

## Valence and excited states of $\text{LiH}^-$

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Valence and excited dipole-bound states of the  $\text{LiH}^-$  anion are calculated with the recently developed electron-attachment equation-of-motion coupled-cluster technique. It is found that the first dipole-bound state of  $\text{LiH}^-$  corresponds to the second dissociation channel  $\text{LiH}^- \rightarrow \text{Li}^-(^1S) + \text{H}(^2S)$ . The second (excited) dipole-bound state of  $\text{LiH}^-$  is below the neutral ground-state potential energy curve only for some range of the Li-H internuclear distance. This state appears at bond lengths larger than  $\approx 2.0 \text{ \AA}$  and decays at Li-H distances longer than  $\approx 4.2 \text{ \AA}$ , where the dipole moment of LiH becomes smaller than the critical value of 2.5 D. The adiabatic electron affinity of LiH calculated at the coupled-cluster level with the iterative inclusion of all single, double, and triple excitations and a large atomic natural orbital basis set is 0.327 eV, almost matching the recently obtained experimental value of  $0.342 \pm 0.012 \text{ eV}$ . [S1050-2947(97)04612-X]

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### I. INTRODUCTION

A stationary dipole field can bind an electron [1–7] if the dipole moment is greater than the critical value of 1.625 D, which corresponds to the  $E=0$  solution of the Schrödinger equation

$$\hat{H}\Psi(\mathbf{r}) = \left[ -\frac{\hbar^2}{2m}\nabla^2 + eq\left(\frac{1}{r_q} - \frac{1}{r_{-q}}\right) \right] \Psi(\mathbf{r}) = E\Psi(\mathbf{r}), \quad (1)$$

where the dipole system consists of fixed point charges  $\pm q$  separated by a distance  $R$ ,  $r_q$  and  $r_{-q}$  are the distances of the electron from the positive and negative charges of the dipole whose moment is  $\mu = qR$ . The energy  $E$  depends only on the product  $qR$ , i.e., the dipole moment, and not on  $q$  and  $R$  separately [8].

Garrett [9–11] considered the influence of rotations on the critical value having added to Eq. (1) the rotational operator  $\hat{H}_{\text{rot}} = (\hbar^2/2I)\hat{J}^2$  (where  $I$  is the moment of inertia of the rotating dipole,  $\hat{J}^2$  is the operator of the square total angular momentum) and obtained the solutions to the equation

$$\left( \hat{H}_{\text{rot}} - \frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}, \mathbf{s}) \right) \Psi(\mathbf{r}, \mathbf{s}) = E\Psi(\mathbf{r}, \mathbf{s}) \quad (2)$$

as functions of  $I$  and  $R$ . Here,  $\mathbf{r}$  measures the position of the electron with respect to the center of the dipole,  $V(\mathbf{r}, \mathbf{s})$  is the interaction potential of the electron with the dipole charges  $\pm q$  separated by the distance  $R=2s$ , and  $\pm s$  designates the nuclear positions relative to the center of the dipole with the unit vector  $\hat{s}$  pointing along the internuclear axis.

Due to coupling with the orbital angular momentum of the electron, the rotor angular momentum is no longer a constant of motion; therefore the operator added to Eq. (2) contributes some positive quantity to the eigenvalue  $E$  and the

overall binding energy of the electron decreases. This leads to an increase in the critical value of the dipole moment up to  $\approx 2.0 \text{ D}$ . On the basis of Garrett's approach and qualitative speculations, Crawford [12] concluded "that any real gas phase molecule or radical with  $\mu \geq 2.0 \text{ D}$  probably can bind an extra electron, and almost certainly if  $\mu > 2.5 \text{ D}$ ." The recent experimental [13] and theoretical studies [14] confirmed the threshold value of 2.5 D: polar molecules with dipole moments greater than 2.5 D are found to bind an extra electron and form dipole-bound states, whereas no such state was found for formaldehyde having a dipole moment of 2.33 D.

The number of excited dipole-bound states is infinite in a stationary dipole field whose dipole moment is greater than 1.625 D. However, this number is finite and depends on the dipole moment value if the dipole is rotating, as simulated by more realistic models of Garrett [9] and Rudge [15].

It was found in theoretical studies [16,17] based on the use of Eq. (2) that a "moment in excess of  $\approx 4.5 \text{ D}$  is required to sustain two electronically excited states." Another study [18] predicted a value of  $\approx 5 \text{ D}$  to be required in order to form the first excited dipole-bound state and almost 10 D to form the second excited dipole-bound state.

