An accurate non-Born–Oppenheimer calculation of the first purely vibrational transition in LiH molecule

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In this work we study the ground and the first vibrationally excited states of LiH molecule. We performed an extensive nonrelativistic variational calculations of the two states without using the Born–Oppenheimer approximation. The results are analyzed and compared with the data extracted from recent experiments. The $0 \leftarrow 1$ transition energy obtained in the calculations converged to a value which is less than a wave number above the transition energy estimated from the available experimental data concerning the LiH rovibrational transitions. We discuss the remaining discrepancy and the procedure used to determine the "experimental" transition frequencies. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2047487]

I. INTRODUCTION

One of the most spectacular achievements of the quantum mechanical calculations of molecular systems that occurred is the early stage of the development of the field (late 1960s–early 1970s) was the very accurate calculations of the ground and excited states of the H_2 molecule performed by Kolos, Wolniewicz, and collaborators.[1] Those calculations helped revise the experimental data and correct some inaccuracies of the initial measurements. Since that time there have been numerous instances of works where the theoretical calculations combined with experimental measurements have helped elucidate various phenomena that occur in molecular systems. However, the precision achieved for diatomic systems with two electrons, such as that in the Kolos and Wolniewicz calculations, has not been achieved for system with three, four, and more electrons. In the present work we show that due to the development of the new very accurate quantum-mechanical methods concerning stationary states of diatomic systems in our laboratory at Arizona, and the new more precise spectral measurements, the theoretical-experimental interaction similar to that for H_2 can now be extended to a diatomic molecular system with four electrons—the LiH molecule.

The work presented here concerns only the ground-state pure vibrational transition (the $0 \leftarrow 1$ transition) in the LiH molecule. Since the energy of that transition is not directly available from the experiment, an extrapolation procedure (described briefly in this work) was used to estimate that energy. The calculations of the ground and first excited pure vibration states of LiH shown in this work have lasted for a year and they have certainly been one of the most time and resource-consuming pieces of work that we have ever performed in our laboratory.

In order to enhance the precision of molecular quantum-mechanical calculations of such properties as excitation energies, electron affinities, and ionization potentials, which are currently measured with the precision exceeding one-tenth or even one hundredth of a wave number, not only the electronic component of the wave function has to be calculated with a very high precision, but also the component describing the motion of the nuclei (vibrational and rotational) and the component describing the coupling of the electronic and the nuclear motions have to be very accurately represented. Thus, the use of an approach that departs from the Born–Oppenheimer approximation is very desirable. The development of such an approach and its implementation has been carried out for several years.[2–17] The centerpiece of the development has been the use of various forms of the explicitly correlated Gaussian functions that are dependent on the distances between the particles (nuclei and electrons) forming the system. Recent calculations have demonstrated that, if extended Gaussian basis sets are used, very accurate results matching quite well the high-resolution experimental data can be obtained. This applies to properties of the ground state as well as excited states.[7,15,17]

As will be described later, our approach is based on separating the center of mass motion of the system from the internal motion and on using the variational method to determine the internal bound states of the system. In separating the center of mass motion we define a new internal coordinate system which is centered on one of the nuclei (called the reference particle). Such a choice does not restrict the types of the molecular systems that can be calculated. It also allows to easily separate calculations of states with different total rotational quantum numbers. In particular, it allows to carry out calculation of the purely vibrational spectrum of

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the system, i.e., calculation of the states that correspond to the zero rotational energy (rotationless states).

Lithium hydride, LiH, one of the lighter heteronuclear diatomics, continues to be the object of intense theoretical and experimental studies. The spectroscopic and structural data up to 1993 have been extensively reviewed by Stwalley and Zemke.[18] More recently, high-resolution spectra of LiH, recorded by the Bernath's group, provided even more accurate results.[19] These very precise experimental or experimentally derived data cover a wide range of internuclear separations and represent an ultimate benchmark that enables a very critical assessment of the performance and reliability of various theoretical approaches in describing a simple four-electron molecular system.

