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Non-Born-Oppenheimer variational calculation of the ground-state vibrational spectrum of LiH^+

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Very accurate, rigorous, variational, non-Born-Oppenheimer (non-BO) calculations have been performed for the fully symmetric, bound states of the LiH^+ ion. These states correspond to the ground and excited vibrational states of LiH^+ in the ground $^2\Sigma^+$ electronic state. The non-BO wave functions of the states have been expanded in terms of spherical N-particle explicitly correlated Gaussian functions multiplied by even powers of the internuclear distance and 5600 Gaussians were used for each state. The calculations that, to our knowledge, are the most accurate ever performed for a diatomic system with three electrons have yielded six bound states. Average interparticle distances and nucleus-nucleus correlation function plots are presented. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2244563]

I. INTRODUCTION

Our previous works concerning non-Born-Oppenheimer (non-Bo) variational calculation of the vibrational spectrum of the H_2 molecule[1,2] where we used 3000 and 5000 explicitly correlated Gaussian functions (ECGFs), respectively, for each state yielded a very similar accuracy for all 15 vibrational transition energies as that achieved a decade ago by Wolniewicz.[3] Since, unlike Wolniewicz's, our approach is not restricted to two-electron systems, we decided to undertake a series of rigorous, variational, non-BO calculations of all vibrational states of a three-electron system in its ground electronic state. The vibrational spectrum of the system we have chosen, the LiH^+ ion, has been studied before using methods based on the BO approximation.[4,5] The present calculations on LiH^+ are not only the first non-BO calculations on this system but also the first non-BO calculations of the vibrational spectrum ever performed for a three-electron diatomic molecule.

In a non-BO calculation one does not assume the separability of the electronic and nuclear motions and the wave function depends explicitly on the coordinates of all particles involved in the system. In such a situation the correlation effects, which in the BO calculations are restricted to electrons, also appear in the relative nucleus-nucleus motion, as well as in the relative motion involving the nuclei and the electrons. For this reason, non-BO calculations are significantly more complicated and time consuming than BO calculations. Moreover, if a high precision of non-BO calculations is required the basis functions used have to explicitly depend on the distances between particles (this is why explicitly correlated Gaussians have been used in the present work), and not only long expansions of the wave function in terms of basis functions must be used but also linear and nonlinear parameters of the basis function have to be extensively optimized.

The non-BO calculations presented in this work were performed using the method we have been developing in the last few years. For a description of the method, we refer the reader to our recent reviews.[6,7] In the next section we will briefly describe the method and its application to calculate the vibrational states of LiH^+. We will also briefly describe the procedure used to optimize the linear and nonlinear parameters of the wave functions. It should be noted that the term "vibrational states" can only approximately describe states with zero total angular momentum considered in this work. This is because if the BO approximation is not assumed, the vibrational motion is coupled with the electronic motion and, strictly speaking, the vibrational quantum number is not a good quantum number.

II. THE NON-BO APPROACH

In the non-BO calculation we start with the nonrelativistic N-particle Hamiltonian in the laboratory Cartesian coordinate system. The particles are electrons and nuclei:

$$\hat{H}_{\rm tot} = -\sum_{i=1}^{N} \frac{1}{2M_i}\nabla^2_{\mathbf{R}_i} + \sum_{i<j=1}^{N} \frac{Q_iQ_j}{R_{ij}}. \tag{1}$$

The masses, charges, and positions of the particles in (1) are denoted as M_i, Q_i, and $\mathbf{R}_i$, respectively. Next we rigorously separate out from $\hat{H}_{\rm tot}$ the motion of the center of mass. This is accomplished by a coordinate transformation. The new coordinate system comprises three laboratory coordinates of the center of mass and $3N-3$ internal Cartesian coordinates. The center of the internal coordinate system is placed at one of the particles (usually the heaviest one) called the reference

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TABLE I. Non-BO total energies of LiH$^+$ vibrational states obtained with 3200, 3600, 4000, 4400, 4800, 5200, and 5600 basis functions. All values are in a.u.

