Full configuration interaction determination of potential energy curve for LiH molecule using cc-pVXZ (X=D, T and Q) basis sets

M.S. Arruda[(a)], F.V. Prudente[(b)], and A.M. Maniero[(b)]
[a]*Instituto de Física, Universidade Federal da Bahia,*
Campus Universitário de Ondina, CEP 40210-340, Salvador, Bahia, Brazil,
e-mail: manuelaarruda@gmail.com
[b]*Instituto de Ciências Ambientais e Desenvolvimento Sustentável Universidade Federal da Bahia,*
R. Prof. José Seabra, Centro, CEP 47805-100, Barreiras, Bahia, Brazil.

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In this work we study the influence of atomic orbital basis sets in the determination of ground state ($X^1\Sigma^+$) potential energy curve of Lithium Hydride diatomic molecule. The electronic energies of LiH are calculated, within the Born-Oppenheimer approximation, at the full Configuration Interaction level using cc-pVXZ (X=D, T and Q) basis sets. From the potential energy curves, the vibrational energy levels and respective spectroscopic constants are determinated for such a state. The present results are compared with experimental and previous theoretical ones published in literature.

Keywords: Atomic orbital; potential energy; lithium hydride.

En este trabajo estudiamos la influencia del conjunto de bases de orbitales atómicos sobre la determinación de la curva de energía potencial (CEP) correspondiente al estado fundamental ($X^1\Sigma^+$) de la molécula diatómica Hidruro de Litio. La energía electrónica del LiH es calculada, en los marcos de la aproximación Born-Oppenheimer, a nivel ICC usando los conjuntos de funciones base cc-pVXZ (X=D,T,Q). A partir de las CEP calculadas, determinamos los niveles de energía vibracional y respectivas constantes espectroscópicas. Los resultados obtenidos son comparados con valores experimentales y teóricos publicados previamente.

Descriptores: Orbitales atómicos; energía potencial; hidruro de litio.

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1. Introduction

In the study of processes involving atoms and molecules it is possible to separate the Schrödinger equation, through the Born-Oppenheimer approximation, in two parts: one related to the nuclear part and the other one to the electronic motions. The nuclear equation relates the molecular dynamics phenomena, including the vibrational and rotational movement, the meta-stable states, photodissociation process and elastic, inelastic and reactive molecular scattering. In this context, the interaction between nuclei is described by a Potential Energy Curve (PEC) in the case of diatomic molecules, which brings the information of a particular electronic state of a molecular system and of repulsion energy between nuclei. On the other hand, the electronic Schrödinger equation describes the motion of electrons considering the nuclei fixed. Its solution gives the eigenvalue of energy for an electronic state of interest. This can be obtained by methods of post-Hartree-Fock electronics correlation. The PEC are then built from a set formed by those solutions to different nuclei geometries.

The main goal of this paper is to analyze the influence of atomic orbital basis set in the determination of ground state ($X^1\Sigma^+$) potential energy curve of Lithium Hydride diatomic molecule. The choice of the this molecule, the simplest neutral heteropolar diatomics, is that the reduced number of electrons permits the test and application of new *ab initio* methodologies (see Refs. 1 to 4 and references therein). Besides the very precise knowledge of experimental spectroscopic data of LiH [5, 6] represents a challenge for theoreticians.

In particular, the Full Interaction Configuration (FCI) method is employed to compute the electronic energies and permanent dipole moments using as atomic orbital the family of correlation consistent polarized valence basis set proposed by Dunning Jr. [7]. Additionally, the electronic energies are also obtained taking into account the basis set superposition error (BSSE). The vibrational energy levels and respective spectroscopic constants are then calculated solving the nuclear radial Schrödinger equation from PECs obtained using the best atomic basis set employed here (with and without the BSSE correction).

The structure of the paper is the following. In the Sec. 2 the technical details of the methodologies utilized to compute potential energy curves, permanent dipole moment functions (PDMF) and vibrational levels are shown. The results of this paper are presented in Sec. 3 while some concluding remarks are done in Sec. 4.

2. Technical details

All potential energy curves and their respective permanent dipole moment functions for the ground state ($X^1\Sigma^+$) of LiH molecule presented here have been performed by using the GAMESS [8,9] package. As it was pointed out previously, the reduced number of electrons of the this system makes

TABLE I. Contractions of the correlation consistent polarized valence basis set [7] for H and Li atoms.

