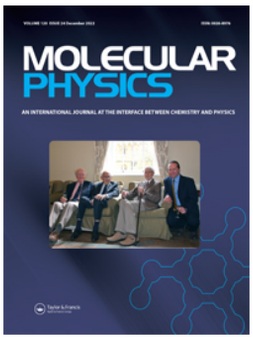

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Molecular Physics

An International Journal at the Interface Between Chemistry and Physics

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/tmph20

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To cite this article: Saeed Nasiri, Toreniyaz Shomenov, Sergiy Bubin & Ludwik Adamowicz (2022) Dissociation energy and the lowest vibrational transition in LiH without assuming the non-Born–Oppenheimer approximation, Molecular Physics, 120:24, e2147105, DOI: 10.1080/00268976.2022.2147105

To link to this article: https://doi.org/10.1080/00268976.2022.2147105

Published online: 18 Nov 2022.

MOLECULAR PHYSICS
2022, VOL. 120, NO. 24, e2147105 (9 pages)
https://doi.org/10.1080/00268976.2022.2147105

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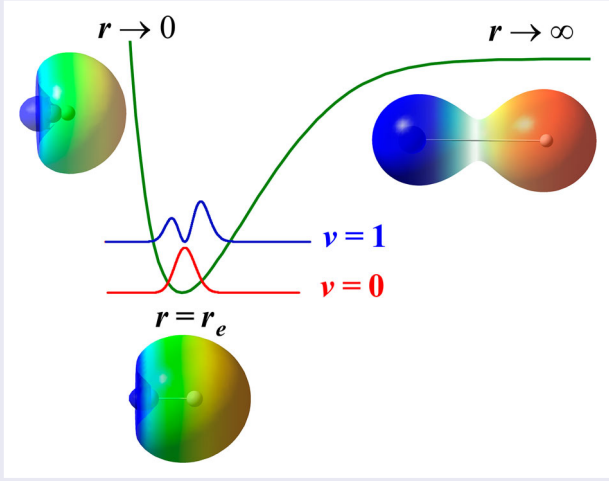
Dissociation energy and the lowest vibrational transition in LiH without assuming the non-Born–Oppenheimer approximation

Saeed Nasiri[a], Toreniyaz Shomenov[a], Sergiy Bubin[a] and Ludwik Adamowicz[b,c,d]

[a]Department of Physics, Nazarbayev University, Nur-Sultan, Kazakhstan; [b]Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ, USA; [c]Department of Physics, University of Arizona, Tucson, AZ, USA; [d]Centre for Advanced Study (CAS), the Norwegian Academy of Science and Letters, Oslo, Norway

ABSTRACT
The fundamental vibrational excitation energy and the dissociation energy of the main isotopologue of lithium hydride (^{7}LiH) are studied by the variational method using all-particle explicitly correlated Gaussian (ECG) basis sets. In this approach, electrons and nuclei are treated on equal footing, i.e. the Born–Oppenheimer approximation is not assumed. The leading relativistic ($\sim \alpha^2$) and the dominating part of the quantum electrodynamics ($\sim \alpha^3$) corrections to the energy levels are accounted for in the framework of the perturbation theory. The fundamental vibrational excitation energy and the dissociation energies obtained in the calculations are well within the error bars of the available experimental data.



ARTICLE HISTORY
Received 30 September 2022
Accepted 5 November 2022

KEYWORDS
Lithium hydride; explicitly correlated gaussians; non-Born–Oppenheimer calculations; relativistic corrections

1. Introduction

The lithium hydride molecule has long been regarded as a 'workbench of theoretical chemistry', on which various electronic structure methods are tested and refined. One interesting aspect of the LiH molecule in the ground electronic state is its electronic density distribution at different values of the internuclear distance. An examination of the dipole moment curve calculated by Shi *et al.* [1] reveals that at and around the equilibrium internuclear distance, the LiH dipole moment is large (with a maximum at around $R = 3$ a.u.), but decreases to zero at larger distances. This indicates that at equilibrium the LiH bond has predominantly an ionic character resulted from the electrostatic interaction of the positively charged lithium ion and the hydrogen anion ($Li^+ + H^-$). However, at larger distances, the LiH bond becomes predominantly covalent (Li + H). This interesting behaviour that has profound implication for the LiH spectral properties, in particular for the transition oscillator strengths, results from an avoided curve crossing that

CONTACT Ludwik Adamowicz ludwik@arizona.edu

occurs when the internuclear distance stretches beyond the equilibrium distance of approximately 3.015 a.u. The crossing involves the potential energy curve representing the ionic LiH and the curve representing the covalently-bonded LiH.

