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Theoretical Determination Of The Spectroscopic Constants Of The H_2 Ground State

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THEORETICAL DETERMINATION OF THE
SPECTROSCOPIC CONSTANTS OF THE H_2 GROUND STATE

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THESIS

Submitted in Partial Fulfillment of the
Requirements for the Degree of
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Albuquerque, New Mexico
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ABSTRACT OF THESIS

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ABSTRACT

Recently the H_2 ground state potential E was calculated in double precision by Kolos and Wolniewicz (KW) using a 100-term wave function. For this KW potential the coefficients in a power series expansion about the potential minimum R_E are here determined by using the pure electronic potential and central differences. Resulting Dunham potential coefficients a_0, a_1, a_2, a_3, a_4, a_5, and a_6 are 79703 cm^{-1}, -1.6031, 1.865, -1.999, 2.048, -2.02 and 2.0, respectively. From these coefficients the spectroscopic constants are found to be $Y_{00} = 8.36$, $Y_{10} = 4406.6$, $Y_{20} = -122.6$, $Y_{30} = 1.2$, $Y_{40} = -0.04$, $Y_{01} = 60.838$, $Y_{11} = -3.041$, $Y_{21} = 0.044$, $Y_{31} = -0.003$, $Y_{02} = -0.04653$, $Y_{12} = 0.001591$, $Y_{22} = -0.00005$, $Y_{03} = 4.965 \times 10^{-5}$, $Y_{13} = -7.7 \times 10^{-7}$ and $Y_{04} = -6.76 \times 10^{-8}$, all in cm^{-1}, for the ground state of H_2.

A detailed examination of the KW potential energy is made. The fluctuation in differences indicates a random computer error ϵ of about 1×10^{-7} a.u. in the KW 100-term energies (which are listed with one additional digit). Moreover, KW values of dE/dR in the range $1.401075 < R < 1.401080$ a.u. lead to a value of a_0 distinct from the value listed above and from a previously determined value. The discrepancy is attributed to inaccuracy in the virial theorem calculation of dE/dR.

Theoretical rotational constants B_v, D_v and H_v are here determined by using rotation-vibration eigenenergies determined by Kolos and Wolniewicz and are compared with the experimental constants. The present computation of B_v, D_v indicates good agreement between theory and experiment. However, it is found that there is a large systematic discrepancy of about 1×10^{-5} cm^{-1} between the theoretical and experimental H_v's. This discrepancy is believed to be due to the experimental analysis in which the I_v values are ignored.

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CHAPTER I

INTRODUCTION

Recently, the potential energy curve for the electronic ground state of the hydrogen molecule was recalculated for $1 \leq R \leq 3.2$ a.u. * in double precision by Kolos and Wolniewicz (KW) using a 100-term expansion for the electronic wave function (Ref 7). This is the most accurate variational treatment of H_2 to date. It is desirable, therefore, to determine the spectroscopic constants associated with this new KW vibrational potential.

A number of theoretical determinations of the spectroscopic constants of the hydrogen molecule have been carried out (Ref 1). These did not make use of the pure electronic potential, the total potential energy minus the repulsive potential between two nuclei. In this thesis a determination making use of the pure electronic energy is reported. Prior to performing the evaluation of the Dunham constants (Ref 4), a detailed examination of the accurcy of the KW potential energy with 54 term, 80 term and 100 term wave functions was made.

* R is the distance between two nuclei. One a.u. of distance $= 5.2917 \times 10^{-9}$ cm

THE POTENTIAL CONSTANTS B_V, D_V AND H_V WERE ALSO DETERMINED AND COMPARED WITH THE EXPERIMENTAL DATA. THIS WAS DONE USING ROTATION-VIBRATION EIGENENERGIES DETERMINED BY KOLOS AND WOLNIEWICZ (REF 7).

CHAPTER II

BACKGROUND

(A.) Born-Oppenheimer Approximation

Let the positions of the nuclei be given by coordinates Z_I. Let the positions of the electrons be given similarly by coordinate X_J. Let the total potential energy of the whole system, consisting of the coulomb-electrostatic interactions between all pairs of charges, nuclei and electrons, be $V(Z_I, X_J)$. Then the Schrodinger equation for the system as a whole is

$$\left[-\sum_i \frac{\hbar^2}{2M_i} \nabla_i^2 - \sum_j \frac{\hbar^2}{2m} \nabla_j^2 + V(Z_i, X_j) \right] \Psi(Z_i, X_j) = W \Psi(Z_i, X_j) \qquad (1)$$

Here $\hbar$ is the Planck constant divided by 2π, ∇_i^2 represents the Laplacian with respect to coordinates of nucleus I, whose mass is M_I and ∇_j^2 is the Laplacian with respect to electron J, with mass M. The exact solution of this equation is very difficult for even the simplest molecule.

In general, the Born-Oppenheimer approximation (Ref 3) is applied to solve the above Schrodinger equation. The first step is to solve a Schrodinger equation which is identical with Eq(1) except that the terms in ∇_i^2, the kinetic energy of the nuclei, are omitted. That is, if we solve for the motion of the electron in the potential energy involving coulomb attractions and repulsions between all particles of the system while holding the nuclear positions fixed. We then have the Schrodinger equation

$$\left[-\sum_j \frac{\hbar^2}{2m}\nabla_j^2 + V(Z_i,X_j)\right] u(Z_i,X_j) = E(Z_i)\,u(Z_i,X_j) \qquad (2)$$

Next, according to the Born-Oppenheimer method, we use $E(Z_I)$ as a potential energy function to discuss the nuclear motion. That is we set up a Schrodinger equation of the form

$$\left[-\sum_i \frac{\hbar^2}{2M_i}\nabla_i^2 + E(Z_i)\right] v(Z_i) = W\,v(Z_i) \qquad (3)$$

When we have solved these two Schrodinger problems, one for the electronic motion and one for the nuclei, then the Born-Oppenheimer theorem states that the energy W of equation (3) forms a good approximation to the energy level of the exact Schrodinger equation (1). In the case of the diatomic molecule, the energy level of the electrons rotating about the nuclei will depend on the distance R between the nuclei, but not on the orientation of the molecule in space. Consequently, the energy $E(Z_I)$ becomes $E(R)$ and $u(Z_I, X_J)$ becomes $u(R, X_J)$.

(B) Dunham Formulas

The energy W of equation (3) for a diatomic molecule is calculated by Dunham using of the W.B.K. method (Ref 4) with the vibrational potential E(R) expanded in a power series

$$E = A_0 \xi^2(1 + A_1 \xi + A_2 \xi^2 + A_3 \xi^3 + A_4 \xi^4 + \ldots) \qquad (4)$$

Here $\xi = (R-R_E)/R_E$, R_E being the equilibrium nuclear separation, A_i are the Dunham constants. This method is valid only in the neighborhood of R_E.