Basis	H atom	Li atom
cc-pVDZ	$(4s, 1d) \rightarrow [2s, 1p]$	$(9s, 4d, 1d) \rightarrow [3s, 2p, 1d]$
cc-pVTZ	$(5s, 2d, 1d) \rightarrow [3s, 2p, 1d]$	$(10s, 5d, 2d, 1f) \rightarrow [4s, 3p, 2d, 1f]$
cc-pVQZ	$(6s, 3d, 2d, 1f) \rightarrow [4s, 3p, 2d, 1f]$	$(12s, 6d, 3d, 2f, 1g) \rightarrow [5s, 4p, 3d, 2f, 1g]$

possible the realization of the Full CI calculation up to fourth excitations. It is known that the accuracy of FCI calculations depends of the atomic basis set employed. In such a case, we have employed the class of cc-pVXZ (X=D, T and Q) basis sets [7]. These basis sets are designed so that functions which contribute similar amounts of correlation energy are included at the same stage, independent of the function type. A step up in terms of quality increases each type of basis functions by one, and adds a new type of higher order polarization functions [10], as it can be seen for H and Li atoms in Table I.

Moreover, the PECs are also determined doing the counterpoise (CP) correction [11] of the basis set superposition error. In such a case, the electronic energy of LiH diatom in a particular internuclear distance (R) as respect of dissociation energy is calculated of the following way:

$$\Delta E_{LiH}^{CP}(R) = E_{LiH}^{LiH}(R) - E_{Li}^{LiH}(R) - E_{H}^{LiH} \qquad (1)$$

where $E_{LiH}^{LiH}(R)$ is the total electronic energy of LiH, and $E_{Li}^{LiH}(R)$ [$E_{H}^{LiH}(R)$] is the electronic energy of Li [H] atom calculated with the normal Li [H] atomic basis functions and with the H [Li] ones located at the H [Li] nuclear position without the H [Li] nucleus present.

The $G(\nu)$ vibrational energy levels (or term values) and the B_ν rotational constants from the different PECs obtained here are determined by using the LEVEL 7.1 program of LeRoy [12]. In this program, the vibrational energies and respective wavefunctions are computed via the numerical integration of the radial Schrödinger equation for the nuclear motion. Moreover, the values of $G(\nu)$ and B_ν of our best PECs considered in the present paper are employed in calculation of spectroscopic constants ω_e, $\omega_e x_e$, B_e and α_e of $X^1\Sigma^+$ electronic state of LiH. This is done minimizing the square deviations between calculated $G(\nu)$ and B_ν and the ones found by following expansions

$$G(\nu) = \omega_e(\nu + \frac{1}{2}) - \omega_e x_e(\nu + \frac{1}{2})^2 + \omega_e y_e(\nu + \frac{1}{2})^3 + \cdots \qquad (2)$$

$$B_\nu = B_e - \alpha_e(\nu + \frac{1}{2}) + \gamma_e(\nu + \frac{1}{2})^2 + \cdots \qquad (3)$$

by using the Powell directions set method [13].

3. Results

The ground state PEC of Lithium Hydride has been computed using three different atomic basis sets (cc-pVXZ, X=D, T and Q) at FCI level. In Fig. 1 these three PECs are displayed for comparision. Since FCI method is based on variational principle, the best atomic basis set employed is the one that provides the lowest energy values. Thus, the lowest electronic energy values are obtained for LiH molecule using the cc-pVQZ basis set that is formed by 85 functions, followed of cc-pVTZ and cc-pVDZ basis that have 44 and 19 functions respectively.

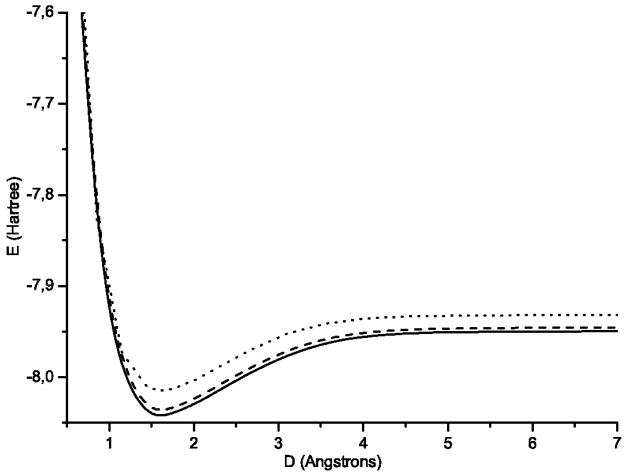

FIGURE 1. Ground state potential energy curves of LiH molecule calculated from $(\cdots)$ FCI/cc-pVDZ, $(--)$ FCI/cc-pVTZ and $(—)$ FCI/cc-pVQZ approaches.