LiH, which is the smallest heteronuclear molecule, has only four electrons and it has been subject to meticulous theoretical calculations from the very early stages of quantum chemistry (see Table 13 in Ref. [2]). It has become a popular benchmark system for testing emerging quantum-mechanical methods for performing electronic-structure molecular calculations and for investigating the capability of the existing methods to produce more accurate results. In past decades, the LiH molecule has been studied using various high-level quantum mechanical methods such as configuration interaction (CI) [3–6], multi-reference configuration interaction (MR-CI) [3, 7–13], coupled-cluster (CC) [14–18] and explicitly correlated Gaussian functions (ECG) [19–24].

A significant interest in the spectral properties of LiH has been in part due to its relevance to astrophysics and astrochemistry. In particular, the role LiH may play in the cooling of primordial clouds [24–27] and its application in monitoring the evolution of stars and interstellar clouds [28] should be mentioned. Lastly, LiH is also a good model system for investigating the validity and limitations of the Born–Oppenheimer (BO) approximation in calculating its bound ro-vibrational states [13].

The focus of this work is the fundamental vibrational transition energy of the ^{7}LiH molecule. Unlike, the standard approach used in the calculations of the molecular ro-vibrational spectra, that is based on assuming the BO approximation, the present approach does not assume this approximation. By treating the electrons and the nuclei on an equal footing, high accuracy is achieved. In the calculations, we use the variational method with the Hamiltonian obtained by separating out the kinetic energy of the centre-of-mass motion from the laboratory all-particle nonrelativistic Hamiltonian. The wave functions of the considered states are expanded in terms of single-centre ECG functions, which are eigenfunctions of the operator representing the square of the total angular momentum of the molecule with the zero total angular momentum quantum number. The total angular momentum includes the electronic angular momentum and the nuclear angular momentum. Thus the states calculated in this work can be called 'pure vibrational states', as they represent the ground and lowest excited internal states in the rotation-less spectrum of the system. However, as the BO approximation is not assumed in the present calculations, the terms 'rotational' and 'vibrational' that are well defined within the BO approach can only be applied loosely to the results of the present calculations. As the coupling of the electronic and nuclear motions is explicitly present in our calculations, the non-BO results are not, strictly speaking, completely equivalent to the BO results. Naturally, in the limit of infinite basis sets used to expand the BO and non-BO wave functions of the system, the non-BO description is more accurate than its BO equivalent.

2. Formalism

Very accurate molecular calculations have to account for the effects associated with the finite mass of nuclei. This can be done using the perturbation theory approach (by far the most common way) or more directly by explicitly including these effects in the (zero-order) Hamiltonian that represents the nonrelativistic energy of the system. In the present work, the latter approach is adopted. The finite nuclear mass (FNM) effects are revealed when the internal motions of the system are considered as a coupled motion of the nuclei and the electrons around the system's centre of mass. Thus, to calculate the energies and the corresponding wave functions of bound states associated with this motion, an internal nonrelativistic Hamiltonian has to be derived. In the approach used here, the starting point in the derivation of such a Hamiltonian is the standard non-relativistic laboratory-frame Hamiltonian comprising operators representing the kinetic and potential energies of the nuclei and the electrons. First, the laboratory frame Hamiltonian is expressed in terms of the Cartesian lab-frame coordinates. Next, a new set of Cartesian coordinates is introduced. These coordinates include the three coordinates, x_{cm}, y_{cm}, and z_{cm}, that represent the position of the centre of mass of the system in the laboratory frame, and $3N-3 = 3n$ internal coordinates, where N is the total number of particles in the system. There are a number of ways to choose the internal coordinates. In the present approach, we use a generalisation of the textbook approach employed in solving the Schrödinger equation for the hydrogen atom, where the internal coordinates are the coordinates of the vector with the origin at the proton and the end at the electron. In the generalised approach used here, the internal coordinates are the coordinates of vectors $\mathbf{r}_i$, $i = 1, \ldots, n$ originating at one of the nuclei (usually the heaviest one in the system; the lithium nucleus in the present work) and ending at the individual electrons and at the other nuclei (the H nucleus in the case of the LiH molecule). When the lab-frame Hamiltonian is expressed in terms of the new coordinates, it rigorously separates into an operator representing the kinetic energy of the motion of the centre of mass and an operator dependent only on the

internal coordinates that represents the internal state of the system [29]. The internal Hamiltonian has the following form:

$$H_{\rm nr}^{\rm int} = -\frac{1}{2}\left(\sum_{i=1}^{n}\frac{1}{\mu_i}\nabla_{\mathbf{r}_i}^2 + \sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{1}{m_0}\nabla'_{\mathbf{r}_i}\nabla_{\mathbf{r}_j}\right) + \sum_{i=1}^{n}\frac{q_0 q_i}{\mathbf{r}_i} + \sum_{i=1}^{n}\sum_{j<i}^{n}\frac{q_i q_j}{\mathbf{r}_{ij}}, \quad (1)$$

