

# Nonrelativistic molecular quantum mechanics without approximations: Electron affinities of LiH and LiD

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We took the complete nonrelativistic Hamiltonians for the LiH and LiH<sup>-</sup> systems, as well as their deuterated isotopomers, we separated the kinetic energy of the center of mass motion from the Hamiltonians, and with the use of the variational method we optimized the ground-state nonadiabatic wave functions for the systems expanding them in terms of *n*-particle explicitly correlated Gaussian functions. With 3600 functions in the expansions we obtained the lowest ever ground-state energies of LiH, LiD, LiH<sup>-</sup>, and LiD<sup>-</sup> and these values were used to determine LiH and LiD electrons affinities (EAs) yielding 0.330 30 and 0.327 13 eV, respectively. The present are the first high-accuracy *ab initio* quantum mechanical calculations of the LiH and LiD EAs that do not assume the Born-Oppenheimer approximation. The obtained EAs fall within the uncertainty brackets of the experimental results. © 2004 American Institute of Physics.

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## I. INTRODUCTION

The LiH<sup>-</sup> systems is the smallest negative ion of a stable molecule and the binding energy of the excess electron in this system has been the subject of several investigations both experimental<sup>1-4</sup> and theoretical.<sup>5-9</sup> The only smaller diatomic anion, according to the theoretical calculations<sup>10,11</sup> is HeH<sup>-</sup>, but its parent neutral system HeH is known to be unbound. Since LiH<sup>-</sup> contains only five electrons it can be calculated with the highest levels of theory available for molecular systems. Thus, from the fundamental view point it represents an excellent model system for testing the accuracy of the calculations. The theoretical interest in the LiH<sup>-</sup> has increased since the electron affinity (EA) of LiH and its deuterated counterpart LiD were measured with the use of the photoelectron spectroscopy by Bowen and co-workers.<sup>4</sup> The adiabatic electron affinities of <sup>7</sup>LiH and <sup>7</sup>LiD determined in that experiment were 0.342±0.012 eV for the former and 0.337±0.012 eV for the latter system. The appearance of these data posed a challenge for theory to reproduce those values in rigorous calculations based on the first principles. Since the two systems are small, it has been particularly interesting to see if the experimental EAs can be reproduced in calculations where the Born-Oppenheimer (BO) approximation is not assumed. The present work undertakes this challenge.

Even though ten years has passed since the paper of Bowen *et al.* was published, the theory based on the BO approximation, except for one very recent multireference configuration interaction (MRCI) calculation by Chang *et al.*,<sup>9</sup> has been unable to produce a value of the LiH adiabatic electron affinity that falls within the experimental un-

certainty bracket. This inability seems somewhat odd, since there is nothing particularly unusual about and fundamentally difficult to describe in the LiH<sup>-</sup>/LiH system. Since the LiH molecule is a polar system (Li<sup>δ+</sup>-H<sup>δ-</sup>) an excess electron in the process of attachment localizes on the electropositive alkali atom in a nonbonding orbital of the neutral molecule. In essence, one should be able to describe this situation well with such methods as the coupled cluster (CO) approach [with single (S), double (D), and triple (T) excitations] or with MRCI method provided that a sufficiently complete basis set is used. However, despite the use of the most advanced techniques and extended basis sets the calculated values (CCSDT of 0.327 eV<sup>7,8</sup> and MRCI of 0.319 eV<sup>7</sup>) have come short of the experimental result.

Over the last decade, we have developed methods in our laboratory which allow us to perform calculations on small atomic and molecular systems without resorting to the BO approximation regarding the separation of the motions of the nuclei and electrons.<sup>12</sup> The only approximation we have made in our approach was the neglect of the relativistic effects. One of the first applications that we ran were the calculations of the electron affinities of H, D, and T (Ref. 13) where we obtained essentially exact agreement with the experiment. The high accuracy of the calculations was achieved by expanding the wave functions of H<sup>-</sup>, D, and T<sup>-</sup> in terms of explicitly correlated Gaussian functions dependent on the interparticle distances (see the following section). Those calculations convinced us that also for electron affinities of small molecules we should be able to obtain very accurate results. However, implementation of a new basis set had to be carried out,<sup>14,15</sup> a considerable effort had to be made in parallelizing the computer code, and access had to

