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Elaine Rothstein

(Ph.D. Thesis)

February 23, 1968

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Contents

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Berkeley, California

February 1968

ABSTRACT

Radio-frequency spectra have been observed in the first rotational state of Li^7H, Li^7D, Li^6H, and Li^6D by the molecular-beam electric-resonance method. Analysis of the spectra has made possible the determination of accurate dipole moments and nuclear-hyperfine interaction constants.

The experimental values are compared to the available quantum mechanical calculations. The polarizable ion model is also compared to the experiment.

I. INTRODUCTION

The first molucular-beam electric-resonance (MBER) spectrometer was constructed in 1947 by H. K. Hughes,[1] who obtained a crude spectrum of CsF. The idea was suggested by I. Rabi as an analogue to the magnetic-resonance molecular-beam spectrometer[2] which had been previously developed. Subsequently, J. W. Trischka introduced a new homogeneous C-field, to obtain higher resolution, and many other improvements.[3] Since then MBER spectroscopy has proven to be a valuable tool in obtaining the molecular electric dipole moments and nuclear hyperfine interaction constants of the alkali halides. For the background and history of MBER spectroscopy, the reader is referred to a book by N. F. Ramsey,[4] a book by K. F. Smith[5] and a review article by P. Kusch and V. W. Hughes.[6]

The present work is a continuation of the radio-frequency studies of the alkali halide molecules using a high resolution electric-resonance spectrometer. The spectrometer used in the present experiments has demonstrated very good resolution, even at strong Stark fields. This has made possible an accurate determination of electric dipole moments, as well as hyperfine interaction constants. This thesis presents the electric-resonance studies of Li^7H, Li^7D, Li^6H, and Li^6D.

This thesis compares the experimental results with all available quantum mechanical calculations. The results of the polarizable ion model are compared to the experiment.

II. EXPERIMENTAL PROCEDURE

A. Introduction

In molecular-beam electric-resonance experiments the molecules effuse from an oven and are focused or defocused onto a detector. In the vacuum between the oven and the detector (see Fig. 1) the inhomogeneous electric fields A and B deflect the molecules along an S-shaped path at resonance. The homogeneous electric field in the C region removes the degeneracy of the $|m_J|$ states. Perpendicularly to the Stark field in the C region, a radiofrequency field induces transitions which are detected as an increased beam intensity at the detector.

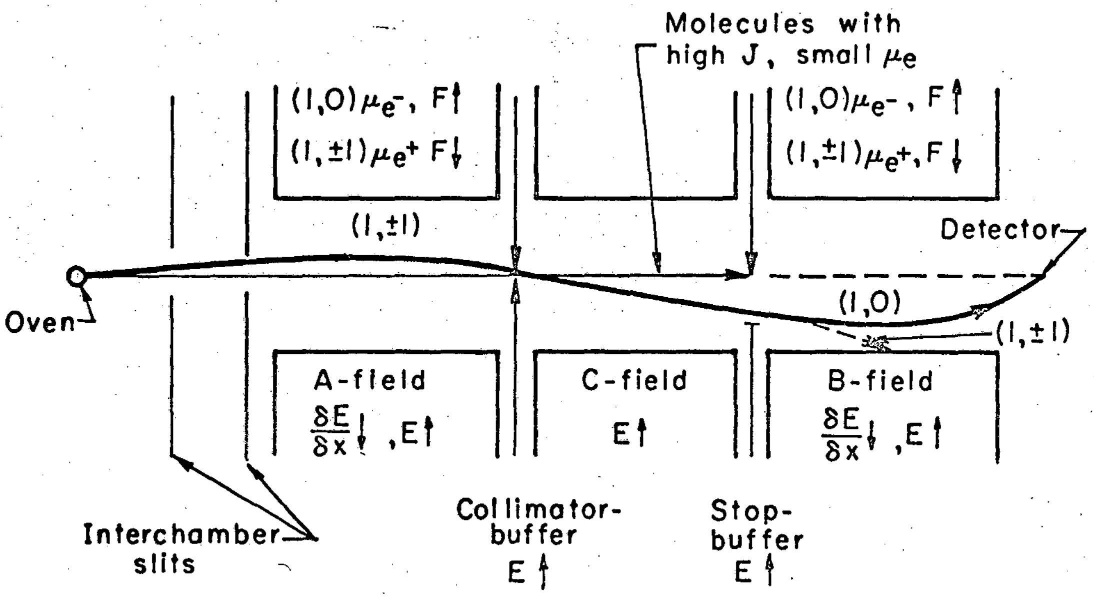

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Fig. 1. A diagram of a typical molecular-beam electric-resonance spectrometer set up for doing "flop-in" experiments.

B. Oven

The ovens used in these experiments were made from type 304 stainless steel with outside diameter of 3/8 inch and a ten-mil wall thickness. The ends of the $6\frac{1}{2}$-inch-long tube were plugged and a $\frac{1}{4}$" × 5 mil slit cut in the center of the tube. The oven was resistance heated by passing current through the tube. When the width of the oven slit is comparable to the mean free path, the situation is called molecular flow or Knudsen effusion. The apparatus was constructed so that this condition is met by the molecules in the oven and by those travelling from the oven to the detector.

Expressing temperature (T) in degrees Kelvin, pressure (p) in mm of mercury and the collision cross section (σ) in cm^2 (where σ is calculated from the hard sphere approximation to be π times the internuclear distance squared), the mean free path is derived from the formula:

$$\lambda = 7.321 \times 10^{-20} \left(\frac{T}{p\,\sigma}\right) \quad \text{in cm.} \tag{1}$$

For LiH at 700° C and 1 mm Hg oven pressure, the mean free path in the oven is 10 mils. In the main chamber (see Fig. 2) with pressures on the order of 1×10^{-6} mm Hg at room temperature, the mean free path is on the order of 147 meters. At the oven slit of width 5 mils and in the vertical length of the main chamber (on the order of 1 meter), one may consider that there are negligible collisions. For a thin-walled aperture the shape of the molecular beam follows the cosine law, with most of the molecules emerging in the forward direction.

After loading a stainless steel oven with lithium hydride and allowing the oven to remain at about two hundred degrees for approximately eighteen hours, the oven chamber pressure dropped rapidly, indicating water trapped in the sample had boiled off. The temperature was then increased to 500° C. After a period of eight hours, the oven chamber pressure dropped a factor of 1000 within a span of twenty minutes. The best spectra (signal to noise of 80 or 100 to 1) were taken at this time. This technique is more an art than a science. In general, better spectra are obtained after the oven has been heated up for a while than at the beginning of a run.

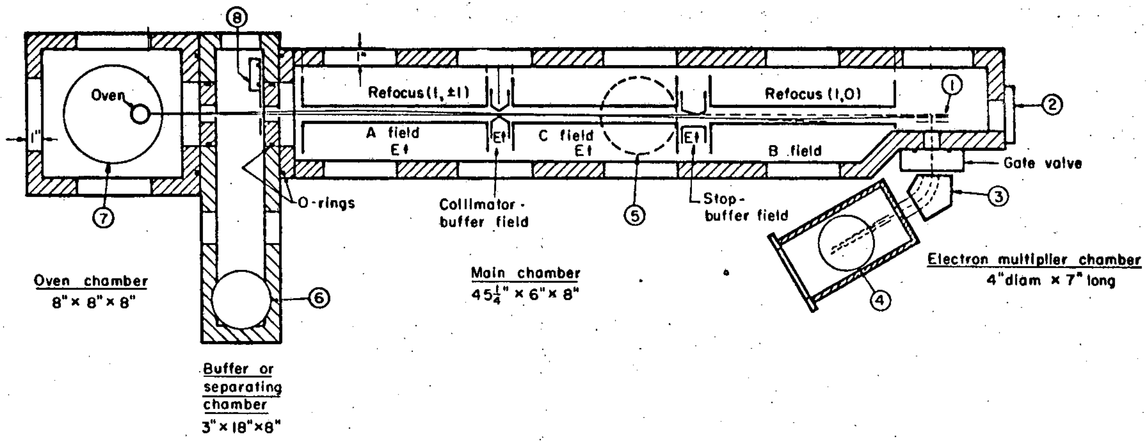

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Fig. 2. Schematic diagram (top view) of the electric-resonance apparatus. Field lengths and displacements are to scale. Field gaps and beam displacements are exaggerated. Unshaded areas in chamber walls represent access ports.

(1) Hot wire and ion accelerator
(2) Glass cover port for optical alignment
(3) Permanent magnet, 60°, 1-cm gap
(4), (5), (6), and (7) Outlets to liquid nitrogen traps and oil diffusion pumps
(8) Gate valve and beam flag

C. Detection

Detection is accomplished by surface ionization on a hot tungsten wire. The intensity is of the order of 10^{12} molecules per second impinging on a one mil by ten mil strip of tungsten maintained at approximately 1200° C. The positive ions are accelerated by an electric field (about 3000 volts for lithium) into the field of a permanent magnet with a radius of curvature of 5 cm.; from there to a fourteen stage NRC electron multiplier, with its first dynode maintained at -3300 volts. Pulses from the electron multiplier can either be fed to an electrometer and displayed on a Leeds and Northrup chart recorder or amplified and fed into a Hewlett-Packard 5253B counter. Radiofrequency is introduced into the transition region and counted on another HP counter for one second simultaneously with one second beam intensity count. The frequency and counts are recorded simultaneously on a HP 562A digital recorder. Average time per spectra is about ten minutes. Several plots of beam intensity versus frequency may be added together to reduce noise, or a multichannel analyzer system may be used.

The analyzer has 100 channels and a time base of 5×10^{-4} seconds per channel. The reference voltage generator reproduces the voltage that the RAMP generator affects in the frequency synchronizer (HP 8708A). This voltage is balanced against that from the frequency generator (HP 608F or 606B) for a particular channel and the frequency recorded. The RAMP generator generates a voltage of 0 to 10 volts, variable in frequency, whose starting pulse is obtained from an UPGEN pulse generator. The frequency synchronizer locks on a particular frequency and sweeps a range up to one megacycle with the help of the RAMP voltage. After sweeping spectra for thirty to sixty minutes, the information (channel number versus counts) is printed out and plotted.

D. Stark Effect

In the absence of an electric field, the dipole moment of a heteronuclear diatomic molecule averages to zero. In the more formal language, a non-degenerate system of definite angular momentum can have no odd electric multipole moments. The electric field twists the dipole and gives it a faster rotation when oriented in the direction of the field.

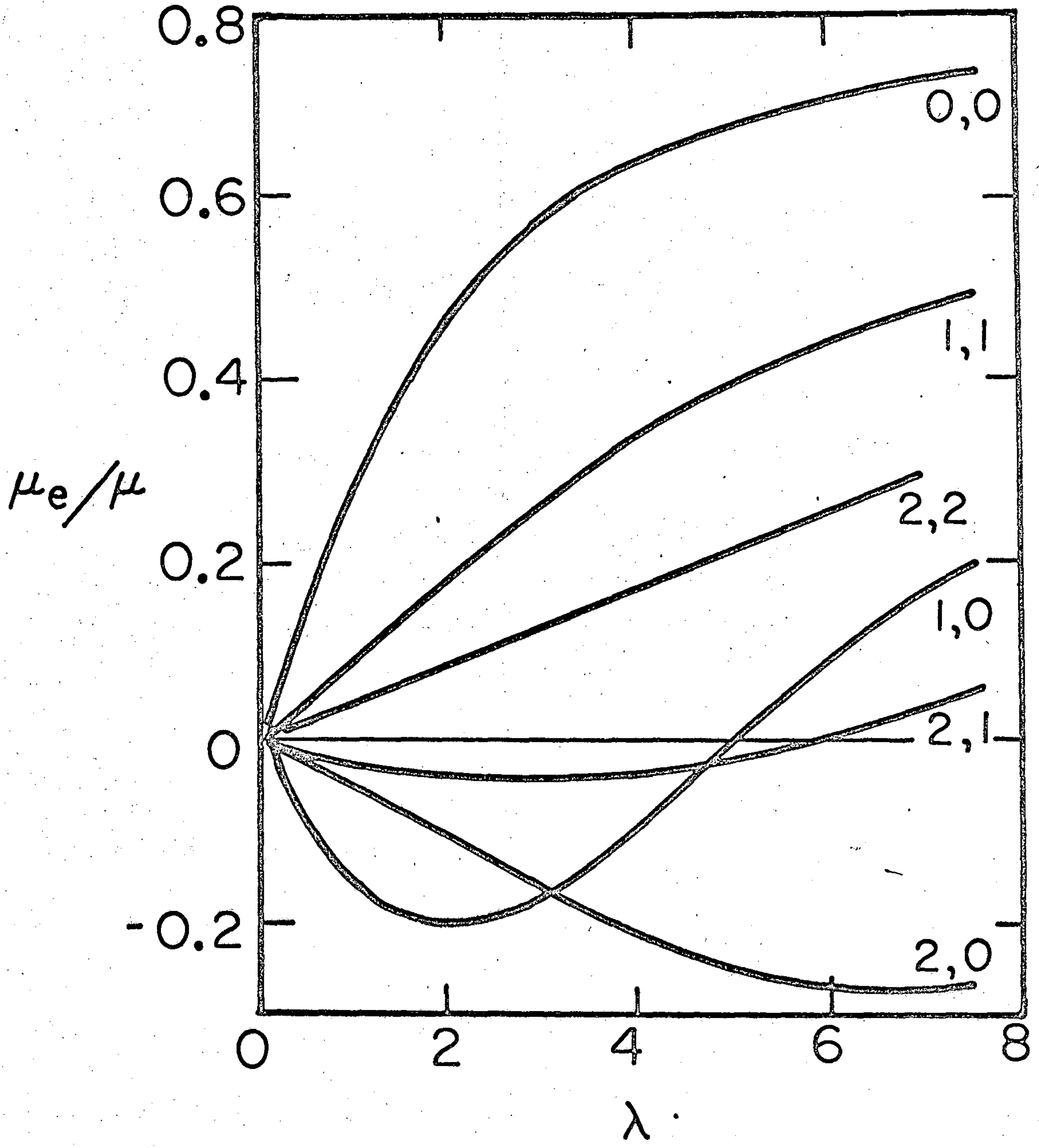

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Fig. 3. The effective electric dipole moment, μ_e, for deflection of a diatomic molecule with a permanent dipole moment, μ. The numbers at the right of each curve represent the $(J, |m_J|)$ states. The dimensionless parameter λ is equal to $\mu E/B$ where E is the electric field and B is the rotational constant.

where

B = rotational constant

J = rotational angular momentum

u = dipole moment

E = Stark field

I_1, I_2 are nuclear spins

c_1, c_2 are spin rotation constants

$c_3 = g_1 g_2 \mu_N^2 (1/r^3)$ where g_1 and g_2 are nuclear g factors and μ_N is the nuclear magneton

c_4 = electron coupled spin — spin interaction

Q_1, Q_2 are nuclear quadrupole moments

q_1, q_2 are gradient of the electric field at nuclei 1 and 2

The molecular beam experiment measures, among other things, the effective dipole moment, which is a product of permanent dipole moment squared and the inverse of the rotational constant. In most cases the rotational constant is known, and the experiment measures the dipole moment. Crawford and Jorgenson[11] measured the rotational constants for Li^7H and Li^7D. Their B_e values as given in their paper could not be isotopically corrected to be consistent with each other. In more recent years, molecular g factors[12] have been measured. These are proportional to the moment of inertia of the electrons. When the B_e values are corrected, as outlined in the following, the rotational constants can be isotopically corrected.