The resulting energy W is expressed as a doubly infinite power series in the quantum numbers v and J in the form

$$F_{VK} = \frac{W}{HC}$$

$$= \sum_{l,j} Y_{l,j} \left(v + \frac{1}{2}\right)^l J^j (J + 1)^j \qquad (5)$$

$$J = 0, 1, 2, \ldots \qquad v = 0, 1, 2, \ldots$$

Here v is the vibrational quantum number, J the rotational quantum number and $Y_{l,j}$ are called spectroscopic constants. The first fifteen $Y_{l,j}$'s are found to be

$$Y_{00} = \frac{B_E}{8}\left(3A_2 - \frac{7}{4}A_1^{\ 2}\right)$$

$$Y_{10} = \omega_E\left(1 + \frac{B_E^{\ 2}}{4\omega_E^2}\left(25A_4 - \frac{95}{2}A_1 A_3 - \frac{67}{4}A_2^{\ 2} + \frac{459}{8}A_1^{\ 2} A_2 - \frac{1155}{64}A_1^{\ 4}\right)\right)$$

$$Y_{20} = \frac{B_E}{2}\left(3\left(A_2 - \frac{5}{4}A_1^{\ 2}\right) + \frac{B_E^{\ 2}}{2\omega_E^2}\left(245A_6 - \frac{1365}{2}A_1 A_5 - \frac{885}{2}A_2 A_4\right.\right.$$
$$- \frac{1035}{4}A_3^{\ 2} + \frac{8535}{8}A_1^{\ 2}A_4 + \frac{1707}{8}A_2^{\ 3} + \frac{7335}{4}A_1 A_2 A_3$$
$$\left.\left. - \frac{23865}{16}A_1^{\ 3}A_3 - \frac{62013}{32}A_1^{\ 2}A_2^{\ 2} + \frac{239985}{128}A_1^{\ 4}A_2 - \frac{209055}{512}A_1^{\ 6}\right)\right)$$

$$Y_{30} = \frac{B_E^2}{2\omega_E}\left(10A_4 - 35A_1A_3 - \frac{17}{2}A_2^2 + \frac{225}{4}A_1^2A_2 - \frac{705}{32}A_1^4\right)$$

$$\begin{aligned} Y_{40} = \frac{5B_E^3}{\omega_E^2}\Big(&\frac{7}{2}A_6 - \frac{63}{4}A_1A_5 - \frac{33}{4}A_2A_4 - \frac{63}{8}A_3^2 + \frac{543}{16}A_1^2A_4 \\ &+ \frac{75}{16}A_2^3 + \frac{483}{8}A_1A_2A_3 - \frac{1953}{32}A_1^3A_3 - \frac{4989}{64}A_1^2A_2^2 \\ &+ \frac{23265}{256}A_1^4A_2 - \frac{23151}{1024}A_1^6\Big) \end{aligned}$$

$$\begin{aligned} Y_{01} = B_E\Big(1 + \frac{B_E^2}{2\omega_E^2}\big(&15 + 14A_1 - 9A_2 + 15A_3 - 23A_1A_2 \\ &+ \frac{21}{2}(A_1^2 + A_1^3)\big)\Big) \end{aligned}$$

$$\begin{aligned} Y_{11} = \frac{B_E^2}{\omega_E}\Big(6(1+A_1) + \frac{B_E^2}{\omega_E^2}\big(&175 + 285A_1 - \frac{335}{2}A_2 + 190A_3 \\ &- \frac{225}{2}A_4 + 175A_5 + \frac{2295}{8}A_1^2 - 459A_1A_2 + \frac{1425}{4}A_1A_3 - \frac{795}{2}A_1A_4 \\ &+ \frac{1005}{8}A_2^2 - \frac{715}{2}A_2A_3 + \frac{1155}{4}A_1^3 - \frac{9639}{16}A_1^2A_2 + \frac{5145}{8}A_1^2A_3 \\ &+ \frac{4677}{8}A_1A_2^2 - \frac{14259}{16}A_1^3A_2 + \frac{31185}{128}(A_1^4 + A_1^5)\big)\Big) \end{aligned}$$

$$Y_{21} = \frac{6B_E^3}{\omega_E^2}\left(5 + 10A_1 - 3A_2 + 5A_3 - 13A_1A_2 + \frac{15}{2}(A_1^2 + A_1^3)\right)$$

$$Y_{31} = \frac{20B_E^4}{\omega_E^3}\Big(7 + 21A_1 - \frac{17}{2}A_2 + 14A_3 - \frac{9}{2}A_4 + 7A_5 + \frac{225}{8}A_1^2$$

$$- 45A_1A_2 + \frac{105}{4}A_1A_3 - \frac{51}{2}A_1A_4 + \frac{51}{8}A_2^2 - \frac{45}{2}A_2A_3 + \frac{141}{4}A_1^3$$

$$- \frac{945}{16}A_1^2A_2 + \frac{435}{8}A_1^2A_3 + \frac{411}{8}A_1A_2^2 - \frac{1509}{16}A_1^3A_2$$

$$+ \frac{3807}{128}(A_1^4 + A_1^5)\Big)$$

$$Y_{02} = -\frac{4B_E^3}{\omega_E^2}\Big(1 + \frac{B_E^2}{2\omega_E^2}\big(163 + 199A_1 - 119A_2 + 90A_3 - 45A_4$$

$$- 207A_1A_2 + \frac{205}{2}A_1A_3 - \frac{333}{2}A_1^2A_2 + \frac{693}{4}A_1^2 + 46A_2^2$$

$$+ 126(A_1^3 + \frac{A_1^4}{2})\big)\Big)$$

$$Y_{12} = -\frac{12B_E^4}{\omega_E^3}\left(\frac{19}{2} + 9A_1 + \frac{9}{2}A_1^2 - 4A_2\right)$$

$$Y_{22} = -\frac{24B_E^5}{\omega_E^4}\Big(65 + 125A_1 - 61A_2 + 30A_3 - 15A_4 + \frac{495}{4}A_1^2 - 117A_1A_2$$

$$+ 26A_2^2 + \frac{95}{2}A_1A_3 - \frac{207}{2}A_1^2A_2 + 90(A_1^3 + \frac{A_1^4}{2})\Big)$$

$$Y_{03} = \frac{16B_E^5}{\omega_E^4}(3 + A_1)$$

$$Y_{13} = \frac{12B_E^6}{\omega_E^5}\Big(233 + 279A_1 + 189A_1^2 + 63A_1^3 - 88A_1A_2$$

$$- 120A_2 + \frac{80}{3}A_3\Big)$$

$$Y_{04} = - \frac{64 B_E^7}{\omega_E^6} (13 + 9 A_1 - A_2 + \frac{9}{4} A_1^2)$$

WITH

$$B_E = \frac{\hbar}{4 \pi c \mu R_E^2}$$

AND

$$\omega_E = \sqrt{4 A_0 B_E}$$

WHERE μ IS THE REDUCED MASS OF THE NUCLEI.

THE ABOVE EQUATIONS ARE CALLED, HERE, DUNHAM FORMULAS.

