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Mass-Reduced Quantum Numbers: Application
to the Isotopic Lithium Hydrides ($\chi^1\Sigma^+$)*

Kwong C. Li[†] and William C. Stwalley[‡]
Department of Chemistry
University of Iowa
Iowa City, IA 52242

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[†] Present address: Department of Chemistry, University of Illinois - Chicago Circle, Chicago, Illinois 60680.

[‡] Also Department of Physics.

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ABSTRACT

The massed-reduced quantum number (MRQN) method of combining isotopic data is applied to the lithium hydride $X^1\Sigma^+$ ground state. The $\Delta G(\eta) = \mu^{1/2} \Delta G(v)$, $B(\eta) = \mu B(v)$ and $D(\eta) = \mu^2 D(v)$ isotopically-combined functions are obtained. An isotopically-combined Rydberg-Klein Rees (ICRKR) potential is constructed using the $G(\eta)$ and $B(\eta)$ functions. Evidence for breakdown of the Born-Oppenheimer approximation is presented and examined. The Dunham, Simons-Parr-Finlan, and Thakkar methods of potential expansion are also applied to lithium hydride and compared to the RKR Potential.

I. INTRODUCTION

The vibrational-rotational spectroscopic analysis of the $A^1\Sigma^+ - X^1\Sigma^+$ system of all four isotopic lithium hydrides, ^7LiH , ^7LiD , ^6LiH and ^6LiD has been reported.⁽¹⁻⁶⁾ The spectroscopic properties of ^7LiH , ^7LiD , ^6LiH and ^6LiD are combined here for comparison using mass-reduced quantum number (MRQN) analysis. The theory of MRQN analysis has been introduced^{7,8} and applied to the $B^1\Pi$ state of the isotopic lithium hydrides, ^7LiH and ^7LiD , and to the $X^2\Sigma^+$ state of isotopic mercury hydrides, HgH , HgD , and HgT . However, the above potentials are highly anharmonic and not typical well-behaved potentials! Here we wish to examine the relatively harmonic and well-behaved $X^1\Sigma^+$ LiH potential. In a future publication we shall examine another anomalous potential, that of the $A^1\Sigma^+$ state of LiH.

The working equations for MRQN may be derived from Dunham's energy expression (for detailed and alternative derivations see Reference 8). Dunham^{9,10} expressed the energy levels

$$E(v,J) = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} Y_{ij} (v + \frac{1}{2})^i [J(J+1)]^j$$

where the Y_{ij} are the Dunham coefficients.

The Y_{ij} are in turn expressible by means of an expansion in inverse powers of μ (or equivalently B_e^2/ω_e^2):

$$Y_{ij} = Y_{ij}^{(0)} + \mu^{-1} Y_{ij}^{(1)} + \mu^{-2} Y_{ij}^{(2)} + \dots \quad (2)$$

where the $Y_{ij}^{(0)}$ are the "classical" coefficients: $Y_{10}^{(0)} = \omega_e$, $Y_{01}^{(0)} = B_e$, $Y_{20}^{(0)} = -\omega_e x_e$, $Y_{11}^{(0)} = -\alpha_e$, $Y_{02}^{(0)} = -D_e$ and, in particular, $Y_{00}^{(0)} = 0$; the $Y_{ij}^{(1)}$ and $Y_{ij}^{(2)}$ are correction terms given by Dunham¹⁰ and by Sandeman.¹¹⁻¹³ Breakdown of the Born-Oppenheimer approximation also introduces additional correction terms, the largest being proportional to μ^{-1} .

Introducing the mass-reduced quantum numbers

$$\eta = (v + \frac{1}{2})\mu^{-\frac{1}{2}} \text{ and } \xi = J(J + 1)\mu^{-1}$$

we have

$$E(\eta, \xi, \mu) = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} Z_{ijk} \eta^i \xi^j \left(\frac{1}{\mu}\right)^k \quad (3)$$

The $Y_{ij}^{(1)}/\mu$ Dunham correction⁹ as described by Herzberg¹⁴ is of the order B_e^2/ω_e^2 , which is largest for the hydride molecules. Even for these, however, the corrections are always less than and usually much less than one part in 1000.¹¹ This means that we can usually truncate the μ^{-1} expansion since uncertainty in experiment and/or theory is usually comparable or larger. Thus equation (3) becomes

$$E(\eta, \xi) \approx \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} Z_{ij0} \eta^i \xi^j \quad (4)$$

From equation (4) we have

$$G(\eta) = \sum_{i=1}^n Z_{i00} \eta^i \text{ or } (\Delta G(\eta) = \mu^{\frac{1}{2}} \Delta G(v + \frac{1}{2})) \quad (5)$$

$$B(\eta) = \sum_{i=0}^n Z_{i10} \eta^i = \mu B(v) \quad (6)$$

$$D(\eta) = \sum_{i=0}^n Z_{i20} \eta^i = \mu^2 D(v) \quad (7)$$

where n is the minimum degree of the polynomial which will best fit $G(\eta)$, $B(\eta)$ or $D(\eta)$ values.

The values of the reduced masses used in the analysis are given in Table I. Since ${}^7\text{LiH}$ is the most abundant, the reduced mass of ${}^7\text{LiH}$ is used as the reference reduced mass; that is, the reference reduced mass $\mu_{{}^7\text{LiH}} \equiv 1$ and the other three isotopic molecules are reduced to ${}^7\text{LiH}$ for comparison.

Table I. Values of the reduced mass μ used in this work in atomic mass units (amu, ^{12}C)^a and referred to reduced mass ($\mu_{^7\text{LiH}} = 1$).