where m_0 is the mass of the reference nucleus and q_0 is its charge, q_i, $i = 1, \ldots, n$, are the charges of the other particles, $\mu_i = m_0 m_i/(m_0 + m_i)$ is the reduced mass of particle i (m_i, $i = 1, \ldots, n$, are the particle masses), $\mathbf{r}_i$, $i = 1, \ldots, n$ is the distance from particle $n+1$ to the reference particle, i.e. particle 1, and $\mathbf{r}_{ij}$ is the distance between particle $j+1$ and particle $i+1$. The prime symbol in Equation (1) denotes the matrix/vector transposition. One can notice that the internal Hamiltonian represents the motion of n particles, whose charges are the original particle charges, but the masses are the reduced masses (because of that, we use the term 'pseudoparticles' in reference to the particles described by the internal Hamiltonian), in the central field of the charge of the reference nucleus. Thus the internal Hamiltonian is invariant upon all rotations about the centre of the internal coordinate system and one can think of it as an 'atom-like' Hamiltonian. The eigenfunctions of this Hamiltonian can be classified using the same symmetries as the wave functions of an atom. These eigenfunctions and the corresponding eigenvalues (energies) represent all modes of the internal motions of the molecule including the electronic, vibrational and rotational motions. In particular, the ground-state solution is spherically symmetric, i.e. it is invariant under 3D rotations.

The following all-particle spherically-symmetric explicitly correlated Gaussian functions are used in the present calculations:

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

where r_1 is the distance between the nuclei (particle 1 is the lithium nucleus while particle 2 is the proton), m_k is an even integer (in this work, m_k is constrained within the range 0–200 and it is regarded as an integer variational parameter), A_k is an $n \times n$ real symmetric matrix of the exponential variational parameters, $\otimes$ denotes the Kronecker product, and I_3 is an 3×3 identity matrix. Note that both A_k and m_k are unique and independently tunable for each basis function, which is indicated by the presence of index k. Vector $\mathbf{r}$ in Equation (2) is a $3n$-component vector formed by stacking the internal Cartesian coordinates, $\mathbf{r}_i$:

$$\mathbf{r} = \begin{pmatrix} \mathbf{r}_1 \\ \mathbf{r}_2 \\ \vdots \\ \mathbf{r}_n \end{pmatrix}. \quad (3)$$

Let us denote $\mathbf{A}_k = A_k \otimes I_3$. $\mathbf{A}_k$ and, by extension, A_k, have to be positive definite in order for Gaussian basis function (2) to be square integrable. To ensure positive definiteness of $\mathbf{A}_k$ we adopt the following Cholesky-factored form for it: $\mathbf{A}_k = (L_k L_k') \otimes I_3$, where L_k is an $n \times n$ lower-triangular matrix of real numbers. In this form, $\mathbf{A}_k$ is automatically positive definite for any real-valued L_k. The elements of matrix L_k are variational parameters that are extensively optimised in the present calculations. The optimisation employs the analytical energy gradient determined with respect to the L_k matrix elements. The enlargement and subsequent optimisation are done using a one-function-at-a-time approach. The initial guess of a new function is generated stochastically based on the values of the nonlinear parameters of the Gaussians already included in the basis set. After being added to the basis set, the new function is variationally optimised and, if it is not linearly dependent with any other functions already present in the basis set, it is included in the set. In the optimisation of the function, the L_k matrix elements and the m_k power of r_1 in the pre-exponential factor of Gaussian (2) are subject to the variational optimisation. Each m_k power is optimised in the 0–250 range and is restricted to be an even integer. This is the only place in the calculation where the m_k power is optimised. After a certain number of Gaussians are added to the basis set, the L_k parameters of all functions in the set generated so far in the calculation are reoptimised, again using a one-function-at-a-time approach. However, as above mentioned, in this reoptimisation, only the L_k matrix elements are varied, while the m_k values kept unchanged. All calculations are performed using our in-house parallel computer code written in Fortran and employing MPI (Message Passing Interface) for communication between parallel processes. It should be noted that the generation of the basis set for each considered state is by far the most time-consuming step of the calculations. It required over a year of continuous computing using about a hundred cores on parallel computer systems equipped with Intel Xeon E5-2695v3 and AMD EPYC 7642 central processing units.