The situation in real molecules can be different. Nonetheless, the results of many-body perturbation theory (MBPT) calculations [14] support a threshold value of about 2.5 D for the first dipole-bound state and confirm the magnitude of the dipole moment of a neutral system is a determining factor for the number of dipole-bound states in the corresponding anion and their binding energies. Hence the critical values of the dipole moment that are required to support the first, second, etc., excited dipole-bound states are definitely of interest.

Computationally, the first excited dipole-bound states have been found for the  $\text{LiH}^-$ ,  $\text{LiF}^-$ ,  $\text{LiCl}^-$ ,  $\text{NaH}^-$ ,  $\text{NaF}^-$ ,  $\text{NaCl}^-$ ,  $\text{BeO}^-$ , and  $\text{MgO}^-$  anions [19–23], formed by polar molecules whose dipole moments exceed 5.8 D. According to the Koopman theorem (KT) approximation,  $\text{LiH}^-$  has four excited dipole-bound states [24] at the equilibrium geometry of LiH, whose dipole moment is 5.88 D; however, correlated calculations are required [25] in order to check the validity of this prediction.

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The recently developed electron-attachment equation-of-motion coupled-cluster (EA-EOMCC) method [26] presents a very convenient way for simultaneously estimating *all* the vertical attachment energies of an extra electron to a target molecule at the coupled-cluster level with single and double excitations (CCSD), which is normally a difficult problem [27]. Since the equilibrium geometrical configuration of a stationary dipole-bound state of an anion does not differ substantially from the ground-state configuration of the corresponding neutral parent [28], the vertical and adiabatic attachment energies of an extra electron in a stationary dipole-bound state are nearly the same.

The aim of the present communication is to determine the number of excited dipole-bound states in LiH<sup>-</sup> at the correlated level of theory and to trace the behavior of these states when stretching the Li—H bond length. Also, in view of the recent accurate measurement of the adiabatic electron affinity  $A_{e,ad}$  of LiH by laser photodetachment spectroscopy [29], it is interesting to compare the experimental data to the results of coupled-cluster calculations for the ground states of LiH and LiH<sup>-</sup>.

## II. COMPUTATIONAL DETAILS

The calculations have been performed with the ACES II suite of programs [30] using the large (Li:  $14s9p4d3f/7s6p4d3f$ ; H:  $8s4p3d/6s4p3d$ ) atomic natural orbital basis of Widmark, Malmqvist, and Roos (WMR) [31], which proved to be reliable in such a difficult case as the electron affinity of the NH radical [32]. The ground states of LiH( $X^1\Sigma^+$ ) and LiH<sup>-</sup>( $X^2\Sigma^+$ ) were optimized at the infinite-order coupled-cluster level with all single and double excitations [33] plus non-iterative inclusion of triple excitations [CCSD(T)] [34–36]. The total energies were recalculated at the CCSDT [37] level with the iterative inclusion of all triples. The EA-EOMCC calculations for the excited dipole-bound states of LiH<sup>-</sup> have been performed with three bases consisting of the WMR basis and sets of diffuse functions, namely, set I: WMR plus seven ‘‘standard’’  $sp$  shells (the exponents are 0.001, 0.0005, 0.0001, 0.00005, 0.00001, 0.000005, and 0.000001) [14,28]; set II: set I plus two more diffuse  $sp$  shells with the exponents of 0.0000005 and 0.0000001; set III: set II plus five  $d$  shells with the exponents of 0.001, 0.0001, 0.00001, 0.000001 and 0.0000001. The diffuse functions were placed at the distance of 3 Å beyond the Li atom along the molecular axis. Note that the smallest exponents in the standard WMR basis sets are 0.007860 and 0.027962 for Li and H, respectively. Thus the additional extensions increase significantly the flexibility of the basis.

