Theoretical study for potential energy curves, dissociation energy and molecular properties for (LiH, H₂, HF) molecules

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ABSTRACT. A theoretical study has been carried out of calculating dissociation energies and potential energy curves (Deng-Fan potential and Varshni potential) and molecular parameters of of ground state of diatomic molecules (LiH, H₂, HF). Dissociation energies and potential energy curves depended on spectroscopic constants (ω_e , $\omega_e x_e$, r_e , α , μ , β .) and our results has been compared with experimental results. Molecular and electronic properties as ϵ_{HOMO} , ϵ_{LUMO} , ionization potentials (IP), electron affinities (EA) and binding energy was performed by using B3P86/6-311++g** method and Gaussian program 03, the results is well in a agreement with that of other researchers.

1. INTRODUCTION

A potential energy curve is a graphical representation of the change in potential energy of the molecule as a function of the distortion of the bond of the molecule from its equilibrium distance. The knowledge of potential energy curves is of prime importance in the study of diatomic molecular spectra [1]. In the calculations of Franck Condon factor, dissociation energy and thermodynamic quantities etc, the studies of potential energy curves are necessary. The empirical potential energy functions like Varshni [2] and Deng-Fan potential [3] are usually applied and the potential energy curves are drawn. Naturally to compute the turning points of various vibrational levels the accurate spectroscopic constants are required. The empirical potential energy functions also require these molecular constants.

Lithium hydride, the simplest stable metallic hydride, and the subject of an extensive review in 1993, continues to generate intense theoretical and spectroscopic interest. In particular, it provides a testing ground for new techniques, permits validation of approximate methods, and the existence of various isotopes allows analysis of the breakdown of the Born-Oppenheimer (BO) approximation. Of additional interest are the mutual neutralization of Li⁺ and H⁻ ions.[4]

Hydrogen fluoride is a chemical compound with the formula HF. This colorless gas is the principal industrial source of fluorine, often in the aqueous form as hydrofluoric acid, and thus is the precursor to many important compounds. HF is widely used in the petrochemical industry and is a component of many super acids. Hydrogen fluoride boils just below room temperature whereas the other hydrogen halides condense at much lower temperatures. Unlike the other hydrogen halides, HF is lighter than air and diffuses relatively quickly through porous substances. Hydrogen fluoride is a highly dangerous gas, forming corrosive and penetrating hydrofluoric acid upon contact with tissue. The gas can also cause blindness by rapid destruction of the corneas[5,6].

Theoretical determination of the dissociation energy of the simplest, prototypical chemical bond in the hydrogen molecule has a long history. It started in 1927, very shortly after the discovery of quantum mechanics, by the work of Heitler and London[7] who approximately solved the Schrödinger equation for two electrons in the Coulomb field of two protons and found that this system is stable against the dissociation to two hydrogen atoms. The approximate dissociation energy they obtained represented only about 60% of the observed value but it could be argued that by virtue of the vibrational principle this was only a lower bound and, consequently, that the new quantum theory satisfactorily explained the hitherto puzzling stability of chemical bond between electrically neutral atoms.

Theoretical calculations of the spectroscopic behavior of simple molecules, such as H₂, LiH and HF are in nearly perfect agreement with experimental data, especially around the equilibrium distance r_e . Still, there is a need for generally valid potential energy (PE) functions for more complicated systems. The ideal solution would be a single PE function, capable of accounting for the spectral data of a great variety of bonds. In a recent review of the question, the divergent behavior of non-ionic and ionic molecules could be understood and accounted for if, in first approximation, the ground state of all bonds was determined by ionic structures. A potential energy function should therefore reproduce dissociation energies in the first place[8,9].

All results of such procedure are presented in this paper for three molecules H₂, HF, and LiH represented by dissociation energies and potential energy curves (Deng-Fan potential and Varshni potential), and Molecular and electronic properties as ϵ_{HOMO} , ϵ_{LUMO} , ionization potentials (IP), electron affinities (EA) and binding energy are calculated by using B3P86/6-311++g** method and Gaussian program 03[10] except binding energy by mathematical equation[11].

