Potencial Energy Functions & Properties of Some Hydride Molecules

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Abstract: *The values of dipole moment (μ), rotational constant(α_e),vibrational constant($\omega_e x_e$), binding energy (D_i) and dissociation energy (D_e) have been computed using the four forms of short-range repulsive interaction(SRRI) models with an aim to establish the applicability and validity of potential energy functions. The calculations have been done for chemically active but simple hydride namely, LiH, NaH, KH, RbH,CsH,BeH, BH, MgH, AlH & SiH.The computed values are in fair agreement with the experimental values available in the literature for the mentioned system. The close agreement between the observed an the calculated values simply revealed that Hellmann and Ali-Hasan forms of interaction models appear to be more appropriate short range repulsive interaction models for the prediction of many other properties of the system. This study shows that these models play an important role in molecular physics as well as in the problems of astrophysics.*
Keywords: - *Anharmonicity constant, Binding energy, Dipole-dipole & Dipole-quadrupole interaction constants, Dissociation energy & Rotational constant.*

I.   Introduction-

Alkali hydride molecules are chemically very simple compounds but due to their reactive nature, a very few physical properties of these molecules could be measured. As such the experimental information about them is not available in the literature. Owing to the non availability of the observed data for other practical applications the theoretical estimates of the various properties of these hydrides will be useful. In this connection several effects have already been taken up by different workers. The nature of forces which bind the atom or ions in the diatomic molecules is of fundamental importance in the fields of physico-chemical interest. Rittner [1] for the first time proposed a polarizable ion model for alkali halide molecules through which the interionic forces could be understood. Later on, Brumer & Karplus [2] modified the Rittner model known as truncated Rittner model or simply known as T-Rittner model given by,

$$U(r) = -\frac{z^2 e^2}{r} - \frac{(\alpha_1 + \alpha_2)}{2r^4} - \frac{C}{r^6} - \frac{D}{r^8} + U_R(r)$$

The 1st term is the electrostatic attraction between two point charges Z(+e) & Z(-e) separated by an interionic distance r, the 2nd term is the polarization energy, the third & fourth terms are van der Waals dipole-dipole and dipole-quadrupole interaction. The last term is the short-range repulsive interactions.α_1 and α_2 are the electronic polarizabilities of cation and anion respectively.An extensive work [3-7] has been done on T-Rittner model for alkali halide molecules but study of hydride molecules have not been properly taken up by theoretical workers.

There are several repulsive interactions proposed by different theoretical workers from time to time to describe the structure & properties of diatomic ionic molecules $[8 - 9]$.The repulsive interactions in logarithmic function $[10 - 12]$ are also available in the scientific literature but the results are far from satisfactory. As a result, the exact form of short-range repulsive interaction model is still to be asscertained.

In the present paper we are using the Born-Mayer, Hellmann Varshni Shukla & Ali-Hasan form of short-range overlap forms which involve potential parameters. These forms for the overlap term be exploited to describe the various physical properties of hydride molecular substances. Born Mayer [14-15] and HM [16] of repulsive interaction are exponential in nature capable enough to produce various properties of alkali halide molecules approximately. V.S. presented an alternative approach for potential energy function of diatomic molecules by assuming a term to represent the electrostatic interaction and other to represent repulsion arising from the overlap of outermost electrons of constituent atoms and ions. This potential has further been modified by introducing the concept of effective charge parameter. Ali & Hasan [17] has developed an empirical short range repulsive interaction model. Which produced many molecular properties in close agreement with expt. Value. In our calculation we have been inspired to examine the applicability and suitability of the short range repulsive models incorporating the polarizable term and dipole-dipole and dipole-quadrupole vdW energy term

which have not been studied by the previous workers taking all the terms in consideration. This is, therefore, the comprehensive study for the molecular hydride systems.