The need to include the $r_1^{m_k}$ factors in the Gaussian basis functions can be explained by analysing the internal Hamiltonian. As pseudoparticle 1 in the internal Hamiltonian (1) is the proton, there is strong Coulombic repulsion between this proton and the charge of the

lithium nucleus (the reference particle) located in the centre of the internal coordinate system. The pair correlation function of the two nuclei that depends on r_1 (the separation between them) must be virtually zero at $r_1 = 0$. At the same time, for a diatomic molecule in its ground state, this pair correlation function sharply peaks at $r_1 \approx R_e$, i.e. at a sphere with the radius approximately equal to the equilibrium bond length of the molecule. For vibrationally excited states, the corresponding pair correlation function has multiple radial peaks, but they are all located away from the origin $r_1 = 0$. As an origin-centred Gaussian function has a maximum at the centre of the coordinate system, it needs to be modified to move its maximum away from the centre of the sphere. This can be accomplished by multiplying the Gaussians by the $r_1^{m_k}$ factors. Such factors, in addition to shifting the Gaussian maxima away from the origin can also effectively describe the radial oscillations of the wave functions corresponding to (radial) vibrational excitations. If the basis functions used in the calculation are spherically symmetric, as is the case for functions (2), then the only excited states they can describe are purely 'vibrational' states, i.e. states with the zero total angular momentum.

The present calculations concern the ground and first excited singlet states of the LiH molecule. In constructing the wave functions for these states, the proper permutational symmetry of the electrons has to be taken into account. This can be achieved using the spin-free formalism [30–32]. The key element of this formalism is the construction of an appropriate permutational symmetry projector, Y. The action of this projector on the spatial part of basis functions yields a combination of terms that otherwise be generated by using the full (spatial plus spin) basis functions and integrating over the electronic spin coordinates. Projector Y implements the desired permutational symmetry properties of the variational wave function. For a system consisting of four electrons (labelled as particles 3, 4, 5 and 6) in a singlet state one possible choice of operator Y is

$$Y = (1 + P_{34})(1 + P_{56})(1 - P_{35})(1 - P_{46}), \quad (4)$$

where permutations P_{ij} exchange the indices of electrons i and j.

Calculations performed at the nonrelativistic level of the theory, even if they are very accurate, are insufficient to determine the total energies and the interstate transition energies with an accuracy comparable with the present-day spectroscopic results. To achieve the spectroscopic accuracy, at least the leading relativistic and QED energy corrections need to be included in the calculations. An approach to account for these corrections that is practical and most frequently used in calculating bound states of light atoms and molecules is based on expanding the total energy of the system in terms of powers of the fine-structure constant, α [33, 34]:

$$E_{\rm tot} = E_{\rm nr} + \alpha^2 E^{(2)}_{\rm rel} + \alpha^3 E^{(3)}_{\rm QED} + \cdots, \quad (5)$$

where $E_{\rm nr}$ is the nonrelativistic energy of the state being considered, the second term, $(\alpha^2 E^{(2)}_{\rm rel})$, represents the leading relativistic correction, the third term $(\alpha^3 E^{(3)}_{\rm QED})$ represents the leading QED correction and so on. Each of these terms is evaluated as an expectation value of a certain effective Hamiltonian. In Equation (5), quantity $E^{(2)}_{\rm rel}$ is the expectation value of the Breit–Pauli Hamiltonian corresponding to the singlet state, $H_{\rm rel}$ [35, 36]. To be used in the present work, $H_{\rm rel}$ is first transformed from the laboratory coordinates, $\mathbf{R}_i$, to the internal coordinates, $\mathbf{r}_i$. $H_{\rm rel}$ includes the following terms: the mass–velocity term ($H_{\rm MV}$), the Darwin term ($H_{\rm D}$), the orbit–orbit interaction term ($H_{\rm OO}$) and the spin–spin Fermi interaction term ($H_{\rm SS}$):

$$H_{\rm rel} = H_{\rm MV} + H_{\rm D} + H_{\rm OO} + H_{\rm SS}. \quad (6)$$

The explicit expressions for the corresponding effective operators in the internal coordinates are (again assuming particles 1 and 2 are nuclei and particles 3-6 are electrons) [29]:

$$H_{\rm MV} = -\frac{1}{8}\left[\frac{1}{m_0^3}\left(\sum_{i=1}^{n}\nabla_{\mathbf{r}_i}\right)^4 + \sum_{i=1}^{n}\frac{1}{m_i^3}\nabla^4_{\mathbf{r}_i}\right], \quad (7)$$

$$H_{\rm D} = -\frac{\pi}{2}\left(\sum_{i=2}^{n}\frac{q_0 q_i}{m_i^2}\delta(\mathbf{r}_i) + \sum_{i=2}^{n}\frac{q_1 q_i}{m_i^2}\delta(\mathbf{r}_{1i}) + \sum_{\substack{i,j=2\\ j\neq i}}^{n}\frac{q_i q_j}{m_i^2}\delta(\mathbf{r}_{ij})\right), \quad (8)$$