CHAPTER III

KOLOS AND WOLNIEWICZ ELECTRONIC ENERGY CALCULATION

(A) The Method of KW Energy calculation

A new improved theoretical potential $E(R)$ for H_2 was determined by Kolos and Wolniewicz. In their calculation, the electronic wave function $u(R,X_J)$ was put forward as an expansion $U = \sum_i C_i U_i$, where u_I is a molecular orbital wave function, in terms of electronic elliptic coordinates and of the interelectronic distance R. The variational method was employed to solve the electronic Schrodinger equation (2) (See Ref 8)

The potential energy calculated is dependent on the approximate wave function chosen. Numerous test runs were made to select the most important terms u_I to be used in the wave functions u. The terms which did not significantly improve the total energy were rejected in subsequent runs. In this way, the ground state potential energy curve of the hydrogen molecule had been calculated in single precision with a 54-term and 80-term expansion for the electronic wavefunction (Ref 8). Recently, a double precision calculation with 80-term and 100-term expansions for the wave function was made to improve the accuracy of the energy curve (Ref 7).

(B) THE APPARENT PRECISION OF THE KW ENERGY CALCULATION

THE DATA'S PRECISION CAN BE CHECKED OUT BY THE USE OF DIFFERENCE TABLES. IT IS BASED ON THE THEORY THAT A SMOOTHLY CHANGING FUNCTION ON AN EQUALLY SPACED MESH WILL EXHIBIT A WELL-BEHAVED DIFFERENCE TABLE IN WHICH HIGHER ORDER DIFFERENCES FOLLOW A REGULAR PATTERN. IF, AT ANY STAGE OF THE DIFFERENCING, THE VALUES SHOW RANDOM FLUCTUATIONS, THIS INDICATES ERROR. OF COURSE, THIS PROCEDURE ONLY REVEALS RANDOM AND NOT SYSTEMATIC ERRORS.

THE DIFFERENCE TABLES ON THE KW POTENTIAL E WITH A 100-TERM WAVE FUNCTION DO NOT SHOW ANY APPARENT FLUCTUATIONS (TABLE 1). THE HIGHER DIFFERENCES OF E ARE LARGE ENOUGH TO HIDE THE POSSIBLE ERRORS WHICH MIGHT EXIST. HOWEVER, THE DIFFERENCE TABLE OF THE PURE ELECTRONIC ENERGY E-1/R FROM THE 100-TERM WAVE FUNCTION DOES SHOW FLUCTUATIONS IN THE HIGHER ORDER DIFFERENCES (TABLE 2). THIS INDICATES A SIGNIFICANT ERROR ϵ IN AT LEAST ONE VALUE OF R. AN ESTIMATED ERROR OF 500×10^{-8} A. U.* IN THE 7TH DIFFERENCE IS CONSISTENT WITH AN ERROR $\epsilon = 1 \times 10^{-7}$ A.U. IN E-1/R.

THE ENERGY IMPROVEMENT IN GOING FROM THE DOUBLE-PRECISION 80 TO THE 100 TERM WAVE FUNCTION WAS DETERMINED AT DIFFERENT VALUES OF R. ONLY THE POINT AT R=1.6 LIES FAR FROM THE SMOOTH CURVE (FIG 1). THE DEVIATION IS ABOUT 0.5×10^{-7} A.U.* IF WE ASSUME $\epsilon_{1.6} = 0.5 \times 10$-7 A.U. IN THE 100 TERM E, E(1.6) FOR THE 100-TERM CALCULATION IS CHANGED FROM -1.16858212, AS LISTED IN REFERENCE 1, TO -1.16858207. THE STRAY POINT IN FIGURE 1 THEN MOVES CLOSE TO THE SMOOTH CURVE, BUT THE FLUCTUATIONS IN THE E-1/R DIFFERENCE TABLE DO NOT VANISH.

*1 A.U. OF ENERGY = 219494.62 CM^{-1}

TABLE 1. Difference Table of Kolos-Wolniewicz 100-Term Energies

R.	E.	$\Delta^1 E$	$\Delta^2 E$	$\Delta^3 E$	$\Delta^4 E$	$\Delta^5 E$	$\Delta^6 E$	$\Delta^7 E$	$\Delta^8 E$	$\Delta^9 E$	$\Delta^{10} E$	$\Delta^{11} E$
1.0	-1.12453881											
		-4039554										
1.2	-1.16493435		3085512									
		-954042		-1542205								
1.4	-1.17447477		1543307		761093							
		589265		-781112		-400039						
1.6	-1.16858212		762195		361054		223429					
		1351460		-420058		-176610		-131268				
1.8	-1.15506752		342137		184444		92161		80523			
		1693597		-235614		-84449		-50745		-51002		
2.0	-1.13813155		106523		99995		41416		29521		33096	
		1800120		-135619		-43033		-21224		-17906		22678
2.2	-1.12013135		-29096		56962		20192		11615		10418	
		1771024		-78657		-22841		-9609		-7488		
2.4	-1.10242011		-107753		34121		10583		7127			
		1663271		-44536		-12258		5482				
2.6	-1.08578740		-152289		21863		5101					
		1510982		-22673		-7157						
2.8	-1.07067758		-174962		14706							
		1336020		-7967								
3.0	-1.05731738		-182929									
		1153091										
3.2	-1.04578647											

$\Delta^i E$ in atomic units multiplied by 10^8.

R and E are in atomic units.

TABLE 2. DIFFERENCE TABLE* OF KOLOS-WOLNIEWICZ 100-TERM PURE ELECTRONIC ENERGY

R	E-1/R	ΔE	$\Delta^2 E$	$\Delta^3 E$	$\Delta^4 E$	$\Delta^5 E$	$\Delta^6 E$	$\Delta^7 E$	$\Delta^8 E$	$\Delta^9 E$	$\Delta^{10} E$	$\Delta^{11} E$
1.0	-2.12453881											
		12627113										
1.2	-1.99826768		-1676393									
		10950720		243509								
1.4	-1.88876048		-1432883		-32558							
		9517836		210952		-3214						
1.6	-1.79358212		-1221932		-35771		6977					
		8295904		175180		3763		5004				
1.8	-1.71062308		-1046752		-32006		1974		2822			
		7249153		143174		5739		-2182		-1051		
2.0	-1.63813155		-903578		-26268		-209		1771		-205	
		6345575		116906		5530		-411		-1256		217
2.2	-1.57467580		-786673		-20738		-631		515		12	
		5558903		96168		4909		104		-1244		
2.4	-1.51908678		-690504		-15829		-517		-729			
		4868399		80339		4392		-626				
2.6	-1.47040278		-610164		-11437		-1143					
		4258235		68902		3249						
2.8	-1.42782044		-541262		-8188							
		371697		60714								
3.0	-1.39065071		-480548									
		3236424										
3.2	-1.35828647											

R AND E IN ATOMIC UNITS.

THE DIFFERENCES ARE IN 10^8 A.U.

*$E-\frac{1}{R}$ AND THE DIFFERENCES ARE CALCULATED BY THE COMPUTER WITH DOUBLE-PRECISION. BECAUSE OF THE ROUNDOFF ERROR, THE DIFFERENCES LISTED HERE ARE NOT EXACTLY THOSE OBTAINED FROM THE LISTED VALUES OF COLUMN 2.