From the theoretical viewpoint, the simplicity of the electronic structure of LiH makes it a good molecule for testing of various theoretical techniques. These include those based on the Born–Oppenheimer (BO) approximations as well as those where the BO approximation is not assumed. The electronic structure of LiH exhibits general features of more complex systems, including the role of triply and quadruply electronic excited configurations in high-level correlated calculations. The fact that only four electrons are involved makes it possible to employ the full CI (FCI) BO approach with a fairly complete basis set. It also enables treatment with methods where the motion of both electrons and nuclei are considered on equal footing. This in turn enables a critical assessment of the performance of various methods relative to the available experimental data.

The number of works reporting both the *ab initio* and semiempirical quantum mechanical calculations of various properties of LiH is rather extended. In the early 1980s Partridge and Langhoff[20] reported MCSCF-CI LiH calculations using the Slater-type basis set. Their potential energy curve (PEC) is often used to this very day. About the same time, Jonsson *et al.*[21] carried out the MCSCF-CI calculations using a sizable Gaussian-type orbital basis set. More recently, Boutalib and Gadea[22] computed both diabatic and adiabatic PECs where they used a nonempirical pseudopotential for the core electrons and the full CI treatment of the valence electrons.

The vibrational analysis represents a good tool for testing the accuracy of the computed PECs in the BO calculations. Generally, in all cases of highly accurate results[20–24] the errors in computed vibrational term values steadily increase with the increasing vibrational quantum number. In other words, the theoretical PECs substantially deviate from the experimentally derived ones—often by several hundreds of wave numbers (cm^{-1}) for large internuclear separations approaching the dissociation region. For this reason, some of the above-mentioned studies focused only on low-lying vibrational levels. Clearly, it is the outer region of the potential, describing the actual bond breaking, where the accuracy of the electronic wave function plays the most significant role. Also in determining the vibrational transitions by a non-BO approach an accurate description of the part of the wave function corresponding to larger internuclear distances is very important.

II. CALCULATIONS

In the non-BO approach we use in this work we start with the nonrelativistic Hamiltonian for LiH consisting of six particles (the first particle is the Li nucleus, the second is the proton, and the remaining four are electrons) written in terms of the laboratory Cartesian coordinates, $\mathbf{R}_i$:

$$\hat{H}_{\text{TOT}} = -\sum_{i=1}^{6} \frac{1}{2M_i}\nabla_i^2 + \sum_{i=1}^{6}\sum_{j>i}^{6} \frac{Q_i Q_j}{R_{ij}}, \quad (1)$$

where the masses and charges of the particles are denoted as M_i and Q_i. The Hamiltonian (1) consists of the kinetic energy operator for each of the six particles and Coulombic interactions between each pair of the particles. $R_{ij} = |\mathbf{R}_j - \mathbf{R}_i|$ are interparticle distances. Next, the Hamiltonian (1) is transformed to separate the center-of-mass Hamiltonian from the rest, thereby reducing the six-particle problem to a five-pseudoparticle problem described by the internal Hamiltonian, $\hat{H}$. In this transformation the laboratory Cartesian coordinate system is replaced by a system whose first three coordinates are the laboratory coordinates of the center of mass, and the remaining 15 coordinates are the Cartesian coordinates in the internal coordinate system whose origin is placed at the lithium nucleus (particle 1 with mass M_1 called the reference particle). The other particles referred to the reference particle using the Cartesian position vectors $\mathbf{r}_i$ defined as $\mathbf{r}_i = \mathbf{R}_{i+1} - \mathbf{R}_1$. The resulting internal Hamiltonian, $\hat{H}$, is

