Rayleigh quotient subject to an orthogonality constraint (for excited states), $E = \min(c'H(\{m_k\},\{L_k\})c)/(c'S(\{m_k\},\{L_k\})c)$, where $H(\{m_k\},\{L_k\})$ and $S(\{m_k\},\{L_k\})$ are the Hamiltonian and overlap matrices, respectively. The minimization with respect to the linear wave-function expansion coefficients, $\{c_k\}$ $(k = 1,\ldots K$, where K is the basis size), leads to the generalized eigenvalue problem,

$$Hc = ESc. \tag{3}$$

The analytical energy gradient with respect to $\{L_k\}$ can be constructed and used to accelerate the energy minimization.[4,6] The calculation of the gradient requires the knowledge of the first derivatives of the Hamiltonian and overlap matrix elements. The expressions for those derivatives can be found in Refs. 4 and 6.

The Gaussian basis set has been generated independently for each considered state in a process starting with a short randomly chosen set of basis functions and involves adding small sets of functions and optimizing them first individually and next together with the other functions already included in the basis set. For the description of possible strategies see Refs. 6, 13, and 14. The process is continued until the basis size reached 10 000. After 10 000 function basis was constructed for each state, several additional optimization cycles of all basis functions were performed.

The leading relativistic corrections of the order of α^2 [α is the fine structure parameter; $\alpha = 7.2973525376\times 10^{-3}$ (Ref. 15)] are determined using the first order perturbation theory approach with the non-BO wave function being the zero-order approximation. For $^7\text{LiH}^+$ the corrections account for the mass–velocity (MV), Darwin (D), spin–spin (SS), and orbit–orbit (OO) effects which in the internal coordinate system for $^7\text{LiH}^+$ are represented by the following operators:[16]

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

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

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

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

As the states considered in this work are represented by spherically symmetric wave functions the spin–orbit interaction is zero. We get the total relativistic correction by summing the MV, D, SS, and OO corrections, $\langle\hat{H}_{\text{REL}}\rangle = \langle\hat{H}_{\text{MV}}\rangle + \langle\hat{H}_{\text{D}}\rangle + \langle\hat{H}_{\text{SS}}\rangle + \langle\hat{H}_{\text{OO}}\rangle$. Due to the indistinguishability of electrons, $\langle\hat{H}_{\text{D}}\rangle$ and $\langle\hat{H}_{\text{SS}}\rangle$ for $^7\text{LiH}^+$ simplify to

$$\langle\hat{H}_{\text{D}}\rangle = \frac{\pi}{2}\left[9\delta(\mathbf{r}_2) + 3\delta(\mathbf{r}_{12}) - 6\delta(\mathbf{r}_{23})\right],\ \langle\hat{H}_{\text{SS}}\rangle = 6\pi\delta(\mathbf{r}_{23}). \tag{8}$$

The results for the lowest two vibrational states of $^7\text{LiH}^+$ were presented in our previous work.[2] Here we only slightly improve them for the largest basis set of 10 000 functions by performing a few additional optimization cycles. The present work focuses on the third, fourth, fifth, and sixth pure vibrational states ($v = 2$–5) of $^7\text{LiH}^+$. The total non-BO nonrelativistic energies and total energies that include the MV, D, SS, and OO relativistic corrections for those states are shown in Table I for different numbers of basis functions. As one can see, for all states the energies are converged within the relative accuracy of approximately 10^{-8}. For the energy values obtained with the largest basis sets we also show in Table I

TABLE I. The convergence of the total nonrelativistic non-BO energies (E_{NR}) and the total energies that include the leading MV, D, SS, and OO relativistic corrections (E_{REL}) for vibrational states of the $^7LiH^+$ ion. All values are in hartrees.