be gained to a large-scale parallel computer system before the calculations of the LiH and LiD electron affinities could be attempted. In the recent months several powerful, state-of-the-art, parallel computer clusters became available to us and we decided to pursue the LiH<sup>-</sup>/LiH and LiD<sup>-</sup>/LiD calculations. As it will be shown here, the electron affinity values obtained in the calculations fall within the uncertainty bracket of the experimental EA values determined by Bowen *et al.*

We should mention that we do not expect the nonadiabatic effects to play a significant role in the LiH and LiD electron affinity calculations. However, by applying the non-BO approach we can directly determine the total energies of the anion and the neutral system in one-step calculations, and we do not need to resort to calculating the electronic potential energy curves for the anion and the neutral first and using them for calculating their nuclear vibration energies in the next step, as it is done in the BO approach. Thus, using the non-BO method we not only make the calculation free of any artifacts that may result from the two-step procedure used in the BO approximation, but we also obtain total and relative energies that, if the basis sets become more complete, approach the true nonrelativistic limits of those quantities free of any approximations.

## II. THE HAMILTONIAN

In the approach we use, we begin with the total nonrelativistic Hamiltonian for a molecular system in the laboratory Cartesian coordinate system. Both the electrons and the nuclei are included in the Hamiltonian. The total number of particles (i.e., the electrons and the nuclei) is set to be  $n + 1$  and their masses, charges, and positions are denoted as  $M_i$ ,  $Q_i$ , and  $\mathbf{R}_i$ , respectively, where  $i = 1, \dots, n + 1$ . The lab-frame Hamiltonian has the following form:

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

where  $R_{ij} = |\mathbf{R}_j - \mathbf{R}_i|$  are interparticle distances. We then make a transformation to separate the center-of-mass Hamiltonian from the rest, thereby reducing the  $n + 1$ -particle problem to an  $n$ -pseudoparticle problem described by the internal Hamiltonian  $\hat{H}$ . In this transformation we place a heavy particle (particle 1 with mass  $M_1$ ; this particle is usually the heaviest nucleus) at the center of the internal coordinate system and we refer the other particles to that center particle using the position vectors  $\mathbf{r}_i$  defined as  $\mathbf{r}_i = \mathbf{R}_{i+1} - \mathbf{R}_1$ . The resulting internal Hamiltonian is

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

This Hamiltonian describes a system containing a heavy particle at the origin of the coordinates with charge  $q_0 = Q_1$  and  $n$  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 second term in the parentheses is the

mass polarization term, which arises from the transformation of the lab-frame coordinate system to the internal coordinate system and which couples the motion of all the particles. In the potential energy terms  $r_i$  and  $r_{ij}$  are defined as  $r_i = |\mathbf{r}_i|$  and  $r_{ij} = |\mathbf{R}_{j+1} - \mathbf{R}_{i+1}| = |\mathbf{r}_j - \mathbf{r}_i|$ .

The model of the molecule described by Hamiltonian (2) resembles an atom as noted by Monkhorst.<sup>16</sup> The pseudoparticles are moving in the spherically symmetric potential generated by the particle placed at the center of the internal coordinate system (an analogy of the atomic nucleus). The pseudoparticles are analogical to electrons. The main difference between this model and an atom is that the internal particles in an atom are all electrons and in the “molecular atom” or “atomic molecule” the internal particles may be both electrons and nuclei (or, as we should more correctly say, pseudoparticles resembling the electrons and the nuclei). Formally this difference manifests itself in the effective masses of the pseudoparticles, in their charges, and in the way the permutational symmetry is implemented in the wave function.

In the present calculations of LiH<sup>-</sup>/LiH and LiD<sup>-</sup>/LiD the lithium atom was placed in the center of the internal coordinate system. For LiH and LiH<sup>-</sup> the internal Hamiltonian described the motion of five and six pseudoparticles, respectively.