The $B_e^{(ionic)}$ values for Li^7H and Li^7D were extracted using the g_J(elec) and $B_e^{(exp)}$ values. Both the g_J(elec) and g_J(nuc) values are inversely proportional to the moment of inertia, or directly proportional to the rotational constant. The measured g_J values and the $B_e^{(ionic)}$ values were isotopically corrected for Li^6H and Li^6D. The $B_e^{(calc)}$ values were calculated and used to find the necessary B_v values.

Using ionic masses in the reduced mass formula and the molecular magnetic moments[12] to find the ionic rotational constants from the data of Crawford and Jorgenson,[11] one obtains 0.56321 for the ratio of the ionic rotational constant of Li^7D to that of Li^7H. The ratio of the reduced ionic masses of Li^7H to that of Li^7D is 0.56329. The value of the equilibrium internuclear distance is 1.59443 ±0.00003 Å. This method was applied to find the corresponding constants for the other two isotopes. These rotational constants as well as vibrational frequencies and molecular magnetic moments are listed in Table I. Preliminary values of the constants for Li^7D and Li^6D were presented by Pearson and Gordy[13] at the Spring American Physical Society meeting. A set of constants for these molecules, using their values for Y_{01} and Y_{11} is listed in Table II.

The fractional error in the Crawford and Jorgenson rotational constants is of the order of 1×10^{-4}. This will produce an uncertainty in the measured dipole moments of the order of 3×10^{-4} Debye. The fractional error between the rotational constants of Pearson and Gordy and those of Crawford and Jorgenson is 5×10^{-4} for Li^7D and produces an uncertainty of 0.0015 D in the dipole moment. For Li^6D there is a 0.0027 D difference between the two possible v = 0 dipole moments, however the u_e (equilibrium dipole moment) values agree.

B. Rotational Constants

Summary of formulas:

$$B_v = Y_{01} + Y_{11}(v + \tfrac{1}{2}) + Y_{21}(v + \tfrac{1}{2})^2$$

$$Y_{01} = B_e[1 + C_{01}(B_e/w_e)^2]$$

$$Y_{11} = B_e(B_e/w_e)[6(1 + a_1) + (B_e/w_e)^2 C_{11}]$$

$$Y_{21} = 6B_e(B_e/w_e)^2 C_{21}$$

a_1 = anharmonicity constant

B_e = equilibrium rotational constant

B_v = rotational constant for vibrational state v

Y_{ij} = Dunham coefficients

C_{ij} = constants

w_e = vibrational frequency at equilibrium

$u^{(ionic)} = M_{(Li+)} \cdot M_{(H^-)}/(M_{(Li+)} + M_{(H^-)})$

$u^{(ionic)} = u$ = reduced mass

M_i = mass of nucleus i in amu

$g_J(nuc.) = Mu \ \ Z_i/M_i^2$

$g_J(total) = g_J(elec.) + g_J(nuc.)$

$u_N \cdot J \cdot g_J$ = rotational magnetic moment

M = proton mass

Z_i = effective nuclear charge

u_N = nm = nuclear magneton

$B_e^{(ionic)} = B_e^{(EXP)}(1-g_J(elec.)u_N/u_o)$

$B_e^{(calc)} = B_e^{(ionic)}/(1-g_J(elec.)u_N/u_o)$ = calculated B_e value

$B_e^{(EXP)}$ = experimentally measured B_e value

$B_e^{(ionic)}$ = derived B_e value

u_o = Bohr magneton

Isotopic correction to w_e and $B_e^{(ionic)}$:

$$\frac{w_e^a}{w_e^b} = \sqrt{\frac{u^b}{u^a}} \qquad (5)$$

$$\frac{B_e^a}{B_e^b} = \frac{u^b}{u^a} \qquad (6)$$

Table I.

	Y_{01}	Y_{11}	Y_{21}	error
$\mathrm{Li}^7\mathrm{D}$	4.23384 cm^{-1}	-0.09198 cm^{-1}	6.7×10^{-4}	0.0004 cm^{-1}
$\mathrm{Li}^7\mathrm{H}$	7.5131 cm^{-1}	-0.2132 cm^{-1}	7.5×10^{-4}	0.0004 cm^{-1}
$\mathrm{Li}^6\mathrm{H}$	7.67090 cm^{-1}	-0.2198 cm^{-1}	14.93×10^{-4}	0.0006 cm^{-1}
$\mathrm{li}^6\mathrm{D}$	4.39015 cm^{-1}	-0.1043 cm^{-1}	4.89×10^{-4}	0.0006 cm^{-1}

	$B_e^{(\mathrm{ionic})}$	B_0	B_1
$\mathrm{Li}^7\mathrm{D}$	4.2360 cm^{-1}	0.12559×10^9 kc	0.122825×10^9 kc
$\mathrm{Li}^7\mathrm{H}$	7.5212 cm^{-1}	0.2220473×10^9 kc	0.215701×10^9 kc
$\mathrm{Li}^6\mathrm{H}$	7.67633 cm^{-1}	0.2266842×10^9 kc	0.2201736×10^9 kc
$\mathrm{Li}^6\mathrm{D}$	4.3933 cm^{-1}	0.130053584×10^9 kc	0.1269558×10^9 kc

	w_e	$g_J^{(\mathrm{elec})}$	g_J meas.[12]	$\mu^{(\mathrm{ionic})}$
$\mathrm{Li}^7\mathrm{D}$	1055.015 cm^{-1}	-0.692 nm	-0.272 nm	1.5651743
$\mathrm{Li}^7\mathrm{H}$	1405.401 cm^{-1}	-1.545 nm	-0.654 nm	0.88164861
$\mathrm{Li}^6\mathrm{H}$	1420.120 cm^{-1}	-1.254 nm		0.86358830
$\mathrm{Li}^6\mathrm{D}$	1074.193 cm^{-1}	-0.7176 nm		1.5091451

$r_e' = 1.59443 \pm 0.00003$ Å

	$B_e^{(\mathrm{calc})}$	$B_e^{(\mathrm{exp})}$[11]
$\mathrm{Li}^7\mathrm{D}$		0.12694414×10^9 kc
$\mathrm{Li}^7\mathrm{H}$		0.22529107×10^9 kc
$\mathrm{Li}^6\mathrm{H}$	0.23002299×10^9 kc	
$\mathrm{Li}^6\mathrm{D}$	0.13165777×10^9 kc	

Table II.

	Y_{01} ($\times 10^9$ kc)	Y_{11} ($\times 10^9$ kc)	Y_{21} ($\times 10^9$ kc)
Li^{7}D	0.12690536	-0.00274461	0.000018
Li^{6}D	0.13161507	-0.00289890	0.000015

	B_0 ($\times 10^9$ kc)	B_1 ($\times 10^9$ kc)
Li^{7}D	0.12553756	0.12282896
Li^{6}D	0.13016937	0.12730047

	B_e	r_e
Li^{7}D	0.12696035×10^9 kc	1.59490 Å
Li^{6}D	0.13467274×10^9 kc	1.59490 Å

Comparing the Crawford and Jorgenson values with the Pearson and Gordy values, the Li^{7}D values agree well. The difference between the two causes an uncertainty of 0.001 D in dipole moment. The Li^{6}D values are quite different. Most of the difference is due to the approximations in the isotope correction.

IV. DATA ANALYSIS AND SPECTRA

A. Fitting the Data

A computer program[14] calculates the matrix elements of $\mathcal{H}$ (defined by equation (4) on page 7) in a $(J\ I_1 I_2 m_J m_1 m_2)$ representation. Since $\mathcal{H}$ is invariant under rotations about the electric field axis, the projection of the total angular momentum on the direction of the electric field (denoted by $m_F = m_J + m_1 + m_2$) is a good quantum number at all values of the electric field. This means that the matrix is diagonal in m_F. The last four terms of $\mathcal{H}$ are usually small and only matrix elements diagonal in J are included for them. Quadrupole matrix elements diagonal in J were included for the smaller quadrupole. Quadrupole matrix elements connecting J and J ±2 for the second quadrupole term are included. The Stark-quadrupole interaction is included for both quadrupole terms.

In calculating J = 1 eigenvalues, only the first four J states are included in the matrix. Since the Stark operator connects J states with J ±1 states only, this amounts to a fourth order perturbation treatment and second order for the quadrupole term.

The computer program diagonalizes the energy matrix by the Jacobi diagonalization method. The elements of the matrix which diagonalizes the energy matrix, or the elements of the transformation matrix are used as coefficients in forming the transformed wave function ϕ in terms of the original basis ψ. The intensity of a transition from ϕ_i to ϕ_j is proportional to the dipole matrix element squared:

$$|\langle\phi_i|\mu|\phi_j\rangle|^2 = |\sum_{K\ell} a_{iK} a_{\ell j} \langle\psi_K|\mu|\psi_\ell\rangle|^2 \qquad (7)$$

The program calculates energy eigenvalues by diagonalizing the energy matrix and calculates the spectral line positions and intensities corresponding to a given set of input parameters according to the selection rules $\Delta m_F = 0, \pm 1, \pm 2$, etc. The unknown parameters are varied to obtain a best fit to the observed spectra.

For the Li^6H and Li^6D spectra, individual transitions could not be extracted from the data. The output from the program described was introduced into a program which plotted the calculated spectra assuming guassian line shapes at each calculated line position and summed the unresolved lines. This plot was compared to the experimental data in order to find the correct parameters. For Li^7H, the single transitions were well described by guassians and the intensities calculated agreed with the experiment; therefore this procedure appears to be justified.

B. Radio-Frequency Spectra of $\mathrm{Li^7H}$

Table III. Experimental and calculated line positions for $\mathrm{Li^7H}$ $v = 0$ at 750 volts (experimental values represent the average of 13 runs)

line	experiment	calculated	composite calculated position
1	3229.4 ±0.2 kc	3229.130	
2	3240.8 ±0.2 kc	3240.917	
3	3251.3 ±0.2 kc	3249.889	3251.5
4		3252.009	
5	3277.75 ±0.4 kc	3273.267	3278.85
6		3277.249	
7		3282.239	
8	3305.3 ±0.2 kc	3304.808	3305.35
9		3307.439	
10	3330.2 ±0.2 kc	3330.317	
11	3364.4 ±0.2 kc	3363.947	3364.3
12		3369.032	
13		3373.017	
14	3376.0 ±0.2 kc	3375.868	3376.0
15		3377.422	
16		3378.004	
17	3432.8 ±0.2 kc	3432.922	
18	3453.35±0.3 kc	3451.325	3453.35
19		3455.730	

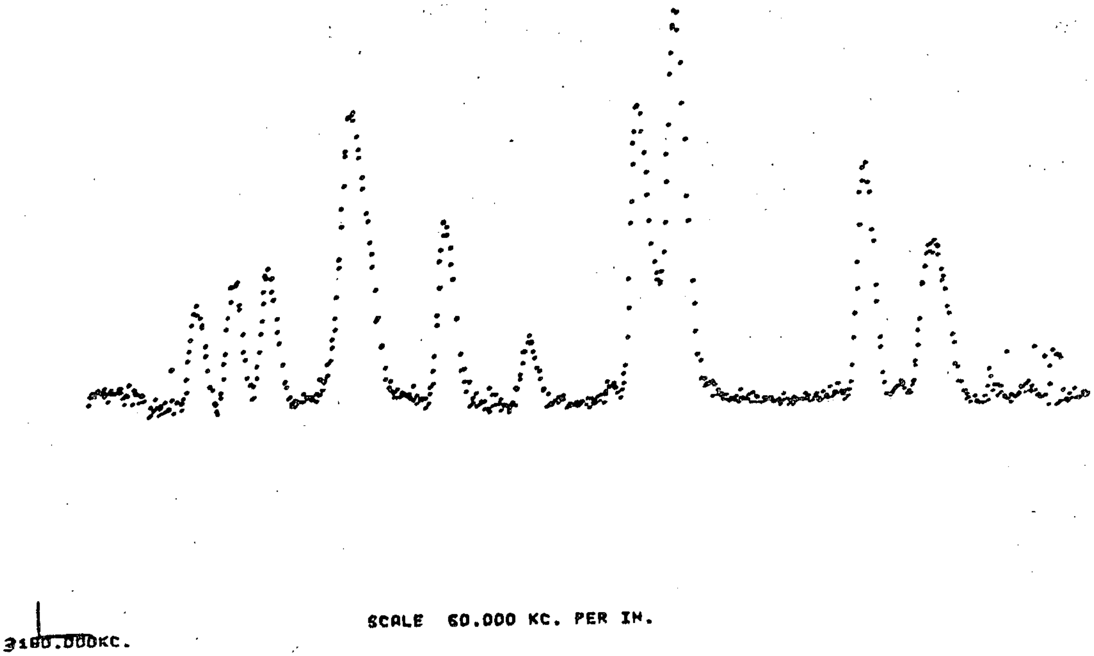

Fig. 4. Li^7H v = 0 experimental data (sum of 13 spectra) at 750 volts.

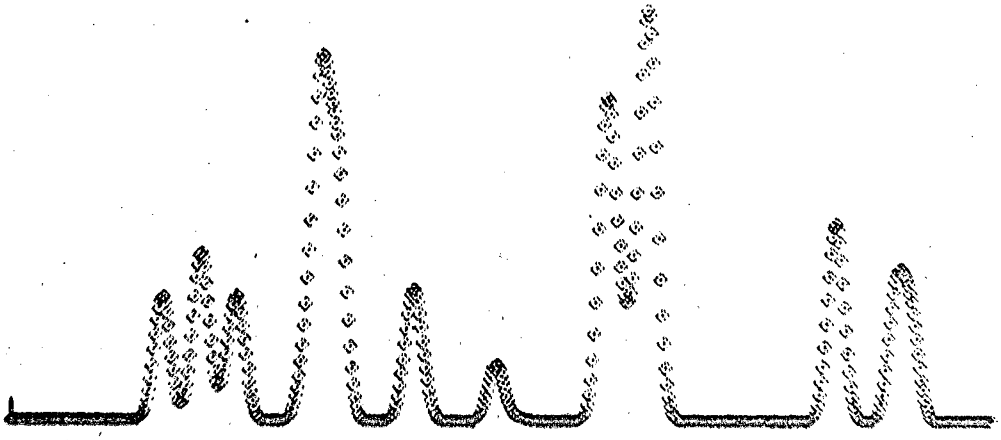

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Fig. 5. Li^7H v = 0 calculated spectra.