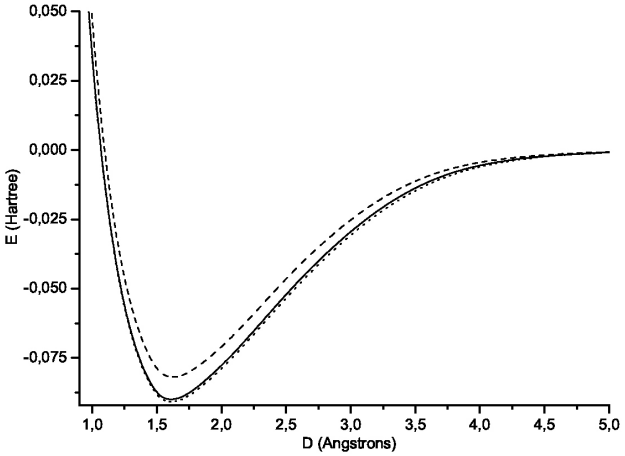

FIGURE 2. Ground state potential energy curves of LiH molecule calculated from $(--)$ FCI/cc-pVDZ(CP), $(—)$ FCI/cc-pVTZ(CP) and $(\cdots)$ FCI/cc-pVQZ(CP) approaches.

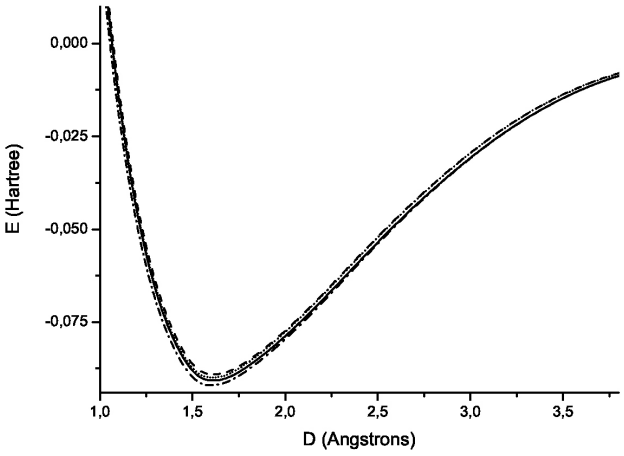

FIGURE 3. Comparison between $(\cdots)$ FCI/cc-pVTZ, $(- \cdot -)$ FCI/cc-pVQZ, $(--)$ FCI/cc-pVTZ(CP) and (—) FCI/cc-pVQZ(CP) potential energy curves of LiH.

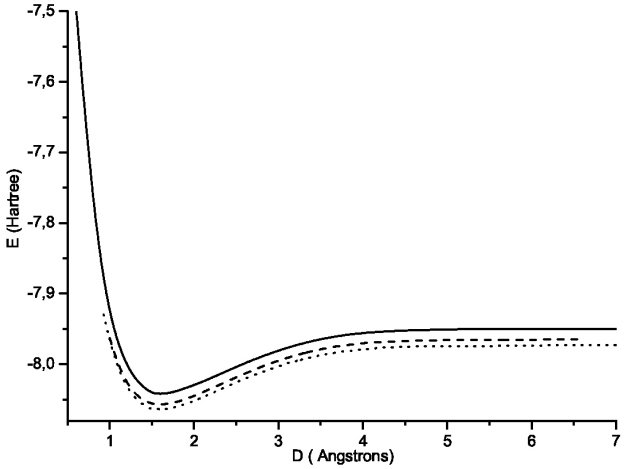

FIGURE 4. Ground state potential energy curves of LiH molecule computed by us (—, FCI/cc-pVQZ), Li and Paldus ($--$, CCSD-[4R]/cc-pVQZ) [2], and Partridge and Langhoff ($\cdots$, CI/Slater) [14].

For the other hand, the potential energy curves determined considering the counterpoise correction of the BSSE are shown in Fig. 2. As in the previous figure, the PEC with higher depth well has been obtained with the cc-pVQZ atomic basis. Note that in such a case, both curves have like asymptotic limit the zero of energy. In order to analyze the effect of CP correction on the determination of PECs, we present the ones generated using the cc-pVTZ and cc-pVQZ with and without the CP approach in Fig. 3 (the last curves are shifted so that the asymptotic limits are coincident). The effect of the CP correction on the PEC is the reduction of depth well when compared with the PEC without CP correction at the same atomic basis set. This explicit an artificial stabilization of the molecule due to basis set superposition error.