## III. THE WAVE FUNCTION

In the calculations of the H, D, and T electron affinities, the wave functions describing the internal ground states of the anions were expanded in terms of following explicitly correlated Gaussians:

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

The above function is a one-center spherically symmetric correlated Gaussian with exponential coefficients forming the symmetric matrix  $A_k$ ,  $\mathbf{r}$  is a  $3n \times 1$  vector of the internal cartesian coordinates  $\mathbf{r}_i$  of the  $n$  pseudoparticles, and  $I_3$  is the  $3 \times 3$  identity matrix.  $\phi_k$  are rotationally invariant functions as required by the symmetry of the internal ground-state problem described by the Hamiltonian (2). This internal ground state corresponds to the total (electron and nuclei) rotational spatial quantum number equal to zero.

To describe bound stationary states of the system, the  $\phi_k$ 's have to be square-normalizable functions. The square integrability of these functions may be achieved using the following general form of an  $n$ -particle correlated Gaussian with the negative exponential of a positive definite quadratic form in the  $3n$  variables:

$$\phi_k = \exp[-\mathbf{r}'(L_k L_k' \otimes I_3)\mathbf{r}]. \quad (4)$$

Here  $L_k$  is an  $n \times n$  lower triangular matrix of rank  $n$  whose elements may vary in the range  $[-\infty, \infty]$ .

Although the basis functions (3) are good for small atoms they are not good for molecules because they cannot well describe the nucleus-nucleus correlation effect, i.e., the wave functions of different nuclei having very small overlap due to their repulsion and heavy masses. In order to describe this effect in diatomic molecules we introduced a Gaussian

basis set involving functions with preexponential multipliers consisting of the internuclear distance  $r_1$  raised to integer, even, non-negative powers,  $m_k$ :<sup>14,15</sup>

$$\phi_k = r_1^{m_k} \exp[-\mathbf{r}'(L_k L_k' \otimes I_3)\mathbf{r}]. \quad (5)$$

The presence of  $r_1^{m_k}$  in Eq. (5) makes the function peak not at the origin as Eq. (4) does but at some distance away from the origin. This distance depends on the value of  $m_k$  and on the exponential parameters  $L_k$ . To describe a diatomic system the maximum of  $\phi_k$  in terms of  $r_1$  should be around the equilibrium internuclear distance of the system. Since their implementation basis functions (5) have been applied in several very accurate non-BO calculations of molecular systems.<sup>15,17-19</sup> In this work we used them to determine the electron affinities of LiH and LiD.

In accordance with the Pauli principle, the basis functions (5) must have proper permutational symmetry so that the product of the spatial and spin part is antisymmetric with respect to interchanging the electron labels. In this work the antisymmetrization was implemented using the standard approach based on Young operators (see, for example, Ref. 20).

#### IV. THE VARIATIONAL METHOD

The ground-state wave function in the present calculations for each of the considered systems, i.e., LiH, LiD, LiH<sup>-</sup>, and LiD<sup>-</sup>, was obtained by directly minimizing the Rayleigh quotient:

$$E(\{c_k\}, \{m_k\}, \{L_k\}) = \min_{\{c_k\}, \{m_k\}, \{L_k\}} \frac{c' H(\{m_k\}, \{L_k\}) c}{c' S(\{m_k\}, \{L_k\}) c} \quad (6)$$

with respect to the linear coefficients  $\{c_k\}$  of the wave function expansion in terms of the basis functions (5), and with respect to the nonlinear exponential parameters  $\{L_k\}$  and pre-exponential powers  $\{m_k\}$  of the basis functions.

The convergence of variational calculations involving correlated Gaussians strongly depends on how one selects the nonlinear parameters in the Gaussian exponentials. Optimization of the parameters usually leads to a significant improvement of the results. Due to a usually large number of basis functions in non-BO calculations that is required to achieve high accuracy of the results, and, consequently, a larger number of the exponential parameters (21 and 15 different  $L_k$  elements for each basis function in case of LiH<sup>-</sup> and LiH, respectively), the optimization represents a serious computational problem. The two most commonly applied approaches to the parameter optimization are: a full optimization, which is very effective when the analytical gradient of the energy functional with respect to the parameters is available; and the method based on a stochastic selection of the parameters.