v	3200	3600	4000	4400	4800	5200	5600
0	−7.783 246 42	−7.783 246 60	−7.783 246 72	−7.783 246 79	−7.783 246 84	−7.783 246 88	−7.783 246 91
1	−7.781 627 05	−7.781 627 57	−7.781 627 95	−7.781 628 20	−7.781 628 45	−7.781 628 66	−7.781 628 85
2	−7.780 433 17	−7.780 434 26	−7.780 434 97	−7.780 435 46	−7.780 435 80	−7.780 436 03	−7.780 436 19
3	−7.779 655 89	−7.779 658 02	−7.779 659 30	−7.779 660 16	−7.779 660 73	−7.779 661 13	−7.779 661 40
4	−7.779 243 63	−7.779 247 15	−7.779 249 15	−7.779 250 34	−7.779 251 07	−7.779 251 56	−7.779 251 91
5	−7.779 038 64	−7.779 075 42	−7.779 084 56	−7.779 087 92	−7.779 089 50	−7.779 090 42	−7.779 090 93

particle and the internal coordinate axes are made parallel to the axes of the laboratory coordinate frame. In the internal coordinate system the particles other than the reference particle are referred to the reference particle using the position vectors $\mathbf{r}_i$, $i=1,\ldots,n$, where $n=N-1$. After the coordinate transformation the laboratory Hamiltonian $\hat{H}_{\text{tot}}$ separates into the Hamiltonian describing the kinetic energy of the center-of-mass motion and the following internal Hamiltonian $\hat{H}$:

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

In (2) $q_0=Q_1$ is the charge of the reference particle, $q_i=Q_{i+1}$ $(i=1,\ldots,n)$ are the charges of the other n particles, $r_{ij}=|\mathbf{r}_j-\mathbf{r}_i|$, and the prime ($'$) is used to indicate vector-matrix transposition. The internal Hamiltonian (2) describes n pseudoparticles with charges q_i and reduced masses $m_i=M_1M_{i+1}/(M_1+M_{i+1})$ moving in the spherical potential of charge q_0. In this work, particle 1, the reference particle, was the Li nucleus, particle 2 was the proton, and particles 3, 4, and 5 were the electrons.

The key element of the non-BO calculation is the selection of the basis set for the expansion of the wave function. Since the internal Hamiltonian $\hat{H}$ is spherically symmetric (i.e., isotropic with respect to any rotation about the center of the internal coordinate system), the basis functions for describing states corresponding to zero angular momentum (i.e., the vibrational states) have to be spherically symmetric as well. In our works concerning non-BO calculations on light diatomic molecular systems (see, for example, Refs. 1, 2, and 8 and references in Refs. 6 and 7), we have shown that the explicitly correlated Gaussians (ECGs) involving functions with preexponential multipliers consisting of the internuclear distance r_1 raised to a non-negative even power m_k,

$$\phi_k = r_1^{m_k}\exp[-\mathbf{r}'(A_k\otimes I_3)\mathbf{r}] = r_1^{m_k}\exp[-\mathbf{r}'\bar{A}_k\mathbf{r}], \qquad (3)$$

are very effective in describing such states. In (3) A_k is a symmetric, positive definite, $n\times n$ matrix, and $\bar{A}_k$ is a Kronecker product of A_k and I_3, $\bar{A}_k=A_k\otimes I_3$, where I_3 is the 3×3 identity matrix.

In accordance with the Pauli principle, the basis functions (3) must have the proper permutational symmetry so that when the spatial and spin parts are combined the resulting function is antisymmetric with respect to interchanging the electron labels. In our calculations the antisymmetrization was implemented using the standard approach based on Young operators, as described in Ref. 9.

In the non-BO calculations we use the variational method and we minimize the energy functional (the Rayleigh quotient)

$$E(\{c_k\},\{m_k\},\{A_k\}) = \min\frac{c'H(\{m_k\},\{A_k\})c}{c'S(\{m_k\},\{A_k\})c} \qquad (4)$$

with respect to the linear expansion coefficients c_k, the basis function exponential parameters $\{A_k\}$, and the preexponential powers $\{m_k\}$. The optimization is done using an algorithm based on analytical derivatives of the functional (4) with respect to the exponential parameters. The optimization of the basis set was performed separately for each state and the basis was grown from a small size to a set of 5600 functions. We believe that with this many functions the total energies are converged to about seventh decimal figure. The convergence is certainly better for the lower lying states than for the higher states due to increasingly more complicated structure (larger number of nodes) in the wave functions of the higher vibrational states. The preexponential powers $\{m_k\}$ in our calculations ranged from 0 to 250 and they were partially optimized for each state. More details on the Hamiltonian transformation, proper symmetrization of the basis functions, and selection of nonlinear parameters for calculations with ECGFs can be found in Refs. 6 and 7. The masses of the