$$\hat{H} = -\frac{1}{2}\left(\sum_i^5 \frac{1}{M_i}\nabla_i^2 + \sum_{i\neq j}^5 \frac{1}{M_1}\nabla_i'\nabla_j\right) + \sum_{i=1}^5 \frac{q_0 q_i}{r_i} + \sum_{i<j}^5 \frac{q_i q_j}{r_{ij}}, \quad (2)$$

where $'$ denotes vector transposition. The Hamiltonian (2) describes a system with the charge of the reference particle placed in the origin of the coordinate system ($q_0 = Q_1$) and five pseudoparticles, or internal particles, which are characterized by the reduced masses $m_i = M_1 M_{i+1}/(M_1 + M_{i+1})$ and charges $q_i = Q_{i+1}$. The pseudoparticles are moving in the spherically symmetric potential of the reference-particle charge. The second term in the parentheses in (2) is the mass polarization term, which couples the motion of all pseudoparticles. In the potential energy terms r_i and r_{ij} are defined as: $r_i = |\mathbf{r}_i|$ and $r_{ij} = |\mathbf{R}_{j+1} - \mathbf{R}_{i+1}| = |\mathbf{r}_j - \mathbf{r}_i|$.

In our works concerning non-BO calculations on small diatomic molecular systems we have shown that the explicitly correlated Gaussian basis set involving functions with pre-exponential multipliers consisting of the internuclear distance, r_1, raised to a non-negative power, m_k,[5,7,16]

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

is capable of very effectively describing noadiabatic zero-angular-momentum states of diatomic systems with σ electrons. The above function is a one-center correlated Gaussian with exponential coefficients forming the symmetric matrix A_k. $\mathbf{r}$ is a 15×1 vector of the internal Cartesian coordinates, $\mathbf{r}_i$, of the five pseudoparticles, and I_3 is the 3×3 identity matrix. ϕ_k are rotationally invariant functions as required by

the symmetry of the internal ground state problem described by the Hamiltonian (2). The presence of $r_1^{m_k}$ in (3) makes the function peak at some distance away from the origin. This distance depends on the value of m_k and on the exponential parameters, A_k. To describe a diatomic system, the maximum of ϕ_k in terms of r_1 should be around the equilibrium internuclear distance of the system. In the variational calculation the maximum of ϕ_k's is adjusted by optimization of m_k's and A_k's.

The ground and excited-state nonadiabatic wave functions for LiH in the present calculations were obtained by directly minimizing the Rayleigh quotient independently for each state:

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

with respect to the expansion coefficients of the wave function in terms of the basis functions, c_k (this is achieved through the diagonalization), the basis-function exponential parameters, $\{A_k\}$, and the pre-exponential powers, $\{m_k\}$.

To achieve the best results in the parameter optimization with the least computational effort, we have recently implemented a hybrid method that combines the gradient-based optimization with the stochastic selection method.[12,13] The strategy is based on alternating the gradient-based and the stochastic-based optimizations in growing the basis set from a small initial set generated in a gradient-based optimization to the final set. The basis set for each vibrational state was generated in a separate calculation. To achieve high accuracy in the calculations we used up to 7200 basis functions for each state. The range of the pre-exponential powers, $\{m_k\}$, used was from 0 to 250, and the powers were optimized for all basis functions. The calculations have been carried out at the University of Arizona Center of Computing and Information Technology with the use of an HP Alpha GS1280 supercomputer. Most calculations have been performed on 16 processors using message passing interface (MPI).

After the wave functions were generated, we calculated the expectation values of the interparticle distances (i.e., the internuclear distance, the distances between the electron and the nuclei, and the interelectron distance) for each state, as well as the squares of the distances. The algorithm for calculating the expectation values of the distances was described before.[17] In the calculations we used the following values for the nuclear masses: $m_{Li}=12786.3933m_e$ (^{7}Li), $m_p=1836.15267261m_e$ taken from Ref. 25. Here, m_e stands for the mass of the electron.