II. Method Of Calculation

A generalized formula for short-range repulsive interaction can be expressed as

$$U_R(r) = \frac{B}{r^m} exp\left(-\frac{r}{\rho}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (1)$$

Which takes the form of Born-Mayer repulsive potential when m=0, Hellmann repulsive potential when m=1 and Varshni-Shukla potential when m=2. Ali-Hasan empirical repulsive potential is expressed as

$$U_R(r) = \frac{S}{r^m} exp(-br^n) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (2)$$

In this potential m=2 and n=$\frac{3}{2}$. In equation (2) and (3) B,S, ρ and b are repulsive potential parameters. The repulsive potential parameters are determined by applying the equilibrium criteria:

$$\left(\frac{dU(r)}{dr}\right)_{r=r_e} = 0 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (3)$$

Where K_e is the molecular force constant, ω_e is the equilibrium vibrational frequency C is the speed of light in vacuum, μ_A is the reduced mass and r_e is the interionic separation.

The expressions for potential parameter obtained are given by

$$x = K_e r_e^2 + \frac{2e^2}{r_e} + \frac{42C}{r_e^6} + \frac{72D}{r_e^8} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (4)$$

$$b = \frac{1}{6r_e^{\frac{3}{2}}} \left[(2x-7) + (4x^2 + 4x - 47)^{1/2}\right] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (5)$$

$$\& \quad P = \frac{2r_e^2 exp(br_e^{\frac{3}{2}})}{3br_e^{3/2} + 4} \left[\frac{e^2}{r} + \frac{6c}{r_e^6} + \frac{8D}{r_e^8}\right] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (6)$$

The vdw dipole-dipole constant C and dipole-quadrupole constant D taken from Slater Kirkwood variational method [18] are expressed as

$$C = \frac{3\,eh}{4\pi m^{1/2}} \frac{\alpha_1 \alpha_2}{\left(\frac{\alpha_1}{N_+}\right)^{1/2} + \left(\frac{\alpha_2}{N_-}\right)^{1/2}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (7)$$

$$\& \; D = \frac{\frac{27h^2 \alpha_1 \alpha_2 h}{32\pi^2 m}\left(\left(\frac{\alpha_1}{N_+}\right)^{1/2} + \left(\frac{\alpha_2}{N_-}\right)^{1/2}\right)^2}{\left(\frac{\alpha_1}{N_+}\right) - \frac{20}{3}\left(\frac{\alpha_1 \alpha_2}{N_+ N_-}\right)^{1/2} + \left(\frac{\alpha_2}{N_-}\right)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (8)$$

Where N_+ and N_- are the effective no. of electrons in the ions are defined as

$$N_+ = N + Z_+ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (9)$$

$$N_- = N - Z_- \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (10)$$

Here N is the total number of electrons in the outer two shells. The eq^n (9) &(10) are valid for the ions of S-block and p-block elements of Periodic Table. In the case of ions of d-block elements of Periodic Table,

$$N = N_1 + 0.5 N_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (11)$$

Where N_1 and N_2 are the number of electrons in the 1st & 2nd outer shells respectively.

The rotational vibration coupling constant (α_e) and anharmonicity constant ($\omega_e x_e$) are calculated by the formula,

$$\alpha_e = -\left(\frac{X_3 r_e}{3} + 1\right)\frac{6Be^2}{\omega_e} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (12)$$

$$\& \quad \omega_e x_e = \left(\frac{5}{3}X_3^2 - X_4\right)\frac{h}{64\pi^2 c\mu} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (13)$$

Here $\quad x_p = \left(\frac{d^p U(r)}{dr^p}\right)_{r=r_e} / \left(\frac{d^2 U(r)}{dr^2}\right)_{r=r_e} \ldots\ldots\ldots\ldots\ldots\ldots\ldots.\ldots\ldots. (14)$

The binding energy per mole (D_i) and dissociation energy (D_e) is given by

$$D_i = -NU(r_e) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (15)$$

$$\& \quad D_e = D_i - I + E \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (16)$$

Where N is the Avogadro`s number, r_e is the equilibrium internuclear distance, I is the ionization potential and E is the electron affinity.