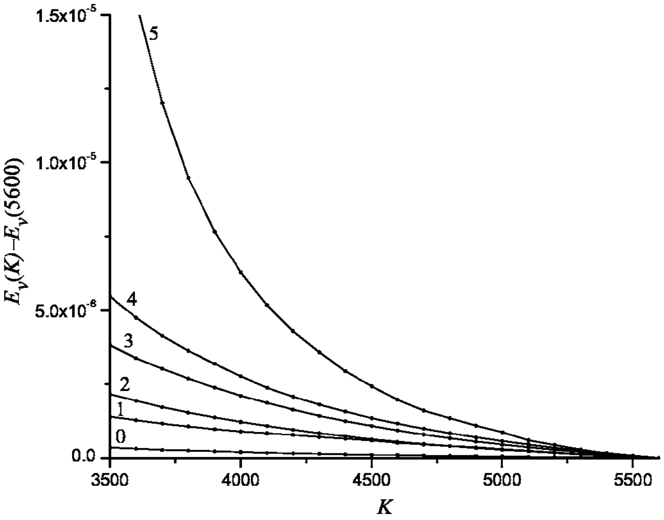

FIG. 1. Convergence of the total energy, E_v, for states with $v=0-5$. K is the number of basis functions.

TABLE II. Transition frequencies for LiH$^+$ vibrational states obtained in this work with 3200, 3600, 4000, 4400, 4800, 5200, and 5600 function basis for each state vs the frequencies of Berriche and Gadea (Ref. 5). All values are in cm^{-1}.

$v' \to v$	3200	3600	4000	4400	4800	5200	5600	Berriche and Gadea
$1 \to 0$	355.411	355.338	355.279	355.241	355.197	355.158	355.125	357.43
$2 \to 1$	262.027	261.901	261.828	261.775	261.757	261.754	261.757	265.61
$3 \to 2$	170.592	170.364	170.240	170.160	170.107	170.070	170.047	172.96
$4 \to 3$	90.480	90.176	90.018	89.945	89.911	89.889	89.874	92.20
$5 \to 4$	44.990	37.691	36.121	35.647	35.460	35.367	35.331	37.45
$6 \to 5$								9.22

Li (^{7}Li isotop) and H nuclei used in the calculations were $m_{\mathrm{Li}}=12\,786.3933m_e$ and $m_p=1836.152\,672\,61m_e$, where m_e stands for the mass of the electron.

III. RESULTS AND DISCUSSION

The previous calculations of Berriche and Gadea[5] of the vibrational spectrum in the ground electronic state of the LiH$^+$ system predicted the existence of seven bound vibrational states. Those calculations were done within the Born-Oppenheimer approximations and the electronic energy was determined with a method that utilized an effective core potential. Thus, they can be expected to be significantly less accurate than the calculations presented in this work. We start the presentation of the results by showing the convergence of the total energies of the ground and excited vibrational states as the function of the size of the basis set. The number of states whose energies we have managed to converge below the dissociation threshold was 6. An attempt made to converge the seventh state below the dissociation threshold failed. With nearly 5000 functions in the basis set the energy was still above the threshold and the convergence pattern did not indicate a realistic possibility of lowering the energy below the threshold. The convergence patterns of the energies of the six vibrational states are shown in Table I. They are also shown on Fig. 1 where, for each state, we plotted the difference between the energy obtained with a particular number of basis functions and the energy obtained with 5600 functions. As mentioned, it takes more basis functions to obtain the same quality of the results for higher excited states than for the lower states because of the larger number of radial nodes in the wave functions of the higher states. Figure 1 demonstrates this trend very well. The curve corresponding to the ground state ($v=0$) is flat, indicating that the energy of this state is already very well converged with 4500 basis functions while the energy of $v=5$ state with that many functions is still far from the same degree of convergence.

