

# LiH potential energy curves for ground and excited states with the free complement local Schrödinger equation method

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## ABSTRACT

The two lowest singlet and triplet  $\Sigma^+$  potential energy curves of LiH were calculated using the free complement (FC) local Schrödinger equation (LSE) method. The overall potential curves and the properties calculated therefrom, like equilibrium bond length, dissociation energy, adiabatic and vertical excitation energies, zero point energy, vibrational spacings, etc., demonstrated the high accuracy of the FC LSE method for both the ground and excited states in comparison to the reference calculations and experiments.

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## 1. Introduction

Knowledge of potential energy curves (PECs) is fundamental to gain insight in structure, reactivity, and spectroscopy of molecules. PECs of excited states are particularly interesting, since they often display unusual shapes that are deviating from the well understood curve shapes of the ground states. Limited applicability of several theoretical and experimental methods to excited states enhances the need for research in that field.

LiH, a simple four-electron neutral heteronuclear molecule, has been a popular test case for PEC calculations over decades. Older works are reviewed in Ref. [1]. A comprehensive pseudopotential full CI study on  $1\Sigma^+$  and  $3\Sigma^+$  PECs was published recently [2]. The potential curve of the second  $1\Sigma^+$  state ( $A^1\Sigma^+$ ) is unusually flat near the minimum [1,2], suggesting interesting spectroscopic phenomena for this state. This is caused by the varying ionicity in different states upon bond stretching, as firstly discussed in detail for the X and  $A^1\Sigma^+$  states by Docken and Hinze using MCSCF wave functions [3].

The free complement local Schrödinger equation (FC LSE) method was proposed to solve the Schrödinger equation of atoms and molecules accurately [4–9]. This was demonstrated already for LiH for its ground-state potential curve [9]. In this letter, we examined in more detail the potential curves of LiH in both ground and excited states with the FC LSE method. We studied the first two  $1\Sigma^+$  (X, A) and  $3\Sigma^+$  (a, c) states. Structural and vibrational properties were evaluated from these potential curves and the results were compared with the existing theoretical and the experimental data.

## 2. Method and computational details

The Born–Oppenheimer LiH Hamiltonian in internal coordinates reads

$$\begin{aligned}
 H = & -\frac{1}{2} \left[ \sum_{i=1}^3 \sum_{j \neq i}^3 \sum_{k > j, k \neq i}^4 \frac{r_{ij}^2 + r_{ik}^2 - r_{jk}^2}{r_{ij}r_{ik}} \frac{\partial^2}{\partial r_{ij} \partial r_{ik}} + \sum_{i=1}^4 \sum_{j \neq i}^4 \left( \frac{\partial^2}{\partial r_{ij}^2} + \frac{2}{r_{ij}} \frac{\partial}{\partial r_{ij}} \right) \right. \\
 & + \sum_{i=1}^3 \sum_{j > i}^4 \sum_{a=1}^2 \frac{r_{ij}^2 + r_{ia}^2 - r_{ja}^2}{r_{ij}r_{ia}} \frac{\partial^2}{\partial r_{ij} \partial r_{ia}} \\
 & \left. + \sum_{i=1}^4 \sum_{a=1}^2 \left( \frac{\partial^2}{\partial r_{ia}^2} + \frac{2}{r_{ia}} \frac{\partial}{\partial r_{ia}} + \sum_{b \neq a}^2 \frac{r_{ia}^2 + r_{ib}^2 - r_{ab}^2}{2r_{ia}r_{ib}} \frac{\partial^2}{\partial r_{ia} \partial r_{ib}} \right) \right] \\
 & - \sum_{i=1}^4 \sum_{a=1}^2 \frac{Z_a}{r_{ia}} + \sum_{i=1}^3 \sum_{j > i}^4 \frac{1}{r_{ij}} + \sum_{a=1}^1 \sum_{b > a}^2 \frac{Z_a Z_b}{r_{ab}}, \quad (1)
 \end{aligned}$$

where the last three terms are potential energy terms, all others are kinetic energy terms.  $i, j, k$  denote electrons,  $a, b$  nuclei.