With the EA-EOMCC method, one obtains the vertical attachment energies for a selection of states having one more electron than the initial parent state. The parent state is described at the CCSD level as

$$|\Psi_{\text{CCSD}}\rangle = e^{\hat{T}}|\Phi_0\rangle, \quad (3)$$

where  $|\Phi_0\rangle$  is a reference Hartree-Fock (HF) determinant and  $\hat{T} = \hat{T}_1 + \hat{T}_2$  is the cluster operator limited to singles and doubles. In the general EOMCC theory [38,39], one defines the transformed Hamiltonian

$$\hat{H} = e^{-\hat{T}}\hat{H}e^{\hat{T}} \quad (4)$$

and  $\hat{H} - E_{\text{CCSD}}$  is diagonalized over a suitable set of configurations. In EA-EOMCC, these configurations comprise the  $1p$  and  $2p1h$  determinants describing states with an additional electron. The final attached states are described as linear combinations

$$\left( \sum_a c_a a^\dagger + \sum_{a,b,j} c_{a,b}^j a^\dagger b^\dagger j \right) e^{\hat{T}}|\Phi_0\rangle, \quad (5)$$

where  $a^\dagger, b^\dagger$  are creation operators for unoccupied orbitals (particles),  $j$  is an annihilation operator for the orbital  $j$  occupied in the reference  $\Phi_0$  state, and  $c_a$  and  $c_{a,b}^j$  are amplitudes. The eigenvalues obtained from the diagonalization are the vertical electron affinities with respect to the CCSD reference state. Hence we obtain *all* the vertical attachment energies to LiH at some fixed Li—H bond length from a single calculation. Also, we have performed separate coupled-cluster [CCSD, CCSD(T), and CCSDT] calculations for the ground states of LiH and LiH<sup>-</sup>, which are more suitable in the present implementation to obtain the  $A_{e,ad}$ .

The  $A_{e,ad}$  of a molecule with respect to a particular  $n$ th anionic state is defined as the difference in the total energies of this anionic state and the ground state of the neutral molecule. Within the Born-Oppenheimer (BO) approximation, one may define the  $n$ th adiabatic electron affinity as

$$\begin{aligned} A_{e,ad}^{(n)} &= E_{\text{tot}}(N, R_e^N) + E_{\text{ZP},N} - E_{\text{tot}}(A, R_e^{A,(n)}) - E_{\text{ZP},A,(n)} \\ &= \Delta E_{\text{el}}^{(n)} + \Delta E_{\text{nuc}}^{(n)}, \end{aligned} \quad (6)$$

where  $R_e^N$  and  $R_e^{A,(n)}$  denote the equilibrium geometrical configurations of the neutral molecule and the  $n$ th state of the anion, respectively, and  $E_{\text{ZP}}$  is the zero point energy.

Vibrational quanta of the LiH and LiH<sup>-</sup> ground states are calculated with the use of the LEVEL 5.2 package [40] which solves the radial one-dimensional Schrödinger equation

$$-\frac{\hbar^2}{2\mu} \frac{d^2\Psi_{vJ}(R)}{dR^2} + V_J(R)\Psi_{vJ}(R) = E_{vJ}\Psi_{vJ}(R), \quad (7)$$

where  $V_J(R)$  are taken as the potential energy curves of molecular ground states ( $J=0$ ), and vibrational quanta  $\Delta G(v + \frac{1}{2}) = E_{v,0} - E_{v-1,0}$ ;  $E_{-1,0} = 0$ .

## III. RESULTS AND DISCUSSION

### A. Ground states of LiH and LiH<sup>-</sup>

Ground-state properties of LiH and LiH<sup>-</sup> have been the subject of numerous theoretical studies (see Refs. [41, 42], and references therein) performed at different levels of theory with Gaussian, Slater, and numerical basis sets. Detailed comparison of the most reliable results for the  $A_{e,ad}$  of LiH and the structure of the LiH<sup>-</sup> anion is presented by Frenking and Koch [43]. In order to check the performance of the CCSD(T)-WMR approach, one can compare our results with the experimental data given in Table I. One can see that the difference between the experimental [44,45] and our computed values is 0.0023 Å for  $R_e$ , 0.0184 cm<sup>-1</sup> for  $B_e$ , 2.26 cm<sup>-1</sup> for  $\omega_e$ , 0.03 D for  $\mu$ , and 0.38 kcal/mol for

TABLE I. Results for the ground states of LiH ( $X^1\Sigma^+$ ) and LiH $^-$  ( $X^2\Sigma^+$ ) obtained at the CCSD(T)-WMR optimized geometries. Bond lengths ( $R_e$ ) are in angstroms, rotational constants ( $B_e$ ) are in  $\text{cm}^{-1}$ , harmonic frequencies ( $\omega_e$ ) are in  $\text{cm}^{-1}$ , dipole moments ( $\mu$ ) are in debyes, dissociation energies ( $D_e$  and  $D_0$ ) are in kcal/mol, total energies (TE) are in hartrees, electron affinities are in eV.