Isotopic species	$\mu(^{12}\text{C})$	$\mu(^7\text{LiH} = 1)$
^7LiH	0.88123	1
^7LiD	1.56487	1.77577
^6LiH	0.86319	0.97953
^6LiD	1.50887	1.71222

^aThe masses in amu for individual atoms are $^7\text{Li} = 7.01600$, $^6\text{Li} = 6.01512$, $\text{H} = 1.00782$ and $\text{D} = 2.01410$.

11. MASS-REDUCED QUANTUM NUMBER ANALYSIS OF SPECTROSCOPIC CONSTANTS

Generally from spectroscopic analysis one obtains the vibrational spacings $\Delta G(v + \frac{1}{2})$ and then from the least square fit of the vibrational spacings, the vibrational constants $\omega_e = \gamma_{10}^{(0)}$, $-\omega_e x_e = \gamma_{20}^{(0)}$, $\omega_e y_e = \gamma_{30}^{(0)}$, $\omega_e z_e = \gamma_{40}^{(0)}$ are obtained. Here the mass-reduced vibrational spacing function $\Delta G(\eta) = \mu^{\frac{1}{2}} \Delta G(v + \frac{1}{2})$ is used to generate the Z_{100} constants of equation (5) rather than the $G(\eta)$ function (which would require pre-determination of zero point energies of each individual isotopic molecule); i.e. the use of $\Delta G(\eta)$ avoids the problem of relative zero point energies.

The qualities of the isotopically-combined least square fits of the mass-reduced rotational constant function, $B(\eta) = \mu B(v)$ and the mass-reduced vibrational spacing function $\Delta G(\eta) = \mu^{\frac{1}{2}} \Delta G(v + \frac{1}{2})$ are shown in Tables II and III. The $B(\eta)$ and $\Delta G(\eta)$ functions of the X state are satisfactorily represented by a least square fit of a three-term polynomial. Plots of the $B(\eta)$ and $\Delta G(\eta)$ vs. μ are shown in Figures 1 and 2. The $D(\eta) = \mu^2 D(v)$ function of the X state is linear and well represented by a two-term polynomial. A plot of $D(\eta)$ vs. μ is shown in Figure 3.

The coefficients of the polynomials Z_{ij0} are listed in Table IV along with the same mass-reduced coefficients obtained by fitting each isotopic molecule individually. The mass-reduced vibrational constants of the four isotopes of lithium hydrides can be calculated from the coefficients of $\Delta G(\eta)$ function. The mass-reduced vibrational and rotational constants of the isotopic molecules are related to one another by the following relationship

$$Z_{ij0}(\ell) \equiv \gamma_{ij}(\ell) \mu^{(i/2 + j)} \quad (8)$$

where $\ell = {}^7\text{LiD}$, ${}^6\text{LiH}$, or ${}^6\text{LiD}$, and μ = reduced masses based on ${}^7\text{LiH}$

Table II. The quality of the isotopically-combined least-square fit of the mass-reduced rotational constant function $B(\eta) = \mu B(v)$ compared to the observed mass-reduced rotational constants for the $X^1\Sigma^+$ state of ^7LiH , ^7LiD , ^6LiH and ^6LiD .

Isotope	v	η	$B(\eta)$ (cm^{-1})		diff. $\times 10^4$
			obs.	fit	
^7LiH	0	0.50000	7.4061	7.4076	-15
	1	1.50000	7.1941	7.1942	-1
	2	2.50000	6.9853	6.9854	-1
	3	3.50000	6.7792	6.7802	-10
	4	4.50000	6.5786	6.5777	9
	5	5.50000	6.3744	6.3767	-23
^7LiD	0	0.37521	7.4360	7.4346	14
	1	1.12563	7.2766	7.2735	31
	2	1.87606	7.1164	7.1143	21
	3	2.62648	6.9610	6.9593	17
^6LiH	0	0.50520	7.4024	7.4065	-41
	1	1.51559	7.1878	7.1909	-31
	2	2.52599	6.9787	6.9800	-13
	3	3.53638	6.7721	6.7728	-7
	4	4.54678	6.5700	6.5683	17
	5	5.55717	6.3646	6.3656	-10
	6	6.56757	6.1651	6.1636	15
	7	7.57797	5.9608	5.9614	-6
^6LiD	0	0.38211	7.4351	7.4331	20
	1	1.14633	7.2725	7.2691	34
	2	1.91056	7.1026	7.1080	-54
	3	2.67478	6.9545	6.9493	52
	4	3.43900	6.7943	6.7926	17
	5	4.20323	6.6309	6.6376	-70
	6	4.96745	6.4876	6.4837	39
	7	5.73167	6.3313	6.3306	7

Table III. The quality of the isotopically-combined least-square fit of mass-reduced vibrational spacing function $\Delta G(\eta) = \mu^{\frac{1}{2}} \Delta G(v + \frac{1}{2})$ compared to the observed mass-reduced vibrational spacings of the $X^1\Sigma^+$ state of ^7LiH , ^7LiD , ^6LiH and ^6LiD .