To generate a FC wave function  $\psi_n$  of order  $n$ , the Hamiltonian  $H$  and the scaling function  $g$  are applied  $n$  times to an initial wave function  $\psi_0$  [4–6]. The  $g$  function of the form,  $g = 1 + \sum_i \sum_a r_{ia}/Z_a + \sum_i \sum_{j > i} r_{ij}$  was used [9] and the initial wave function used is written in the valence-bond type formula,

$$\begin{aligned}
 \psi_0 = & \left. \begin{aligned} & c_1 e^{-\alpha r_{Li,1}} e^{-\alpha r_{Li,2}} e^{-\beta r_{H,3}} e^{-\gamma r_{Li,4}} \\ & + c_2 e^{-\alpha r_{Li,1}} e^{-\alpha r_{Li,2}} e^{-\beta r_{H,3}} e^{-\delta r_{Li,4}} \\ & + c_3 e^{-\alpha r_{Li,1}} e^{-\alpha r_{Li,2}} e^{-\beta r_{H,3}} e^{-\beta r_{H,4}} \end{aligned} \right\} 3\Sigma^+ \left. \right\} 1\Sigma^+. \quad (2)
 \end{aligned}$$

It contains two covalent terms ( $\phi^{\text{cov}}$ ) for all  $\Sigma^+$  states. They describe the Li atom in the  $1s^2 2s$  and  $1s^2 3s$  configuration, respectively. The ionic  $\text{Li}^+\text{H}^-$  term ( $\phi^{\text{ion}}$ ) in the last line of Eq. (2) was included for the  $1\Sigma^+$  states. The exponents were  $\alpha = 3.2$ ,  $\gamma = 0.8$ ,  $\delta = 0.4$  for Li and  $\beta = 1.2$  for H.  $\alpha$  had roughly been optimized and  $\gamma$  and  $\delta$  were chosen the literatures [3,10–12]. The FC wave function  $\psi_n$  is written

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as a linear combination of  $M_n$  independent, non-diverging complement functions  $\phi_i$  [4,7,8],

$$\psi_n = \sum_i^{M_n} c_i \phi_i. \quad (3)$$

Order  $n = 4$  wave functions have been used throughout this study. The number of the complement functions was 3392 for the  $^3\Sigma^+$  states and 4341 for the  $^1\Sigma^+$  states.

The coefficients  $c_i$  were determined with the LSE procedure for interatomic distances  $R$  from 1.7 to 40.0 a.u. as solutions to the matrix eigenvalue problem  $\mathbf{Ac} = \mathbf{BcE}$ .  $A_{\mu i} = H\phi_i(r_\mu)$  and  $B_{\mu i} = \phi_i(r_\mu)$  were evaluated at  $10^7$  Monte Carlo sampling points  $r_\mu$  [9] that have been generated for each  $R$  according to the density  $\rho_\mu = \psi_0(r_\mu)^2$  using the Metropolis algorithm [13]. We actually solved  $\mathbf{Qc} = \mathbf{HcE}$  with  $\mathbf{Q} = \mathbf{A}^\dagger \mathbf{A} = \langle H\psi | H\psi \rangle$  and  $\mathbf{H} = \mathbf{A}^\dagger \mathbf{B} = \langle H\psi | \psi \rangle$  [9,14]. The eigenvectors  $\mathbf{c}$  were determined via diagonalization of the Gram–Schmidt orthonormalized  $\mathbf{Q}$  matrix in a Davidson iteration like procedure. Energies for the three lowest states were calculated from  $\mathbf{E} = \mathbf{c}^\dagger \mathbf{A}^\dagger \mathbf{Bc} / \mathbf{c}^\dagger \mathbf{B}^\dagger \mathbf{Bc}$  with  $\mathbf{B}^\dagger \mathbf{B} = \langle \psi | \psi \rangle$ . A measure of the covalent nature of  $^1\Sigma^+$  states as a function of  $R$  was obtained as the contribution of all covalent terms to the wave function  $\psi_n$ , that means as  $\sum_i \sum_j c_i^{cov} c_j^{cov} \langle \phi_i^{cov} | \phi_j^{cov} \rangle$ .