Property	LiH		LiH $^-$	
	This work	Expt. <sup>a</sup>	This work	Expt. <sup>b</sup>
$R_e$	1.5976	1.5957	1.6600	$1.724 \pm 0.025$
$B_e$	7.4947	7.5131	6.9419	$6.43 \pm 0.18$
$\omega_e$	1403.39	1405.65	1213.84	$920 \pm 80$
$\mu$	5.85 <sup>c</sup>	5.88	4.69	
$D_e$	57.68 <sup>d</sup>		48.27 <sup>d</sup>	
$D_0$	55.67 <sup>d</sup>	56.05	46.54 <sup>d</sup>	$46.53 \pm 0.48$
Level	TE (LiH)	TE (LiH $^-$ )	$A_{e,\text{ad}}$ , <sup>e</sup> this work	
SCF	-7.987 301 2	-7.996 706 7	0.268	
MBPT [2]	-8.041 174 7	-8.051 795 6	0.301	
CCSD	-8.052 843 0	-8.063 990 1	0.315	
CCSD+T[CCSD]	-8.052 975 9	-8.064 412 9	0.323	
CCSD(T)	-8.052 974 3	-8.064 405 4	0.323	
CCSDT	-8.052 997 5	-8.064 578 5	0.327	

<sup>a</sup>See Refs. [44, 45].

<sup>b</sup>See Ref. [29].

<sup>c</sup>The HF value is 6.01.

<sup>d</sup>The CCSDT level.

<sup>e</sup>The experimental value is  $0.342 \pm 0.012$ , see Ref. [29].

$D_0$ , i.e., the present values are superior compared to the results of the most accurate previous studies [43] and are close to those obtained recently at the explicitly correlated CCSD(T)-R12/9s8p6d5f level [46].

The experimental constants of LiH $^-$  were obtained on the basis of a Franck-Condon analysis of the laser photodetachment spectrum of LiH $^-$  and are rather different from our values. Our values are in closer agreement with the values obtained by other advanced theoretical methods [43,47,48]. Since our constants, including vibrational quanta presented in Table II, for LiH are in nice agreement with the reliable experimental data, and our results for LiH $^-$  are expected to be only slightly less accurate, we can recommend our values for LiH $^-$  spectroscopic constants. The  $A_{e,\text{ad}}$  value of LiH calculated at the CCSDT level equals 0.327 eV and is very close to the lower bound of the experimental value of 0.342

$\pm 0.012$  eV. Our computed dissociation energy  $D_0$  of LiH $^-$  matches the center of the experimentally obtained range ( $46.54$  vs  $46.53 \pm 0.48$  kcal/mol). The coupled-cluster electron affinities of the Li and H atoms are 0.616 and 0.723 eV, respectively, being in good agreement with the experimental value of 0.618 049(20) [49] for Li and 0.754 209(3) eV [50] for H. Table I shows the CCSD  $A_{e,\text{ad}}$  of LiH to be only marginally smaller than the CCSDT  $A_{e,\text{ad}}$ . Therefore, we anticipate that the CCSD wave function of LiH has to be a good reference function for the EA-EOMCC calculations, which have proven to yield rather accurate binding energies (BE) of dipole-bound electrons [52].

Table II presents the first eight vibrational quanta of ground-state LiH and LiH $^-$  calculated according to Eq. (7) with the use of potential energy curves presented in Fig. 1. Computed spacings between energies of vibrational levels are in nice agreement with experimental data available for LiH [51]. As is seen from Tables I and II, anharmonic cor-

TABLE II. Vibrational quanta  $\Delta G(v + \frac{1}{2})$  ( $\text{cm}^{-1}$ ) of LiH and LiH $^-$  calculated according to Eq. (7) All values are in  $\text{cm}^{-1}$ .

Level	$\Delta G(v + \frac{1}{2})$		Level	$\Delta G(v + \frac{1}{2})$	
	LiH	LiH $^-$		LiH	LiH $^-$
$v=0$	1391.9	1142.3	$v=4$	1225.2	956.0
$v=1$	1357.4 <sup>a</sup>	1122.2	$v=5$	1183.4	906.1
$v=2$	1312.6 <sup>b</sup>	1062.7	$v=6$	1141.8	906.1
$v=3$	1268.0 <sup>c</sup>	1006.7	$v=7$	1100.7	809.2

<sup>a</sup>Experimental value is 1359.8, see Ref. [51].