2. THEORY

Dissociation energy and potential energy functions:

The height of an asymptote of a potential energy curve, above the lowest vibrational level, is equal to the work that must be done in order to dissociate that molecule, and is known as the heat of dissociation or dissociation energy D_0 . Another constant D_e is also the dissociation energy but it is taken as a height of an asymptote from x-axis or measured from minima of the potential energy curve. The relation between D_0 and D_e is here[12]

$$D_e = D_0 + G(0) \quad (1)$$

$$\text{where } G(0) = \omega_e/2 - \omega_e x_e/4 + \omega_e y_e/8 + \dots \quad (2)$$

$$D_e = \Delta G_{\text{max}}(v) \quad (3)$$

The relation in defining the dissociation energy D_e in terms of molecular constants is

$$D_e = \omega_e^2 / 4\omega_e x_e \quad (4)$$

Varshni function and Deng-Fan Potential function:

One of functions of potential is Varshni function which is different from Morse function by term(r/r_e) so the function had written as [13]:

$$U(x) = D_e \left(1 - \frac{r}{r_e} e^{-\beta x} \right)^2 \quad (5)$$

$$x = r - r_e$$

$$\beta = \left[\frac{8\pi^2 \mu (\omega_e x_e) c}{h} \right]^{1/2} \quad (6)$$

where β , r_e and D_e have the same physical significant as in the Morse potential function and $\omega_e x_e$: the anharmonicity constant, μ : reduced mass, c : speed of light and h : plank constant.

On the other hand, another function of potential called Deng-Fan potential function has the form[3]:

$$U_{\text{Deng-Fan}}(r) = P_1 + \frac{P_2}{e^{\alpha r} - 1} + \frac{P_3}{(e^{\alpha r} - 1)^2} \quad (7)$$

$$P_1 = D_e ; P_2 = -2D_e (e^{\alpha r_e} - 1) ; P_3 = D_e (e^{\alpha r_e} - 1)^2 ; \alpha: \text{ spectroscopic parameter}$$

Ionization potentials (IP), Electron affinities (EA) and Binding energy

The B3P86/6-311++g** method has been carried out using the Gaussian 03 programs [10] for the molecular and electronic properties of the LiH, H₂, HF. In this investigation, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy were used to estimate the IP and EA in the framework of Koopmans, theorem[14]:

$$\text{IP} = -\varepsilon_{\text{HOMO}} \quad \text{and} \quad \text{EA} = -\varepsilon_{\text{LUMO}} \quad (8)$$

and binding energies [11]:

$$\text{B.E} = D_e + \text{IP} + \text{EA} \quad (9)$$

3. RESULTS AND DISCUSSION

In the present work, the spectroscopic parameters for three diatomic molecules (LiH, H₂, HF) are summarized in table1 [15, 16, 17], dissociation energy is obtained using (eq.4) compared with another energy. and potential energy curves for two functions began with Varshni potential function for ground $^1\Sigma^+$ state (eq. 13) and other function "Deng- Fan potential function " for ground $^1\Sigma^+$ state (eq. 14).

Table 1. Spectroscopic parameters of ground state of LiH, H₂, HF molecules measured in (cm⁻¹) and r_e in (Å°)

Molecule	Spectroscopic parameters of ground state $^1\Sigma^+$					
	ω_e	$\omega_e x_e$	r_e	B_e	α	$\mu(g) \times 10^{-23}$
LiH	1405.64	23.20	1.5956	7.5137	1.79983	0.880
H₂	4401.21	121.33	0.7416	60.853	1.44055	0.503
HF	4138.38	89.94	0.917	20.953	0.97103	0.160

The D_e values of these molecules are found to be (21291.2 cm⁻¹ for LiH), (39913.14 cm⁻¹ for H₂) and (47602.95 cm⁻¹ for HF) for ground state $^1\Sigma^+$, that dissociation due to approaching the bond length (r) from infinity values, where this is one of three conditions of potential curve. These results are in good agreement with the experimental values[18] as in table below.

Table 2. Dissociation energy of ground state of LiH, H₂, HF molecules measured in (cm⁻¹)

Molecule	Dissociation energy	
	calc.	expt. [18]
LiH	21291.2	20291.5
H₂	39913.14	38283.1
HF	47602.95	49405.5

These theoretical values are agreement rather with experimental results but there are simple different led us also to simple different in potential curves because our potential functions (Varshni and Deng-Fan) are depended on dissociation energy for LiH, H₂ and HF molecules. In calculating Varshni potential for these molecules (eq. 5) is used for the ground state $^1\Sigma^+$, and here are the results in table (3) and figures (1,2,3).