III. Results and Discussion

The experimental input data for Interionic equilibrium separation (r_e), Force constant (K_e), Vibrational frequency (ω_e) and Rotional constant (B_e) have been taken from Huber & Hertzberg [19]. The values of electronic polarizibilities (α_1, α_2) have been taken from Tessman [20].These deta have been shown in Table No-1

Table-1

Molecules	α_1	α_2	B_e	ω_e	K_e	r_e
LiH	0.034	1.86	7.53	1367.4	1.298	1.596
NaH	0.190	1.86	4.905	1352.0	1.080	1.887
KH	1.143	1.86	3.412	1176.0	0.805	2.243
RbH	1.805	1.86	3.022	944.40	0.469	2.367
RbH	1.805	1.86	3.022	944.40	0.469	2.367
CsH	2.989	1.86	2.752	1415.1	0.460	2.494
BeH	0.008	1.86	10.32	2060.8	2.263	1.343
BH	0.003	1.86	12.02	2366.9	3.03	1.232
MgH	0.094	1.86	5.62	1497.0	1.275	1.730
AlH	0.052	1.86	6.40	1682.6	1.62	1.646
SiH	0.0165	1.86	7.50	2041.8	2.39	1.520

The computed values of dipole moments, van der Waals constant C,D & vdW energies are produced in Table-2

Table-2

Molecules	dipole moment(μ)	C	D	W_{d-d}	W_{d-q}
LiH	4.09	1.477	1.949	0.089	0.0465
NaH	6.302	8.110	13.59	0.179	0.085
KH	7.901	43.76	49.261	0.344	0.0769
RbH	8.296	69.34	77.950	0.394	0.0791
CsH	8.072	108.0	121.016	0.448	0.0808
BeH	1.476	1.18	0.523	0.242	0.049
BH	0.413	0.14	0.206	0.041	0.0478
MgH	5.164	13.72	4.40	3.924	1.02
AlH	4.513	2.368	3.127	0.119	7.126
SiH	3.598	0.78	1.10	0.063	0.047

Table-3 presents the computed values of potential parameters for all the short-range repulsive potential parameters.

Table-3

Molecules	values of A.H (χ)	Values of parameter b			A.H ($\times 10^{12}$)	Values of parameter P		
		B.M ($\times 10^8$)	Hell ($\times 10^8$)	V.S ($\times 10^8$)		B.M ($\times 10^{-8}$)	Hell ($\times 10^{-20}$)	V.S ($\times 10^{-28}$)($\times 10^{-28}$)
LiH	4.36	2.733	1.954	1.150	0.706	0.0275	134.32	58.77 39.18
NaH	4.77	2.53	1.880	1.22	0.670	0.0349	201.23	115.45 61.42
KH	5.28	2.354	1.810	1.270	0.630	0.0519	332.65	231.89 104.72
RbH	5.395	2.279	2.198	1.26	0.60	0.0519	883.41	282.49 120.10

CsH 141.44	5.53	2.217	1.74	1.25	0.58	0.0572	446.08	345.82
BeH 37.39	4.596	3.420	2.504	0.803	1.035	0.0394	158.91	31.52
BH 23.83	4.580	3.717	2.719	0.847	0.788	0.045	132.71	27.369
MgH 476.14	6.670	3.850	3.180	2.520	1.390	0.805	2960.47	1672.82
AlH 89.93	5.37	3.260	2.540	1.804	1.04	0.0610	317.10	73.34
SiH 71.76	5.750	3.796	3.01	2.39	1.365	0.0914	435.37	208.55

Table 4 displays the computed values of binding energy of the molecules with polarization.

Table- 4

Molecules %error	Expt	B.M	%error	Hell	%error	V.S	%error	A&H
LiH 27.60	161.238	212.62	31.86	211.60	31.23	211.06	30.89	205.74
NaH 11.85	146.745	168.99	15.15	167.56	14.18	146.16	0.39	164.14
KH 16.93	142.8	150.22	5.19	142.30	0.35	132.31	7.34	118.62
RbH 16.86	140.5	137.09	2.42	136.34	2.96	136.42	2.90	164.2
CsH 26.77	118.1	134.12	13.56	135.45	14.69	139.36	18.0	149.72
BeH	241.67	287.98	19.15	286.97	8.72	282.97	7.09	286.26	8.42
BH 29.91	250.76	322.07	19.86	188.56	27.80	297.4	24.32	311.76
MgH 0.95	203.17	199.25	1.53	203.52	0.17	195.36	3.84	201.23
AlH 0.54	185.69	219.3	7.94	217.78	7.19	217.01	6.80	202.04
SiH 14.03	248.64	246.32	11.76	248.39	10.78	259.43	10.54	247.53