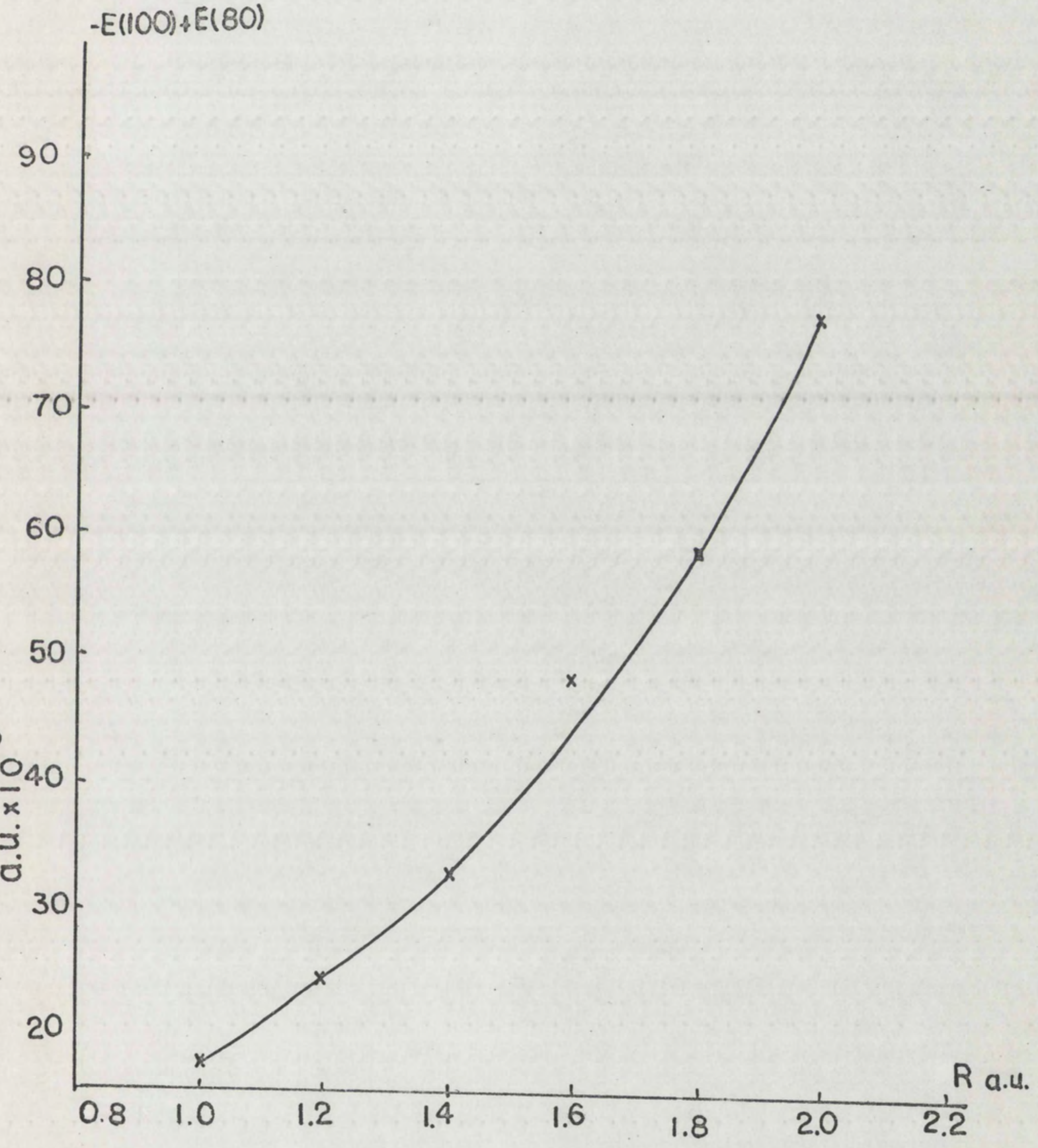

FIGURE 1. ENERGY IMPROVEMENT IN GOING FROM 80 TERM TO 100 TERM

Indeed, the difference table of E-1/R from the 80 term wave function shows the same pattern of fluctuations as in E-1/R fron the 100 term wave function. This means comparable computer error already existed in the 80 term energies.

Of course, it is very difficult to spot the errors by a simple inspection. However, if we assume $\epsilon_{1.6} = 1.0 \times 10^{-7}$ and $\epsilon_{2.6} = 1.5 \times 10^{-7}$ the fluctuation in the E(100)-1/R difference table vanishes (Table 3). On this basis, we assume the error for the 100 term potential is about 1×10^{-7} a.u.

It is important to note that the roundoff errors propogating through a table may also disrupt a difference pattern. However, the maximum possible error of the n-th difference, due to the round-off of all constituent entries to K decimal places, should not exceed the value $E_{MAX} = \pm 2^{N-1} \times 10^{-K}$ (Ref 9). In our case, the fluctuations in the difference tables are much larger than this E_{MAX}. The main source of fluctuation does, therefore, come from errors other than computer round-off.

It was found that the energy improvements E(100) -E(80) (in double-precision) and E(80) -E(54) (in single precision) were quite smooth. For example, when the difference table of improvements is calculated over the range $1.4 \leq R \leq 1.6$ a.u. the second difference shows a constant value of zero well within computer error (Table 4-1 and Table 4-2). This fact will be used when the potential expansion's constants are determined.

TABLE 3. THE HIGHER DIFFERENCES OF ENERGY E-1/R WITH 100 TERMS

A) BEFORE CORRECTION			B) AFTER CORRECTION		
Δ^6	Δ^7	Δ^8	Δ^6	Δ^7	Δ^8
6977			7177		
	-5004			-5353	
1974		2822	1824		3360
	-2182			-1993	
-209		1771	-169		1611
	-411			-382	
-631		515	-551		191
	104			-191	
-517		-729	-742		90
	-626			-101	
-1143			-843		

TABLE 4. THE ENERGY IMPROVEMENT, E(100)-E(80) AND E(80)-E(54),* AND THEIR DIFFERENCE TABLES NEAR R = 1.4 A.U.

R	E(100)-E(80) $\times 10^8$ A.U.	DIFFERENCE 1ST	DIFFERENCE 2ND	E(80)-E(54) $\times 10^{-7}$ A.U.	DIFFERENCE 1ST	DIFFERENCE 2ND
1.2	-24			-48		
		-3			3	
1.3	-27		-2	-45		-3
		-5			0	
1.4	-32		-1	-45		0
		-6			0	
1.5	-38		-1	-45		2
		-5			2	
1.6**	-43			-43		

* THE ERROR IN E(54) IS ± 2.5 × 10^{-7}, AS INDICATED BY BECKEL AND SATTLER (REF 2)

** $E_{1.6}$ (100) SMOOTHED WAS USED, I.E -1.16858207 AND NOT THE VALUE LISTED BY KOLOS AND WOLNIEWICZ

CHAPTER IV

POTENTIAL EXPANSION COEFFICIENTS

(A) Determination of E_E and R_E

The KW potential energy near the minimum position, 1.401075 a.u. $\leq R \leq$ 1.401080 a.u., has been calculated accurately up to 14 significant figures (Ref 7). When the difference table of the energy E was made over this range (Table 5), the third difference shows a constant value of zero within $\pm 2 \times 10^{-14}$. Thus, the potential function E can be expressed as a quadratic power series,

$$E = E_E + A_0(R-R_E)^2$$

The constants E_E, R_E and A_0 can then be determined from any three data points in this region. The results are

$$R_E = 1.4010783\underset{2}{\underline{7}}$$

$$E_E = -1.1744749830177\underset{1}{\underline{8}}$$

$$A_0 = 0.18\underset{5}{\underline{5}}$$

Numbers below underlines indicate position and magnitude of errors due to computor precision of E's.