Table IV. Li^7H v = 0 results and comparison.

	this work	Wharton, Klemperer and Gold (ref. 15)
eqQ_{Li}	346.75 ±0.25 kc	346 ±1
c_H	-9.05 ±0.05 kc	-8 ±1
c_{Li}	10.025 ±0.075 kc	10 ±1
c_3	0.45318 ±0.001 kc	
c_4	0 ±0.3 kc	
dipole	5.8820 ±0.0004 D	5.882 ±0.003

Table V. Experimental and calculated line positions for $\mathrm{Li}^7\mathrm{H}$ v = 0 at 750 volts (experimental values represent the average of 12 runs).

line	experiment	calculated	composite calculated
1	interference with v = 0 spectra	3459.121	
2		3470.567	
3		3479.247	
4		3481.296	
5	3506.55 ±0.3	3501.227	3506.8
6		3505.228	
7		3509.907	
8	3533.05 ±0.4	3531.770	3532.3
9		3534.227	
10	3556.7 ±0.3	3556.403	
11	3588.6 ±0.3	3588.121	3588.5
12		3593.235	
13		3597.231	
14	3600.0 ±0.3	3599.388	3599.6
15		3601.433	
16		3601.914	
17	3654.1 ±0.2	3654.438	
18	3674.35 ±0.5	3672.338	3674.15
19		3676.539	

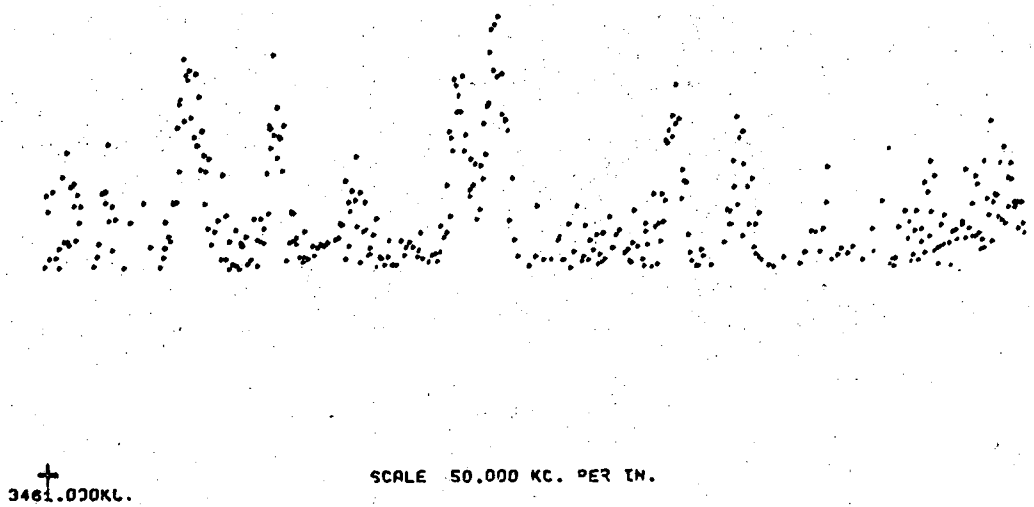

Fig. 6. Li^7H v = 1 experimental data (sum of 12 sets of data) at 750 volts.

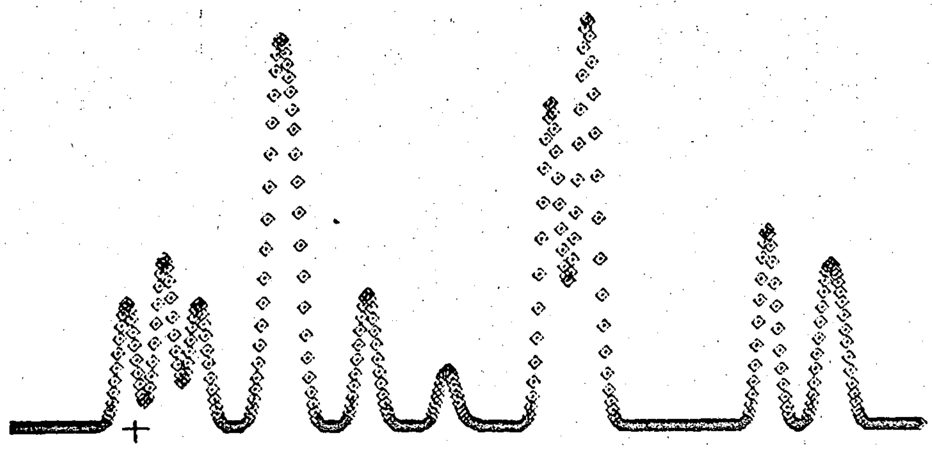

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Fig. 7. Li^7H v = 1 calculated spectra.

Table VI. Li^7H v = 1 results and comparison with previous work.

	this work	Wharton, Klemperer, and Gold
eqQ_{Li}	332 ±0.5	328 ±4
c_H	-9 ±0.5	-6 ±2
c_{Li}	9.8 ±0.1	10 ±2
c_3	0.43828 ±0.001	
c_4	0 ±0.5	
dipole	5.9905 ±0.0004	5.990 ±0.003

C. Radio-Frequency Spectra of Li^6H

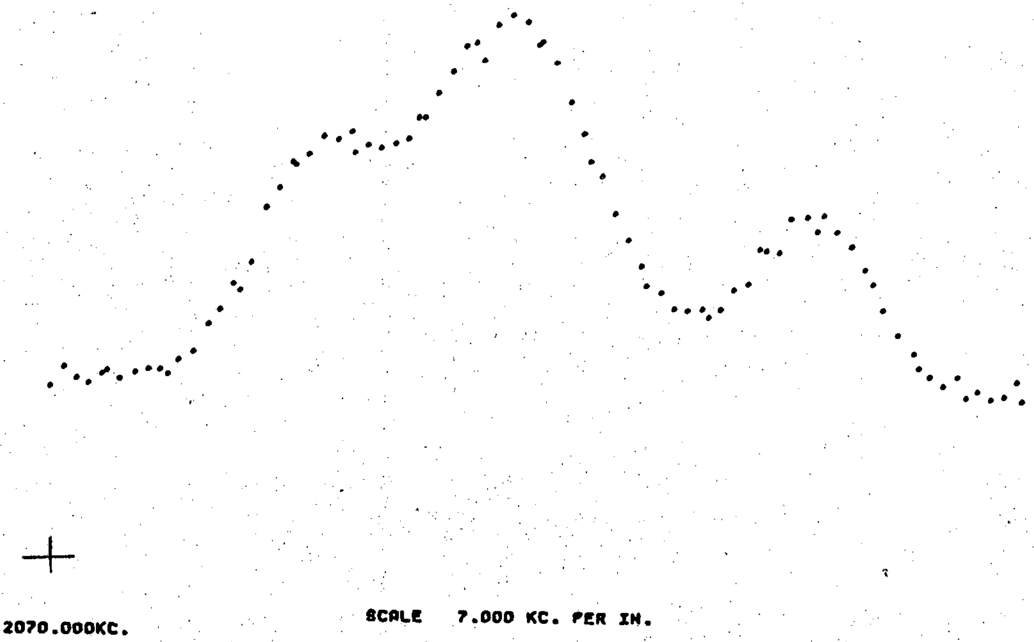

Fig. 8. Li^6H v = 0 data (sum of six runs) at 600 volts.

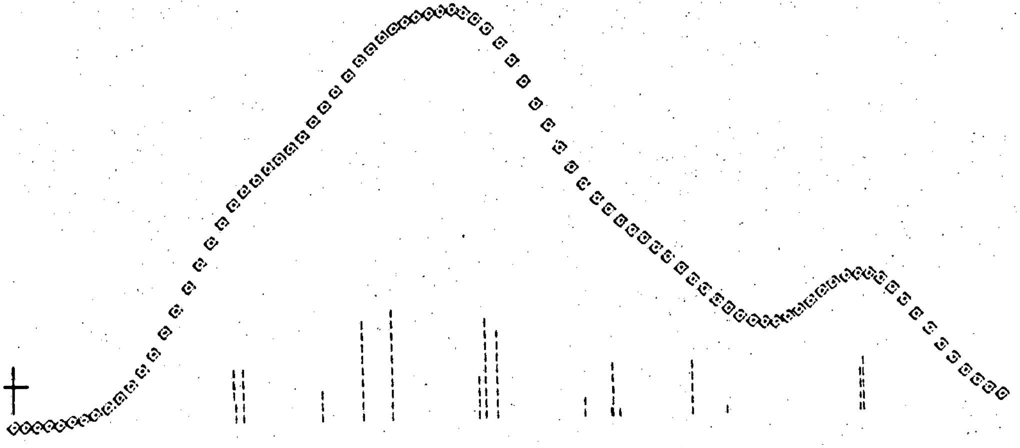

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Fig. 9. Li^6H v = 0 calculated spectra.

Table VII. Li^6H v = 0 results.

	this work	Wharton, Klemperer, and Gold
eqQ_{Li}	7.2 ±0.8 kc	
c_H	-9.3 ±0.7 kc	
c_{Li}	3.9 ±0.5 kc	
c_3	0.171109 ±0.001 kc	
c_4	0 ±0.3 kc	
dipole	5.8836 ±0.0012 kc	5.884 ±0.003

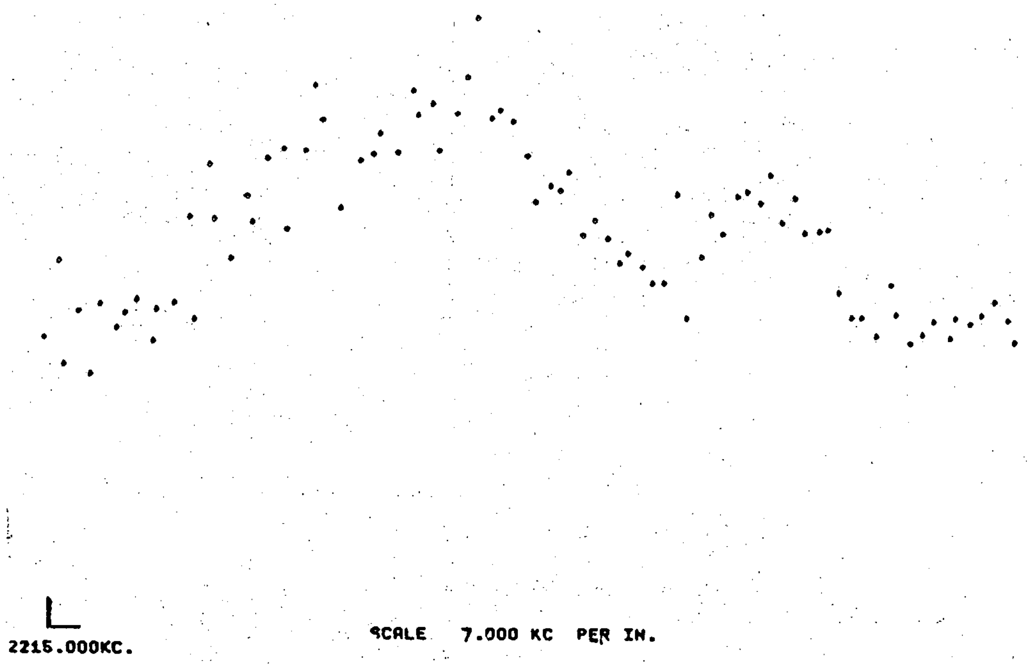

Fig. 10. Li^6H v = 1 experimental data (sum of seven sets of data) at 600 volts.

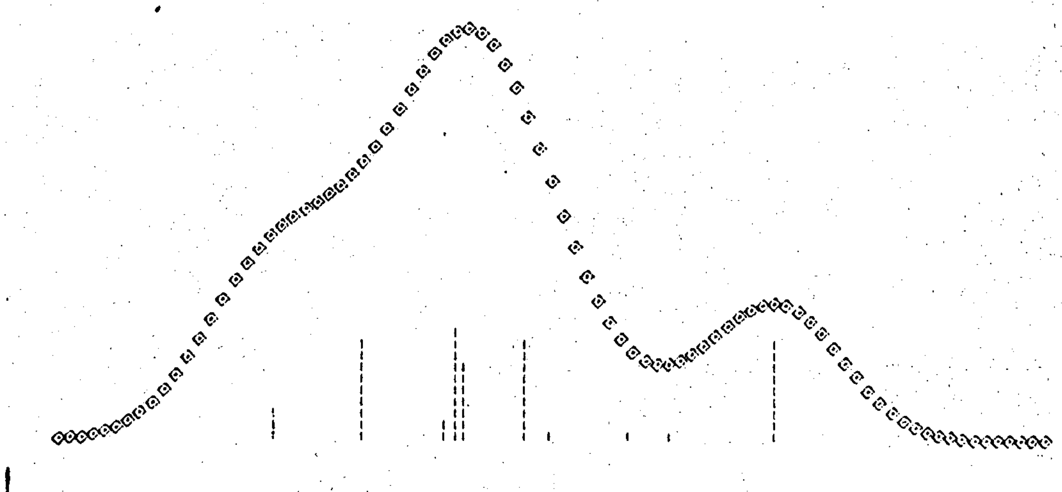

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Fig. 11. Li^6H v = 1 calculated spectra.

Table VIII. Li^6H v = 1 results from this work.

eqQ	7.2 ±0.8
c_H	-9.3 ±0.7
c_{Li}	3.9 ±0.5
c_3	0.1658819 ±0.001
c_4	0 ±0.3
dipole	5.9929 ±0.0016

D. Radio-Frequency Spectra of Li^6D

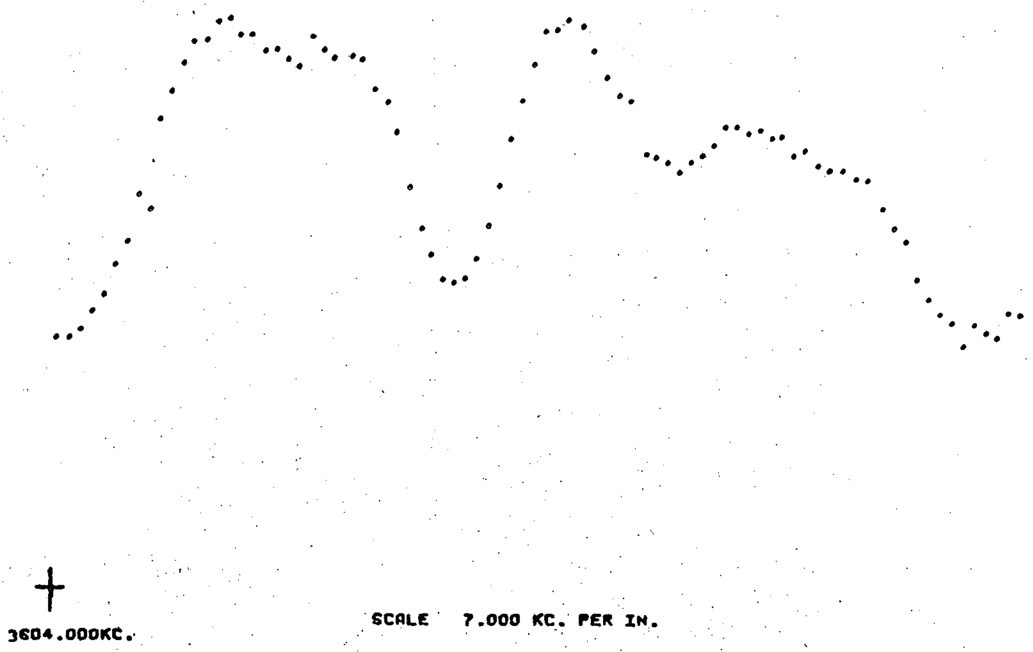


Fig. 12. Li^6D v = 0 experimental data (sum of 11 sets of data) at 600 volts.