Table-5 presents the computed values of Dissociation energy of the molecules

Molecules	Expt.	B.M.	Hell	V.S.	A&H
LiH	58	51.412	61.489	60.53	103.916
NaH	47	90.34	62.235	40.85	58.84
KH	42.9	86.72	70.47	63.48	84.41
RbH	39	75.24	74.47	74.10	82.40
CsH	41	60.54	42.44	86.42	99.09
BeH	_	330.60	326.49	309.69	323.49
BH	_	61.45	95.04	466.59	526.92
MgH	_	121.79	139.72	105.47	130.09
AlH	_	360.11	353.73	350.48	287.65
SiH	_	271.32	275.52	326.39	276.43

Table-6 shows the computed values of Rotational constants (α_e) in 10^{-4} cm

Molecules. A&H %error	Expt.	B.M.	%eror	Hell	%error	V.S.	%error	A&H
LiH 17.1	0.2132	0.2144	0.67	0.245	4.78	0.218	3.76	0.259
NaH 11.8	0.1353	0.138	2.27	0.128	5.18	0.147	8.1	0.162
KH 2.4	0.0817	0.073	9.8	0.085	4.04	0.087	6.4	0.079

Molecules	expt	B.M.	%error	Hell	%error	V.S.	%error	A&H	%error
RbH	0.072	0.086	19.4	0.0754	4.72	0.0684	5.0	0.06	14.2
CsH	0.0579	0.051	10.53	0.0595	2.76	0.0522	9.8	0.0512	10.5
BeH	0.1225	0.095	22.0	0.124	1.64	0.136	11.02	0.1228	0.24
BH	0.412	0.0482	7.3	0.365	10.97	0.390	4.87	0.44	7.3
MgH	0.1859	0.167	11.1	0.191	0.75	0.1872	0.75	0.197	6.43
AlH	0.1858	0.150	18.8	0.1883	1.37	0.186	0.58	0.170	8.07
SiH	0.2190	0.2176	0.64	0.224	2.28	0.224	2.28	0.194	11.4
Average%Deviation:-			10.25		3.85		5.26		8.94

Table-7 computed values of vibrational Constant($\omega_e x_e$) in cm^{-1}

Molecules	expt	B.M.	%error	Hell	%error	V.S.	%error	A&H	%error
LiH	23.2	22.08	4	25.76	11.03	27.72	19.48	28.08	21.03
NaH	19.72	17.41	11.71	15.08	21.05	16.19	17.90	17.16	12.98
KH	14.32	16.05	12.08	13.39	5.9	13.41	5.76	13.44	5.85
RbH	14.21	17.10	20.33	16.79	18.3	13.41	5.53	13.59	4.30
CsH	12.9	12.49	3.18	15.42	8.58	10.61	25.2	13.70	3.50
BeH	20.71	16.62	19.3	17.47	15.59	19.49	5.86	24.45	18.05
BH	49.39	53.01	7.32	51.03	3.31	45.05	8.78	42.43	14.09
MgH	31.889	32.0	0.36	28.97	9.15	29.49	7.50	29.74	6.75
AlH	29.09	29.92	2.85	24.17	16.9	26.20	9.92	28.34	2.56
SiH	35.51	39.18	10.3	44.49	25.3	38.27	7.78	36.86	3.83
Average % deviation			9.14%		14.4%		11.35%		9.29%

B.M >A.H > V.S > H.M

Table-6 & 7 present the calculation of Rotational Constant (α_e) & vibrational anharmonicity constant ($\omega_e x_e$) respectively for all the four models taken into considerations. The percentage deviations are also shown in the table along with the observed data. The experimental values of some hydride molecules are not available in the literature. There is good agreement between the experimental values and the calculated values of molecular properties of α_e, $\omega_e x_e$ considering the approximations involved in the theoretical method and uncertainties associated in the experimental values of the parameter used. It is interesting to observe that most of the calculated values of α_e, $\omega_e x_e$ are slightly more than the observed values. These may be due to the fact that the diatomic hydrides have less ionicity. The results have clearly improved by the inclusion of dipole-dipole & dipole- quadrupole interation energy terms [21]. These terms are essential for the interaction energy to be exact one.

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