In the present calculations we applied a hybrid method that combines the gradient-based optimizations with the stochastic selection method. In this approach we first generated a relatively small basis set for each of the studied systems using the full gradient optimization that provided a good starting point for the next step of the optimization. In this next step we applied the following strategy. We incrementally increased the size of the basis set by including one

function at a time with randomly selected values of the nonlinear parameters and of the preexponential power. After including a function into the set, we first optimized the power of its preexponential factor using the finite-difference approach and next we optimized the nonlinear parameters in its exponent with the analytical-gradient approach. After adding several new basis functions using this approach (this number was 25 in most cases) the whole basis was reoptimized by means of the gradient approach applied consecutively to each basis function, one function at a time. This continued until the number of basis functions reached 3600 for each considered system. Three thousand and six hundred was a practical limit of the number of functions that we could use with the computer resources available to us for the calculations. In the final phase of the calculations those resources consisted of an Athlon MP Linux Beowulf cluster and HP Alpha GS1280 supercomputer located at the University of Arizona Center of Computing and Information Technology; on each of the systems we used 32 processors for the calculations.

#### V. MASS VALUES

In the calculations we used the following values for the nuclear masses:  $m_{\text{Li}} = 12\,786.3933m_e$  (<sup>7</sup>Li isotope),  $m_{\text{D}} = 3670.482\,965\,2m_e$ ,  $m_{\text{H}} = 1836.152\,672\,61m_e$  taken from Ref. 21, where  $m_e$  stands for the mass of the electron.

#### VI. RESULTS AND DISCUSSION

The convergence of the energy values for LiH, LiD, LiH<sup>-</sup>, and LiD<sup>-</sup> in terms of the number of the basis functions is shown in Table I. In Table II we show the values of the LiH and LiD electron affinities calculated as the difference of the energies of the anion and the neutral system for all lengths of the basis set for which the total energies are reported. A question can be raised whether it is appropriate to use the total energies obtained with the same length of the basis set for LiH<sup>-</sup> and LiH (or LiD<sup>-</sup> and LiD) in the electron affinity calculation. Since LiH<sup>-</sup> has one more electron than LiH, it should require more basis functions for LiH<sup>-</sup> than for LiH to achieve a similar level of accuracy of the results. This is indeed showing in the convergence of the results presented in Table I. Certainly the 3600-term energy for LiH is better converged than the 3600-term energy for LiH<sup>-</sup>. It should be mentioned that the LiH and LiD variational energies obtained in this work are the lowest non-BO ground-state energies ever obtained for these systems. The same is true about the LiH<sup>-</sup> and LiD<sup>-</sup> energies, though in this case the final values are not as tightly converged as the energies for LiH and LiD. Also, no one has ever attempted a variational, high-accuracy, non-BO calculation of the ground state of a five-electron system such as LiH<sup>-</sup> or LiD<sup>-</sup>.

Now returning to the question concerning the procedure used in the EA calculation in this work, the justification of our approach is as follows: First of all, we decided to carry out the calculations for all the systems considered in this work as accurately as the resources available to us permitted. We should mention that the work presented here represents several months of continuous computing. Second, since the

TABLE I. Nonadiabatic variational ground-state energies of the  $\text{LiH}^-$ ,  $\text{LiH}$ ,  $\text{LiD}^-$ , and  $\text{LiD}$  molecules obtained with different basis set sizes. All energies in atomic units.