We have compared the present results with the full CI (FCI) results of a standard quality. The reference full CI calculations were carried out with the cc-pVQZ basis sets [15] at the experimental  $r_e$  of the ground state (3.015 a.u. [1]) only, and with the cc-pV5Z basis sets [15] for  $R = 1.7$ –40.0 a.u. using the MOLPRO program package [16].

### 3. Potential energy curves

For the ground state, the shape and the total energies of the FC LSE curve (Fig. 1) agree with the previous FC LSE results within the fluctuation range of the data points due to Monte Carlo sampling [9]. Near the dissociation limit of the singlet states, the fluctuation range is observed to be in the order of magnitude of  $10^{-4}$  a.u. At long bond distances  $R$ , only about 60% of the complement functions have non-zero contribution to the wave function, whereas at the equilibrium distance region, almost all the complement functions contribute, so that the quality of the wave function should be better near the equilibrium distance than near the dissociation limit and therefore the fluctuation error must be smaller near the equilibrium distance region than  $10^{-4}$  a.u. The obtained FC LSE curve is considerably (about  $10^{-2}$  a.u.) lower in energy than the FCI/cc-pVTZ [9], MRCCSD-[4R]/cc-pVQZ [17] and other reference curves [3,18] from the literature. It is also lower in about the same energy than the presently calculated curve of FCI/cc-pV5Z (Fig. 1) and the

shapes of the two curves are quite the same. For example, the total energies at  $r_e = 3.015$  a.u. were  $-8.070\,309$  a.u. with FC LSE,  $-8.053\,640$  a.u. with FCI/cc-pV5Z, and  $-8.042\,694$  a.u. with FCI/cc-pVQZ. The comparison with  $-8.070\,533$  a.u. obtained from a 2400-term explicitly correlated Gauss function considered as the best Ref. [19], shows furthermore, that the FC LSE energy is correct in absolute value within the estimated fluctuation range. Table 1 shows an equally close agreement at  $R = 40.0$  a.u. between the X state energy and the most accurate atomic energies [9].

The excited state FC LSE PECs in Fig. 1 also display the similar shapes to those of the FCI/cc-pV5Z curves. For the two higher excited states, A and c, we expect that the qualities of the FC wave functions are slightly less accurate than that of the ground state, because of the comparably lower quality of the initial wave function (Eq. (3)) to describe the excited states containing an electron in a 2p orbital of a Li atom. The second term in Eq. (3) works to improve the states in the sense of using a double instead of a single zeta ansatz for that state.

The broad minimum of the  $A^1\Sigma^+$  state PEC [1–3,10] is known to result from the avoided crossings of the diabatic ionic  $-1/R$  curve of  $\text{Li}^+\text{H}^-$  and diabatic covalent potentials [2,3]. Therefore, the ionic nature in singlet states exchanges from the X state into the A (and higher)  $^1\Sigma^+$  states upon bond extension, followed by reestablishment of purely covalent character for even larger  $R$ . The covalent density contribution evaluated here, which increased towards pure covalency for increasing  $R$ , supports this finding. Additionally, the covalent character starts to dominate in the X state already for smaller  $R$  than in the higher states. The FC LSE  $a^3\Sigma^+$  PEC is repulsive in nature. Its known shallow minimum of less than  $2 \times 10^{-5}$  a.u. [20,21] could not be resolved due to fluctuations of this order of magnitude. The avoided crossing between the c and d states, indicated by a shoulder in the c state PEC at around  $R = 4.0$  a.u., is in accord with the literature [2].

As shown in Table 1, all PECs reveal the dissociation of LiH into the neutral atoms with H in the 1s and Li in the  $1s^2 2s$  and  $1s^2 2p$  configurations for the X and a state and the A and c state, respectively. The ground state at  $R = 40.0$  a.u. is obtained in best agreement with the Ref. [22,23] within the fluctuation range, indicating, that the dissociation limit is already fully reached.