III. ESTIMATION OF THE PURELY VIBRATIONAL GROUND-STATE TRANSITION ENERGY FROM THE INFRARED AND MICROWAVE SPECTRA

The available infrared (IR) and microwave (MW) spectral data of LiH comprised of pure rotational and vibration-rotational transitions of ^{7}LiH, ^{6}LiH, ^{7}LiD, and ^{6}LiD and include: 4,[27] 6,[28] 22,[29,30] 29,[32] and 261[19] pure rotational lines corresponding to $\Delta v=0$ up to $v=3$ and $J=45$; and 4,[31] 526,[26] and 678[19] rotation-vibrational lines with $\Delta v=1$, 2 up to $v=6$ and $J=28$. To estimate the purely vibrational $\nu_{0\rightarrow1}$ tran-

TABLE I. Mass-dependent Dunham constants (in cm^{-1}) for ^{7}LiH in the ground $X^1\Sigma^+$ electronic state.

Y_{10}	1405.499821(805)
Y_{20}	−23.169757(709)
$Y_{30}\times10^1$	1.71706(261)
$Y_{40}\times10^3$	−1.84815(423)
$Y_{50}\times10^4$	−1.05908(250)
Y_{01}	7.5137310546(966)
$Y_{02}\times10^4$	−8.58573863(540)
$Y_{03}\times10^7$	1.0804023(459)
$Y_{04}\times10^{11}$	−1.75336(149)
$Y_{05}\times10^{15}$	3.0470(193)
$Y_{06}\times10^{19}$	−3.6590(861)
Y_{11}	−0.21639167(279)
$Y_{21}\times10^{13}$	2.024691(216)
$Y_{12}\times10^5$	1.590311(704)
$Y_{22}\times10^8$	−9.7657(360)
$Y_{31}\times10^5$	−2.40638(566)
$Y_{13}\times10^{10}$	−6.8697(201)
$Y_{32}\times10^8$	−1.42540(409)
$Y_{23}\times10^{11}$	−6.17000(255)
$Y_{14}\times10^{13}$	−2.6533(405)
$Y_{41}\times10^6$	−2.13497(465)
$Y_{15}\times10^{17}$	7.00(243)
$\hat{\sigma}$	1.0912
σ_{SD} cm^{-1}	0.0010
$F/10^{16}$	2.6426
$\nu_{0\rightarrow1}$ cm^{-1}	1359.7083(19)

sition frequency of ^{7}LiH, we employed in the calculations 549 pure rotational and vibration-rotational transitions of ^{7}LiH (including duplicated lines) extracted from the basic set of the spectral lines. These spectral data were fitted to the Dunham energy formula:[33,34]

$$E_{vJ} = \sum_{i,j} Y_{ij}\left(v+\frac{1}{2}\right)^i \left[J(J+1)\right]^j \qquad (5)$$

using a weighted nonlinear least-square routine with weights taken as inverse squares of the uncertainties of the experimental data. To obtain the best set of the Dunham constants, Y_{ij}, from the spectra, we used the following criteria: the minimum number of fitted parameters consistent with the minimum value of the normalized standard deviation $\hat{\sigma}\approx1$, the maximum value of the F statistic, and the optimal value of the estimated standard error σ_i of each fitted parameter i and of the correlation coefficient $cc(i,j)$ between the parameters i and j. The results of the calculations are presented in Table I. The uncertainty provided in the parentheses was estimated as the standard deviation in units of the last quoted digit in the values of the fitted Dunham constants.

The purely vibrational $\nu_{0\rightarrow1}$ transition frequency of ^{7}LiH was calculated using the relation

$$\nu_{0\rightarrow1} = E_{10} - E_{00} = 1359.7083(19)\ cm^{-1} \qquad (6)$$

and the values of the energy terms (5) including the Dunham constants taken from Table I. The standard error of the calculated frequency was estimated from the errors of the fitted Dunham constants Y_{ij}.

TABLE II. Convergence of the total energies of the $v=0$ and $v=1$ states and the $1\leftarrow 0$ transition energy for LiH.