In the case of slightly lower accuracy of the calculated energy value for the $v+1$ state than for the v state the transition energies, $E_{v+1}-E_v$, are usually slightly overestimated. Thus, our calculated transition energies shown in Table II should provide upper bounds to the exact results. In Table II we not only include the transition energies obtained with the largest basis set of 5600 functions but we also show how the energies converge with the number of basis functions. The convergence pattern allows us to estimate the accuracy of our calculations. It is safe to state that this accuracy is of the order of 0.1 cm^{-1}. Further extension of the basis set size would certainly lead to higher accuracy. However, at this point, after over six months of continuous calculations, we have reached the limits of our computer capabilities.

In Table II we also compare our transition energies with those of Berriche and Gadea[5] All their energies are higher than ours by 2–4 cm^{-1}. To what extent this is an effect of not assuming the Born-Oppenheimer approximation in our calculations and/or to what extent this results from inaccuracies of the potential energy curve calculated by Berriche and Gadea, it is, at this point, difficult to say.

Finally, in Table III we present the expectation values of the interparticle distances and their squares for the six bound vibrational states obtained with 5600 basis functions for each state. Those include lithium nucleus-proton ($r_{\mathrm{Li}\text{-}p}$), lithium nucleus-electron ($r_{\mathrm{Li}\text{-}e}$), proton-electron ($r_{p\text{-}e}$), and electron-electron ($r_{e\text{-}e}$) distances. The results show that the internuclear distance increases, as expected, with the vibrational excitation. It also can be noticed that the average value of the proton-electron distance parallels the average value of the electron-electron distance. This indicates that when the vibrational excitation moves the nuclei further apart, two elec-

TABLE III. Mean interparticle distances of LiH$^+$ and mean squares of the interparticle distances calculated with 5600 basis functions for each state. Here, $r_{\mathrm{Li}\text{-}p}\equiv r_1$, $r_{\mathrm{Li}\text{-}e}\equiv r_2$, $r_{p\text{-}e}\equiv r_{12}$, and $r_{e\text{-}e}\equiv r_{23}$. All values are in a.u.

v	$\langle r_{\mathrm{Li}\text{-}p}\rangle$	$\langle r_{\mathrm{Li}\text{-}e}\rangle$	$\langle r_{p\text{-}e}\rangle$	$\langle r_{\mathrm{e}\text{-}\mathrm{e}}\rangle$	$\langle r^2_{\mathrm{Li}\text{-}p}\rangle$	$\langle r^2_{\mathrm{Li}\text{-}e}\rangle$	$\langle r^2_{p\text{-}e}\rangle$	$\langle r^2_{e\text{-}e}\rangle$
0	4.329 22	1.829 63	3.415 24	3.208 63	18.9229	6.962 33	13.9343	13.9400
1	4.821 88	1.995 62	3.742 09	3.538 07	23.8518	8.634 60	17.2254	17.2837
2	5.536 66	2.236 90	4.215 53	4.017 66	31.8581	11.355 4	22.5621	22.7244
3	6.681 00	2.622 09	4.973 88	4.784 55	46.7935	16.414 0	32.5126	32.8408
4	8.706 93	3.300 29	6.319 15	6.136 98	79.7911	27.519 0	54.5023	55.0501
5	12.721 0	4.638 19	8.990 11	8.808 71	170.743	57.953 0	115.130	115.918