$$\hat{H}_{\rm OO} = -\frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\frac{q_0 q_j}{m_0 m_j} \times\left[\frac{1}{r_j}\nabla'_{\mathbf{r}_i}\nabla_{\mathbf{r}_j} + \frac{1}{r_j^3}\mathbf{r}'_j(\mathbf{r}'_j\nabla_{\mathbf{r}_i})\nabla_{\mathbf{r}_j}\right] + \frac{1}{2}\sum_{i=1}^{n}\sum_{j>i}^{n}\frac{q_i q_j}{m_i m_j} \times\left[\frac{1}{r_{ij}}\nabla'_{\mathbf{r}_i}\nabla_{\mathbf{r}_j} + \frac{1}{r_{ij}^3}\mathbf{r}'_{ij}(\mathbf{r}'_{ij}\nabla_{\mathbf{r}_i})\nabla_{\mathbf{r}_j}\right], \quad (9)$$

and

$$H_{\mathrm{SS}} = -\frac{8\pi}{3} \sum_{\substack{i,j=2 \\ j>i}}^{5} \frac{q_i q_j}{m_i m_j} \left(\mathbf{s}_i' \mathbf{s}_j\right) \delta\left(\mathbf{r}_{ij}\right). \tag{10}$$

In the last expression, $\mathbf{s}_i$ denotes the spin operator of the ith pseudoparticle. For the LiH states considered in this work, $\mathbf{s}_i'\mathbf{s}_j = -3/4$. The relativistic corrections for a particular state are calculated as the expectation values of the above operators using its nonrelativistic non-BO wave function.

The leading QED correction, $E^{(3)}_{\mathrm{QED}}$ in Equation (5), represents the two-photon exchange, vacuum polarisation and electron self-energy effects. The largest contribution to $E^{(3)}_{\mathrm{QED}}$ arises from the term which includes the Bethe logarithm, $\ln k_0$ (see Refs. [37, 38] for more information). The main difficulty in computing the QED correction lies in accurate determination of that term. To our knowledge, there has not been any calculation of $\ln k_0$ for LiH. However, it is well known that the dominant contribution to $\ln k_0$ in atoms comes from the inner shell electrons. Based on this, we make an approximation and use the following $\ln k_0$ values reported for the Li and H atoms, i.e. 5.178 080 [39] and 2.984 129 [40], respectively, to determine $\ln k_0$ for LiH. Thus the QED correction for LiH molecule is estimated as

$$\begin{aligned} H^{(3)}_{\mathrm{QED}} \approx \frac{4\,q_0}{3} & \left(\frac{19}{30} - 2\ln\alpha - \ln k_0(\mathrm{Li})\right) \\ & \times \left\langle \sum_{i=2}^{5} \delta\left(\mathbf{r}_{\mathrm{Li}-i}\right) \right\rangle \\ & + \frac{4\,q_{\mathrm{H}}}{3} \left(\frac{19}{30} - 2\ln\alpha - \ln k_0(\mathrm{H})\right) \\ & \times \left\langle \sum_{i=2}^{5} \delta\left(\mathbf{r}_{\mathrm{H}-i}\right) \right\rangle. \end{aligned} \tag{11}$$

3. Results

Table 1 presents the calculations of the total non-Born–Oppenheimer nonrelativistic (nr) energies, the leading relativistic (rel) corrections, and some key expectation values for the LiH ground and first excited states, as well as the corresponding values for the Li and H atoms. The results shown in the table are obtained with the basis sets of sizes that increase from 11,000 to 17,000 and from 8000 to 11,000 for the LiH and Li species, respectively. The energies and the expectation values are extrapolated to an infinite basis set size (for more information, see Ref. [41]). The extrapolated values are shown in the table along with the corresponding estimated uncertainties. As one can see, all LiH expectation values are well converged but, as expected, the convergence rate is relatively faster for the ground state than for the first excite state. The basis sets used to calculate the results shown in Table 1 are calculated using basis sets obtained in a basis-set growing process. In this process, we start from a small set of Gaussians with nonlinear parameters chosen by a combination of a random and physically-motivated choices. Then several steps are performed, where in each step the basis set is enlarged by addition of a subset of new Gaussians and variationally optimising them with the a procedure that employs the analytical energy gradient. The enlargement and subsequent optimisation are done using a one-function-at-a-time approach. After a newly added function is variationally optimised it is checked for linearly dependency with the functions already included in the set. If not linear dependency is found, the function is included in the basis set. As mentioned, the L_k matrix

Table 1. Variational non-Born–Oppenheimer nonrelativistic energies (E_{nr}) of the ground ($v = 0$) and first excited ($v = 1$) vibrational states of the LiH molecule. Results obtained with basis sets with different sizes are shown.