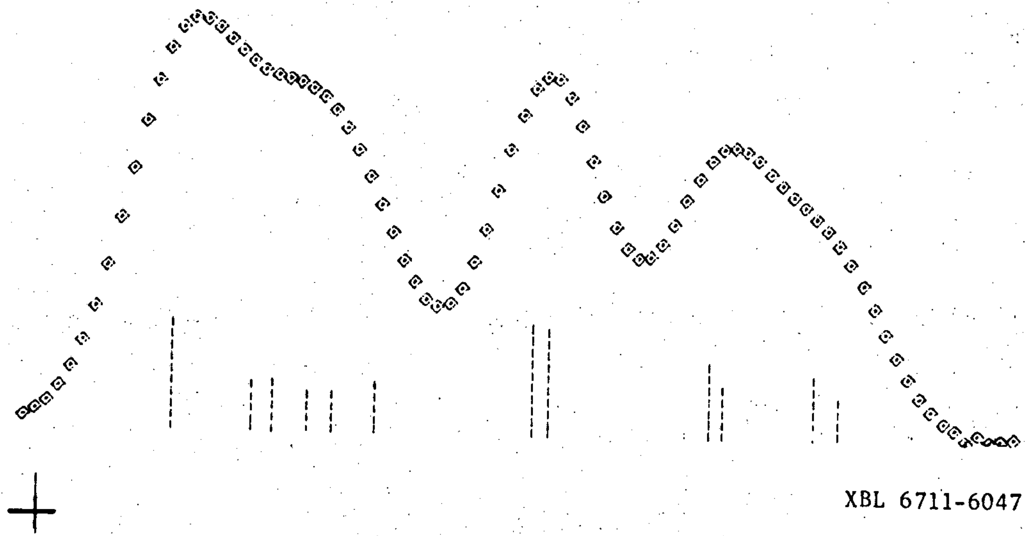


Fig. 13. Li^6D v = 0 calculated spectra.

Table IX. Li^6D v = 0 results.

eqQ_{Li}	7.5 ±1 kc
eqQ_D	33 ±1 kc
c_{Li}	3.2 ±1 kc
c_D	-1.3 ±0.5 kc
c_3	0.026385 ±0.001 kc
c_4	0 ±0.3 kc
dipole	5.8667 ±0.0012 D
	5.8694 ±0.0010 D (using rotational constants of Pearson and Gordy.)

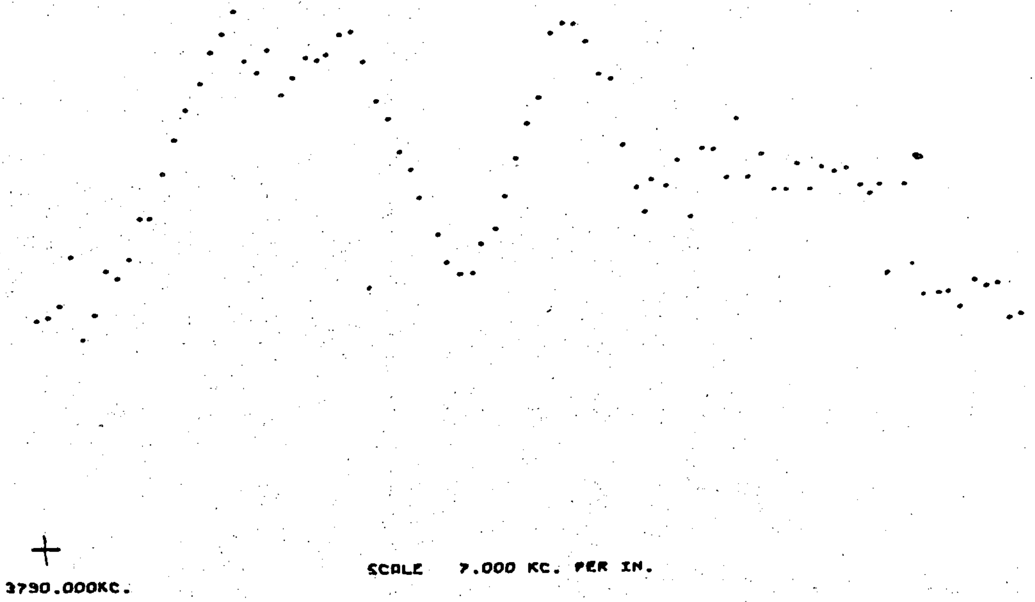
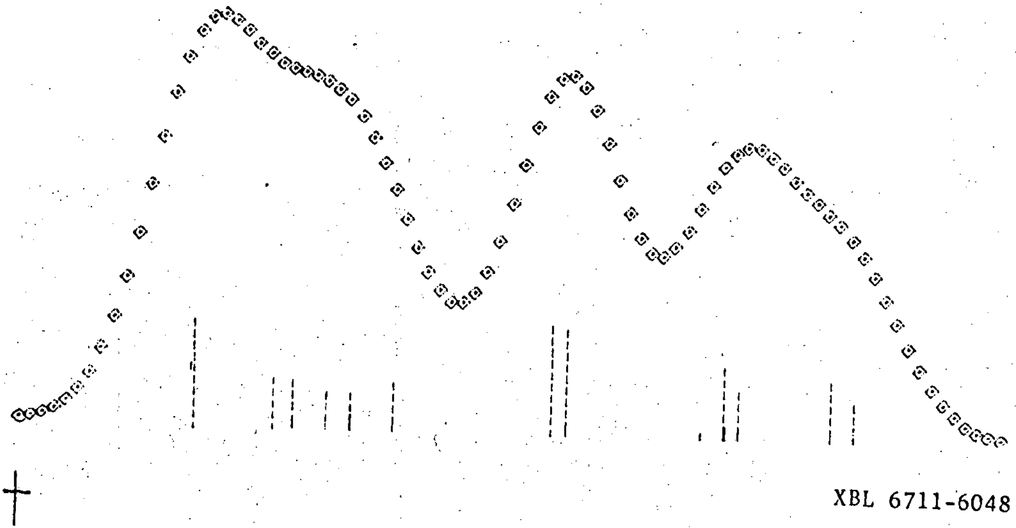


Fig. 14. Li^6D v = 1 experimental data (sum of five sets of data) at 600 volts.



XBL 6711-6048

Fig. 15. Li^6D v = 1 calculated spectra.

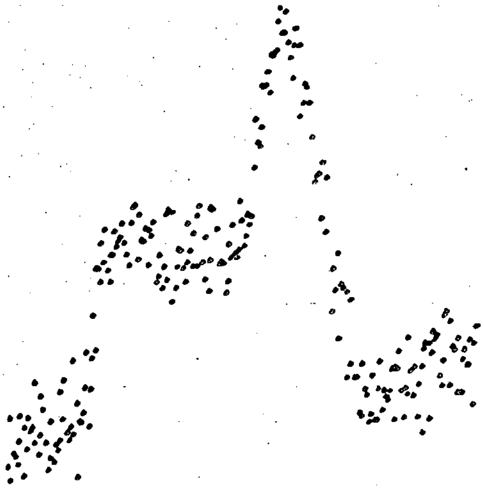
Table X. Li^6D v = 1 results.

eqQ_{Li}	7.5 ±1
eqQ_D	33 ±1
c_{Li}	3.2 ±1
c_D	-1.3 ±0.5
c_3	0.025770 ±0.001
c_4	0 ±0.3
dipole	5.9443 ±0.0012 5.9523 ±0.0010 (using rotational constants of Pearson and Gordy.)

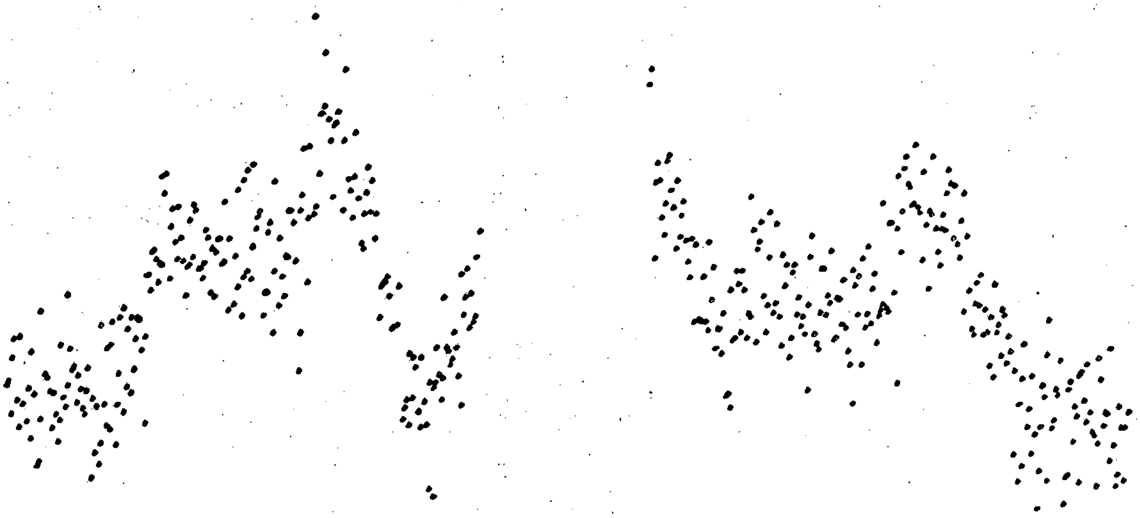
E. Radio-Frequency Spectra of Li^{7}D

Table XI. Li^{7}D $v = 0$ experimental and calculated line positions at 750 volts.

line	experimental	calculated	composite calculated
Ia	5761.901 ±0.4	5761.964	
Ib	5777.528 ±0.2	5776.802 5777.844	5777.4
IIa	5801.430 ±0.8	5801.213	
IIb	5816.676 ±0.5	5815.205 5818.251	5816.7
IIIa	5829.242 ±0.7	5831.624	
IIIb	5844.627 ±0.7	5845.154 5848.627	5846.2
IVa	5890.103 ±0.2	5890.696	
IVb	5899.705 ±0.3	5900.009	
IVc	5914.354 ±0.2	5912.355 5916.755	5914.4
Va	5960.431 ±0.3	5960.356	
Vb	5974.646 ±0.5	5974.198 5977.758	5976.0



Sec. 1. Lines Ia, Ib.

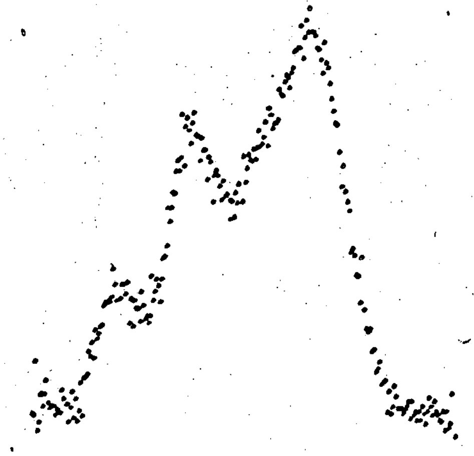


Sec. 2. Lines IIa, IIb.

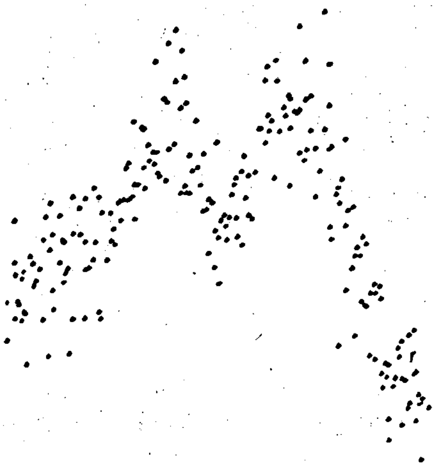
Sec. 3. Lines IIIa, IIIb.

XBL 6711-6049

Fig. 16. Li^7D v = 0 experimental data.



Sec. 4. Lines IVa, IVb, IVc.



Sec. 5. Lines Va, Vb.

XBL 6711-6050

Fig. 17. Li^7D v = 0 experimental data continued from Fig. 16.

Table XII. Li^7D v = 0 results and comparison

	this work	Wharton, Klemperer, and Gold (ref. 15.)
eqQ_D	33 ±1	33 ±1
eqQ_{Li}	349 ±1	349 ±1
c_D	0 ±1	
c_{Li}	5.5 ±0.25	5.5 ±1
c_3	0.054842 ±0.001	
c_4	0 ±0.3 kc	
dipole	5.8689 ±0.0005 D	5.868 ±0.003
	5.8677 ±0.0005 D (using rotational constants of Pearson and Gordy)	

The values of the dipole moments for the isotopes were fitted to the equation $\mu = \mu_e + (v + \frac{1}{2})\cdot\mu_I$. The values of μ_e and μ_I as well as a summary of the experimental values of u_o and u_1 are listed in Table XIII. The errors listed arise from several sources. The error due to uncertainty in the rotational constants of Crawford and Jorgenson is 3×10^{-4} Debye for Li^7H and Li^7D and 5×10^{-4} D for Li^6H and Li^6D. Errors due to the rotational constants of Pearson and Gordy are not known. The errors due to their measurements of the frequency are of the order of 1 ppm and will produce a 3 ppm dipole moment error. The fitting error, due to uncertainties in the other molecular constants, is 3×10^{-4} D. The error due to variation in the full width at half maximum of the guassians used to approximate the shape of the resonance distribution contributes 0.001 D in the case of Li^6H and Li^6D. This occurs in the case of these two isotopes because the spectra is not well spread out and many lines overlap. The errors due to C field measurement and frequency calibration are 80 ppm and are negligible.

Lawrence, Anderson, and Ramsey,[12] measured the rotational magnetic moments of Li^7H and Li^7D. From their data they calculated the sign and magnitude of the electric dipole moment. For the purposes of making the isotope correction, the equation for the isotope shift of the molecular g factor, u_R/J (where u_R is the rotational magnetic moment and J the rotational quantum number) can be represented as:

$$g_b - (A_a/A_b)\, g_a = -2\, M\mu_e \Delta X/eA_b \qquad (8)$$

A = moment of inertia
M = proton mass
e = electronic charge
ΔX = displacement of the center of mass

$\mu_e = e\,(\Sigma Z_i)(D-d)$, the dipole moment and D and d are the distance from the center of mass to the centroids of the nuclear charge and of the electronic charge, respectively. The result is $u_e = +5.9 \pm 0.5$ Debye, with the dipole pointing toward the lithium nucleus. This convention is the same as that used in the ionic model.

Table XIII.

	μ_o	μ_1	μ_e	μ_I
Li^7H	5.8820 ±0.0004	5.9905 ±0.0004	5.82775	0.1085
Li^6H	5.8836 ±0.0012	5.9929 ±0.0016	5.82895	0.1093
Li^6H	5.8667 ±0.0012	5.9443 ±0.0012	5.8279	0.0776
*	5.8694 ±0.0010	5.9523 ±0.0010	5.82795	0.0829
Li^7D	5.8689 ±0.0005			
*	5.8677 ±0.0005			

*Using rotational constants of Pearson and Gordy.

The value $u_e/(du/dr)_{r=r_e} r_e = 1.8 \pm 0.3$ was extracted by James, Norris, and Klemperer[16] from measurements of the relative line intensities of the rotational fine structure. Li^7H was heated to 1000° C in order to obtain appreciable absorption. Line intensities in the 0-1 and 1-2 rotation vibration band of LiH at 7μ were measured. Assuming the second derivative to be zero, u_I calculated from this experiment is 0.06893 Debye.