In Fig. 4, our PEC using the cc-pVQZ basis is displayed to comparison with the one obtained by Partridge and Langhoff [14], who have used the truncate CI method and the Slater basis set, and with the one calculated by Li and Paldus [2] by employing the energy-corrected CCSD-[4R] approach and the cc-pVQZ basis. In such a figure it is clear that the lowest potential energy curve was obtained by using Slater basis and truncate CI.

In order to compare with previous theoretical and experimental results, we have estimated the dissociation energy (D_e) and the equilibrium geometry (R_e) from the spline fit of our *ab initio* points. These results are presented in Table II jointly with the theoretical ones obtained by Partridge and Langhoff [14], Gadéa and Leininger [4] and Lundsgaard and Rudolph [15], and with the experimental ones obtained by Chan *et al.* [5]. In particular, Gadéa and Leininger employed

TABLE II. Spectroscopic constants for the ground state of LiH molecule. All constants are given in cm^{-1}, except for R_e (Å).

	D_e (cm^{-1})	R_e (A)	ΔD_e (cm^{-1})	ω_e	$\omega_e x_e$	B_e	α_e
cc-pVDZ	18186	1.582	2098	1366.0	30.317	7.319	0.1448
cc-pVTZ	19933	1.596	351	1415.3	27.003	7.503	0.1983
cc-pVQZ	20396	1.616	112	1411.3	37.343	7.612	0.2476
cc-pVDZ (CP)	18144	1.600	2140	1370.2	23.626	7.303	0.1755
cc-pVTZ (CP)	19749	1.604	535	1401.2	28.932	7.426	0.1948
cc-pVQZ (CP)	20109	1.618	175	1401.3	26.173	7.472	0.2088
Slater[a] [14]	19991	1.556	293	1394.8	20.856		
CPP [4]	20349	1.595	65				
LR [15]	20102	1.595	182	1406.2	23.578	7.516	0.2124
EXP [5]	20284	1.595		1405.7[b]	24.164[b]	7.521[b]	0.2196[b]
				1405.1[c]	22.680[c]	7.513[c]	0.2153[c]

[a] Results from Ref. 15

[b] From Dunham-type coefficients without their adiabatic corrections

[c] From Dunham-type coefficients with their adiabatic corrections

TABLE III. Experimental vibrational energy levels of ground state of LiH molecule and the differences between various computed values and the experimental ones. The last row lists the absolute mean error ($|\Delta|_{av}$). Values are in cm^{-1}.

ν	Exp [1]	FCI cc-pVQZ	FCI cc-pVQZ(CP)	CCSD-[4R] [2] cc-pVQZ	LR [15]	CI [14] Slater	CPP [4]
0	697.9	-0.8	3.5	0.4	0.2	5.6	2.2
1	2057.6	-9.7	10.7	2.2	0.2	18.3	2.2
2	3372.5	-19.8	17.3	2.8	0.4	27.5	2.5
3	4643.4	-23.2	22.1	3.0	0.8	6.5	2.8
4	5871.1	-20.4	25.0	3.5	1.2	26.1	3.2
5	7056.6	-13.5	26.7	4.7	1.8	25.7	3.8
6	8200.4	-3.6	27.2	6.6	2.6	25.0	4.6
7	9303.0	8.4	26.7	9.1	3.4	16.1	5.5
8	10364.7	21.9	25.1	12.1	4.4	36.8	6.4
9	11385.9	36.1	22.8	15.5	5.7	50.2	7.7
10	12366.4	50.8	19.8	19.1	7.4	61.0	9.5
11	13306.0	65.3	16.8	22.9	9.6	55.7	11.6
12	14204.1	79.3	14.1	26.8	12.5	68.0	14.5
13	15059.6	92.5	12.0	30.5	16.2	80.0	18.2
14	15870.8	105.0	10.6	33.8	21.0	97.8	23.0
15	16635.2	116.8	10.1	36.5	27.1	114.9	29.1
16	17349.5	127.3	11.6	38.2	34.9	117.7	37.0
17	18008.7	136.2	15.7	38.2	44.7	130.6	46.7
18	18606.6	142.4	23.9	35.9	57.1	153.4	59.1
19	19134.5	146.5	36.3	29.9	72.7	183.4	74.7
20	19581.1	147.5	55.1	18.4	92.2	214.9	94.2
21	19932.1	143.3	82.9	-1.7	116.2	268.6	118.2
22	20169.8	134.0	120.4	-37.8	144.6	380.3	146.6
$\|\Delta\|_{av}$		71.5	27.7	18.7	30.8	98.4	32.9

a pseudopotential approach with the inclusion of CPP corrections and Lundsgaard and Rudolph used the FCI method with an atomic basis composed of five s-functions contracted from ten s-basis and augmented with five $p-$ and four $d-$orbitals to Li atom and triple zeta ANO basis set to H atom. In the fourth column, we have listed the absolute mean error between theoretical and experimental dissociation energies. The results most nearly of experimental data were those ones obtained by Gadéa and Leininger. However, the present results computed with cc-pVQZ basis including the CP correction show a good agreement with the experimental ones.