TABLE 5. The Difference Table of E near R_E

		Differences**		
R*	E*	1st	2nd	3rd
1.401075	-1.17447498301568			
		-106		
1.401076	-1.17447498301674		37	
		- 69		- 1
1.401077	-1.17447498301743		36	
		- 33		2
1.401078	-1.17447498301776		38	
		5		- 2
1.401079	-1.17447498301771		36	
		41		
1.401080	-1.17447498301730			

*R and E are in atomic units.

** The differences in atomic units are multiplied by 10^{14}.

(B) Use of Simultaneous Equations to Determine the Potential Expansion's Constants

Assume the potential E can be expanded in a Taylor's series about the equilibrium separation R_E:

$$E(R) = E_E + A_0(R-R_E)^2 + A_1(R-R_E)^3 + A_2(R-R_E)^4 + \ldots \quad (6)$$

Suppose that we wish to fit a truncated form of equation (6), i.e., a polynomial, to a set of numerically determined values of E. For a given subdomain of R, we must truncate the series such that all retained terms make a contribution to E greater than computer error (Ref 1). That is to say, if we want the polynomial to represent the function accurately, the absolute value of the first neglected term must be less than or equal to ϵ, the computer error.

$$|A_{n-1}(R-R_E)^{n+1}| \sim \epsilon$$

or

$$|R-R_E| \sim |\epsilon / A_{n-1}|^{1/(n+1)} \quad (7)$$

Now, since the potentials for the ground state of H_2 behave approximately like a sum of a quadratic term and a coulomb repulsion term in the vicinity of the minimum (Ref 2), that is,

$$E \sim \frac{1}{R} + A'(R-R_E)^2 + \text{small terms},$$

we have $A_{n-1} \sim \frac{1}{R_E^{n+2}}$ for $N > 2$.

If we substitute this A_{N-1} in equation (7), the proper range of R can be calculated as

$$|R - R_E| \sim |\epsilon R_E^{N+2}|^{\frac{1}{n+1}} \quad (8)$$

For the potential from the 100-term wave function being considered here, $\epsilon = 1 \times 10^{-7}$ a.u. and $R_E \sim 1.4$ a.u., if we choose $N = 7$, then $|R - R_E| \sim 0.2$. Hence, a 7th order polynomial can be fitted to the KW potential from the 100-term wave function, if we choose the data in the range $1.2 \leqq R \leqq 1.6$.

In the KW energy data from the 100-term wave function, there are only four data points available between $1.2 \leq R \leq 1.6$ a.u. (exclude R = 1.4*). Then clearly it is impossible to solve for the constant in the expansion.

$$E = E_E + A_0(R-R_E)^2 + A_1(R-R_E)^3 + \ldots + A_5(R-R_E)^7 \qquad (9)$$

We may attempt to use the virial theorem to calculate dE/dR (the applicability of the virial theorem will be discussed later) to double the data. This is, we get 4 more equations from

$$dE/dR = 2A_0(R-R_E) + 3A_1(R-R_E)^2 \ldots + 7A_5(R-R_E)^6 \qquad (10)$$

such that we have enough equations to determine the potential expansion's constants A_0 to A_5. This calculation was done on the IBM 360 computer using a double precision Gaussian elimination program. The determined constants are listed as follows:**

E_E: -1.1744749

A_{-1}: $-0.00000\underline{1}$

A_0: $0.18498\underline{8}$

A_1: $-0.2115\underline{5}$

A_2: $0.176\underline{4}$

A_3: $-0.1\underline{3}88$

A_4: $0.0\underline{9}4$

A_5: $-0.\underline{0}2$

The bar under a number indicates the position at which the error should occur. The error is approximated by the formula

$$(\Delta A_{N-2})\ (R-R_E)^N \sim \epsilon \sim 10^{-8}$$

Which gives

$$\Delta A_{N-2} \sim 10^{-8+N}$$ as a rough estimate.

---

*Because the equation determined from the data point R = 1.4, $E_{1.4} - E_E = 21 \times 10^{-8} \sim A_0 \times 10^{-6} + A_1 \times 10^{-9}$ is not accurate enough to determine A_N.

**A_{-1} is the coefficient of the linear term in the Taylor's expansion.

(C) Use of $E-1/R$ to Determine A_N's

The potential energy $E(R)$ in the nuclear motion problem has included a term $1/R$, which is the electrostatic energy between two nuclei. This term causes a singularity at $R = 0$. However, the function $E(R)-1/R$ has no singularity at $R = 0$ and hence is better behaved than $E(R)$ near $R = 0$. This increases the convergence radius of the power series from R_E to the whole range.

The energy $E-1/R$ can be expanded in a power series

$$E-1/R = E_E' + A_{-1}'(R-R_E) + A_0'(R-R_E)^2 + A_1'(R-R_E)^3 \ldots \quad (11)$$

Since $\frac{1}{R} = \sum_{n=0} \frac{(-1)^n (R-R_E)^n}{R_E^{n+1}}$

the relation between A_N' and A_N is

$$A_n = A_n' + (-1)^{n+2} / R_E^{n+3} \quad (12)$$

Now $A_2 \sim 0.176$ and $1/R_E^5 \sim 0.185$, therefore $A_2' \sim 0.009$; similary $A_3' \sim -0.007$. Hence A_N' for $N > 2$ is expected to be much smaller than A_N. Hence $E-1/r$ is not only better behaved than E but a power series with a given number of terms can be used over a much wider range of R for $E-1/R$ than for E.

The constants A_N' can be calculated by using Stirling's central difference formula. Stirling's formula can be expected to yield more accurate A_N' than a forward or backward difference formula. The estimated errors of the A_N' can be easily determined from the difference table.

To use the central difference formula for higher differences, we must have a sufficient number of equally spaced data points. However, the new KW energies from the 100-term wave function are listed between $1.0 \leq R \leq 3.2$ a.u. only. They are not sufficient to yield central differences (with the center at $R = 1.4$) higher than the 4th, since the equidistant mesh is 0.2. Thus, we have to use the old values of the KW potential, which are listed between $0.4 \leq R \leq 3.7$, to get more information about the higher order central differences.

As we have shown previously in Table 4, if R is near the minimun position R_E, the second differences for E(100)-E(80) and E(80)-E(54) are zero well within the computor error of the 54 term calculation. This means the terms additional to 54 in the wave function contribute less to the 2nd differences than the computor error. This will be illustrated more clearly if we examine the table 6.