Basis size	LiH	$\text{LiH}^-$	LiD	$\text{LiD}^-$
1000	-8.066 320 55	-8.067 254 33	-8.077 781 28	-8.078 598 43
1200	-8.066 344 54	-8.067 282 73	-8.077 947 15	-8.078 755 07
1400	-8.066 364 91	-8.067 305 93	-8.078 079 91	-8.078 886 51
1600	-8.066 382 95	-8.067 328 05	-8.078 220 84	-8.079 034 83
1800	-8.066 394 98	-8.067 342 16	-8.078 305 36	-8.079 122 38
2000	-8.066 404 08	-8.067 353 33	-8.078 375 66	-8.079 198 77
2200	-8.066 410 99	-8.067 361 28	-8.078 427 11	-8.079 255 49
2400	-8.066 415 54	-8.067 366 13	-8.078 460 14	-8.079 290 81
2600	-8.066 420 68	-8.067 372 08	-8.078 487 53	-8.079 319 85
2800	-8.066 423 53	-8.067 375 14	-8.078 510 89	-8.079 343 70
3000	-8.066 425 81	-8.067 377 49	-8.078 529 33	-8.079 362 48
3200	-8.066 427 87	-8.067 379 62	-8.078 544 06	-8.079 377 59
3400	-8.066 429 41	-8.067 381 23	-8.078 558 05	-8.079 391 62
3600	-8.066 430 70	-8.067 382 51	-8.078 568 87	-8.079 404 45

variational approach has been used in this work and the  $\text{LiH}$  ( $\text{LiD}$ ) energy at a particular basis set size is better converged than the  $\text{LiH}^-$  ( $\text{LiD}^-$ ) energy, the calculated electron affinity is always lower than the result would be in the limit of the complete basis set. Thus, by calculating the EA at the basis set with the same size for the anion and for neutral system and by incrementally increasing the size of the basis, we could monitor the EA convergence and be sure that all the EA values we calculated including the final value (this being the 3600-term result) are lower bounds to the true EA.

With this in mind, let us now look at the results. As shown in Table II our best results for  $\text{LiH}$  and  $\text{LiD}$  electron affinities obtained with the 3600-term expansions of the wave functions for  $\text{LiH}^-/\text{LiH}$  and  $\text{LiD}^-/\text{LiD}$  are 0.330 30 and 0.327 13 eV, respectively. Even though, as stated, both values represent lower bounds to the true EAs, they both are within the uncertainty brackets of the experimental results of  $0.342 \pm 0.012$  eV ( $\text{LiH}$ ) and  $0.337 \pm 0.012$  eV ( $\text{LiD}$ ) obtained by Bowen and co-workers.<sup>4</sup> It should be added that we have estimated extrapolated values of the total energies of  $\text{LiH}^-/\text{LiH}$  and  $\text{LiD}^-/\text{LiD}$  at the infinite basis set limit and from those we calculated EAs. Though, we do not show here

TABLE II. Convergence of the electron affinities of  $\text{LiH}$  and  $\text{LiD}$  (in eV) in terms of the number of the basis functions.

Basis size	LiH	LiD
1000	0.311 86	0.308 69
1200	0.315 72	0.312 18
1400	0.318 78	0.315 12
1600	0.322 13	0.318 56
1800	0.324 10	0.320 56
2000	0.325 76	0.322 33
2200	0.326 98	0.323 66
2400	0.327 75	0.324 49
2600	0.328 36	0.325 12
2800	0.328 91	0.325 68
3000	0.329 35	0.326 13
3200	0.329 70	0.326 48
3400	0.330 04	0.326 82
3600	0.330 30	0.327 13
Experiment <sup>a</sup>	$0.342 \pm 0.012$	$0.337 \pm 0.012$

<sup>a</sup>Reference 4.

those extrapolated values due to obvious uncertainties in the extrapolation procedure, we can say that, though they moved the predicted EAs slightly more towards the centers of the experimental uncertainty brackets, they still tend to be located at the lower ends of the brackets. Whether one should attribute any significance to this finding can only be answered by a more accurate experiment. Also, if a new generation of parallel computers become available, the present non-BO calculations can be carried out to a higher precision.