<sup>b</sup>Experimental value is 1314.8, see Ref. [51].

<sup>c</sup>Experimental value is 1270.9, see Ref. [51].

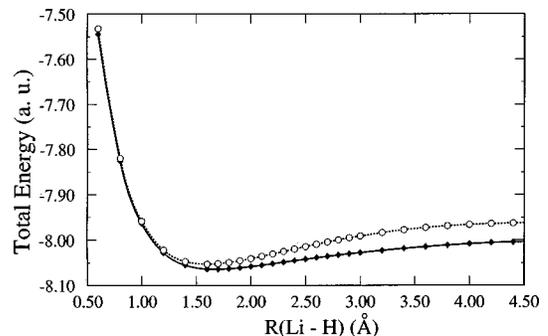


FIG. 1. CCSD-WMR total energies of the LiH  $X^1\Sigma^+$  (open circles) and LiH $^-$   $X^2\Sigma^+$  (diamonds) ground states.

TABLE III. Energies of the vertical attachment of an extra electron to the ground state of  $\text{LiH}$  ( $X^1\Sigma^+$ ) calculated by the EA-EOMCC method with three basis sets (see Sec. III) together with the eigenvalues of the lowest unoccupied orbitals (taken with the opposite sign, i.e., the  $kT$  binding energies). All values are in eV. Numbers in brackets are powers of ten.

State	Set I		Set II		Set III		Numerical
	EOMCC	KT	EOMCC	KT	EOMCC	KT	KT <sup>a</sup>
Valence	0.3010	0.2134	0.2976	0.2071	0.2986	0.2079	0.213
1st excited	0.0026	0.0019	0.0026	0.0018	0.0030	0.0022	0.0023
2nd excited	-0.5[-4]	-0.7[-4]	0.2[-4]	0.1[-4]	0.3[-4]	0.2[-4]	0.2[-4]
3rd excited	-0.0004	-0.0003	-0.4[-5]	-0.4[-5]	-0.2[-5]	-0.3[-5]	0.2[-6]

<sup>a</sup>See Ref. [24].

rections to the main vibrational frequency of  $\text{LiH}$  are smaller than those of  $\text{LiH}^-$  (43 and  $72\text{ cm}^{-1}$ , respectively).

### B. Excited states of $\text{LiH}^-$

The results of our EA-EOMCC calculations at the equilibrium bond length of the  $\text{LiH}$  ground state are presented in Table III together with the eigenvalues (taken with the opposite sign) of the three lowest unoccupied molecular orbitals (MOs). The latter correspond to the  $KT$  binding energies of an extra electron, which have been considered to be good estimates for the vertical BE of loosely bound electrons [41].

The vertical attachment energy required for an extra electron to form the valence state of  $\text{LiH}^-$  is close to the  $A_{e,\text{ad}}$ , see Table I, because the difference in the equilibrium bond lengths of  $\text{LiH}$  and  $\text{LiH}^-$  is small ( $0.065\text{ \AA}$ ) and the potential energy curves (PEC) of both species are rather flat, see Fig. 1. The BE of the dipole-bound electron in the first excited state depends slightly on the extensions of basis set I. The largest BE of  $0.0030\text{ eV}$  was obtained with basis set III and is close to the value of  $0.0028\text{ eV}$  obtained previously [22] in a complicated CCSD calculation with a numerical (“infinite”) basis set. The  $KT$  BEs of the valence and first excited states are approximately one-third smaller than the CCSD BEs, i.e., the correlation contribution constitutes half the  $KT$  binding energy.

The second excited state was found after including some very diffuse functions (sets II and III). However, the binding energy of an extra electron in this state is only  $0.22\text{ cm}^{-1}$  (set III) at the equilibrium geometry of  $\text{LiH}$ , being about 35 times

smaller than the rotational constant of  $\text{LiH}$ . Since the BO EA should exceed by  $\frac{1}{20}$  to  $\frac{1}{10}$  the value of the rotational constant in order for a polar molecule to attach an extra electron [53], the second excited state should not be bound near the equilibrium bond length of  $\text{LiH}$  if one adds the rotational operator [9–11] to the molecular BO Hamiltonian. Further diffuse basis extensions could lead to the appearance of the third excited state, as has been found with the use of a numerical basis set [24]. However, this state should not be bound either if one goes beyond the BO approximation.