TABLE 6-A. The Energy Improvement E(100)-E(54)

R	E(100)-E(54) $\times 10^{-7}$ A.U.	Differences 1st	2nd	3rd	4th	5th
1.0	-55					
		5				
1.2	-50		-4			
		1		4		
1.4	-49		0		-16	
		1		-12		34
1.6	-48		-12		18	
		-11		6		
1.8	-59		-6			
		-17				
2.0	-76					

TABLE 6-B. THE ENERGY IMPROVEMENT E(80)-E(54)

R	E(80)-E(54)	DIFFERENCES				
	x 10^{-7} A.U.	1ST	2ND	3RD	4TH	5TH
0.6	-88					
		19				
0.8	-69		-4			
		15		-5		
1.0	-54		-9		11	
		6		6		-15
1.2	-48		-3		-4	
		3		2		-10
1.4	-45		-1		-14	
		2		-12		28
1.6	-43		-13		14	
		-11		2		
1.8	-54		-11			
		-22				
2.0	-76					

TABLE 6-C. THE PROPAGATION OF COMPUTER ERROR $\epsilon = 3 \times 10^{-7}$.
(IF WE ASSUME AN ERROR ϵ OCCURS)

	DIFFERENCES				
$\epsilon \times 10^7$	1ST	2ND	3RD	4TH	5TH
0		0			
	0		3		
0		3		-12	
	3		-9		30
3		-6		18	
	-3		9		-30
0		3		-12	
			-3		
0		0			

IT CAN BE SEEN FROM TABLES 6-A AND 6-B THAT THE FIFTH DIFFERENCES ARE $\sim \pm 10 \times 3 \times 10^{-7}$ WHICH IS CONSISTENT WITH THE ESTIMATED ERROR OF 2.5×10^{-7} IN THE ENERGIES CALCULATED WITH THE 54 TERM WAVE FUNCTION.

THE ABOVE FACT ENABLES US TO COMPUTE THE HIGHER DIFFERENCES FROM THE KW ENERGY WITH 54 TERM AND 80 TERM WAVE FUNCTIONS. IT SHOULD BE MENTIONED THAT MIXING THE DATA IN THE SECOND COLUMN OF THE DIFFERENCE TABLE WILL PRODUCE DISCONTINUITIES OF THE ORDER OF 50×10^{-7} AND THE ERRORS IN DIFFERENCES WILL MULTIPLY ACCORDINGLY.

THE CENTRAL DIFFERENCES, THEN, ARE DETERMINED AS FOLLOWS: (Y_0 TO $\Delta^4 Y_0$ COME FROM THE ENERGY WITH 100 TERMS, $\Delta^5 Y_0$ TO $\Delta^6 Y_0$ FROM SINGLE PRECISION 80 TERMS, AND $\Delta^7 Y_0$ TO $\Delta^{10} Y_0$ FROM 54 TERMS.*)

$Y_0 = -1.88876048$

$\Delta^1 Y_0 = 0.102342\underset{14}{\underline{78}}$

$\Delta^2 Y_0 = -0.014328\underset{2}{\underline{8}}3$

$\Delta^3 Y_0 = 0.002272\underset{4}{\underline{3}}0$

$\Delta^4 Y_0 = -0.000325\underset{6}{\underline{5}}8$

$\Delta^5 Y_0 = -0.00015\underset{35}{\underline{48}}6$

$\Delta^6 Y_0 = 0.00024\underset{50}{\underline{48}}$

$\Delta^7 Y_0 = -0.0003\underset{125}{\underline{479}}$

$\Delta^8 Y_0 = 0.0003\underset{2}{\underline{6}}$

$\Delta^9 Y_0 = -0.0005\underset{45}{\underline{43}}$

$\Delta^{10} Y_0 = 0.0005\underset{6}{\underline{7}}6$

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*THE DIFFERCE TABLES OF THE ENERGY WITH 80 TERMS AND 54 TERMS WAVE FUNCTION ARE SHOWN IN APPENDICES.

Accordingly these central differences were used in the Stirling's central formula (Appendix II) to determine the expansion's constants A' of E - 1/R. Finally, from equation (12), we get the following KW potential expansion's constants, which are far more accurate than the most accurate previous theoretical calculation by Beckel and Sattler. (Ref 1)

TABLE 7. KW Potential Expansion Coeiffcients

N	$(-N)^N/R_E^{N+3}$	A_N'	A_N
0	0.36359066	$-0.17859\underset{6}{\underline{3}}$	$0.18499\underset{6}{\underline{8}}$
1	-0.25950772	$0.0478\underset{5}{\underline{4}}$	$-0.2116\underset{5}{\underline{7}}$
2	0.18521999	$-0.0094\underset{3}{\underline{2}}$	$0.175\underset{3}{\underline{8}}$
3	-0.13219817	$-0.002\underset{18}{\underline{25}}$	$-0.134\underset{2}{\underline{4}}$
4	0.09435458	$0.0040\underset{3}{\underline{0}}$	$0.098\underset{3}{\underline{4}}$
5	-0.06734426	$-0.00\underset{12}{\underline{18}}7$	$-0.06\underset{1}{\underline{9}}$
6	0.04806602	$0.001\underset{4}{\underline{6}}$	$0.05\underset{4}{\underline{0}}$

CHAPTER V

VIRIAL THEOREM AND ITS APPARENT ACCURACY

Applying the virial theorem to the diatomic molecule in the Born-Oppenheimer Approximation, we find (Appendix III)

$$\frac{dE}{dR} = \left(\frac{V}{2E} - 1\right)\frac{2E}{R}$$

where V is the potential for the electronic problem. The above formula and the values of V/2E given in (Ref 7) enable us to calculate the derivatives dE/dR.

To test the accuracy of the virial theorem in the diatomic molecular system, we will interpolate between known energies with an Hermite polynomial. The polynomial is fitted to the energy E and its derivatives dE/dR at several internuclear separations.

Suppose we use the following data to evaluate E at R = 1.35, 1.39, 1.4011, 1.41, 1.45 and compare with known values.

R	E	dE/dR
1.3	-1.17234623	-0.04469065
1.4	-1.17447477	-0.00039974
1.5	-1.17285408	-0.03100757
1.6	-1.16858212	-0.05311410

The results are as follows:

R	1.35	1.39	1.4011
Interpolated value	-1.17396284	-1.17445199	-1.17447498
Known value	-1.1739627 2.5	-1.17445199	-1.17447498

R	1.41	1.45
Interpolated value	-1.17446041	-1.17405610
Known value	-1.17446041	-1.1740558 2.5

The interpolated values compare well with the known values. Hence dE/dR as derived from the virial theorem appears consistent in accuracy with E.

However, a question arises when we try to use the virial theorem to calculate A_0. The procedure is as follows:

At first, we apply the virial theorem to calculate dE/dR at R = 1.401075, 1.401076, ----, 1.401080 and make a difference table.