Total FC LSE energies for excited states are always considerably lower than the full CI energies calculated here. Table 2 summarizes vertical excitation energies  $\Delta E$  to estimate the relative position of the excited state PECs with respect to the ground state. Excitations into the  $^3\Sigma^+$  states are particularly interesting, since the  $^1\Sigma^+$  and  $^3\Sigma^+$  wave functions are structurally different. For the excitation into the  $a^3\Sigma^+$  state, MR-CCSD calculations with Gauss-type orbitals gave  $\Delta E = 3.200$  eV at 3.015 a.u. [18] and pseudopotential full CI calculations  $\Delta E = 3.330$  eV at 3.000 a.u. [24]. The FC LSE value is

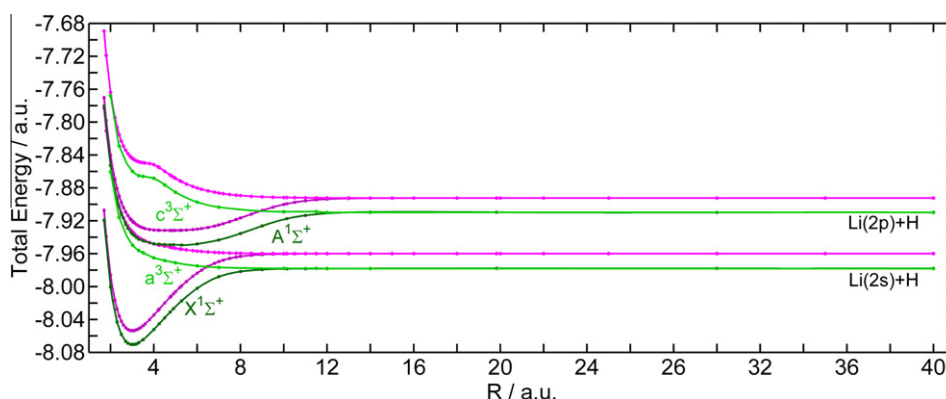


Fig. 1. Lowest two  $^1\Sigma^+$  FC LSE (dark green),  $^3\Sigma^+$  FC LSE (light green),  $^1\Sigma^+$  FCI/cc-pV5Z (dark magenta), and  $^3\Sigma^+$  FCI/cc-pV5Z (light magenta) potential energy curves of LiH for interatomic distances between 1.7 and 40.0 a.u.

**Table 1**

FC LSE energies (a.u.) for  $1^1\Sigma^+$  and  $3^3\Sigma^+$  states at  $R = 40.0$  a.u. compared to accurately calculated atomic energies (a.u.) for two Li configurations.

Atom <sup>a</sup>	$1^1\Sigma^+$		$3^3\Sigma^+$		
Li( $1s^22s$ )	-7.9780	X	-7.9778	a	-7.9781
Li( $1s^22p$ )	-7.9102	A	-7.9098	c	-7.9097

<sup>a</sup>  $E(H) = -0.5000$  a.u.,  $E(Li)$  for  $1s^22s$  from FC LSE,  $n = 6$  [9], excited states from variational calculations with fully correlated basis, Refs. [22,23].

**Table 2**

Full CI and FC LSE vertical excitation energies  $\Delta E$  from the ground state into the excited states.

State	$\Delta E$ (FCI/QZ <sup>a</sup> ) eV	$\Delta E$ (FCI/5Z <sup>a</sup> ) eV	$\Delta E$ (FC LSE) eV
a	3.257	3.264	3.286
A	3.614	3.622	3.649
c	5.704	5.699	5.726

<sup>a</sup> XZ abbreviates cc-pVXZ Dunning basis set [15].

within this range. In general, FC LSE lies at the continuation of the full CI data with increasing quality of the basis set for all states except for the c state. For the c state, the effect of missing Li(2P) function in the initial  $\psi_0$  given by Eq. (2) must be examined.

#### 4. Vibrational analysis

Structural properties for the X and A state were obtained from an extension of the Morse function,  $F = c_1 + \sum_{k=2}^N c_k [1 - e^{-\alpha(r-r_e)}]^k$  with  $N = 10$  as described by Dunham [25], which was fitted to the FC LSE data in a least squares procedure. Special care has been taken, that  $F$  satisfactorily represents the dissociation limit. Dissociation energies  $D_e$  were obtained as difference between the total energy at 40.0 a.u. and the fitted energy minimum. For adiabatic excitation energies  $T_e$ , the minimum energies of both contributing states were used.