The calculations of LiH molecule appeared the maximum value of varshni potential is at (r = 1 Å°) that mean the minimum value of bond length give us maximum potential in ground state of this molecule. At bond length (r = 1.5956 Å°), the potential equal (zero), then the potential increase by increasing bond length until reach at the point which happen in it the dissociation because that the diatomic molecules dissociate when the value of (r) increase to determinate limit. The calculations of H₂ molecule appeared the maximum value of varshni potential is at (r = 0.4 Å°) which equal (111574.11 cm⁻¹), this value is large that due to taken small value for bond length, but when bond lengths begin increasing we note degreasing in values of potential until the value (r=r_e) after that when (r) increase, the potential curve increase also until reach to dissociation limit. Also for HF molecule, behavior the potential curve is similar to previous curves but there are one different which is we not high value for potential at large values of bond length that due to this molecule has large dissociation energy being larger that dissociation energies for LiH and H₂ molecules.

Table 3: Varshni potential for ground state $^1\Sigma^+$ of LiH, H₂, HF molecules measured in (cm⁻¹)

Molecule	LiH	H ₂	HF
	r (Å) U _{Varsh} (r)	r (Å) U _{Varsh} (r)	r (Å) U _{Varsh} (r)
	1 97750.47	0.4 111574.1	0.4 8096.72
	1.2 30382.62	0.5 47486.18	0.5 7870.38
	1.4 5110.41	0.6 12992.08	0.6 5659.3
	1.5956 0	0.7416 0	0.7 2974.84
	1.6 1.7691	0.8 1285.06	0.8 908.47
	1.8 2627.6	0.9 7112.29	0.917 0
	2 7176.25	1 14276.41	1 447.45
	2.2 11393.08	1.2 26251.77	1.2 4638.28
	2.4 14651.8	1.4 33313.8	1.4 11458.31
	2.6 16961.48	1.6 36884.03	1.6 18922.4
	2.8 18520.3	1.8 38563.06	1.8 25795.31
	3 19540.9	2 39322.46	2 31533.55
	3.2 20195.92	2.2 39657.99	2.2 36035.51
	3.4 20610.58	2.4 39803.97	2.4 39421.65
	3.6 20870.52	2.6 39866.77	2.6 41894.48
	3.8 21032.3	2.8 39893.57	2.8 43661.35
	4 21132.42	3 39904.92	3 44903.78
	4.2 21194.11	3.2 39909.7	3.2 45766.82
	4.4 21231.98	3.4 39911.71	3.4 46360.66
	4.6 21255.16	3.6 39912.89	3.6 46766.21
	4.8 21269.31	3.8 39913.03	3.8 47041.5
	5 21277.93	4 39913.09	4 47227.44
		4.2 39913.12	4.2 47352.51
		4.4 39913.13	4.4 47436.34
		4.6 39913.13	4.6 47492.35
		4.8 39913.13	4.8 47529.68
		5 39913.13	5 47554.5

To calculate Deng-Fan potential for all previous molecules eq. (7) is used for the ground state $^1\Sigma^+$ by depending on dissociation energy, bond length, spectroscopic constants in table 1, and here are the results of Deng-Fan potential for all molecules in table (4) and figures (4,5 and 6).

The calculations of LiH molecule appeared the maximum value of Deng-Fan potential is at ($r = 5 \text{ Å}$) that mean there are difference in the behavior of this curve comparing with Varshni potential for this molecule. value of bond length give us maximum potential in ground state of this molecule at maximum bond length in our calculating. At bond length ($r = r_e$), the potential equal (zero), the dissociation happen after that because the diatomic molecules dissociate when the value of (r) increase to determinate limit. The calculations of H_2 molecule appeared converge between Deng-Fan potential and Varshni potential as the behavior. behavior of potential curve of HF

molecule is different rather than behavior of curve in Varshni potential that is due to form and parameters of each suggested function. At the end all results for to functions compared with experimental results[9,18] as shown in figure (7, 8 and 9).