R	dE/dR x 10^6 a.u.	First difference
1.401075	-1.24773	
		0.36941
1.401076	-0.87832	
		0.36941
1.401077	-0.50891	
		0.36942
1.401078	-0.13949	
		0.36941
1.401079	0.22992	
		0.36941
1.401080	0.59933	

The second difference shows a constant value of zero within $\epsilon = 2 \times 10^{-11}$ a.u. Thus, dE/dR can be expressed as a linear equation over the region i.e.,

$$dE/dR = 2A_0(R-R_E)$$

A_0 can then be determined as $A_0 = \frac{1}{2(R_2-R_1)} \left(dE/dR\,\big|_2 - dE/dR\,\big|_1 \right) =$

$$0.1847\underset{2}{\underline{1}}$$

It is clear that the value determined in this way is not consistent with the value of the previous results, $A_0 = 0.18499\underset{6}{\underline{8}}$. This indicates that the 100-term wave function was not sufficient to yield values of $V/2E$ accurate up to the 11 significant digits tabulated in Reference 1. The consistency of that difference of dE/dR is perplexing, however.

CHAPTER VI

SPECTROSCOPIC CONSTANTS FROM DUNHAM'S FORMULAS

The potential in equation (4) can be converted into the Dunham form

$$E(R) = a_0 \xi^2 (1 + a_1 \xi + a_2 \xi^2 + a_3 \xi^3 \ldots)$$

if we set

$$a_0 = c A_0 R_E^2$$

$$a_i = \frac{A_i}{A_0} R_E^i \quad \text{with } i = 1, 2, \ldots\ldots N,$$

where $\xi = (R-R_E)/R_E$ and c, the conversion factor is equal to 219474.62 cm^{-1}/a.u.

The most accurate A_i's are those found in Table 7. From these, the Dunham coefficients were found to be

$a_0 \doteq 7970\underset{2.6}{\underline{3.3}}\ \text{cm}^{-1}$

$a_1 = -1.603\underset{4}{\underline{1}}$

$a_2 = 1.86\underset{36}{\underline{54}}$

$a_3 = -1.99\underset{3}{\underline{9}}$

$a_4 = 2.04\underset{6}{\underline{8}}$

$a_5 = -2.0\underset{4}{\underline{2}}$

$a_6 = 2.\underset{1}{\underline{0}}$

These a's were used in Dunham's formulas to determine the KW spectroscopic constants. The KW spectroscopic constants determined from the present data are shown in Table 8, along with the constants of Beckel and Sattler (Ref 1) and the experimental constants of Herzberg and Howe (Ref 6), and Fink, Wiggins and Rank (Ref 5).

TABLE 8. COMPARISON OF KW AND EXPERIMENTAL SPECTROSCOPIC CONSTANTS (IN CM^{-1})

	KW		EXPERIMENTAL	
CONSTANT	PRESENT	BECKEL-SATTLER	HERZBERG-HOWE	FINK-WIGGINS-RANK
Y_{00}	$8.3\underset{8}{\underline{6}}$	$8.\underset{4}{\underline{4}}$		
ω_E	$4406.\underset{2}{\underline{1}}$	$4406.\underset{7}{\underline{2}}$		$4403.18\underset{2}{\underline{6}}$
Y_{10}	$4405.\underset{8}{\underline{3}}$	$440\underset{3}{\underline{2}}$*	4400.39	$4401.21\underset{6}{\underline{7}}$
Y_{20}	$-122.\underset{4}{\underline{8}}$	$-12\underset{2}{\underline{2}}$	$-121.8\underset{5}{\underline{1}}$	$-121.3\underset{3}{\underline{4}}3$
Y_{30}	$\underset{1.5}{\underline{1.2}}$		$0.72\underset{2}{\underline{4}}$	$0.81\underset{7}{\underline{4}}5$
Y_{40}	$-0.0\underset{6}{\underline{4}}$			
B_E	$60.89\underset{6}{\underline{2}}$	$60.89\underset{6}{\underline{4}}$		$60.86\underset{8}{\underline{7}}9$
Y_{01}	$60.87\underset{6}{\underline{2}}$	$60.8\underset{1}{\underline{2}}$*	60.864	$60.85\underset{7}{\underline{9}}1$
Y_{11}	$-3.04\underset{3}{\underline{4}}$	$-3.0\underset{2}{\underline{3}}$	-3.0763	$-3.0\underset{14}{\underline{78}}3$
Y_{21}	$0.04\underset{5}{\underline{4}}$		0.0601	$0.06\underset{7}{\underline{8}}6$
Y_{31}	$-0.00\underset{17}{\underline{32}}$		-0.0048	$-0.00\underset{15}{\underline{07}}0$
Y_{02}	$-0.0465\underset{1}{\underline{3}}$	$-0.046\underset{1}{\underline{5}}$	-0.04659	$-0.0047\underset{3}{\underline{1}}0$
Y_{12}	$0.00159\underset{4}{\underline{1}}$	$0.001\underset{1}{\underline{6}}$	0.001616	$0.002\underset{5}{\underline{7}}4$
Y_{22}	$-0.0000\underset{1}{\underline{5}}$		-0.0000143	$-0.000\underset{2}{\underline{4}}0$
$Y_{03} \times 10^5$	$4.96\underset{2}{\underline{5}}$	$4.9\underset{1}{\underline{8}}$		$4.\underset{5}{\underline{9}}$
$Y_{13} \times 10^7$	$-7.\underset{3}{\underline{7}}$			$-5\underset{5}{\underline{5}}$
$Y_{04} \times 10^8$	$-6.75\underset{7}{\underline{8}}$	$-6.7\underset{5}{\underline{9}}$		

*THE CONSTANTS Y_{10} AND Y_{01} DERIVED BY BECKEL AND SATTLER USED THE VAN VLECK'S NUCLEAR-ELECTRONIC CORRECTIONS. COMPARABLE CORRECTIONS WERE NOT APPLIED IN THE PRESENT CALCULATIONS. HOWEVER THEY YIELD $Y_{01} = 60.838$ CM^{-1}, $Y_{11} = -3.041$, $Y_{10} = 4406.\underset{8}{\underline{6}}$, $Y_{20} = -122.6$.

THE AGREEMENT BETWEEN THE PRESENT AND BECKEL AND SLATTLER'S KW SPECTROSCOPIC CONSTANTS IS VERY GOOD. HOWEVER, THERE ARE SOME DISCREPANCIES BETWEEN THE PRESENT KW AND EXPERIMENTAL SPECTROSCOPIC CONSTANTS. THE CONSTANTS Y_{10}, Y_{20}, Y_{11} AND Y_{01} APPEAR TO DIFFER FROM EXPERIMENTAL VALUES. WHEN THE VON VLECK'S NUCLEAR - ELECTRONIC CORRECTIONS ARE APPLIED FOR Y_{01}, Y_{10}, THESE DISCREPANCIES ARE NOT REMOVED, BUT RATHER BECOME LARGER. THE DISCREPANCIES IN Y_{01} AND Y_{11} ARE COUPLED TO THE DISCREPANCY BETWEEN THE THEORETICAL AND EXPERIMENTAL VALUES OF R_E(REF 1). THE DISCREPANCIES BETWEEN THE KW AND EXPERIMENTAL VALUES OF Y_{10} AND Y_{20} MIGHT BE ATTRIBUTED TO AN UNSATISFACTORY FIT OF POWER SERIES TO EXPERIMAL DATA (REF 6).