In the calculations, the powers  $m_k$  in the preexponential factors in the basis functions (5) were allowed to vary in the interval of 0–200 and, as mentioned, only even values were used. The obtained distributions of  $m_k$ 's have the mean values of 70.0, 74.1, 67.6, 67.9, and the standard deviations of 49.7, 50.4, 49.3, 49.7 for  $\text{LiH}$ ,  $\text{LiD}$ ,  $\text{LiH}^-$ , and  $\text{LiD}^-$ , respectively. A slightly higher mean power for  $\text{LiD}$  than for  $\text{LiH}$  can be explained by a more localized vibrational component of the wave function for the former than for the latter system. Lower mean powers for the anions than for the neutral systems result from two opposing effects: First, the bond lengths for the anions are slightly longer than for the neutral counterparts (see the following paragraph) which should require larger powers. Second, due to the weakening of the bonds in the anions, the vibrational components of their wave functions become more delocalized resulting in lowering of the powers. Apparently the second effect dominates over the first one.

Finally in Table III we present expectation values of the internuclear distance and its square for  $\text{LiH}$ ,  $\text{LiD}$ ,  $\text{LiH}^-$ , and  $\text{LiD}^-$ . Here we see trends that can be easily understood considering that the attachment of an excess electron weakens slightly the Li-H bond and that increasing the mass of H by

TABLE III. Expectation values of the internuclear distance,  $r_1 \equiv r_{\text{LiH}}$ , and its square (in a.u.) calculated with the 3600-term basis sets.

System	$\langle r_1 \rangle$	$\langle r_1^2 \rangle$
$\text{LiH}^-$	3.214 708	10.393 91
$\text{LiH}$	3.061 047	9.419 733
$\text{LiD}^-$	3.199 737	10.283 62
$\text{LiD}$	3.049 131	9.334 349

switching to D results in making the vibrational component of the total wave function more localized resulting in a slight contraction of the average length of the bond. This contraction is very similar in going from LiH and LiD and from  $\text{LiH}^-$  to  $\text{LiD}^-$ .

## VII. SUMMARY

To summarize, in this work we applied explicitly correlated Gaussians with preexponential factors dependent on powers of the internuclear distance to determine the electron affinities of LiH and LiD in the rigorous quantum-mechanical variational calculations based on first principles without assuming the Born-Oppenheimer approximation. The only approximation was the neglect of the relativistic effects. Very accurate, the best to date, ground-state energies were obtained for LiH, LiD,  $\text{LiH}^-$ , and  $\text{LiD}^-$ . The key point that allowed us to obtain high precision results was the combination of stochastic selection of the basis functions with the use of the analytical gradient for optimization of the Gaussian nonlinear parameters. The calculations place the predicted EAs of LiH and LiD within the uncertainty brackets of the results obtained with the photoelectron spectroscopy experiments of Bowen and co-workers.<sup>4</sup>

In their paper Chang *et al.*<sup>9</sup> examined the disagreement between the experimental assignment of Sarkas *et al.*<sup>4</sup> and their theoretical results regarding the vibrational level spacing in the ground electronic state of the LiH anion and proposed a theoretically motivated reinterpretation of the Sarkas *et al.* experimental photodetachment spectra. The problem of the vibrational level spacing can be addressed in our non-BO calculations because the use of fully spherically symmetric basis set allows us to calculate not only the ground state but also all bound excited states with the total rotational quantum number equal to zero (i.e., the vibrational states). Since in the calculations that do not assume the BO approximation these states may include coupling between the electronic and vibrational degrees of freedom, the use of the term “vibrational” to describe these states is approximate. While in the lower lying states this coupling is usually very small, it may significantly increase in higher states (such an effect occurs, for example, in the  $\text{HD}^+$  ion).<sup>22</sup> Excited state calculations

using our non-BO approach are more time consuming but almost equally accurate as the ground-state calculations, as we demonstrated in the recent work on  $\text{H}_2$ .<sup>18</sup> When more computer resources become available to us, we will attempt the calculations of the lowest excited (vibrational) states of LiH, LiD,  $\text{LiH}^-$ ,  $\text{LiD}^-$  to verify the reassignment of the Sarkas *et al.* experimental spectra proposed by Chang *et al.*

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