v	Basis size	E_{NR}	E_{REL}
0	8000	−7.783246990	−7.783882722
	9000	−7.783247003	−7.783882729
	10 000	−7.783247012	−7.783882743
	10 000[a]	−7.783247013(40)	−7.783882745(40)
1	8000	−7.781629259	−7.782264896
	9000	−7.781629361	−7.782264989
	10 000	−7.781629443	−7.782265073
	10 000[a]	−7.781629462(500)	−7.782265092(500)
2	8000	−7.780436646	−7.781072167
	9000	−7.780436710	−7.781072241
	10 000	−7.780436751	−7.781072284
	10 000[a]	−7.780436775(200)	−7.781072308(200)
3	8000	−7.779662109	−7.780297589
	9000	−7.779662198	−7.780297665
	10 000	−7.779662259	−7.780297716
	10 000[a]	−7.779662289(200)	−7.780297744(200)
4	8000	−7.779252835	−7.779888262
	9000	−7.779252943	−7.779888410
	10 000	−7.779253010	−7.779888469
	10 000[a]	−7.779253045(150)	−7.779888504(150)
5	8000	−7.779092179	−7.779727584
	9000	−7.779092296	−7.779727704
	10 000	−7.779092361	−7.779727814
	10 000[a]	−7.779092394(150)	−7.779727846(150)

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

an estimate of the remaining uncertainty. The convergence is expected to be somewhat better for the lower states than for the higher ones. The remaining uncertainty estimates, however, do not show monotonic growth with the excitation level, which we attribute to artifacts of the extrapolation. For variational calculations of this kind the extrapolation often gives a poor estimate of the infinite basis set limit (variations by a factor of 2–3 or even more depending on the model and set of points used are not uncommon).

The additional iterations performed for the basis sets of 10 000 functions produced a noticeable improvement of the energy. That improvement, as expected, increases with the excitation level and it is the largest for the $v = 5$ state and the lowest for the $v = 2$ state.

The total energies with and without the relativistic corrections have been used to calculate transition energies between the adjacent states. These transition energies obtained for the different basis set sizes are shown in Table II. As one can see, the transition energy values are probably converged to about 0.01–0.05 cm^{-1}. The expected contribution of missing higher order relativistic and QEDeffects (in particular for upper vibrational level transitions where they naturally tend to cancel out more) is likely not to exceed the value of 0.05 cm^{-1}. Thus, we believe that the accuracy for our predicted frequencies is not worse than 0.1 cm^{-1} or even a smaller value. It is worth mentioning that the best previous calculations performed with the standard approach based on the BO potential energy curve

TABLE II. The convergence of the pure vibrational transition energies $^7LiH^+$ ions determined with and without the leading relativistic corrections (in cm^{-1}).

$v' \rightarrow v''$	Basis size	$E_{NR}^{v''} - E_{NR}^{v'}$	$E_{REL}^{v''} - E_{REL}^{v'}$
1 → 0	8000	355.051	355.072
	9000	355.031	355.053
	10 000	355.015	355.037
	10 000[a]	355.011(50)	355.034(50)
2 → 1	8000	261.748	261.774
	9000	261.757	261.778
	10 000	261.766	261.787
	10 000[a]	261.765(50)	261.786(50)
3 → 2	8000	169.991	170.000
	9000	169.986	170.000
	10 000	169.981	169.998
	10 000[a]	169.980(20)	169.997(20)
4 → 3	8000	89.825	89.837
	9000	89.821	89.821
	10 000	89.820	89.819
	10 000[a]	89.819(20)	89.818(20)
5 → 4	8000	35.260	35.265
	9000	35.258	35.271
	10 000	35.258	35.260
	10 000[a]	35.259(15)	35.260(15)

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

by Gadéa and Leininger[17] predicted the fundamental $^7LiH^+$ transition to be at 353.9 cm^{-1}, which differs from the present very accurate result by more than a wavenumber.

In summary, the goal of this work is to continue very accurate determination of the vibrational spectra of small diatomic systems with more than two electrons with an approach that does not assume the Born–Oppenheimer approximation and which includes the leading relativistic corrections. By using large sets of explicitly correlated Gaussian functions in the calculations and by variationally optimizing their nonlinear parameters with a gradient-based method we are able to generate pure vibrational transition energies of $^7LiH^+$ with an accuracy of 0.1 cm^{-1} or better. As those transitions are not yet measured, the predictions generated in this work can guide and stimulate future experimental attempts.

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