In order to see the behavior of the dipole-bound states, we have performed EA-EOMCC calculations with the basis set II for a number of Li-H distances ranging from 1.0 to  $3.5\text{ \AA}$ . The ground-state potential energy curves of  $\text{LiH}$  and  $\text{LiH}^-$ , presented in Fig. 1, are similar to those published previously [47,54]. The behavior of the excited states as a function of internuclear separations is displayed in Fig. 2 relative to the  $\text{LiH}$  ground-state curve. As is seen, the attachment energy required to form the first excited state of  $\text{LiH}^-$  increases when going to larger bond lengths. This state corresponds to the dissociation channel  $\text{LiH}^- \rightarrow \text{Li}^-(^1S) + \text{H}(^2S)$ , which is asymptotically higher than the main channel  $\text{LiH}^- \rightarrow \text{Li}(^2S) + \text{H}^-(^1S)$  by the difference in the electron affinities of Li and H of about  $0.13\text{ eV}$ .

The behavior of the ground-state  $\text{LiH}$  dipole moment as a function of the Li—H bond length is shown in Fig. 3. Since the restricted HF (RHF) wave function of the  $\text{LiH}$  ground state corresponds to the  $\text{Li}^+ + \text{H}^-$  dissociation limit, the RHF dipole moment increases permanently when stretching the bond length. One needs to use an unrestricted  $M_S=0$  HF wave function, when going to bond lengths larger than

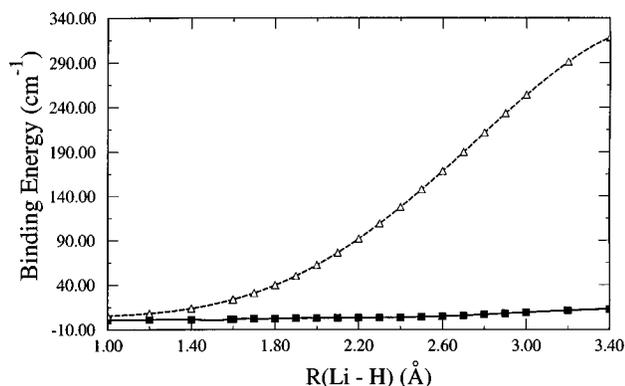


FIG. 2. EA-EOMCC binding energies of the first (open triangles) and second (solid boxes) excited states of  $\text{LiH}^-$  plotted with respect to the total energy of the ground-state  $\text{LiH}$  molecule.

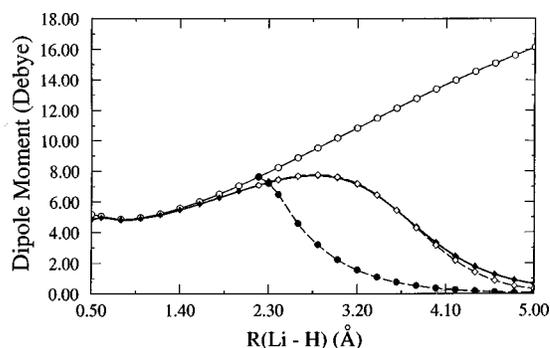


FIG. 3. HF and CCSD dipole moments of  $\text{LiH}$  as functions of the internuclear separation. Open circles—RHF, solid circles—UHF, open diamonds—CCSD-RHF, solid diamonds—CCSD-UHF.

$\approx 2.3$ – $2.5$  Å, in order to simulate the  $\text{Li}(^2S) + \text{H}(^2S)$  dissociation limit, where the dipole moment vanishes. The unrestricted HF (UHF)  $M_S=0$  curve in Fig. 3 is obtained from calculations where the  $M_S=1$  UHF wave function of LiH at  $R(\text{Li}-\text{H})=5.0$  Å has been used as a guess for the  $M_S=0$  wave function at this separation with subsequent stepping towards smaller bond lengths. Figure 3 shows the correct behavior of the UHF dipole moment at increasing internuclear separation.