Considering the energy of interaction of the magnetic moment of the i^{th} nucleus with the surrounding magnetic field using the rigid rotor approximation as described in a paper by White,[17] the energy of interaction is $-\vec{u}_i \cdot \vec{H}$. The magnetic moment $\vec{u}_i = g_I u_{ON} \vec{I}_i$ where g_I is the gyromagnetic ratio of the nucleus, u_{ON} is the nuclear magneton and I_i the spin angular momentum. The field at the i^{th} nucleus is:

$$\vec{H} = -\sum_{j \neq i} q_j \frac{(\vec{v}_j \times \vec{r}_{ij})}{c(r_{ij})^3} \quad , \qquad (9)$$

q_j is the charge of the j^{th} particle of the molecule, v_j its velocity and r_{ij} the radius vector from the i^{th} nucleus to this particle. This sum can be divided into two parts, the sum over nuclei and the sum over electrons.

Assuming that closed shell electrons can be accounted for by the use of effective charge q_j' equal to the nuclear charge minus the number of inner shell electrons, then the electronic term deals with valence electrons. The theory assumes that only one electron at a time will enter an excited state, and that this electron will be a valence electron. The resultant formula for the magnetic interaction in a linear molecule is:

$$W' = c\vec{I}\cdot\vec{J} = \frac{\mu_{ON} g_I}{A_x} \left[4\mu_{OB} \langle \frac{1}{r^3} \rangle_{AV.} \sum_n \frac{|(0|L_x|n)|^2}{E_n - E_o} - \sum_j \frac{q_j'}{c r_{ij}} \right] \vec{I}\cdot\vec{J} \qquad (10)$$

A_x = moment of inertia of nuclear frame (component)

μ_{OB} = Bohr magneton

μ_{ON} = nuclear magneton

$\langle \frac{1}{r^3} \rangle_{AV.}$ = averaged over excited electronic wave functions

L_x = component of electronic angular momentum in x direction

E_n = energy of n^{th} excited state

The x component of the electronic contribution to the molecular g factor

$$\left[g_J(\text{elec})\right]_x = \left[\frac{u_J}{u_{ON}}\right]_x = \frac{2u_{oB}}{u_{oN}A_x} \sum_n \frac{|(0|L_x|n)|^2}{E_n - E_o} \qquad (11)$$

is related to the electronic contribution to the spin-rotation constant.

The spin rotation interaction is proportional to the nuclear g factor and to the rotational constant. Correcting the Li^7H spin rotation constants (c_H = -9.1 and c_{Li} = 10.0) for the isotope effects, the constants obtained for Li^6H are c_H = -9.3 and c_{Li} = 3.9; for Li^6D they are c_D = -0.8 and c_{Li} = 2.3 and for Li^7D they are c_D = -0.9 and c_{Li} = 5.6.

The experimental values (listing the H or D first and then the Li) for Li^6H are -9.3 ±0.7, 3.9 ±0.5; for Li^6D, -1.3 ±0.5, 3.2 ±1 and for Li^7D 0 ±1, 5.5 ±0.5. The isotopically corrected values are all within experimental error.

The spin rotation interaction arises from the reaction between a magnetic moment and the magnetic field at that nucleus. For a diatomic molecule AB, the field at nucleus A is due to nucleus B and to the electrons. For hydrogen molecules[17] and for the lithium hydrides the contribution from the nucleus is larger than that from the electrons. For Li^7H at the hydrogen nucleus, the Li nucleus contributes -11.4 kc and the electrons +2.4 kc for a grand total of -9 kc.

The spin-spin interaction (c_3) as calculated, were sufficient to explain the data, without the need to adjust the calculated values. There is no evidence for the scalar spin-spin interaction constant c_4 in the literature nor in the experiments.

V. MOLECULAR CONSTANTS

Because the LiH molecule is the simplest polar molecule, having only four electrons, there exists a wealth of calculations and theoretical discussion on this subject. Although the solution to the quantum mechanical problem involves approximations, especially in the form of the wave function, the results are encouraging. Calculations of the quadrupole coupling constants, spin rotation constants, and dipole moment are available. These are one-electron operators and Hartree Fock wave functions should give good values. The best test of theory involves calculation of derivatives of these quantities and comparison with $(eqQ)_I$ and u_I. For this, functions at various internuclear distances are needed. There are not too many of these calculations available, but wherever available these have been compared to the experiment. This is summarized in Table XIV. In this table the conversion constant 27.2097 ev = 1 au has been used where necessary.

Introduction to the Discussion: In Table XIV the calculations are listed in order of their "goodness" as given by the "energy criteria"— i.e. the calculation giving the lowest energy is listed first. As can be seen from the table, success in predicting the molecular properties does not always follow the same order. In the following paragraphs a brief description and discussion of each of the calculations is given. For ease in referring to the table, the discussion is identified by the calculation number appearing in the first column of Table XIV.

A. Calculation 12

Ransil[30] reported wave functions for first row diatomic molecules a few years ago. The wave functions have also been used by others to calculate molecular properties. He did self-consistent field calculations with three kinds of basis sets. They are called SAMO, BAMO, and BLMO because of the way in which the orbital exponent was chosen. The orbital exponent in the Slater orbital $S_{nlm} = N_n(\xi)r^{n-1}e^{-\xi r}Y_l^m(\theta,\phi)$ was chosed using Slater's rules in the SAMO calculation. For LiH, values 6.41 D, 1.34 ev, and -7.96666 au for dipole moment, dissociation energy and molecular energy were obtained. The BAMO used best atomic ξ values determined from variational calculations on atoms. The values for the

Table XIV. Calculated Molecular Properties

calcn no.	researcher	ref.	$\mu_{eq.}$ †	μ_I †	eqQ(D) ‡	$eqQ_I(Li^7)$ ‡	c_{Li} ‡	c_H ‡	energy[18] §
	Experiment		5.83	0.11	33	-14.75	10.14	-9.08	-8.0703
1	Bender and Davidson	19	5.965		30.5				-8.0606
2	Browne and Matsen	20	5.96	0.09	34.2				-8.0561
3	Matsen and Browne	21	5.57						-8.04379
4	Ebbing	22	5.96						-8.04128
5	Kahalas and Nesbet	23							
5a	third calculation		5.831		39.24	45.85			-8.0171
5b	fifth calculation		5.8875		35.31	-18.91			-8.0171
6	Robinson, Stuart, and Matsen	24	6.18						-8.0074
7	Karo and Olsen	25	6.05	.059					-7.99412
8	Platas and Matsen	26	5.86						-7.9882
9	Ormand and Matsen	27	5.57						-7.9858
10	Csizmadia	28	6.0079	0.122					-7.984206
11	Miller et al.	29	6.04						-7.9820
12	Ransil	30							
12a	BLMO*		5.92						-7.96992
12b	SAMO*		6.41						-7.96666
12c	BAMO*		6.48						-7.96598

† units used are Debye

‡ units are kc/sec

§ energy is in atomic units

* SAMO refers to Slater Atomic (MO) calculation, BAMO refers to Best Atomic (MO) calculation, BLMO refers to Best Limited (MO) calculation.

Table XIV. continued

calcn no.	researcher	ref.	$\mu_{eq.}$ †	μ_I †	eqQ(D) ‡	$eqQ_I(Li^7)$ ‡	c_{Li} ‡	c_H ‡	energy[18] §
13	Kolker and Karplus	31, 32							
13a	BLMO*				38.1		-38.6	-17.0	-7.96992
13b	SAMO*				45.3		-37.3	-17.9	-7.96666
13c	BAMO*				46.1		-37.2	-18.0	-7.96598
13d		31, 33			35.5				
14	Kern and Lipscomb	34							-7.96992
14a	calculation I						-6.0	-5.6	
14b	calculation II						-1.7	-18.1	
15a	Stephens and Lipscomb	35					9.51	-9.51	-7.96992
15b		36					9.56	-9.60	-7.96922

† units used are Debye

‡ units are kc/sec

§ energy is in atomic units

* SAMO refers to Slater Atomic (MO) calculation, BAMO refers to Best Atomic (MO) calculation, BLMO refers to Best Limited (MO) calculation.

same molecular constants as before are 6.48 D, 1.31 ev, and -7.96598 au. The BLMO is the 'best limited molecular orbital' calculation. The orbitals are constructed of inner and valence shell Slater type orbitals only. The orbital exponent was optimized with respect to molecular energy. The dipole moment, dissociation energy, and molecular energy are 5.92 D, 1.41 ev, and -7.96992 au. The experimental values are 5.83 D, 2.516 ev, and -8.0703 au. The BLMO calculation makes no great improvement in energy over the SAMO or BAMO but does improve the dipole moment calculation significantly.

B. Calculation 13

The quadrupole moment, Q, is a measure of the departure of the nucleus from being spherical. The quadrupole coupling constant, eqQ, involves the product of two quantities, the nuclear quadrupole moment and the gradient of the electric field at the nucleus. Using three of Ransil's[30] wave functions, Kolker and Karplus[31] calculated the deuteron quadrupole coupling constant eqQ_D/h for LiD. The SAMO gave 45.3 kc/sec, the BAMO gave 46.1 and the BLMO 38.1 kc/sec. They used a quadrupole moment of 2.82×10^{-27} cm^2. Using LiD wave functions, computed by Ransil,[33] at a number of internuclear distances and averaging over molecular vibrations, their latest value was 35.5 kc/sec. They calculated $(eqQ)_v$ for several vibrational states, fitting them to the equation $(eqQ)_v = (eqQ)_{eq} + (eqQ)_I \cdot (v+\frac{1}{2})$ and in this way "averaged over molecular vibrations" to find $(eqQ)_{eq}$. The BLMO is not much improvement in energy calculations but is significantly better for eqQ calculations.

Using the SCF-LCAO-MO functions of Ransil,[30] Kolker and Karplus[32] made a variation-perturbation calculation to obtain values of the nuclear magnetic shielding constants. These are related to the spin-rotation constant. For a nucleus of magnetic moment u_N in an atom or molecule that is acted upon by a uniform magnetic field H, the shielding tensor σ_N is defined by the relation:

$$\Delta E(u_N, H) = -u_N \cdot H + u_N \cdot \sigma_N \cdot H \ . \qquad (12)$$

The electrons interact with the external field creating an additional field $-\sigma_N \cdot H$ at the nucleus. The shielding tensor can be expressed as a sum of a diamagnetic part $\sigma_N{}^d$ and a paramagnetic part $\sigma_N{}^p$. Once a choice of gauge for the field had been made $\sigma_N{}^d$ can be calculated from ground state wave functions. $\sigma_N{}^p$ is more difficult to evaluate; it requires several approximations. $\sigma_N{}^p$ is related to the spin-rotation constant. Using the rigid nuclear framework assumption[17] and the formula:

$$\langle \sigma_N{}^p \rangle = \frac{-e^2}{3mc^2} \left\{ \frac{Z_{N'}}{R} - \frac{h}{4g} \frac{I}{M} c_N \right\} \qquad (13)$$

$Z_{N'}$ = charge of the other nucleus

R = internuclear distance

I = moment of inertia of molecule

M = proton mass

m = electron mass

c_N = spin-rotation constant

g = proton g factor

Values of the spin-rotation constant could be calculated from the paramagnetic part of the shielding tensor. The spin-rotation constants for H using the SAMO, BAMO, and BLMO functions, in that order, were -17.9, -18.0, and -17.0 kc/sec and the constants for Li were -37.3, -37.2, and -38.6 kc/sec. The experimental values are -9.08 and 10.14. The calculations are very far from experiment.

C. Calculation 14

Kern and Lipscomb[34] used Ransil's wave function[30] to calculate spin rotation constants for Li^7 and H in Li^7H. The magnetic field can be described as $\nabla X (\vec{A} + \nabla f(r))$. The choice of Δf or the gauge, is arbitrary. They chose:

$$\nabla f = -\vec{H} + \frac{b\vec{R}}{2} \qquad (14)$$

where R is the vector from nucleus A to nucleus B and b is a dimensionless parameter, H is the external magnetic field. In their first calculation (I), b was chosen using the assumption that average excitation energies cancel. In particular that:

$$\langle \Delta E_1 \rangle_{av} = \langle \Delta E_2 \rangle_{av} \tag{15}$$

$$\langle \Delta E_1 \rangle_{AV} = \frac{\langle 0 | M_{xAu} r_{Au}^{-3} P_{yu} | 0 \rangle}{\sum_{n=1}^{\infty} (En-Eo)^{-1} \langle 0 | M_{xAu} r_{Au}^{-3} | n \rangle \langle n | P_{yu} | 0 \rangle} \tag{16}$$

$$\langle \Delta E_2 \rangle_{AV} = \frac{\langle 0 | M_{xAu} r_{Au}^{-3} M_{xAu} | 0 \rangle}{\sum_{n=1}^{\infty} (En-Eo)^{-1} \langle 0 | M_{xAu} r_{Au}^{-3} | n \rangle \langle n | M_{xAu} | 0 \rangle} \tag{17}$$

where M_{xAu} and P_{yu} are the x and y components of angular and linear momentum respectively of electron u for nucleus A. The zeros are ground state wave functions and n corresponds to the nth excited state. In a second calculation (II), b was chosen such that the origin is at the center of electronic charge. The reported values for the spin-rotation constant for Li^7 for calculations I and II are -6.0 and -1.7 kc/sec; for H the values are -5.6 and -18.1 kc/sec.

D. Calculation 5

Kahalas and Nesbet[23] made several series of calculations on LiH. They made various refinements in the basis set; they varied parameters in some runs to see how the computed values changed. From two of their runs, eqQ_I values were calculated. One of these gives a reasonable agreement with experiment. In their third series of runs, they included three π orbitals, two on Li and one on H. Also utilized were Li orbitals in the 1s shell with different radial parts. There were thirteen orbitals in all. Without configuration interaction, the dipole moment computed was 5.831 D at 3.02 au. The molecular energy is -7.9853664 au eqQ for D in Li^7D is 39.24 kc/sec using $Q_D = +2.738 \times 10^{-27}$ cm^2. q/2e is made up of the sum of nuclear and electronic parts, opposite in sign and nearly equal in magnitude. q/2e at equilibrium is -0.02001720 au. Using these orbitals and allowing configuration interaction, it was found that configurations with a large contribution to the electric field gradient also give a large contribution to the energy. The minimum energy is -8.0171 au at R = 3.0581 au. The experimental value is -8.0703 au. q/2e at equilibrium is -0.02070 a_H^{-3} (a_H is a Bohr orbital equal to 5.29167×10^{-9} cm).

In the fourth series of runs, the orbital exponent of the dσ orbital was varied and the result compared to the second series in which no dσ orbitals were used. There is a 7% change in the q/2e value, a 0.01% change in the minimum energy and a 1% change in the dipole moment. This implies that the agreement of calculated electric field gradient and experiment is a sensitive test for the accuracy of a wave function.

The fifth set of runs included dσ orbitals, 9σ orbitals and two π orbitals. Without configuration interaction eqQ for D in Li^7D is calculated as 35.31 kc/sec and a dipole moment of 5.8875 D at R = 3.02 au. The minimum energy is -7.9859698 au. The q/2e value is -0.01668187 a_H^{-3}. With configuration interaction the minimum energy was -8.0171 au at R = 3.0423 au. q/2e was -0.01660 a_H^{-3}.