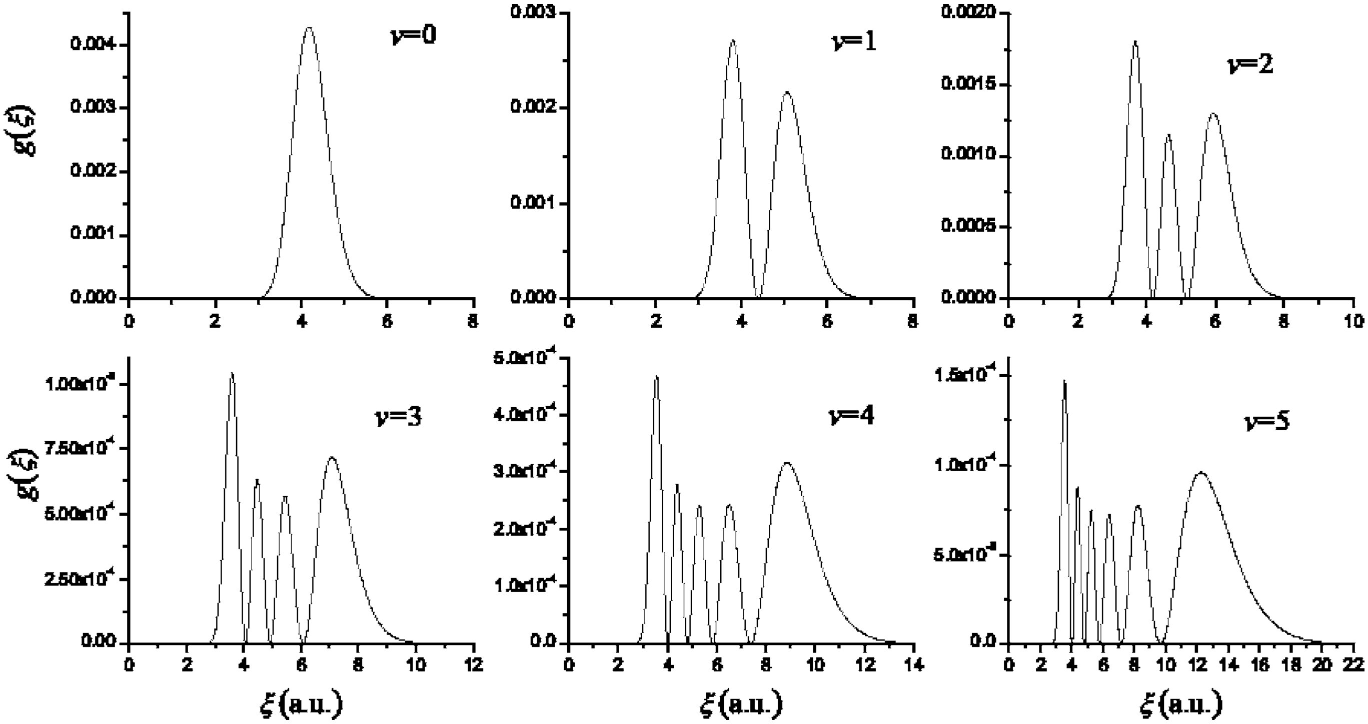

FIG. 2. Nucleus-nucleus correlation function for $v=0-5$ vibrational states of LiH$^+$.

trons stay with the Li nucleus and one moves away with the proton. Thus, at the limit LiH$^+$ dissociates into Li$^+$ and H.

The increase of the internuclear distance with the vibrational excitation is the result of the radial function describing the system becoming increasingly more diffuse and oscillating more. This effect is shown in Fig. 2 where the nucleus-nucleus correlation function, which is the same as one-pseudoparticle density corresponding to pseudoparticle 1 (i.e., pseudoproton), is plotted for all vibrational states we calculated in this work. This function is defined as (see Ref. 10)

$$g(\boldsymbol{\xi}) = \langle \Psi(\mathbf{r})|\delta(\mathbf{r}_1-\boldsymbol{\xi})|\Psi(\mathbf{r})\rangle, \tag{5}$$

where $\Psi(\mathbf{r})$ is the total wave function of the system under consideration.

IV. SUMMARY

In this work we performed very accurate non-BO calculations on fully symmetric bound states of the LiH$^+$ ion and we found six such states. These states are conventionally called vibrational states although, if the BO approximation is not assumed, the vibrational quantum number is, strictly speaking, not a good quantum number due to the coupling between the electronic and vibrational motions. We estimated that the accuracy of our vibrational transition energies calculated as differences between the energies of adjacent energy levels is about 0.1 cm^{-1} in relation to the exact transitions (calculated without including relativistic corrections). This makes, to our knowledge, the present calculations the most accurate ever performed for a diatomic system with three electrons.

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