The CCSD dipole moment converges to zero independently of whether UHF or RHF reference wave functions are used. One might expect the CCSD RHF solution to converge to the closed shell  $\text{Li}^+ + \text{H}^-$  excited state. However, the convergence procedure in the CCSD calculation is such that the ground state is obtained although certain CCSD amplitudes take on rather large values (of about unity). However, the accuracy of the solution is acceptable, and this is due to the fact that the CCSD approach corresponds to the full configuration interaction (full-CI) method in the frozen-core approximation, i.e., for two valence electrons, which are well separated in energy from the  $1s^2$  core electrons of the Li atom. The largest dipole moment corresponds to  $R(\text{Li}-\text{H}) \approx 3$  Å, which is twice as long as the equilibrium bond length. Such a shift of the maximum value of the dipole moment can be explained qualitatively as due to the increase in the ionicity when going from a more covalent bonding near equilibrium to larger bond lengths (weaker ionic bonding). The subsequent lowering of the dipole moment is due to the dissociation into two noninteracting neutral atoms.

Although our calculations are not to wave number accuracy, at bond lengths corresponding to the largest dipole moment values, the BE of an extra electron trapped into the second excited state rises to  $\approx 9$   $\text{cm}^{-1}$ , whereas the rotational constant of LiH decreases to  $\approx 2$   $\text{cm}^{-1}$ . The behavior of the rotational constant and the BO binding energy of an extra electron in the second excited state is presented in Fig. 4, together with the curve describing assumed threshold values for the BO binding energy required by an extra electron to form an observable dipole-bound state. This threshold curve is obtained by the multiplication of  $B_e$  by a factor of  $\frac{1}{10}$ , which was proposed [53] as an upper bound of the ratio between  $B_e$  and  $\mu$  required for an extra electron to be bound. As is seen from Fig. 4, the second excited dipole-bound state is bound under the above approximations at  $R(\text{Li}-\text{H}) > 2$  Å, and should disappear at the distances where the dipole moment drops below the critical value of 2.5 D.

The physical significance of this result is a difficult issue. It might be possible that the second excited state of  $\text{LiH}^-$  can be produced experimentally if neutral target molecules are excited to higher vibrational levels following low-energy electron attachment, by an analogy with the well-developed

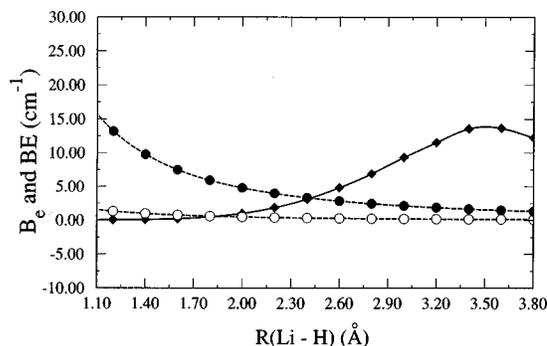


FIG. 4. BO binding energy of an extra electron in the second dipole-bound excited state and the rotational constant of the LiH ground state as a function of the internuclear separation. Solid circles— $B_e$ , open circles— $\frac{1}{10}B_e$ , solid diamonds—binding energy.

procedure for producing ground-state dipole-bound anions [55]. This excited state can at best exist as a resonance state [56]. To further investigate this issue theoretically, it is necessary to consider the coupling to the continuum and to go beyond the Born-Oppenheimer approximation. Experimentally, such states may possibly be observable in photodetachment or electron scattering experiments.

#### IV. CONCLUSION

The adiabatic electron affinity of LiH calculated at the CCSDT level with the large atomic natural orbital Widmark-Malmqvist-Roos basis almost matches ( $0.327$  vs  $0.342 \pm 0.012$  eV) the recently obtained experimental value.

The  $\text{LiH}^-$  anion possesses two excited states. The first state is the “usual” dipole-bound state, excited with respect to the conventional (valence) state of  $\text{LiH}^-$ , and corresponds to the second dissociation channel  $\text{LiH}^- \rightarrow \text{Li}^-(^1S) + \text{H}(^2S)$ , whereas the second dipole-bound state is transient. The Born-Oppenheimer binding energy of the latter state is  $\approx 0.2$   $\text{cm}^{-1}$  at the neutral equilibrium geometry, which is too small to form a stationary dipole-bound state. However, at bond lengths longer than  $\approx 2.0$  Å, the BO binding energy of an extra electron exceeds the value of the rotational constant, and this may allow the formation of an anionic dipole-bound state, which could be observable under suitable experimental conditions.

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