Vibrational properties for the X and the A state were obtained from Dunham parameters of  $F$  [25]. Vibrational energy levels  $G_v$  and their spacings  $\Delta G_v = G_{v+1} - G_v$  were only calculated for  $v = 0, 1$ . This accounts for the limitation of the Dunham method to purely in or decreasing spacings as known for Morse type potentials.

Structural and spectroscopic properties shown in Table 3 allow us to gain insight into the quantitative performance of FC LSE for the calculation of ground and excited A state PECs. For the X state, FC LSE values are compared to experiment [1], all-electron (AE [27]) and pseudopotential (PP [2,24]) full CI properties, each with large Gaussian basis sets, and to PP based Diffusion Quantum

**Table 3**

Comparison of FC LSE structural and vibrational properties to other calculations and experiment.

X state	$r_e$ a.u.	$G_0$ cm <sup>-1</sup>	$\Delta G_0$ cm <sup>-1</sup>	$\Delta G_1$ cm <sup>-1</sup>	$D_e$ eV	
FC LSE	3.013	695.41	1356.87	1312.79	2.521	
DMC <sup>a</sup>	2.995(0)	697.0(2)	1359.7(3)	1314.0(7)	2.534(0)	
FCI/PP <sup>b</sup>	3.003	695.7	1355.81	1311.43	2.523	
FCI/AE <sup>c</sup>	3.015	697.72	1359.66	1314.68	2.492	
Expt. <sup>d</sup>	3.015	697.94	1359.71	1314.89	2.515	
A state	$r_e$ a.u.	$G_0$ cm <sup>-1</sup>	$\Delta G_0$ cm <sup>-1</sup>	$\Delta G_1$ cm <sup>-1</sup>	$D_e$ eV	$T_e$ eV
FC LSE	5.173	136.05	298.42	301.57	1.076	3.296
FCI/PP <sup>b</sup>	4.862	130.00	278.43	310.93	1.077	3.287
Expt. <sup>d</sup>	4.906	131.30	280.84	312.97	1.076	3.272

<sup>a</sup> Ref. [26], standard deviations in parentheses.

<sup>b</sup> PP = pseudopotential, Refs. [2,24].

<sup>c</sup> AE = all-electron, Ref. [27].

<sup>d</sup>  $\Delta G(X)$  [28],  $\Delta G(A)$  [29], all others Ref. [1].

Monte Carlo (DMC) results [26]. DMC is also subject to fluctuations caused by random sampling and was likewise analyzed following the concept of the Dunham procedure [26]. Agreement between DMC and experiment for vibrational quantities justifies the use of this data analysis, although the DMC  $r_e$  is shifted to a considerably smaller value. Comparison of AE [27] and PP [2,24] full CI calculations in the X state discovers the expected lower accuracy of the PP based properties. FC LSE calculations are in good agreement with experiment.  $r_e$  deviates by 0.002 a.u., whereas DMC gives the largest deviation. Vibrational level based FC LSE quantities deviate by at most 2.84 cm<sup>-1</sup>. Here FCI/AE and DMC calculations are closer to experiment, whereas FCI/PP calculations deviate more. For  $D_e$ , the agreement with experiment is best with FC LSE.

FCI/PP is the only theoretical reference for A state properties. The agreement between FCI/PP and experiment is closer in the A state than as it was observed in the X states (except for  $r_e$ ). Inverse behavior occurs for FC LSE. Except for  $D_e$ , FCI/PP gives values closer to experiment than those from FC LSE. Therefore the questions emerge, whether the determination of parameters from experimental data of such a shallow minimum is done accurately, and whether the full CI calculations based on the pseudo potential is even valid to the excited states of complex electronic structure that is different from the ground state.

#### 5. Conclusion

The PECs of the lowest two  $1^1\Sigma^+$  (X, A) and  $3^3\Sigma^+$  (a, c) states of LiH show that the FC LSE method can be used for accurate calculations of ground and excited states of molecules [9]. In contrast to full CI, FC LSE does not only render correct curve shapes and energy differences, but also gives accurate absolute energies. A disadvantage of the present FC LSE algorithm is the slight fluctuation of the curve data due to Metropolis-Monte Carlo sampling. A way to get smooth FC LSE PECs has been prepared by introducing the rational local sampling method by one of the authors [30]. This will furthermore pave the way to the LSE calculations using larger FC wave functions.

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