Using the experimental values for eqQ/h for Li^7H at v = 0 and v = 1 in the equation:

$$(eqQ)_v = (eqQ)_e + (eqQ)_I \cdot (v+\tfrac{1}{2}) \qquad (18)$$

values of $(eqQ)_e = 354.13$ kc/sec and $(eqQ)_I = -14.75$ kc/sec were obtained. Expanding the molecular quantity about $\xi = (R-R_e)/R_e$ and averaging over vibrational states, using the anharmonic oscillator approximation:

$$(eqQ)_v = (eqQ)_e + \left[-3a_1\frac{B_e}{W_e}\left(\frac{deqQ}{d\xi}\right) + \frac{B_e}{W_e}\left(\frac{d^2eqQ}{d\xi^2}\right)\right]_{\xi=0} \cdot (v+\tfrac{1}{2}) \qquad (19)$$

$(eqQ)_I$ can be equated to the term in brackets and the first term is the same as the previous equation.

From the third set of calculation using $(eqQ)_e$ and the calculated q/2e, the nuclear quadrupole moment for Li^7 is $-3.6410420 \times 10^{-26}$ cm^2. $(eqQ)_I$ is 45.85 kc/sec. From the fifth set of calculations $Q(Li^7) = -4.62772 \times 10^{-26}$ cm^2 and $(eqQ)_I = -18.91$ kc/sec. This last value agrees better with the experimental value of -14.75 kc/sec.

E. Calculation 15

Stevens, Pitzer, and Lipscomp[35] used parts of a σ basis set of eleven orbitals derived by Kahalas and Nesbet[23] or four of Ransil's[30] best σ orbitals and a π basis set of fourteen orbitals to calculate spin-rotation constants. The best values were 9.51 kc/sec for Li and -9.51 kc/sec for H. Stevens and Lipscomb[36] in a later calculation, tested the orbital set for completeness. The energy was optimized at -7.96992 at R = 3.015 au. The spin-rotation constants and molecular magnetic moment were calculated at three distances. The final values were corrected for vibration. For v = 0 the values were $c_{Li} = 9.45$, $c_H = -9.42$ and $u_J/J = -0.6677$. For v = 1 the values were 9.24, -9.07, and -0.6536. The equilibrium values, using the formula: $\langle c\rangle_v = \langle c\rangle_{eq} + \langle c\rangle_I\cdot(v+\frac{1}{2})$, were $c_{Li} = 9.56$ kc/sec, $c_H = -9.60$ kc/sec and $u_J/J = -0.6748$ nm. The values of the first coefficient were -0.21, 0.35, and 0.0141. The experimental equilibrium values are $c_{Li} = 10.14$, $c_H = -9.08$ and $u_J/J = -0.654$.[12] This calculation agrees nicely with experiment.

F. Calculation 7

A value of μ_I can be computed using the anharmonic oscillator approximation and computed values of the first and second dipole moment derivatives. The equation is:

$$\mu_I = -3a_1 \frac{B_e}{W_e} \left(\frac{d\mu}{\partial\xi}\right) + \frac{B_e}{W_e} \left(\frac{\partial^2\mu}{\partial\xi^2}\right) \qquad (20)$$

In paper I, by Karo and Olsen,[25] a valence bond approach using numerical Hartree-Fock Li orbitals and a 1s hydrogen orbital as a basis function was undertaken. The ground state VB description uses a filled 1s Li shell and a covalent bond describing the pairing of the 2sLi and the 1sH. In another calculation an s,p hybrid was used instead of the 2s orbital. The CI(configuration interaction) treatment was superimposed on the Heitler-London type VB approximation. Calculation of energy, binding energy, and dipole moment in the range 2 to 8 au were made. The dissociation energy at the equilibrium distance was 1.669 ev, the dipole moment +6.05 D, and the energy -7.99412 au. From the information presented, the values -1.0 D/Å and 0.86 D/Å^2, were calculated for the first and second dipole derivatives. The computed value of u_I is 0.05902 Debye. Compare this to 0.1085 D, the experimental value. In paper II,[37] a SCF LCAO-MO approach was used. The AO's (the same as in paper I) were used to form MO's. Six configurations were included. At the internuclear distance, the results were the same as in paper I. The VB approach is expected to be more accurate at larger distances, but this could not be confirmed.

G. Calculation 4

Ebbing,[22] used a self-consistent field procedure which included configuration interaction. He used 7σ orbitals and 3π orbitals and as much as 53 configurations. The energy was calculated as -8.04128 au at an internuclear distance of 2.99 au; the dipole was +5.96 D.

H. Calculation 11

Miller, Friedman, Hurst, and Matsen[29] did a valence-bond calculation. They considered twenty configurations. Only six of them were of great importance: $1s^2 2s 1s(H)$, $1s^2 2p 1s(H)$, $1s^2 1s^2(H)$, $1s^2 2s^2$, $1s^2 2p^2$, and $1s^2 2s 2p$. A dipole moment of +6.04 D was calculated; ionization energy was 7.52 ev, and total molecular energy -7.9820 au (experimental energy is -8.0703 au).

I. Calculation 9

Ormand and Matsen[27] used a ten-term wave function in elliptical coordinates. In this coordinate system, the center of coordinates is not on either atom. After variation of the orbital exponent and minimization of the energy, the best calculated energy was -7.9858 au. The dipole moment calculated was +5.574 D.

J. Calculation 8

Platas and Matsen[26] included "hydrogen atom polarization" by including the structure $Li^+(1s^2)H^-(1s2p)$ in configuration interaction.

They used five Slater orbitals and six of the more important configurations in their calculation. The energy calculated was -7.9882 au and dipole was +5.86 Debye.

K. Calculation 3

Matsen and Browne[21] argue that AOC (atomic orbital configuration) methods are in practice more advantageous than SCF-MO (self-consistent field molecular orbital) methods. Even though SCF-MO's lend themselves to perturbation theory easily, AOC give accurate results with the use of modern computational methods. They constructed a twenty-term wave function from twenty-one atomic orbitals. Their results are at equilibrium internuclear distance R = 3.075 au, energy = -8.04379 au, binding energy of 1.793 ev, and dipole moment of 5.57 D.

L. Calculation 2

In a later calculation, Brown and Matsen[20] used mixed orbital sets composed of both Slater-type orbitals and elliptical orbitals. The Slater-type orbitals provide a good representation of the inner shell electrons and the elliptic orbitals provide good electronic distributions for delocalized valence electrons. They used a valence bond configuration interaction method with up to twenty-eight configurations. The orbital exponents for the Slater-type orbitals making up the core, were taken from an eight-term calculation of the Li atom which gave an energy of -7.470 au compared to the experimental value of -7.479 au. The orbital exponents for the elliptical orbitals were determined from a twelve-term calculation of LiH using only a $1s^2$ configuration for the Li core. They calculated an energy of -8.0561 au and a quadrupole coupling constant of 34.2 kc/sec for D in LiD. The dipole moments for the zero, first and second vibrational states were calculated at 5.93 D, 6.00 D, and 6.05 D. Fitting this to the formula:

$$\langle u\rangle_v = \langle u\rangle_{eq} + \langle u_I\rangle\cdot(v+\tfrac{1}{2}) + \langle u\rangle_{II}\cdot(v+\tfrac{1}{2})^2 \qquad (21)$$

The equilibrium value is 5.96 D, and the first and second coefficients are 0.09 and -0.04. The experimental equilibrium dipole moment is 5.83 D and u_I is 0.11 D.

M. Calculation 6

Recognizing that the neglect or incomplete allowance for electronic correlation is an important source of error in calculations, Robinson, Stuart, and Matsen[24] used different orbitals for different electrons in valence-bond wave functions. The three most important configurations are (1s,1s',2s;h), (1s,1s',2p;h), and (1s",1s"';h",h"'); primes indicate different orbital exponents. The lowest energy was -8.0074 au. The dipole moment associated with this energy is 6.18 D.

N. Calculation 10

Using gaussian-type functions, Csizmadia[28] calculated energy and dipole moment at various values of internuclear distance. The equilibrium internuclear distance was 3.02 au. Using a six-term gaussian the energy, u_{eq} and u_I values, are -7.975811 au, 5.9179 D, and 0.043. With an eleven-term function the values are -7.969016 au, 6.0929 D, and 0.056. With a sixteen-term function the energy, equilibrium dipole moment, and first dipole moment coefficient are -7.970022, 6.0139 D, and 0.057. With twenty-one terms the values are -7.985366 au, 6.0079, and 0.122.

O. Calculation 1

Bender and Davidson[19] devised an iterative procedure for simultaneous calculation of natural orbitals and energy. With this procedure they have calculated a wave function that gives the lowest energy yet calculated. Löwdin[38] introduced the concept of natural spin orbitals and equations for computing them. These orbitals, which diagonalize the first order density matrix, form an orthonormal set. The occupation number of each orbital gives a direct measure of its importance in the wave function. With forty-five configurations the energy calculated at $R = 3.0147$ au is -8.0606 au. The equilibrium dipole moment is 5.9650 D and $eqQ_d = 30.5$ kc/sec ($q_D = 0.0460$ au).

VI. POLARIZABLE ION MODEL FOR LITHIUM HYDRIDE

Bonding in the alkali halide molecules is generally assumed to be strongly ionic and this has been the basis of several attempts[39,40,41] to propose a simple ionic model of the alkali halides. Since the electron affinity of hydride ion is only 0.715 ev as compared to over 3 ev for the halide ions one would expect a completely ionic description of LiH to be somewhat less satisfactory than for the lithium halides. Nonetheless, the large dipole moment of LiH (5.83 D) indicates substantial ionic character and the ionic model should give at least an approximate description of the molecule. Rittner[42] used such an ionic model, consisting of polarizable ions, to predict and correlate the dipole moments and dissociation energies of the alkali halides. He assumed that the alkali halide molecule is composed of two ions, each of which is polarized by the electrostatic field of the other. Using the same approach as Debye,[39] who first treated the polarizable ion problem, the total molecular dipole moment can be expressed as:

$$u = er - (u_1 + u_2) \quad . \tag{22}$$

Here +e and -e are the charges on the ions; u_1 and u_2 are the induced dipole moments, and r is the internuclear separation. Designating the electrostatic field at the center of each ion as E_1 and E_2 and the dipole polarizabilities as α_1 and α_2, the induced moments can be written as:

$$u_1 = \alpha_1 E_1 = \alpha_1 \left(\frac{e}{r^2} + \frac{2\mu_2}{r^3} \right) \tag{23}$$

$$u_2 = \alpha_2 E_2 = \alpha_2 \left(\frac{e}{r^2} + \frac{2u_1}{r^3} \right) \tag{24}$$

Solving these equations simultaneously and substituting into Eq. (22), we obtain:

$$u = er - \left(\frac{r^4 e(\alpha_1 + \alpha_2) + 4re\alpha_1\alpha_2}{r^6 - 4\alpha_1\alpha_2} \right) \tag{25}$$

Using the crystal lattice theory of Born,[40,41] Rittner expressed the potential energy as:

$$W = \Phi + Ae^{-r/p} \tag{25a}$$

The Φ term arises from electrostatic interactions between the ions: charge-charge, charge-dipole, and dipole-dipole interactions. This is written as

$$\Phi = \frac{-e^2}{r} - \frac{e^2(\alpha_1+\alpha_2)}{2r^4} - \frac{2e^2\alpha_1\alpha_2}{r^7} \qquad (26)$$

The remaining term of the potential energy is the exponential repulsion term, $Ae^{-r/p}$.

The repulsion constants, A and p, are determined by use of the relationships:

$$\left(\frac{dW}{dr}\right)_{r=r_e} = 0 \qquad (27)$$

$$\left(\frac{d^2W}{dr^2}\right)_{r=r_e} = K \qquad (28)$$

The force constant, k, is related to the vibrational frequency, ν_o, by the relationship:

$$\nu_o = \frac{1}{2\pi}\sqrt{K/\mu_A} \qquad (29)$$

where $\frac{\nu_o}{c} = w_e$ (the vibrational constant) and u_A is the reduced mass. Thus the experimental values of the equilibrium internuclear distance, r_e, and the vibrational constant, w_e, are input data for this version of the ionic model.

Honig et al.[43] extended Rittner's model to predict the Dunham coefficient a_1.[44] The potential energy W(r) can be expanded about r_e and written as:

$$W(r-r_e) = W(r_e)+(r-r_e)\overset{0}{\cancel{W'}}(r_e)+\frac{(r-r_e)^2}{2!}W''(r_e)+\frac{(r-r_e)^3W'''(r_e)+}{3!} \qquad (30)$$

or written in the usual Dunham form as:

$$W = W_e + a_o\xi^2 + a_oa_1\xi^3 + \ldots \tag{31}$$

where $\xi = \frac{r-r_e}{r_e}$ and $a_o = Kr_e^2/2$ and the second Dunham coefficient is defined as:

$$a_1 = \frac{r_e^3 W'''(r_e)}{3!a_o} \tag{32}$$

The coefficient a_1 can therefore be calculated knowing the form of the potential energy curve and compared to the experimental value:

$$a_1 = -\frac{\alpha_e w_e}{6B_e^2} - 1 \tag{33}$$

As additional input data for the ionic model, one needs reasonable estimates of the effective polarizabilities of the positive and negative ions. The values of the polarizabilities that are usually extracted from experimental data or calculated are large distance, low-field, polarizabilities; that is they are the polarizabilities when the perturbing charge is entirely outside the electron distribution of the ion.

A commonly used set of polarizabilities is that of Pauling.[45] Klemperer et al.[46,47,48] examined the model for the alkali halides and found that the experimental dipole moments did not agree with the predictions— the calculated values being too small in all cases. They argued that the polarizabilities should exhibit a saturation effect in diatomic molecules and decrease with field strength. They forced the dipole moments to agree with experimental values by decreasing the halide polarizabilities and then calculated the values of the dissociation energy, W_e, and the Dunham coefficient, a_1.

Cohen,[49] however, has shown that the polarizabilities do not necessarily decrease with increasing field strength, as Klemperer has argued. Therefore Klemperer's explanation for the apparent decrease in polarizabilities might not be correct.

Recently Burns[50] has calculated the dipole, quadrupole, octupole, and hexadecapole polarizabilities of F^- and Cl^- in order to determine the antishielding factors for an interpretation of the quadrupole coupling constants in the alkali halides. The polarizabilities were calculated for the alkali halide internuclear distances and were often much smaller than those for the free ion. These polarizabilities also exhibited a variation with internuclear separation, that is they increased with increasing r. These results seem consistent since it would be expected that the polarizability should decrease with charge penetration. At alkali halide internuclear distances the positive alkali core penetrates the electron density of the large halide ion, but the electron density is penetrated only for a few of the alkali ions, and thus this penetration effect is primarily important in the case of the halide polarizabilities. This effect should be much more extreme in the case of the large diffuse H^- ion.

It seems reasonable to expect the polarizabilities to fit an S-shaped curve varying from zero at $r = 0$ to the free ion value at some finite r value, R. This R value, approximates the limit of the electron distribution contributing to the polarizability.