Table 4: Deng-Fan potential for ground state $^1\Sigma^+$ of LiH, H₂, HF molecules measured in (cm⁻¹)

Molecule	LiH		H ₂		HF	
	r (Å)	U _{Deng-Fan} (r)	r (Å)	U _{Deng-Fan} (r)	r (Å)	U _{Deng-Fan} (r)
	1	7552.82	0.3	86483.15	0.4	79523.41
	1.2	2313.93	0.4	29109.29	0.5	33110.52
	1.4	415.6	0.5	9319	0.6	13287.7
	1.5956	0	0.6	2223	0.7	4574.64
	1.6	0.16	0.7416	0	0.8	1018.18
	1.8	274.54	0.8	212.69	0.917	0
	2	870.48	1	2665.02	1	327.93
	2.2	1606.95	1.2	5824.28	1.2	2647.55
	2.4	2391.78	1.4	8827.53	1.4	5665.94
	2.6	3177.36	1.6	11488.28	1.6	8674.31
	2.8	3939.35	1.8	13799.77	1.8	11455.4
	3	4665.94	2	15801.31	2	13958.24
	3.2	5352.11	2.2	17539.76	2.2	16891.81
	3.4	5966.63	2.4	19057.76	2.4	18125.8
	3.6	6600.3	2.6	20391.42	2.6	19945.98
	3.8	7164.95	2.8	21570.45	2.8	21528.73
	4	7692.96	3	22619.08	3	22949.32
	4.2	8186.85	3.2	23557.05	3.2	24229.57
	4.4	8649.17	3.4	24400.49	3.4	25388.05
	4.6	9082.38	3.6	25162.68	3.6	26440.53
	4.8	9488.79	3.8	25854.56	3.8	27400.34
	5	9870.54	4	26485.28	4	28278.79
			4.2	27062.44	4.2	29085.53
			4.4	27592.61	4.4	29828.77
			4.6	28081.14	4.6	30515.58
			4.8	28532.71	4.8	31152.01
			5	28951.34	5	31743.34

Fig. 4 Deng -Fan potential for ground state of LiH molecule

Fig. 5 Deng -Fan potential for ground state of H₂ molecule

Fig.6 Deng -Fan potential for ground state of HF molecule

Fig.7 Varshni and Deng-Fan potential comparing with experimental for ground state of LiH molecule

Fig.8 Varshni and Deng-Fan potential comparing with experimental for ground state of H_2 molecule

Results of electronic properties of all previous molecules are calculated by depending on B3P86/6-311++g** method method using the Gaussian 03 programs [10] and equation (8). Binding energy calculated from equation (9), these results in table (5) and converge with results of other researcher[19]. We noted that the ionization potential for H_2 molecule is larger than it for LiH and HF molecules that due to the small value of HOMO energy that lead to obtaining on high binding energy higher than other molecules. Also we noted the higher value of electron affinities was for LiH molecule which give us the lower value of binding energy comparing with the other molecules. These results appeared also that the ionization potential necessary to remove an electron from the neutral atom. The ionization energy is one of the primary energy considerations used in quantifying chemical bonds.

Table 5: Results of of ϵ_{HOMO} , ϵ_{LUMO} , ionization potentials (IP), electron affinities(EA) and binding energy of LiH, H_2 , HF molecules

Molecule	$\epsilon_{HOMO}(ev)$	$\epsilon_{LUMO}(ev)$	IP(ev)	EA(ev)	B.E (kcal/mol)
LiH	-5.321	-1.321	5.321	1.321	153.1171
H_2	-11.810	2.713	11.810	-2.713	449.0261
HF	-11.422	0.973	11.41	-0.973	421.9398

5. CONCLUSIONS

The potentials of LiH, H_2 and HF molecules by using Varshni function and Deng – Fan function for ground $^1\Sigma^+$ state are agreement rather than experimental results and the important notice that bond length (r) with spectroscopic constants have an effect upon values of the potential. In general all values of potentials in beginning be high and degrease with increasing bond length and after ($r=r_e$) be increasing in the values with increasing values of (r). behavior of potential curve of HF molecule is different rather than behavior of curve in Varshni potential that is due to form and parameters of each suggested function. Dissociation energies for all molecules for ground $^1\Sigma^+$ state very convergence with experimental dissociation energies. The ionization potential for H_2 molecule is larger than it for LiH and HF molecules and the higher value of electron affinities was for LiH molecule which give us the lower value of binding energy.

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