In Fig. 5, we are comparing our calculated permanent dipole moment functions with the ones obtained by Partridge and Langhoff [14]. We have noticed that the PDM curves have the same behavior for all basis used by us and for the Slater basis. For small distances into nuclei the most closed curve to Partridge and Langhoff results is the cc-pVQZ one and for larger distances our PDM function most closed to Partridge and Langhoff ones is the one obtained using the cc-pVTZ basis.

A good way to test the accuracy of basis set is through of vibrational energy levels. By using the PEC's that have been obtained in this work, we solved the radial Schrodinger equation by using the LEVEL 7.1 program [12]. The experimental $G(\nu)$ obtained by Chan *et al.* [5] is showed jointly with the differences between various computed values and the experimental ones in Table III. The considered theoretical results are the present ones obtained using the cc-pVQZ basis set with and without the CP correction and those ones calculated by Li and Paldus using the CCSD-[4R] method with cc-pVQZ basis [2], besides those ones computed by Gadéa and Leininger [4] and by Lundsgaard and Rudolph [15]. In the last row lists the absolute mean errors ($|\Delta|_{av}$). The Li and Paldus result is the one that shows o lesser $|\Delta|_{av}$. Moreover, the use of counterpoise correction of BSSE improves our FCI calculations with a significative reduction of $|\Delta|_{av}$ when compared with the ones without such a correction.

Finally, the spectroscopic constants are calculated as described in Sec. 2. In particular, we have considered all vibrational term values and rotational constants in calculation

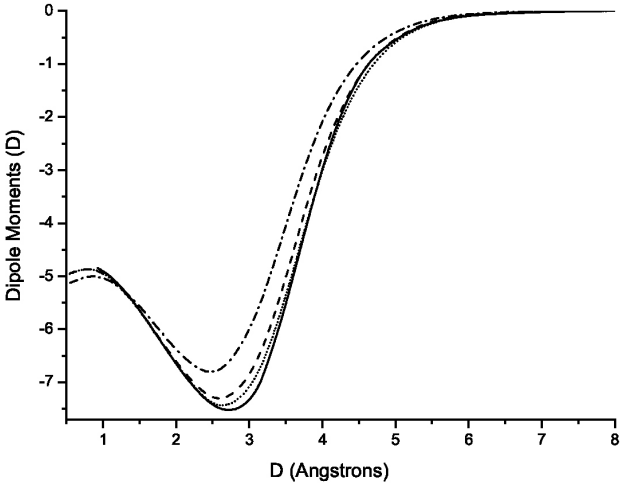

FIGURE 5. Permanent dipole moment functions of $X^1\Sigma^+$ state of LiH using $(-\cdot-)$ FCI/cc-pVDZ, $(--)$ FCI/cc-pVTZ, $(\cdots)$ FCI/cc-pVQZ and (—)CI/Slater [14] approaches.

of spectroscopic constants employng expansions up to order 9. The results of ω_e, $\omega_e x_e$, B_e and α_e are presented in Table II and are compared with others theoretical and experimental ones. The Lundsgaard and Rudolph results are the most accurate when compared with experimental ones, but they considered only 12 vibrational levels to compute the spectroscopic constants. Our results obtained within CP approach are always closer to experimental ones than the results calculated without considering the CP correction.

4. Concluding remarks

In the present work we showed a FCI theoretical study of Lithium Hydride diatomic molecule. The influence of atomic orbital basis sets and the effect of the CP approach in the calculation of the ground state potential energy curves of the this molecule were analyzed. Thus, our best result was obtained with the cc-pVQZ basis set and when the counterpoise correction of the basis set superposition error is employed. A study using a improved class of basis set as the aug-cc-pVXZ, X=D, T and Q, ones is planned in the future. Moreover, we will employ the potential adiabatic correction due to finite nuclei mass that accounts for the Born-Oppenheimer breakdown to improve the theoretical results.

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