	Basis	E_{nr}	$\langle H_{\mathrm{MV}}\rangle$	$\langle H_{\mathrm{OO}}\rangle$	$\langle\delta(\mathbf{r}_e)\rangle$	$\langle\delta(\mathbf{r}_{\mathrm{H}-e})\rangle$	$\langle\delta(\mathbf{r}_{e-e})\rangle$
^{7}LiH	11000	−8.06643882	−79.0464	−0.4730659	3.45138	0.095029	0.0916646
$v = 0$	13000	−8.06643893	−79.0538	−0.4730653	3.45175	0.095057	0.0916489
	15000	−8.06643902	−79.0622	−0.4730649	3.45213	0.095078	0.0916462
	17000	−8.06643913	−79.0624	−0.4730643	3.45214	0.095082	0.0916458
	∞	−8.06643918(6)	−79.0626(2)	−0.4730640(3)	3.45215(1)	0.095085(3)	0.0916456(3)
^{7}LiH	11000	−8.06024277	−79.0273	−0.4724646	3.45082	0.094250	0.0915880
$v = 1$	13000	−8.06024309	−79.0284	−0.4724645	3.45088	0.094253	0.0915799
	15000	−8.06024336	−79.0291	−0.4724673	3.45093	0.094263	0.0915629
	17000	−8.06024367	−79.0325	−0.4724711	3.45112	0.094270	0.0915600
	∞	−8.06024395(28)	−79.0346(22)	−0.4724733(23)	3.45123(10)	0.094274(4)	0.0915585(15)
^{7}Li	8000	−7.477451930722	−78.531157	−0.44549103389	4.61310856419		0.181401118390
	9000	−7.477451930726	−78.531153	−0.44549103386	4.61310856427		0.181401118405
	11000	−7.477451930729	−78.531153	−0.44549103389	4.61310856432		0.181401118411
	∞	−7.477451930732(3)	−78.531150(3)	−0.44549103378(11)	4.61310856437(6)		0.181401118417(6)
H	∞	−0.499727839712	−0.62364031	−0.00054373	0.31830989		

Note: Some additional optimisation steps are involved in generation the largest set of 17,000 ECGs. The values in the parentheses are uncertainties due to the finite size of the basis set used. All energies and expectation values are expressed in atomic units.

elements and the m_k power in the r_1 preexponential factor are subject to the optimisation. Also, as mentioned, the m_k powers are optimised in the 0–200 range and are restricted to be even integers. After a certain number of Gaussians are added, the nonlinear parameters of all function in the basis set generated so far are reoptimised, again using a one-function-at-a-time approach. In this reoptimisation, however, only the L_k matrix elements are varied, while the m_k values are kept unchanged.

The $0 \rightarrow 1$ transition energy calculated using non-relativistic energies ($E_{\rm nr}$), non-relativistic energies and the relativistic correction ($E_{\rm nr+rel}$), and non-relativistic energies and the relativistic and QED corrections ($E_{\rm nr+rel+QED}$) are shown in Table 2. In addition to the values calculated in the present work, some most accurate values obtained in previous experimental and theoretical studies are also shown in the table. All of the previous calculations [5, 12, 13, 24, 42] have been performed assuming the Born–Oppenheimer approximation; although, adiabatic correction has been included in the calculations performed by Holka *et al.* [13] and Tung *et al.* [24] which makes their values more accurate than those obtained in other studies. It is worth mentioning that only the transition energy previously calculated by Tung *et al.* [24] is within the experimental uncertainty. As it is shown in Table 2, the value of 1 359.739(64) cm^{-1} obtained in the present work for the $0 \rightarrow 1$ transition is in excellent agreement with the experimentally determined values [2, 43, 44]. A comparison of the transition-energy values obtained in the ECG calculations with and without assuming the BO approximation reveals the importance of accounting for the coupling between the motion of the electrons and nuclei. As shown by Holka *et al.* [13] and confirm by the present calculations, the non-adiabatic correction is already important for the ground state of the LiH molecule.