Isotope	$(v + \frac{1}{2}) + \frac{1}{2}$	η	$\Delta G(\eta) \text{ (cm}^{-1}\text{)}$		diff.
			obs.	fit	
^7LiH	1	1.00000	1359.77	1359.86	-0.09
	2	2.00000	1314.85	1315.01	-0.16
	3	3.00000	1270.91	1271.01	-0.10
	4	4.00000	1227.72	1227.85	-0.13
	5	5.00000	1185.51	1185.53	-0.02
^7LiD	1	0.75042	1371.29	1371.19	0.10
	2	1.50085	1337.36	1337.29	0.07
	3	2.25127	1303.98	1303.88	0.10
^6LiH	1	1.01040	1359.19	1359.39	-0.20
	2	2.02079	1313.99	1314.09	-0.10
	3	3.03119	1269.50	1269.65	-0.15
	4	4.04158	1226.05	1226.07	-0.02
	5	5.05198	1183.27	1183.36	-0.09
^6LiD	1	0.76422	1370.65	1370.56	0.09
	2	1.52845	1336.24	1336.06	0.18
	3	2.29267	1301.99	1302.05	-0.06
	4	3.05689	1268.82	1268.53	0.29
	5	3.82112	1235.57	1235.51	0.06
	6	4.58534	1203.06	1202.98	0.02

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Figure 1. The mass-reduced rotational constant function $B(\eta) = \mu B(v)$ (in cm^{-1}) for the $X^1\Sigma^+$ states of ${}^7\text{LiH}$, ${}^7\text{LiD}$, ${}^6\text{LiH}$, and ${}^6\text{LiD}$, plotted as a function of mass-reduced vibrational quantum number η .

Figure 2. The mass-reduced vibrational spacing function $\Delta G(\eta) = \mu^{1/2} \Delta G(v + \frac{1}{2})$ (in cm^{-1}) for the $X^1\Sigma^+$ states of ^7LiH , ^7LiD , ^6LiH , and ^6LiD , plotted as a function of mass reduced vibrational quantum number η .

Figure 3. The mass-reduced centrifugal distortion function $D(\eta) = \mu^2 D(v)$ for the $X^1\Sigma^+$ states of ${}^7\text{LiH}$, ${}^7\text{LiD}$, ${}^6\text{LiH}$ and ${}^6\text{LiD}$ is plotted as a function of mass-reduced vibrational quantum number η .

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Table IV. Coefficients of the polynomial fits of mass-reduced functions and the coefficients obtained by fitting each isotopic molecule of lithium hydride individually. For comparison, the individually fitted spectroscopic constants are mass-reduced (equation 8) to ${}^7\text{LiH}$, using μ_k from Table I.

Coefficient	I.C. ^a	${}^7\text{LiH}$	${}^7\text{LiD}$	${}^6\text{LiH}$	${}^6\text{LiD}$
$Z_{100} (\approx \omega_e)$	1405.534	1405.629	1405.743	1405.236	1405.592
$Z_{200} (\approx -\omega_e x_e)$	-23.0633	-23.1950	-23.1516	-23.0074	-23.0344
$Z_{300} (\approx \omega_e y_e)$	0.14132	0.16333	0.16169	0.13688	0.13776
$Z_{010} (\approx B_e)$	7.5163	7.5133	7.5168	7.5118	7.5178
$Z_{110} (\approx -\alpha_e)$	-0.21889	-0.21514	-0.21602	-0.21813	-0.21705
$Z_{210} (\approx \gamma_e) (\times 10^4)$	29.986	15.671	14.953	32.643	18.293
$Z_{020} (\approx -D_e) (\times 10^4)$	-8.549	-8.548	-8.577	-8.462	-8.519
$Z_{120} (\approx -\beta_e) (\times 10^4)$	0.197	0.1440	0.2030	0.1861	0.2501

^a Isotopically combined.

$\mu \equiv 1$. The zero point energies of each isotopic molecule are calculated from these Z_{i00} (IC) vibrational constants and compared with the zero point energy obtained by fitting $G(v)$ or $\Delta G(v)$ vs. $v + \frac{1}{2}$ and calculating $G(0) - G(-\frac{1}{2})$ in Table V.

Table V. The zero point energies (in cm^{-1}) of ^7LiH , ^7LiD , ^6LiH , and ^6LiD as obtained by various polynomial fits.

State	Isotope	Zero Point Energy		
		$G(v)$ vs. $(v + \frac{1}{2})^a$	$\Delta G(v)$ vs. $(v + \frac{1}{2})$	$\Delta G(\eta)$ vs. η
$X^1\Sigma^+$	^7LiH	697.01	697.04	697.02
	^7LiD	524.26	524.20	524.13
	^6LiH	703.99	704.07	704.20
	^6LiD	533.81	533.74	533.71

^a The $G(v)$ s are with respect to $G(-\frac{1}{2}) = 0$.

III. CONSTRUCTION OF ISOTOPICALLY-COMBINED RKR POTENTIAL CURVES.

Once the $B(\eta)$ and $G(\eta)$ functions are defined, the mass-reduced RKR^{7,8,15-17} potential curves can be constructed. The isotopically-combined RKR outer (R_+) and inner (R_-) turning points and B and G values compared with the values obtained by treating the isotopes individually in Table VI. Note the agreement of $G(v)$ and $G(\eta)$ to within 0.2 cm^{-1} at small v and to within 2.1 cm^{-1} at large v . A comparison of the mass-reduced equilibrium internuclear distance, R_e , with various R_e obtained by individual analysis of the isotopic molecules is shown in Table VII. The agreement among the values is excellent.