In choosing values for the effective polarizabilities in the ionic model of LiH, the Li^+ ion presents no serious difficulty. The ion is small and penetration of its electron distribution is unimportant at the equilibrium internuclear distance. In addition the polarizability is small and accurate values are available. Some of the reported values are given in Table XV. Of these the most accurate are undoubtebly the 0.0283 of Edlén,[51] obtained from an analysis of spectroscopic data; and the 0.0286 of Baber and Hassé,[61] which they calculated using a wave function of the Hylleraas type. A brief summary of the methods used in calculating polarizabilities is given in the Appendix.

The situation for H^- is much less satisfactory; here, as mentioned above, penetration of its electron distribution by the small Li^+ ion should have a large effect on its effective polarizability. A number of values for the infinite distance polarizability of H^- ion are available in the literature. Some of these are given in Table XV. Of these the 31.4 of Schwartz[52] should be by far the most accurate. He used an 18-parameter wave function of the Hylleraas type.

That a large reduction in the effective polarizability of H^- is necessary for even an approximate description of LiH by the ionic model can be seen by calculating the dipole moment using Eq.(25). Using internuclear distance $r = 1.59443$ Å, 31.4×10^{-24} cm^3 as the dipole polarizability of the hydride ion,[52] and 0.028×10^{-24} cm^3 as the polarizability[53] of Li^+, the dipole moment calculated is -69.5 Debye. The lithium end of the molecule is negative! Even using the smallest H^- polarizability in Table XV helps only slightly— the sign is still wrong.

Unfortunately no calculations are available for the effect of penetration on the polarizability of H^- ion, and there are only a few calculations for other ions. Callaway[54] has calculated a polarization potential for some of the alkali ions, by perturbation theory, which vanishes at the origin. Allowing r_1 and r_2 to denote the core electronic coordinates and r_v to represent the valence electron, the polarization potential $V_p(r_v)$, is given by:

$$V_p(r_v) = \left(\frac{2}{r_v^{\,2}}\right)\sum_i \int_o^{r_v} u_i^{(o)}(r_1)r_1\cos\theta \; u_i^{(1)}(r_1,r_v)dr_1 \qquad (34)$$

He used numerical values of the perturbed wave functions, which were computed by Sternheimer. Self-consistent wave functions were used for the unperturbed core functions. These were computed by Löwdin[65] for Na and Li; by Hartree and Hartree[66] for K. Multiplying his potential by r^4, where r is the distance from the core, if one neglects quadrupolarizability and higher order terms, equating this to dipole polarizability one obtains numerical values for polarizability versus distance. These are plotted for K^+, Na^+, and Li^+ in Figs. 18 through 20. The infinite distance polarizabilities obtained from these plots, agree reasonably well with values obtained by Sternheimer; these are summarized in Table XV. A distance corresponding to the "ionic radius" (Pauling[67]) is indicated on the figures. All the polarizabilities are characterized by a very

Table XV. Dipole polarizabilities

ion	Callaway	other methods	ref.	
H$^-$	18.2 Å^3	13.8	49	Cohen, coupled HF
		31.4	52	Schwartz, exact calculation
		16.7	55	Yoshime and Hurst
		13.4	56	Wikner and Das
		14.9	57	Sternheimer
		10.0	45	Pauling
		38.7	51	Edlén
		17.33	51	Edlén
		7.56	58	Schwartz
		30.2	59	Geltman
Li$^+$	0.030 Å^3	0.0307	57	Sternheimer
		0.0305	56	Wikner and Das
		0.024	60	Mayer and Mayer
		0.0304	55	Yoshime and Hurst
		0.0286	61	Baber and Hassé
		0.0283	51	Edlén
		0.027	58	Schwartz
		0.0280	49	Cohen, coupled HF
		0.0304	62	Dalgarno and McNamee, uncoupled HF
		0.0281	62	Dalgarno and McNamee, coupled HF
Na$^+$	0.148 Å^3	0.148	51	Edlén
		0.140	49	Cohen, coupled HF
		0.152	63	Sternheimer
K$^+$	1.274 Å^3	1.26	64	Sternheimer
		0.811	51	Edlén

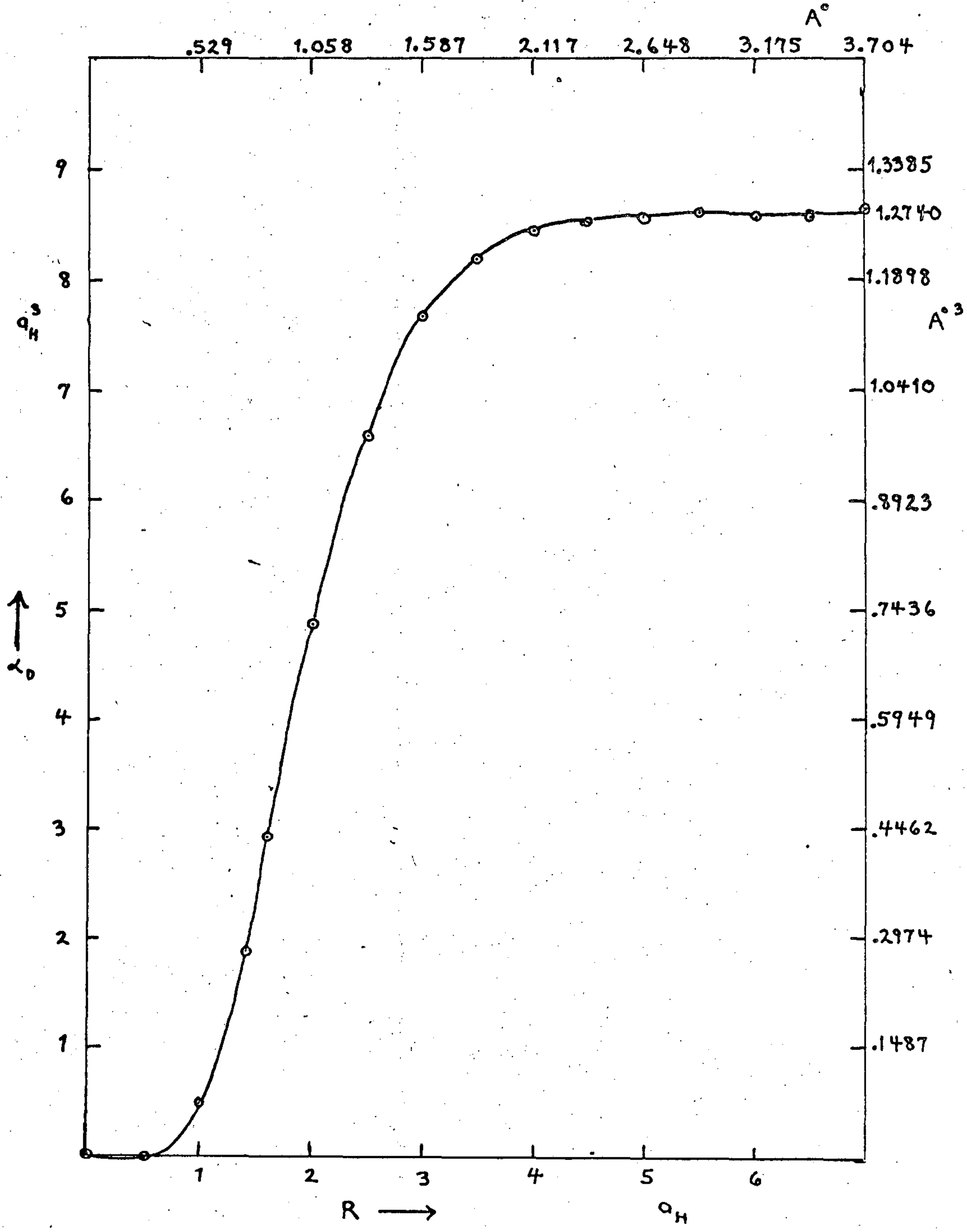


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Fig. 18. Variation of K^+ polarizability with distance (Callaway).

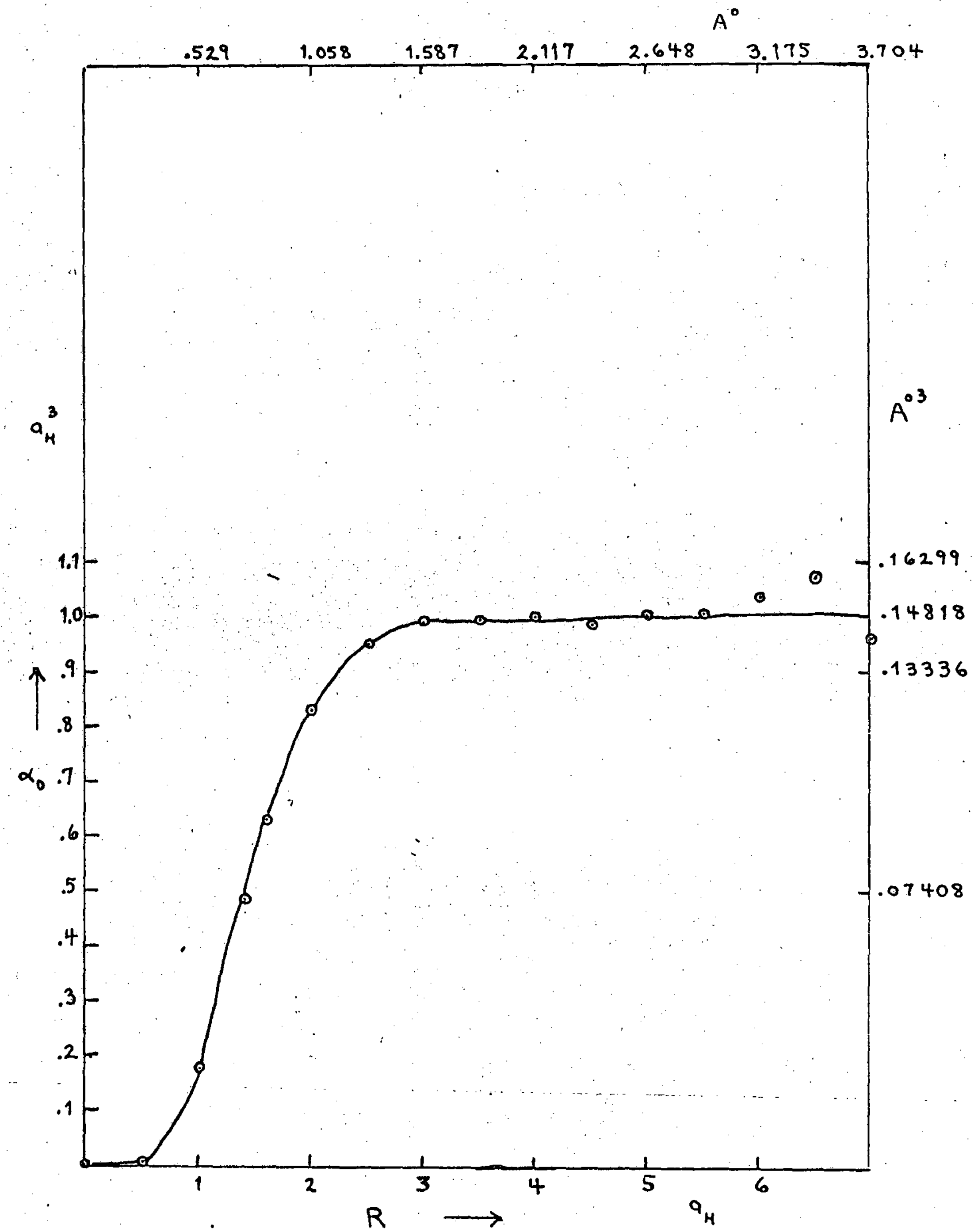

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Fig. 19. Variation of Na^+ polarizability with distance (Callaway).

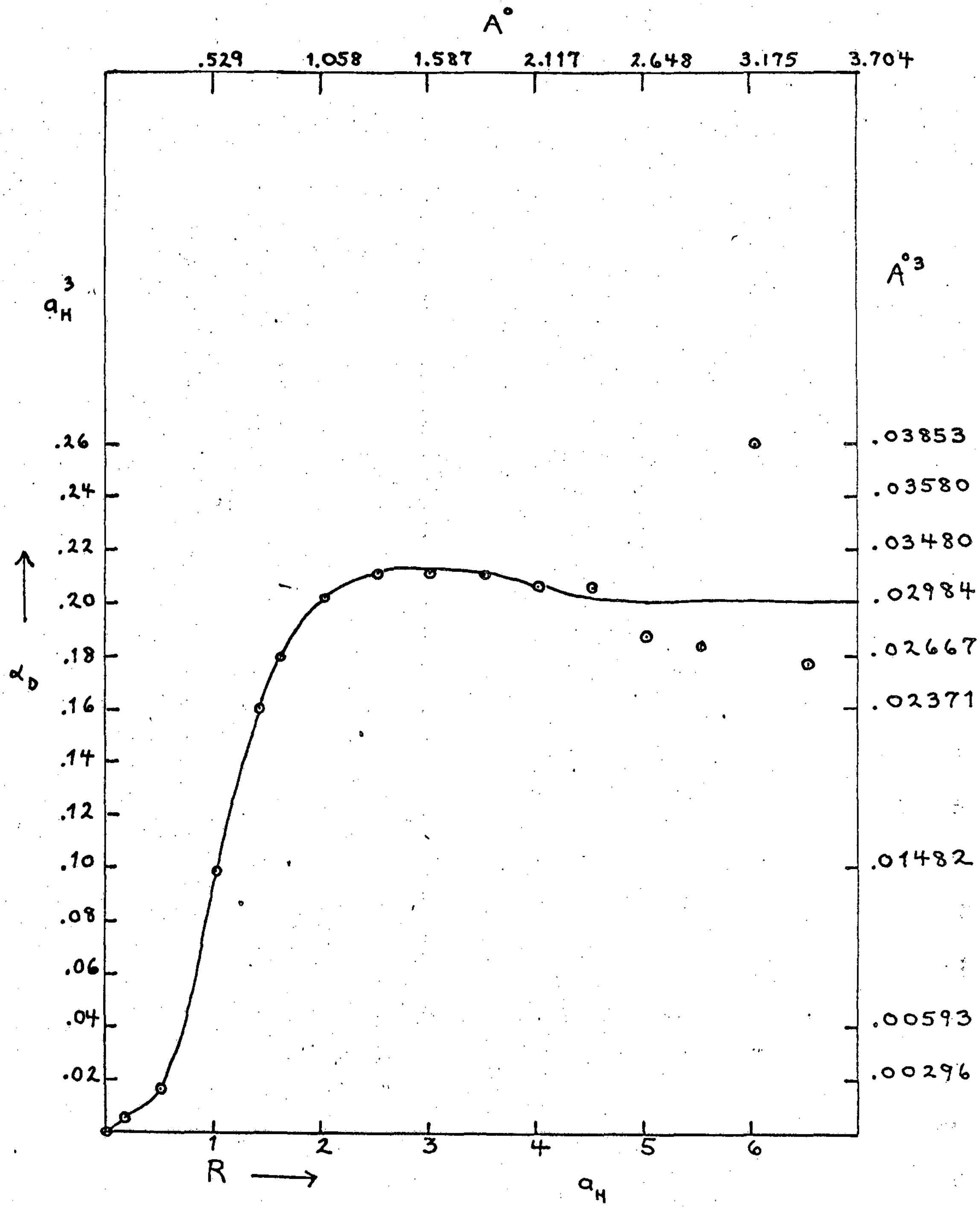

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Fig. 20. Variation of Li^+ polarizability with distance (Callaway).

rapid decrease at about the ionic radius.