Basis size	$E_{v=0}$ (a.u.)	$E_{v=1}$ (a.u.)	ΔE (cm^{-1})
600	−8.0662087891	−8.0536511868	2756.075
1000	−8.0663205454	−8.0599201018	1404.735
1400	−8.0663649058	−8.0600552028	1384.820
1800	−8.0663949787	−8.0601256333	1375.962
2200	−8.0664109879	−8.0601607151	1371.776
2600	−8.0664206788	−8.0601830903	1368.992
3000	−8.0664258061	−8.0601985695	1366.720
3400	−8.0664294133	−8.0602099557	1365.013
3800	−8.0664315836	−8.0602176154	1363.808
4200	−8.0664328306	−8.0602215005	1363.229
4600	−8.0664337160	−8.0602249770	1362.661
5000	−8.0664344512	−8.0602278602	1362.189
5400	−8.0664350896	−8.0602302335	1361.809
5800	−8.0664356223	−8.0602321600	1361.503
6200	−8.0664360871	−8.0602337740	1361.250
6600	−8.0664364808	−8.0602352083	1361.022
7000	−8.0664368012	−8.0602363664	1360.838
7000[a]	−8.0664368421	−8.0602365718	1360.802
7200	−8.0664370924	−8.0602373298	1360.691
Experiment			1359.7083(19)

[a]Results obtained by performing additional optimization of the 7000-term basis set.

IV. RESULTS AND DISCUSSIONS

The goal of the present calculations has been to determine if the non-BO approach utilizing explicitly correlated Gaussian functions can provide a sufficient level of accuracy to predict the $0\leftarrow 1$ pure vibrational transition within approximately a wave number from the experimental value. The transition energy in the present work was determined as the difference of the total non-BO energies of the ground and the first excited rotationless state. The two energies have been calculated using the above-described approach.

It should be realized that an accurate non-BO calculation for a system with five pseudoparticles is a very demanding computational task. Even with the use of a highly parallel version of the code and almost continuous access to a 16-processor segment of the computer the present calculations have lasted for over a year. Obviously, the calculations could have been continued to generate even more precise predictions. However, after achieving our goal of converging the $0\leftarrow 1$ transition energy to less than a wave number in comparison to the value derived from the available experimental rovibrational transitions, we decided to stop the calculations and present the results. If in the future we will gain access to computational resources with a clock that is about 100 times faster than what is available to us at present, we will return to the LiH calculations not only to refine the result for the $0\leftarrow 1$ vibrational transition, but also to calculate higher vibrational transitions. At this point the barrier for pursuing such a project lies more in the limitations of the computer hardware than of the software.

The first series of the results we show concerns the convergence of the total non-BO energies of the ground and the first excited state as the number of the basis functions increases. These results are presented in Table II. In the table

we also show the convergence of the $0\leftarrow 1$ transition energy and its comparison with the value derived from the experiment using the procedure described in the previous section. Since it can be exacted that within the same number of basis functions the energy of the ground state is better converged than the energy of the first excited state (due to the more complicated structure of the excited-state wave function requiring more basis functions to reach comparable precision as for the ground state), the transition energy calculated as the difference of total energies of the two states should provide, in practice, an upper bound to the result one should get at the complete basis set limit. Inspection of the transition energies presented in Table II shows that this is indeed the case. The calculated transition energy decreases as the number of basis functions increases and it is converging to the experimental energy. Our best value for the transition energy of 1360.691 cm^{-1} is slightly less than a wave number higher than the value of 1359.7085 cm^{-1} obtained based on the available experimental rovibrational transitions. It is clear that if the calculations continued and more functions were added to the basis set, the agreement between the calculations and the experiment would improve. However, with 7200 basis functions we reached the practical limit of the computational resources available to us at the present time.