The differences between the mass-reduced vibrational spacings and the experimental spacings of the four isotopes of the X state were shown in Table III. The hydrides vibrational spacing differences are consistently slightly more negative than the mass-reduced vibrational spacings, while the deuterides are consistently slightly more positive. A comparison of the energy difference $\Delta V(R)$ between the individual RKR $X^1\Sigma^+$ potential energy curve and the isotopically-combined RKR (ICRKR) $X^1\Sigma^+$ potential energy curve of X at various internuclear distances is given in Table VIII and Figure 4. Definite differences between the hydride and deuteride potential curves in both states are again indicated. If this difference is interpreted in terms of the breakdown of the Born-Oppenheimer approximation (principally the adiabatic correction), this implies that the outer turning points of the potential curve of the hydrides (where $\Delta V(R)$ is negative) are shifted slightly outward. A second possibility is that the semiclassical approximation used in deriving the RKR equation is more seriously deficient for the hydrides than for the deuterides. However, on the basis of our (unpublished) experience with similar molecules we feel the Born-Oppenheimer breakdown is the

Table VI. Rydberg-Klein-Rees potential energy curve of the $X^1\Sigma^+$ state of Lithium Hydride.

Isotope	v	n	$B(v)$ (cm^{-1})		$G(v)$ (cm^{-1})		$R_-(\text{\AA})$		$R_+(\text{\AA})$	
							RKR $R_-(v)$	ICRKR $R_-(n)$	RKR $R_+(v)$	ICRKR $R_+(n)$
^7LiH	$-\frac{1}{2}$	0.00000	7.5133	7.5163	0.00	0.00		1.5953	1.5957	
	0	0.50000	7.4061	7.4076	697.94	698.01	1.4458	1.4456	1.7780	1.7778
	1	1.50000	7.1941	7.1942	2057.72	2057.88	1.3532	1.3531	1.9367	1.9366
	2	2.50000	6.9853	6.9853	3372.58	3372.89	1.2967	1.2967	2.0607	2.0606
	3	3.50000	6.7795	6.7801	4643.43	4643.89	1.2549	1.2548	2.1717	2.1716
	4	4.50000	6.5769	6.5776	5871.16	5871.74	1.2214	1.2213	2.2760	2.2759
	5	5.50000	6.3774	6.3769	7056.66	7057.27	1.1934	1.1934	2.3765	2.3765
^7LiD	$-\frac{1}{2}$	0.00000	4.2330	4.2327	0.00	0.00		1.5953	1.5953	
	0	0.37521	4.1875	4.1867	524.81	524.74	1.4638	1.4639	1.7511	1.7513
	1	1.12563	4.0927	4.0960	1553.89	1553.70	1.3808	1.3809	1.8836	1.8838
	2	1.87606	4.0078	4.0068	2557.46	2557.23	1.3293	1.3295	1.9853	1.9855
	3	2.62648	3.9193	3.9190	3536.02	3535.68	1.2907	1.2908	2.0750	2.0752
^6LiH	$-\frac{1}{2}$	0.00000	7.6688	7.6734	0.00	0.00		1.5953	1.5957	
	0	0.50520	7.5571	7.5613	705.08	705.30	1.4453	1.4449	1.7793	1.7789
	1	1.51599	7.3382	7.3412	2078.34	2078.83	1.3524	1.3520	1.9391	1.9387
	2	2.52599	7.1242	7.1258	3405.97	3406.58	1.2957	1.2955	2.0639	2.0636
	3	3.53638	6.9138	6.9143	4688.76	4689.42	1.2537	1.2535	2.1758	2.1755
	4	4.54678	6.7058	6.7055	5927.48	5928.24	1.2200	1.2199	2.2809	2.2807
	5	5.55717	6.4988	6.4850	7122.94	7123.90	1.1920	1.1919	2.3823	2.3821
	6	6.56757	6.2916	6.2923	8275.90	8277.28	1.1682	1.1681	2.4817	2.4815
	7	7.57797	6.0829	6.0859	9387.17	9389.26	1.1476	1.1476	2.5803	2.5798
^6LiD	$-\frac{1}{2}$	0.00000	4.3907	4.3900	0.00	0.00		1.5953	1.5952	
	0	0.38211	4.3425	4.3414	534.41	534.34	1.4624	1.4628	1.7526	1.7528
	1	1.14633	4.2468	4.2456	1581.98	1581.74	1.3790	1.3792	1.8866	1.8868
	2	1.91056	4.1524	4.1515	2603.14	2602.79	1.3273	1.3274	1.9895	1.9897
	3	2.67478	4.0593	4.0588	3598.28	3597.82	1.2884	1.2885	2.0805	2.0807
	4	3.43900	3.9674	3.9673	4567.80	4567.24	1.2570	1.2571	2.1649	2.1650
	5	4.20323	3.8768	3.8768	5512.07	5511.44	1.2305	1.2305	2.2453	2.2454
	6	4.96745	3.7874	3.7869	6431.49	6430.77	1.2076	1.2076	2.3231	2.3232
	7	5.73167	3.6992	3.6975	7326.45	7325.62	1.1874	1.1875	2.3991	2.3993

Table VII. Comparison of the equilibrium internuclear distances, R_e , of various isotopic combination of lithium hydride.^a

Isotope	$R_e (\text{\AA})$	
	RKR	ICRKR
⁷ LiH	1.5957	1.5953
⁷ LiD	1.5953	1.5953
⁶ LiH	1.5958	1.5953
⁶ LiD	1.5952	1.5953

^a E. F. Pearson and W. Gordy, Phys. Rev. A 177, 59 (1969) give an isotopically combined value $R_e = 1.59490 \pm 0.00002 \text{ \AA}$ from microwave spectra of ⁶LiD and ⁷LiD, in excellent agreement with the present results.