The dipole polarizabilities of F^- and Cl^- calculated by Burns[50] are shown in Fig. 21. He used the variation of parameters method to calculate the polarizabilities for the F^- and Cl^- ions at several values of r and assumed a cancellation of the $p \rightarrow s$ and $s \rightarrow p$ contributions to the dipole calculation. Sternheimer[68] has shown that these terms do not cancel in the case of the halides. However these contributions are reasonably small and Burn's calculations should give at least a qualitative description of the variation of polarizability with distance. It is evident from Fig. 21 that the decrease in polarizability as one approaches a distance corresponding to the "ionic radius" is even more extreme for the larger, more loosely bound halides than for the alkali ions.

Thus it is probably reasonable to expect an even larger effect for the very large and loosely bound H^- ion. It is difficult to give a definite meaning to "ionic radius" for H^-, nonetheless, Pauling[67] gives a value of 2.08 Å, obtained by extrapolation from other ions. At the equilibrium internuclear distance in LiH, 1.59 Å, the Li^+ ion is "inside" the "ionic radius". Thus one is led to expect a very small effective polarizability for H^- in the LiH molecule.

Since there are no quantitative calculations of the effect of penetration on the polarizability of H^- we will adopt the procedure of Rice and Klemperer and force the effective polarizability of H^- to fit the measured dipole moment of LiH. Using $u_e = 5.828$ D, $r_e = 1.596$ Å, $\alpha_1 = 0.028$ Å^3 in Eq. 25, we find $\alpha_2 = 0.914$ Å^3 —a very small but perhaps not unreasonable value in view of the preceding arguments. Using these values (and $w_e = 1405.65$ cm^{-1}) we can calculate the dissociation energy (to the ions), W, from Eq. 25a; the second Dunham coefficient, a_1, from Eq. 32; and the change of the dipole moment with vibrational state, u_I, from Eq. 25, and Eq. 20 on page 45. Table XVI compares the results of this calculation with experiment. Also shown are the results of a similar calculation for LiF. LiF is the alkali halide expected to most closely resemble LiH and is generally considered an ionic molecule.

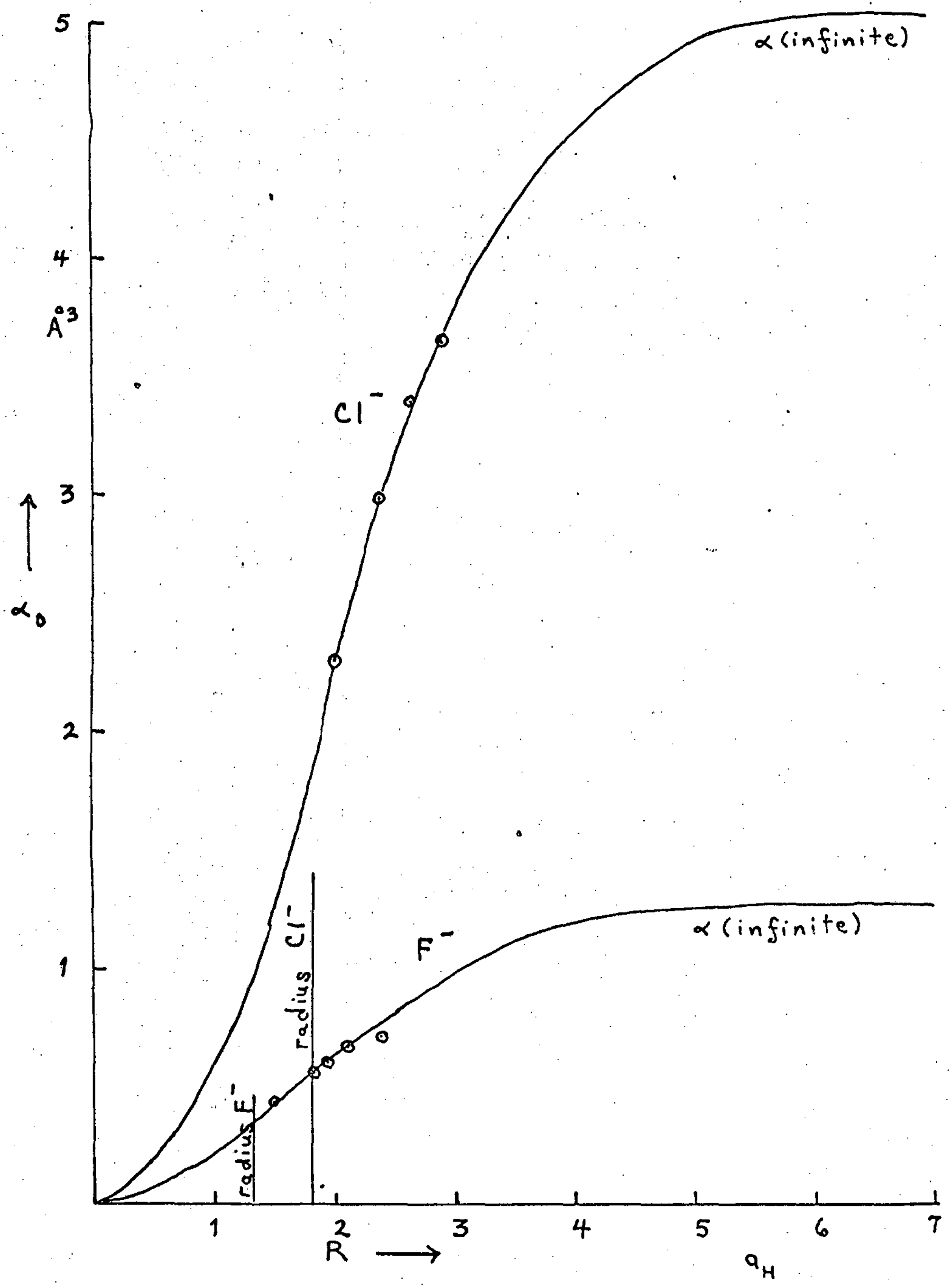

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Fig. 21. Variation of F⁻ and Cl⁻ polarizability with distance (Burns).

As can be seen from Table XVI (and not unexpectedly) the simple ionic model gives a somewhat poorer description of LiH than of LiF. The calculated quantities deviate from experiment in the same direction for both molecules but the deviations are considerably larger for LiH.

Table XVI. Simple ionic model

		calculated	experiment	ref.
LiH				
	W	7.00 ev	7.17 ev	
	a_1	-1.02 ev	-1.88 ev	
	u_I	0.122 D	0.109 D	
LiF				
	W	7.88 ev	7.93 ev	69
	a_1	-2.39 ev	-2.70 ev	
	u_I	0.094 D	0.082 D	

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APPENDIX

In calculating polarizabilities quantum mechanically, there are several ways to proceed. Variational calculations, perturbation techniques, Sternheimer's method, coupled and uncoupled Hartree-Fock methods, oscillator strength formulas, or Thomas-Fermi model calculations.

If an external charge Z' is located at $\vec{r}\,'$ and r' is large, the interaction potential can be written as:

$$V(\vec{r},\vec{r}\,') = -Z'\sum_{i=1}^{N}\sum_{K=1}^{\infty} \frac{r_i^{\,K}}{r'^{\,K+1}} P_K(\cos\theta_i)$$

$$V(\vec{r},\vec{r}\,') = Z'\sum_{K=1}^{\infty} \frac{V_{K(\vec{r})}}{r'^{\,K+1}}$$

The perturbed wave function $\psi_K(\vec{r})$ can be expanded as:

$$\psi_K(\vec{r}) = \psi_o(\vec{r}) + Z'\psi_1^{(K)}(\vec{r}) + Z'^2\psi_2^{(K)}(\vec{r}) + \ldots.$$

$$E_K = E_o + Z'E_1^{(K)} + Z'^2E_2^{(K)} + \ldots.$$

The wave equation of the perturbed system: $(H + Z'V_K - E_K)\psi_K = 0$ can be replaced by the sequence: $(H-E_o)\psi_o = 0$,
$(H-E_o)\psi_1^{(K)}+(V_K-E_1^{(K)})\psi_o = 0$, etc.
This may be solved formally by the approximation:

$$\psi_1^{(K)}(\vec{r}) = \sum_t{}' \, a_t^{(K)}\psi_t(\vec{r})$$

where $\psi_t(\vec{r})$ is the eigenfunction of the tth excited state of the unperturbed system, satisfying the equation:

$$(H-E_t)\psi_t(\vec{r}) = 0$$

The general formula for the polarizability is:

$$\alpha_{2L} = 2\sum_t{}' \frac{|(\psi_t^*, V_L\psi\partial|^2}{E_t-E_o}$$

where the prime means to exclude t = 0 in the sum.

This formula can be used to derive values of dipole polarizabilities for atoms for which oscillator strengths are known. The electric dipole oscillator strengths corresponding to the transition from state ψ_o to state ψ_t is defined by:

$$f_{ot} = \frac{2}{3}(E_t-E_o)|(\psi_t^*, \sum_{i=1}^{N} r_i\psi_o)|^2$$

Substituting this into the preceding equation, the polarizability formula is:

$$\alpha_{ot} = \sum_t{}' f_{ot}/(E_t-E_o)^2$$

Geltman[59] arrived at the value 30.2 Å^3 for the H$^-$ polarizability using this method. Donath[70] essentially used the oscillator strength formula. The wave functions of some of the discrete states were derived from variational methods and used in some parts of the sum.

α_d is sensitive to the adopted representation of the unperturbed wave function. Baber and Hasse[61] chose $\psi_1^{(1)}$ for Li$^+$ as

$$\psi_1^{(1)}(r_1,r_2) = \{(ar_1+br_1^2+cr_1^3)\cos\theta_1+(ar_2+br_2^2+cr_2^3)\cos\theta_2\}\,\psi_o$$

For ψ_o they used a six-parameter wave function and found 0.02862 Å^3 for the polarizability.

In the Hartree approximation the unperturbed function is written in the form:

$$\psi_o(\vec{r}) = \prod_{i=1}^{N} u_i^{(o)}(\vec{r}_i)$$

The first order perturbed wave function is defined by:

$$\psi_1(\vec{r}) = \sum_{i=1}^{N} \frac{u_i^{(1)}(r_i)}{u_i^{(o)}(r_i)} \psi_o(\vec{r})$$

The polarizability is given by the following formulas:

$$\overline{V_L(r_i)} = r_i^L P_L(\cos\theta_i) - (u_i^{(o)}, r_i^L P_L(\cos\theta_i)\, u_i^{(o)})$$

$$\alpha_{2L} = \sum_{n\ell} \alpha_{2L}(n,\ell)$$

$$\alpha_{2L}(n,\ell) = -2 \sum_{\substack{n'\ell' \\ \neq n\ell}} \frac{|u(n',\ell'), \overline{V}_L u(n,\ell)|^2}{\epsilon^{(o)}(n'\ell') - \epsilon^{(o)}(n\ell)}$$

The $(n\ell)$ summation is over the occupied orbitals and $(n'\ell')$ is over all possible orbitals and includes an integration over the continuum. In the Sternheimer procedure, in summing over all shells there occurs a near cancellation of contributions from transitions between occupied orbitals. The cancellation is not complete because $v_i(r_i)$ differ for different electron shells and $u(n\ell)$ are not members of the same complete set. Upward transitions from the outermost shells provide the major contribution to the polarizability. For Na$^+$, Sternheimer[63] finds

$\alpha_d(2s\text{-}p) = 0.117$ and $\alpha_d(2p\text{-}s) = -0.098$. The largest contribution to α_d is $\alpha_d(2p\text{-}d) = 0.133$. The net polarizability is 0.152 Å^3.

In the evaluation of the self-consistent interaction potential $V_i(r_i)$, Sternheimer solves an equation numerically. This numerical integration is one of the chief characteristics of the Sternheimer procedure.

Instead of a perturbation approach, a variational approach using a trial function such as:

$$u_i^{(1)}(r_i) = \lambda \overline{v_1(r_i)} u_i^{(o)}(r_i)$$

or a more flexible trial function such as

$$u_i^{(1)}(r_i) = (a + br_i + cr_i^2)V_1(r_i)u_i^{(o)}(r_i)$$

which was used by Wikner and Das[56] can be used.

Sternheimer modified the uncoupled Hartree approximation by using Hartree-Fock orbitals. Parkinson[71] used anti-symmetrized combinations of product type

$$\prod_{i=1}^{N} u_i^{(o)}(r_i)$$

solutions. In the uncoupled Hartree-Fock approximation, unphysical transitions between occupied orbitals, such as occur in the Sternheimer procedure, are removed. The unperturbed wave function is written as an antisymmetrized product of one electron orbitals.

$$\psi_o(\vec{r}) = \mathcal{A} \prod_{i=1}^{N} u_i^{(o)}(r_i)$$

The first order perturbed wave function is:

$$\psi_1(\vec{r}) = \sum_{i=1}^{N} \mathcal{A} \prod_{i \neq j} u_i^{(o)}(r_i)\, u_j^{(1)}(r_j)$$

The polarizability is given by the formula:

$$\alpha_{2L} = -2 \sum_{i} \left\{ (u_i^{(o)}, \bar{V}_L u_i^{(1)}) - \sum_{\substack{k \\ \text{parallel spins}}} (u_K^{(o)} \bar{V}_L u_i^{(o)})(u_i^{(1)}, u_K^{(o)}) \right\}$$

Alternately a variational method can be used with the trial function

$$u_i^{(1)}(r_i) = \lambda\, \overline{V_1(r_i)}\, u_i^{(o)}(r_i)$$

which yields the formula:

$$\alpha_d = \frac{4}{9} \sum_{i=1}^{N} \frac{\left\{ (u_i^{(o)}, r_i^2 u_i^{(o)}) - \sum_{j \neq i} |(u_i^{(o)}, r_i u_j^{(o)})|^2 \right\}^2}{D_i}$$

$$D_i = N + \frac{2}{3} \sum_{i} \sum_{j} \iint_{//\,\text{spins}} u_i^{(o)}(r_i)\, u_K^{(o)}(r_i)\, u_i^{(o)}(r_K)\, u_K^{(o)}(r_K) \frac{\left[r_i^2 - \vec{r}_i \cdot \vec{r}_K \right]}{|r_i - r_K|}\, dr_i\, dr_K$$

The values obtained using the uncoupled approximation are much smaller, generally, than those from the Sternheimer procedure. The fully coupled approximation usually gives lower bounds for polarizabilities.[62] The values from the Sternheimer, uncoupled Hartree-Fock and coupled Hartree-Fock for Li^+ are 0.0307, 0.0304, and 0.0281, as an example. The previous formulas for polarizabilities from the uncoupled perturbation method remain valid in the fully coupled Hartree-Fock approximation. The wave function is written differently, as:

$$\psi(\vec{r}) = \mathcal{A} \prod_{i=1}^{N} \left\{ u_i^{(o)}(r_i) + u_i^{(1)}(r_i) + \ldots. \right\}$$

The perturbed orbitals are coupled both by direct and exchange interactions in the Hamiltonian. The polarizabilities derived in this way are more exact; they are correct to first order. For polarizabilities derived from the uncoupled approximation there is a non-vanishing first order correction.

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