In Table 3, the calculated dissociation energies (D) from the ground and first excited states are shown along with the available experimental and theoretical values. As one can see, the obtained dissociation value from the ground state, using the non-relativistic energies ($D_{\rm nr}$ =19 590.176(12)) is not as accurate as the ones obtained with including the relativistic, ($D_{\rm nr+rel}$ = 19 589.751(12)) and QED ($D_{\rm nr+rel+QED}$ = 19 589.762(12)) corrections. It is worth mentioning that the computed QED correction in the present work is a very raw estimation. The correction could be improved using more accurate expression for the QED correction. As mentioned before, all previous calculations were performed with assuming the BO approximation [13, 24]. Even though the adiabatic correction was included in those previous calculations, the results are not as accurate as obtained in the present work. The non-Born–Oppenheimer nonrelativistic wave functions obtained for ^{7}LiH with the largest basis sets generated for the two lowest states in this work are used to calculate some expectation values of the interparticle distances and their squares. The expectation values of the interparticle Dirac delta functions are also calculated. The results are shown in Table 4. In addition to the calculated

Table 2. Comparison of the calculated and experimental $0 \rightarrow 1$ transition energies (ΔE) of ^{7}LiH in cm^{-1}.

Basis	$\Delta E_{\rm nr}$	$\Delta E_{\rm nr+rel}$	$\Delta E_{\rm nr+rel+QED}$
11000	1359.877	1359.907	1359.901
13000	1359.829	1359.867	1359.858
15000	1359.790	1359.841	1359.829
17000	1359.745	1359.800	1359.789
∞	1359.696(62)	1359.748(64)	1359.739(64)
FCI [5][a]			1359.66
(MR-CISD+Q) [12][b]			1358.64(549)
FC LSE [42][c]			1356.87
(MR-CISD+Q_p) [13][d]			1361.03
(MR-CISD+Q_p) + adiabatic + rel [13][e]			1360.30
BO-ECG [24][f]			1360.24
BO-ECG+ad [24][g]			1359.77
Experimental [43][h]			1359.71(20)
Experimental [2]			1359.71
Experimental [44]			1359.7085(20)

Note: [a]Full Configuration-Interaction/(42 s18 p10 d).
[b]The internally contracted configuration interaction in the single and double space (MRCISD) levels with four electrons distributed among the five orbitals (MRCISD+Q) arising from the 1 s, 2 s and 2 p atomic orbitals in the multiconfigurational self-consistent-field (MCSCF) part of the calculations has been used.
[c]Free complement (FC) local Schrödinger equation (LSE) method.
[d]Multireference configuration interaction with singles and doubles with Pople-variant correction (MR-CISD+Q_p)/cc-pwCVXZ (X = Q, 5, 6).
[e]The 'adiabatic' represents the sum of the diagonal and mass-dependent diagonal Born–Oppenheimer, BO breakdown corrections; 'rel' represents relativistic Mass–Velocity and Darwin contributions.
[f]Born–Oppenheimer calculations with 2400 ECG basis functions.
[g]In the BO-ECG calculations, the adiabatic correction was included.
[h]The largest uncertainty which was estimated by authors.

Table 3. Comparison of the calculated and experimental dissociation energies (D) of ^{7}LiH in cm^{-1}.

State	Basis	$D_{\rm nr}$	$D_{\rm nr+rel}$	$D_{\rm nr+rel+QED}$
$v = 0$	11000	19590.097	19589.651	19589.668
	13000	19590.120	19589.681	19589.695
	15000	19590.142	19589.716	19589.727
	17000	19590.164	19589.739	19589.750
	∞	19590.176(12)	19589.751(12)	19589.762(12)
	(MR-CISD+Q_p) [13][a]			19606.7
	(MR-CISD+Q_p)+ adiabatic + rel [13][b]			19593.8
	BO-ECG+AD [24][c]			19590.1
	Experimental [2]			19589.8(3)
$v = 1$	11000	18230.221	18229.744	18229.767
	13000	18230.292	18229.814	18229.837
	15000	18230.351	18229.876	18229.898
	17000	18230.419	18229.939	18229.960
	∞	18230.480(61)	18230.002(63)	18230.023(63)

Notes: [a]Multireference configuration interaction with singles and doubles and with Pople-variant corrections (MR-CISD+Q_p)/cc-pwCVXZ (X = Q, 5, 6).
[b]The 'adiabatic' represents the sum of the diagonal and mass-dependent diagonal Born–Oppenheimer, BO breakdown corrections; 'rel' represents relativistic Mass–Velocity and Darwin contributions.
[c]In the BO-ECG calculations, the adiabatic correction was included.
[d]The inverted perturbation approach with adiabatic correction.

Table 4. Results of the non-BO ECG calculations for ^{7}LiH performed in this work. The average values of the interparticle distances ($\langle r_{ij} \rangle$), the most probable distance between Li and H nuclei ($r^{\mathrm{mp}}_{\mathrm{Li-H}}$), obtained with the largest basis sets generated in this work for ^{7}LiH. The results are compared with the calculated equilibrium bond lengths (r_e), and the vibrationally averaged bond lengths for the $v = 0$ and $v = 1$ states (the $\langle r_0 \rangle$ and $\langle r_1 \rangle$ values, respectively), obtained in the BO ECG [24], MRCISD+Q [12], and exFCI [46] calculations. All values are in atomic units.