Table VIII. The differences $\Delta V(R)$ and $\delta V(R)$ (in cm^{-1}) between the RKR potential curves calculated for each isotope individually and the isotopically combined RKR (ICRKR) potential curve, calculated directly and calculated using Le Roy's equations, respectively (see text). The turning points $R_{\pm}(v)$ (in $\text{\AA}$) from the ICRKR potential (Table VI) are also given. Note that $\Delta V(R_e)$ is taken as zero; only evidence for the change in Born-Oppenheimer breakdown with the internuclear distance is presented here.

Isotope	v	at $R_-(v)$			at $R_+(v)$		
		$R_-(v)$	ΔV	δV	$R_+(v)$	ΔV	δV
^7LiH	0	1.4456	-1.8	- 1.6 (0.4)	1.7778	1.3	1.1 (0.3)
	1	1.3531	-2.6	0.2 (0.7)	1.9366	1.1	0.4 (0.4)
	2	1.2967	1.2	0.9 (1.2)	2.0606	1.7	0.7 (0.5)
	3	1.2548	-1.3	- 3.1 (6.2)	2.1716	1.8	1.9 (2.1)
	4	1.2213	-0.7	- 7.0 (9.6)	2.2759	1.6	- 0.7 (2.9)
	5	1.1934	----	-13.5 (22.6)	2.3765	1.4	3.7 (5.9)
^7LiH	0	1.4449	-3.7	- 4.3 (0.6)	1.7789	3.0	3.2 (0.4)
	1	1.3520	-7.3	- 6.6 (2.0)	1.9387	4.3	3.7 (1.0)
	2	1.2955	-4.7	- 4.0 (3.5)	2.0636	3.9	1.9 (1.4)
	3	1.2535	-6.2	- 2.0 (6.2)	2.1755	4.2	1.3 (2.1)
	4	1.2199	-3.1	- 8.9 (7.4)	2.2807	3.1	2.7 (2.2)
	5	1.1919	-3.6	- 5.5 (8.4)	2.3821	3.2	2.0 (2.2)
	6	1.1681	-4.0	-----	2.4815	3.7	-----
^6LiD	0	1.4639	1.7	1.2 (0.3)	1.7513	-1.4	- 1.1 (0.2)
	1	1.3809	1.5	5.7 (1.2)	1.8838	-1.7	- 3.3 (0.6)
	2	1.3295	4.4	5.3 (1.4)	1.9855	-1.5	- 2.6 (0.7)
	3	1.2908	3.6	5.2 (3.2)	2.0752	----	- 2.4 (1.3)
^6LiD	0	1.4628	4.3	1.9 (0.8)	1.7528	-1.9	- 1.4 (0.6)
	1	1.3792	3.4	6.3 (2.7)	1.8868	-2.2	- 3.6 (1.5)
	2	1.3274	4.4	14.0 (6.0)	1.9897	-3.0	- 6.9 (2.7)
	3	1.2885	6.1	17.7 (7.0)	2.0807	-2.0	- 7.2 (2.8)
	4	1.2571	4.0	5.4 (7.9)	2.1650	-2.1	- 3.1 (3.2)
	5	1.2305	3.2	30.0 (8.2)	2.2454	-2.1	-10.9 (2.9)
	6	1.2076	2.9	-----	2.3232	-2.3	-----
	7	1.1875	4.5	-----	2.3993	-3.3	-----

Figure 4. A comparison of the energy differences $\Delta V(R)$ and $\delta V(R)$ (see text) in cm^{-1} versus internuclear distance R in $\text{\AA}$. The ΔV difference is the difference between the individual isotope RKR potentials and the ICRKR potential (Table VI). The $\delta V(R)$ difference is calculated from the $\delta R_{\pm}$ differences calculated in Table VIII below plus the potential slope. For clarity, the error bars on the δV values are omitted.

major contributor to the potential difference reported here. We are also planning to test this in the following way: we have calculated the quantum mechanical energy levels for model hybrid potentials which closely match experiment. We shall treat the eigenvalues as "spectroscopic data" and calculate regular and isotopically-combined spectroscopic constants and RKR potentials and then make the ΔV and δV comparisons discussed here. Any differences would then be due to breakdown of the semiclassical approximation only. This is because the Born-Oppenheimer approximation would hold exactly since we use the same potential for each isotope. In what follows we shall assume the Born-Oppenheimer breakdown is dominant and speak in those terms exclusively.

Using the definition $\Delta[R_{\pm}(v)] \equiv [R_{\pm}(v) - R_{\pm}(\eta)]$, one sees in Table VI that $\Delta[R_{+}(v)] > 0$ for the hydrides. At R_{+} , where $\Delta V(R)$ is usually negative, there is also a shift slightly outward (or $\Delta[R_{-}(v)] > 0$), compared to the mass-reduced RKR potential turning points. The deuterides exhibit the exact opposite trend, i.e. $\Delta[R_{+}(v)] < 0$ and $\Delta[R_{-}(v)] < 0$ compared to the mass-reduced RKR potential turning points. Looking first at the outer turning points, one sees the potentials of the hydrides are further out than for the deuterides, while at the inner wall the potentials of the deuterides are inside the hydrides. In order to determine the overall change of the potential, the magnitude of the $\Delta[R_{+}(v)]$ and $\Delta[R_{-}(v)]$ has to be determined.