The availability of the wave functions describing the rotationless internal motion of LiH in the ground and excited states allowed the calculation of the expectation values of the interparticle distances and their squares. The averaged interparticle distances are presented in Table III. The values of the distances are shown with six figures after the decimal point. By examining the convergence of the result with the number of basis functions one can conclude that at least five of those six figures are fully converged. As expected, the average internuclear distance ($\langle r_1 \rangle$) increases with the vibrational excitation. In the ground state this distance is equal to 3.061043 a.u. and increases to 3.155022 a.u. for the first excited state. The averaged electron-nucleus distances, as well as the interelectron distance, also increase when the system is excited from the ground to the first vibrational state.

V. CONCLUSIONS

The non-BO calculations of the $0\leftarrow 1$ pure vibrational transition in LiH performed in this work show that the non-BO method we developed can be successfully applied to perform very accurate calculations of the ground and excited states of a diatomic molecular system with four electrons. Although only two vibrational states are calculated, the procedure would not be any different for higher excited states. Due to the increasing number of the radial nodes in terms of the r_1 coordinate in those states it is certain that more basis functions will be needed, but the accuracy of the calculations should not be any lower than the accuracy of the results presented in this work. As mentioned, at present our computer resources do not allow to undertake calculations of higher excited states of LiH and an access would be needed to a computer two orders of magnitude faster than what we have available to us at the present time to carry out such work. However, if we gain such access, the LiH system may

TABLE III. Expectation values of the interparticle distances, $r_{Li-H} \equiv r_1$, $r_{Li-e} \equiv r_2$, $r_{H-e} \equiv r_{12}$, $r_{e-e} \equiv r_{23}$ and their squares (in a.u.) calculated with different basis sets.

Basis size	$\langle r_{Li-H} \rangle$	$\langle r_{Li-e} \rangle$	$\langle r_{H-e} \rangle$	$\langle r_{e-e} \rangle$	$\langle r_{Li-H}^2 \rangle$	$\langle r_{Li-e}^2 \rangle$	$\langle r_{H-e}^2 \rangle$	$\langle r_{e-e}^2 \rangle$
$v=0$								
4000	3.061030	1.971926	2.565076	2.955914	9.419625	6.585597	7.744938	10.96573
5000	3.061037	1.971931	2.565090	2.955926	9.419677	6.585666	7.745061	10.96588
6000	3.061045	1.971934	2.565100	2.955935	9.419730	6.585711	7.745147	10.96598
7000	3.061043	1.971934	2.565102	2.955937	9.419721	6.585720	7.745168	10.96601
7200	3.061041	1.971933	2.565101	2.955936	9.419707	6.585717	7.745166	10.96601
$v=1$								
4000	3.155133	2.007055	2.624313	3.008832	10.10555	6.866740	8.171164	11.39475
5000	3.155045	2.007023	2.624280	3.008796	10.10497	6.866565	8.171009	11.39459
6000	3.155028	2.007016	2.624283	3.008795	10.10486	6.866562	8.171078	11.39466
7000	3.155022	2.007014	2.007014	3.008797	10.10482	6.866578	8.171124	11.39472
7200	3.155013	2.007010	2.624282	3.008793	10.10477	6.866553	8.171102	11.39469

become a new model where the high-precision molecular quantum calculations and the experimental spectral results can be tested in the way three decades ago they were tested for H_2 and its isotopomers. Since LiH has a more complex electronic structure than H_2, such testing will provide better verification of the reliability of the computational approach, as well as the accuracy of the experimental data.

Finally we should mention that efforts have been undertaken by other workers to apply the conventional BO approach corrected with the use of the perturbation theory for the nonadiabatic, as well as relativistic effects, in calculations of rovibrational levels of two- and three-atom systems. Some calculations of this type have achieved very high accuracy. An example of such works is the recent study of rovibrational states of the water molecule performed by Polyansky et al.[35] where all experimentally characterized band origins were reproduced with a root-mean-square error of about 0.75 cm^{-1}.

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