		$v = 0$	$v = 1$
$\langle r_{\mathrm{Li-H}} \rangle$		3.06103822(10)	3.15499498(115)
$\langle r_{\mathrm{Li-H}} \rangle$	BO-ECG [24] [a]	3.06029188	3.15422580
$\langle r_{\mathrm{Li-H}} \rangle$	BO-CCSD(T) [b]	3.01121476	3.10857192
$\langle r_{\mathrm{Li-e}} \rangle$		1.97193362(9)	2.00700575(43)
$\langle r_{\mathrm{H-e}} \rangle$		2.56510499(19)	2.62428379(42)
$\langle r_{\mathrm{e-e}} \rangle$		2.95594018(21)	3.00879600(42)
$\langle r^2_{\mathrm{Li-H}} \rangle$		9.4197061(10)	10.1046534(74)
$\langle r^2_{\mathrm{Li-e}} \rangle$		6.5857455(13)	6.8665877(20)
$\langle r^2_{\mathrm{H-e}} \rangle$		7.7452199(19)	8.1711883(15)
$\langle r^2_{\mathrm{e-e}} \rangle$		10.9660755(26)	11.3948241(15)
r_e	BO-ECG [24][a]	3.0141(6)	
r_e	BO-CCSD(T) [b]	3.039	
r_e	MCSCF-CI-4 [9][c]	3.025	
r_e	FC LSE [42][d]	3.013	
r_e	MR-CISD+Q$_p$ [13][e]	3.01390	
r_e	(MR-CISD+Q$_p$)+adiabatic + rel [13][f]	3.01375	
r_e	exFCI [46][g]	3.028	
r_e	Experiment [47]	3.016	
r_e	Experiment [2]	3.015217	
r_e	Experiment [48]	3.01394640(32)	
r_e	Experiment [44]	3.01523597(9)	

Notes: [a]Born–Oppenheimer calculations with 2400 ECG basis functions [24].
[b]Coupled-cluster singles and doubles and noniterative triple excitations. The aug-cc-pV5Z [49] basis set has been used. The calculations were carried out using the Gaussian 16 software package [50].
[c]The configuration-interaction with single and double replacements from MCSCF reference state.
[d]Free complement (FC) local Schrödinger equation (LSE) method.
[e]Multireference configuration interaction with singles and doubles method with Pople-variant correction (MR-CISD+Q$_p$)/cc-pwCVXZ (X = Q, 5, 6).
[f]The 'adiabatic' represents sum of the diagonal and mass-dependent diagonal Born–Oppenheimer, BO breakdown corrections; 'rel' represents relativistic Mass–Velocity and Darwin contributions.
[g]The all-electron extrapolated FCI were used.

values in the present work, some other quantities which were obtained in the BO calculations, such as r_e, r_0 and r_1, are shown in the table. Due to explicitly including the coupling between the motion of electrons and the nuclei in the present non-BO calculations, the agreement between the values obtained in the present work and those obtained in the previous BO calculations is not particularly good. This is consistent with the conclusions expressed in some previous BO works that adiabatic and non-adiabatic effects are not negligible in calculating properties of diatomic molecules [13,45].

4. Summary

In this work, we present the most accurate non-Born–Oppenheimer calculations performed thus far for the LiH molecule in the ground and first vibrationally excited states. All-particle explicitly correlated Gaussian basis functions are used in the calculations. The calculations involve extensive optimisation of the nonlinear parameters of the Gaussians performed separately for each state. The basis set for each state is grown to include up to 17,000 functions. The nonrelativistic non-BO wave functions are used to calculate the leading relativistic and QED corrections. The corrections are added to the non-BO nonrelativistic energies and results are used to calculate the ^{7}LiH dissociation energies for the two states, as well as the $0 \rightarrow 1$ transition energy. The obtained results are well within the uncertainties of the available experimental data and can serve as a useful benchmark for future theoretical studies and spectroscopic measurements of LiH.

The linear and non-linear parameters of all non-BO wave functions for the two considered states of the LiH molecule generated in this work will be provided to the interested reader upon request.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

This work has been supported by Nazarbayev University (faculty development grant no. 021220FD3651) and the National

Science Foundation (grant no. 1856702). L.A. acknowledges the support of the Centre for Advanced Study (CAS), the Norwegian Academy of Science and Letters, in Oslo, Norway, which funds and hosts our research project titled: Attosecond Quantum Dynamics Beyond the Born–Oppenheimer Approximation, during the 2021–22 academic year. The authors are grateful to the University of Arizona Research Computing and Nazarbayev University Academic Computing for providing computational resources for this work.

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