The change of the RKR turning points and in potential can be examined in a different way using LeRoy's equations¹⁸ for estimating error bounds for computed RKR turning points. The errors (indicated by δ to distinguish them from the Δ values obtained above) in the difference and sum of the turning points calculated for level v are

$$\delta[R_{+}(v) - R_{-}(v)] \approx \frac{1}{2} < \delta E_x / [G(v) - G(x)] > [R_{+}(v) - R_{-}(v)], \quad (9)$$

and

$$\delta[R_-(v) + R_+(v)] \approx -\frac{1}{2} < \delta B_X/B_X > [R_+(v) + R_-(v)]. \quad (10)$$

In cases where the errors δE_X and δB_X are small, the average values in equations (9) and (10) may be replaced by

$$\begin{aligned} < \delta E_X/[G(v) - G(x)] > \approx - \delta(\Delta G_{v-1/2})/\Delta G_{v-1/2}, \\ < \delta B_X/B_X > \approx \delta B_V/B_V. \end{aligned}$$

By taking the sum and difference of equations (9) and (10)

$$\delta[R_+(v)] \approx \frac{1}{2}[R_+(v) + R_-(v)] \{ < \delta E_X/[G(v) - G(x)] > - < \delta B_X/B_X > \} \quad (11)$$

$$\delta[R_-(v)] \approx \frac{1}{2}[R_+(v) - R_-(v)] \{ < \delta E_X/[G(v) - G(x)] > + < \delta B_X/B_X > \} \quad (12)$$

If the (signed!) differences in Tables III and II between $\Delta G(v)$ and $\Delta G(\eta)$, and between $B(v)$ and $B(\eta)$ are taken as the "errors", and used in equations (11) and (12), the change of RKR turning points can be calculated. There is, of course, also still a statistical error arising from δE_X and δB_X (the original point of Le Roy's work).

Table IX and Figure 5 show these changes of the RKR turning points calculated for ^7LiH , ^6LiH , ^7LiD and ^6LiD using Le Roy's equations.¹⁸ In the X state of the deuterides, the $\delta[R_+(v)]$ and $\delta[R_-(v)]$ are all negative but $\delta[R_+(v)]$ in general changes more than $\delta[R_-(v)]$ giving a net narrowing effect (see $\delta[R_+(v) - R_-(v)]$) on the potential curve. In the hydrides, an overall broadening is predicted by this calculation. There is also a consistent shift of the average distance (see $\delta[R_+(v) + R_-(v)]$) to larger distance in the hydrides and smaller distance in the deuteride.

The effect of the statistical error of $\Delta G(v)$ and $B(v)$ on the turning points is given in parenthesis in Table IX for comparison with the $\delta[R_+(v)]$

Table IX. The effect of the differences (with definite sign) between the observed $\Delta G(v)$ and $B(v)$ values and the mass-reduced $\Delta G(n)$ and $B(n)$ functions on the RKR turning points. The numbers in parentheses are the errors due to statistical ($\pm$) measurement errors of $\Delta G(v)$ and $B(v)$. For example, for $^7\text{LiH } v = 0$, the distance shifts from the mass-reduced potentials are $+0.3 (\pm 0.7)$, $+32.2 (\pm 6.5)$, $+16.0 (\pm 3.6)$ and $+16.2 (\pm 3.6)$ femtometers ($10^{-5} \text{ \AA}$).

Species	v	$\delta(\text{fm})$			
		$\delta[R_+(v) - R_-(v)]$	$\delta[R_+(v) + R_-(v)]$	$\delta[R_-(v)]$	$\delta[R_+(v)]$
^7LiH	0	0.3 (0.7)	32.2 (6.5)	16.0 (3.6)	16.2 (3.6)
	1	1.8 (0.6)	2.3 (6.9)	-0.3 (3.7)	2.1 (3.7)
	2	4.6 (0.3)	2.4 (8.4)	-1.1 (4.3)	3.5 (4.3)
	3	3.6 (0.1)	25.7 (36.7)	11.1 (18.3)	14.7 (18.3)
	4	5.8 (2.1)	-24.5 (46.5)	15.2 (24.3)	-9.4 (24.3)
	5	1.0 (3.0)	61.8 (96.9)	30.4 (50.0)	31.4 (50.0)
^6LiH	0	4.5 (4.2)	88.7 (18.5)	42.1 (6.3)	46.6 (6.3)
	1	4.4 (3.8)	70.8 (16.4)	33.2 (10.1)	37.6 (10.1)
	2	2.9 (2.3)	31.9 (23.5)	14.5 (12.9)	17.4 (12.9)
	3	5.5 (6.0)	17.2 (30.9)	5.8 (18.4)	11.3 (18.4)
	4	0.8 (7.4)	45.5 (29.8)	22.3 (18.6)	23.2 (18.6)
	5	4.5 (8.3)	28.6 (28.6)	12.0 (18.4)	16.6 (18.4)
^7LiD	0	-3.6 (1.0)	-30.5 (5.8)	-13.5 (3.4)	-17.1 (3.4)
	1	-1.8 (0.3)	-70.2 (13.9)	-34.2 (7.1)	-36.0 (7.1)
	2	-1.7 (0.3)	-48.1 (12.4)	-23.2 (6.3)	-24.9 (6.3)
	3	-3.0 (0.8)	-40.4 (21.5)	-18.7 (11.5)	-21.7 (11.5)
^6LiD	0	-2.7 (2.5)	-43.4 (16.1)	-20.3 (9.3)	-23.1 (9.3)
	1	-1.7 (1.0)	-76.7 (31.0)	-37.5 (16.0)	-39.2 (16.0)
	2	-4.3 (2.3)	-126.0 (49.7)	-60.9 (26.0)	-65.2 (26.0)
	3	-1.8 (2.0)	-126.3 (47.2)	-62.3 (24.6)	-64.1 (24.6)
	4	-10.5 (4.1)	-42.8 (51.3)	-16.2 (27.7)	-26.6 (27.7)
	5	-2.4 (4.1)	-182.5 (45.2)	-90.0 (24.6)	-92.5 (24.6)

Figure 5. The effect of the differences (with definite sign) between the observed $\Delta G(v)$ and $B(v)$ values and the mass-reduced $\Delta G(\eta)$ and $B(\eta)$ functions on the RKR turning points (given in Table IX) as a function of the energy (E , in cm^{-1}) of the vibrational level involved. The following turning point differences (all in $\text{fm} = 10^{-5} \text{ \AA}$) are plotted: (a) $\delta[R_+(v) - R_-(v)]$, $\delta[R_+(v) + R_-(v)]$, (c) $\delta[R_-(v)]$ and (d) $\delta[R_+(v)]$.

assumed to be caused by Born-Oppenheimer breakdown. The $\delta[R_{\pm}(v)]$ of the hydrides are just slightly above the noise due to statistical errors, but in the deuterides the $\delta[R_{\pm}(v)]$ are certainly greater than the effect due to the statistical error. Finally, it should be emphasized that there is always a consistent difference between the hydrides and deuterides; that is the deuteride values are uniformly greater than hydride values, indicating Born-Oppenheimer breakdown. In physical terms the lithium deuteride potential curves are narrower than those of lithium hydrides.

For a more meaningful comparison with our earlier ΔV values (Figure 4 and Table VIII), we have converted the $\delta R_{\pm}$ values of Table IX into $\delta V(R_{\pm})$ values by multiplying them by the local slope of the potential ($dV/dR|_{R=R_{\pm}}$). These δV values are also given in Figure 4 and Table VIII. Note that there is very good agreement in overall trends, with minor differences arising from the large statistical fluctuations. Note also that our results are sensitive only to the change in Born-Oppenheimer breakdown with internuclear distance; the relative positions of the $V(R_e)$ must be obtained independently (the electronic isotope shift).⁷

IV. OTHER METHODS OF POTENTIAL EXPANSION

In addition to the RKR method of obtaining potential curves from spectroscopic data, the Dunham¹⁹ method is also widely used. The Dunham potential is expanded as a function of $\left[\frac{R-R_e}{R_e}\right]$ in the following form:

$$V(R) = a_0 \left[\frac{R-R_e}{R_e}\right]^2 \left(1 + a_1 \left[\frac{R-R_e}{R_e}\right] + a_2 \left[\frac{R-R_e}{R_e}\right]^2 + a_3 \left[\frac{R-R_e}{R_e}\right]^3 + \dots\right) \quad (13)$$

where the constants $\{a_0, a_1, a_2, a_3, \dots\}$ can be calculated from Dunham coefficients, Y_{ij} . The Dunham expansion, however, at most converges in the region defined by $0 < R < 2R_e$ (3.1906 Å here).

Recently Simons, Parr, and Finlan¹⁹ (SPF) have expanded the potential in terms of $\left[\frac{R-R_e}{R}\right]$ in the following form:

$$V(R) = b_0 \left[\frac{R-R_e}{R}\right]^2 \left(1 + b_1 \left[\frac{R-R_e}{R}\right] + b_2 \left[\frac{R-R_e}{R}\right]^2 + b_3 \left[\frac{R-R_e}{R}\right]^3 + \dots\right) \quad (14)$$

where Y_{ij} constants are now functions of $\{R_e, b_0, b_1, b_2, b_3, \dots\}$. Thakkar²⁰ proposed a generalized potential expansion of the form

$$V(R) = e_0(p) \lambda^2(p) [1 + e_1(p) \lambda + e_2(p) \lambda^2 + e_3(p) \lambda^3 + \dots] \quad (15)$$

where $\lambda(p) = \text{SGN}(p) \left[1 - \left[\frac{R_e}{R}\right]^p\right]$; SGN is +1 for $p > 0$ and -1 for $p < 0$, and $\{e_0, e_1, e_2, e_3, \dots\}$ are constants which depend on the value of the parameter p . The Thakkar expansion reduces to the Dunham expansion when $p = -1$ and $e_i \rightarrow a_i$ while $p = 1$ and $e_i \rightarrow b_i$ yields the SPF expansion. The choice of $p = -a - 1$ was used as suggested by Thakkar for diatomics. The a_i, b_i , and e_i coefficients of potential expansion for Dunham, SPF, and Thakkar respectively were obtained using the values in Table IV. The a_i, b_i , and e_i are listed in Table X. A difference plot $V(R)$ of Dunham, SPF, and Thakkar potential with the isotopically combined RKR is shown in Figure 6. The Dunham potential expansion better reproduces the RKR potential than the Thakkar

Table X. The potential expansion coefficients for the Dunham [Eq. 13; a_i] the SPF [Eq. 14; b_i] and the Thakkar [Eq. 15 with $p = -a_1 - 1 = 0.90762785$; e_i]. R_e is 1.5953 Å. I. C. coefficients were obtained using the values of the mass-reduced Dunham expansion coefficients Z_{100} and Z_{110} while individual isotope coefficients are obtained from Y_{10} and Y_{11} (Ref. 7).

Coefficients	I. C.	^7LiH	^7LiD	^6LiH	^6LiD
a_0	65708.05533161	65743.17828521	65722.91161168	65719.34802867	65700.71132530
a_1	-1.90762785	-1.89285136	-1.89575233	-1.90535055	-1.89969906
a_2	2.50317975	2.42047979	2.43903484	2.49606689	2.46840469
a_3	-2.67882616	-2.63236783	-2.70622401	-3.07613776	-2.75767211
a_4	1.85096439	2.73266941	2.96627777	4.55595834	2.78492663
b_0	65708.05533161	65743.17828521	65722.91161168	65719.34802867	65700.71132530
b_1	0.09237215	0.10714864	0.10424767	0.09464945	0.10030094
b_2	-0.21970381	-0.25807428	-0.24822215	-0.21998475	-0.23069248
b_3	-0.11187429	-0.30755682	-0.32459863	-0.52397348	-0.28224769
b_4	-0.58764748	-0.15288546	-0.13201718	0.08243298	-0.31637760
e_0	79763.27632283	82469.31200471	81910.74966449	80178.82881648	81166.26140335
e_1	0.00000000	0.00000000	0.00000000	0.00000000	0.00000000
e_2	-0.31011832	-0.37693654	-0.36056925	-0.31325239	-0.33354967
e_3	-0.11211128	-0.37387594	-0.39857223	-0.66716388	-0.34224581
e_4	-0.82491703	-0.10560756	-0.06895374	0.31022277	-0.37120673

Figure 6. The differences $\Delta V(R)$ in cm^{-1} between the Dunham, SPF, or Thakkar potentials and the ICRKR potential for the $X\ ^1\Sigma^+$ state of LiH are given as a function of internuclear distance R in $\text{\AA}$.

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expansion which in turn is better than the SPF expansion for the inner wall of the potential. At the outer potential wall the Thakkar expansion better reproduces the RKR potential compared to the SPF expansion while the Dunham expansion is the worst of the three methods.

V. DISCUSSION

The isotopically combined RKR (ICRKR) potential of lithium hydride has been constructed using the mass-reduced quantum number (MRQN) method. This ICRKR potential was then compared to the RKR potentials constructed from data for individual isotopes at various internuclear distances. The differences of the potentials are attributed to Born-Oppenheimer approximation breakdown. The narrowing or broadening of the potentials was also estimated using Le Roy's equations.¹⁰ Definite differences exist between the hydride and deuteride potentials. More accurate rotational constant, $B(v)$, and vibrational constant, $G(v)$, values are required to examine the Born-Oppenheimer approximation breakdown more quantitatively. Analysis is in progress using a computer program by Albritton²¹ which calculates precise rotational and vibrational constants by incorporating the correlation between the constants obtained from different bands. Also additional ^7LiH spectra have been obtained and are being analyzed.²² Results will be reported in future publications.

Finally we note that RKR²³ or Dunham³ potentials for $X^1\Sigma^+$ LiH have been previously reported. Our results are in excellent agreement with these in regions of overlap. However, our potentials include additional vibrational levels and, more importantly, our best potential (ICRKR) includes data for all four isotopic variants and should be the most accurate now published. Visually however (see Fig. 1 of Ref. 24), all these potentials are virtually indistinguishable from each other or from the full "hybrid" potential recently reported.²⁴

REFERENCES

1. G. Nakamura, Z. Phys. 59, 218 (1930).
2. G. Nakamura, Japan J. Phys. 7, 33 (1931).
3. F. H. Crawford and T. Jorgensen, Jr., Phys. Rev. 47, 358 (1935); Phys. Rev. 47, 932 (1935); Phys. Rev. 49, 745 (1936).
4. T. Jorgensen, Jr., Ph.D. Thesis, Harvard University (1935).
5. G. Ennen and Ch. Ottinger, Chem. Phys. Lett. 36, 16 (1975).
6. K. C. Li, Ph.D. Thesis, University of Iowa (1976); K. C. Li and W. C. Stwalley, J. Mol. Spectrosc., in press (1977).
7. K. R. Way and W. C. Stwalley, J. Chem. Phys. 59, 5298 (1973); W. C. Stwalley, K. R. Way and R. Velasco, J. Chem. Phys. 60, 3611 (1974).
8. W. C. Stwalley, J. Chem. Phys. 63, 3062 (1975).
9. J. L. Dunham, Phys. Rev. 41, 713 (1932).
10. J. L. Dunham, Phys. Rev. 41, 721 (1932).
11. I. Sandeman, Proc. R. Soc. Edinb. 54, 1 (1938).
12. I. Sandeman, Proc. R. Soc. Edinb. 56, 130 (1939).
13. I. Sandeman, Proc. R. Soc. Edinb. 60, 210 (1940).
14. G. Herzberg, Spectra of Diatomic Molecules (D. Van Nostrand, N. Y., 1950).
15. R. Rydberg, Z. Phys. 73, 376 (1931).
16. O. Klein, Z. Phys. 76, 226 (1932).
17. A. L. G. Rees, Proc. Phys. Soc. Lond. 59, 998 (1947).
18. R. J. Le Roy, J. Chem. Phys. 52, 2683 (1970).
19. G. Simons, R. G. Parr, and J. M. Finlan, J. Chem. Phys. 59, 3229 (1973).
20. A. J. Thakkar, J. Chem. Phys. 62, 1693 (1975).
21. D. L. Albritton, Private Communication.
22. F. B. Orth and W. C. Stwalley, unpublished.
23. R. J. Fallon, J. T. Vanderslice and E. A. Mason, J. Chem. Phys. 32, 1453 (1960).
24. W. C. Stwalley, W. T. Zemke, K. R. Way, K. C. Li and T. R. Proctor, J. Chem. Phys. 66, 5412 (1977); erratum 67, xxxx (1977).