THE EXPERIMENTAL CONSTANTS ARE GENERALLY OBTAINED THROUGH LEAST SQUARES FIT TO POLYNOMIALS OF DIFFERENT ORDER. THE VALUES OBTAINED FROM DIFFERENT ORDERS OF POLYNOMIALS ARE NOT CONSISTENT WITHIN THE EXPERIMENTAL ERROR. FOR H_2 GROUND STATE, HOWEVER, SHAFI AND BECKEL (REF 10), USING AN EXPRESSION OTHER THAN A POWER SERIES OBTAIN A CONSISTENT SET OF VIBRATIONAL CONSTANTS. THEIR VALUES OF $Y_{10} = 4402.8$ AND $Y_{20} = -122.9$ ARE MUCH CLOSER TO OUR VALUES HERE. IT IS BELIEVED THAT THE PRESENT CALCULATION OF KW SPECTROSCOPIC CONSTANTS IS MORE ACCURATE THAN THE EXPERIMENTAL VALUES.

CHAPTER VII

THE ROTATIONAL CONSTANTS B_v, D_v AND H_v

(A) DETERMINATION OF B_V, D_V AND H_V

(I) FROM DUNHAM'S CONSTANTS

THE ROTATIONAL CONSTANTS B_V, D_V AND H_V IN THE VIBRATIONAL STATE V ARE GIVEN RESPECTIVELY BY THE FOLLOWING FORMULAS

$$B_V = Y_{01} + Y_{11}(v+\tfrac{1}{2}) + Y_{21}(v+\tfrac{1}{2})^2 + Y_{31}(v+\tfrac{1}{2})^3+ \ldots\ldots\ldots\ldots (13)$$

$$D_V = Y_{02} + Y_{12}(v+\tfrac{1}{2}) + Y_{22}(v+\tfrac{1}{2})^2 + Y_{32}(v+\tfrac{1}{2})^3+ \ldots\ldots\ldots\ldots (14)$$

$$H_V = Y_{03} + Y_{13}(v+\tfrac{1}{2}) + Y_{23}(v+\tfrac{1}{2})^2 + Y_{33}(v+\tfrac{1}{2})^3+ \ldots\ldots\ldots\ldots (15)$$

IF WE SUBSTITUTE THE DUNHAM'S CONSTANTS Y_{IJ} DERIVED PREVIOUSLY INTO THESE FORMULAS, WE GET B_V, D_V AND H_V OF THE GROUND STATE H_2 AS FOLLOWING:

$$B_V = 60.87\underset{6}{\underline{2}} - 3.04\underset{3}{\underline{4}}\ (v+\tfrac{1}{2}) + 0.04\underset{5}{\underline{4}}\ (v+\tfrac{1}{2})^2 - 0.00\underset{17}{\underline{32}}\ (v+\tfrac{1}{2})^3 \ldots (16)$$

$$D_V = 0.0465\underset{1}{\underline{3}} - 0.00159\underset{4}{\underline{1}}(v+\tfrac{1}{2}) + 0.0000\underset{1}{\underline{5}}(v+\tfrac{1}{2})^2+ \ldots\ldots\ldots\ldots (17)$$

$$H_V = 4.96\underset{2}{\underline{5}} \times 10^{-5} - 7.\underset{3}{\underline{7}} \times 10^{-7}\ (v+\tfrac{1}{2})+ \ldots\ldots\ldots\ldots\ldots\ldots (18)$$

IN COLUMN 3 OF TABLE 9 (A), 9 (B) AND 9 (C) ALL THE B_V, D_V AND H_V VALUES THUS OBTAINED ARE COLLECTED. THESE NUMERIAL VALUES ARE RELIABLE IN PARTICULAR FOR THE FIRST FEW V VALUES.

TABLE 9. COEFFICIENTS OF POWERS OF $J(J + 1)$ IN EXPANSION OF ENERGY LEVELS

(A) B_v cm^{-1}

v	LEAST SQUARE FIT	DUNHAM'S FIT	HERZBERG-HOWE	FINK-WIGGINS-RANK
0	59.339	$59.3\underset{1}{\underline{6}}$	59.3392	$59.33\underset{12}{\underline{62}}$
1	56.378	$56.3\underset{1}{\underline{9}}$	56.3685	$56.37\underset{19}{\underline{22}}$
2	53.483	$53.4\underset{4}{\underline{9}}$	53.4754	$53.48\underset{4}{\underline{2}}3$
3	50.635	$50.7\underset{7}{\underline{4}}$	50.6257	
4	47.805	$47.\underset{3}{\underline{7}}7$	47.801	
5	44.970	$44.\underset{5}{\underline{9}}2$	44.958	
6	42.102	$42.\underset{6}{\underline{0}}6$	42.096	
7	39.158	$39.\underset{9}{\underline{1}}7$	39.145	
8	36.089	$3\underset{1}{\underline{6}}.2$	36.088	
9	32.839	$3\underset{2}{\underline{3}}.2$	32.833	
10	29.313	$3\underset{2}{\underline{0}}.1$	29.311	
11	25.406	$2\underset{3}{\underline{6}}.3$	25.399	
12	20.919	$2\underset{4}{\underline{3}}.4$	20.923	
13	(15.548)		15.582	
14	(8.656)		8.770	

TABLE 9. (CONTINUED)

(B) $D_v \times 10^2$ CM^{-1}

V	LEAST SQUARE FIT	DUNHAM'S FIT	HERZBERG-HOWE	FINK-WIGGINS-RANK
0	4.572	$4.57\underline{5}_{1}$	4.599	$4.5\underline{83}_{13}$
1	4.413	$4.42\underline{6}_{3}$	4.370	$4.3\underline{88}_{15}$
2	4.279	$4.28\underline{6}_{7}$	4.277	$4.0\underline{80}_{17}$
3	4.146	$4.1\underline{57}_{13}$	4.097	
4	4.016	$4.0\underline{4}_{2}$	3.971	
5	3.899	$3.9\underline{3}_{3}$	3.854	
6	3.808	$3.8\underline{3}_{4}$	3.779	
7	3.727	$3.7\underline{4}_{6}$	3.677	
8	3.654	$3.6\underline{6}_{7}$	3.653	
9	3.653	$3.5\underline{9}_{9}$	3.638	
10	3.675	$3.\underline{53}_{11}$	3.660	
11	3.808	$3.\underline{48}_{13}$	3.784	
12	4.054	$3.\underline{45}_{15}$	4.136	
13	4.693		4.927	
14	6.10		8.467	

TABLE 9. (CONTINUED)

(C) $H_v \times 10^5$ CM^{-1}

V	LEAST SQUARE FIT	DUNHAM'S FIT	HERZBERG-HOWE	FINK-WIGGINS-RANK
0	4.96	$4.94\underset{2}{\underline{5}}$	5.2	$4.\underset{33}{\underline{87}}$
1	4.70	$4.84\underset{6}{\underline{9}}$		3.97
2	4.90	$4.77\underset{8}{\underline{3}}$		3.87
3	4.80	$4.7\underset{1}{\underline{0}}$	3.75	3.68
4	4.55	$4.6\underset{1}{\underline{2}}$	3.50	
5	4.35	$4.5\underset{2}{\underline{4}}$	3.42	
6	4.39	4.46	3.32	
7	4.17	4.38	3.25	
8	3.56	4.31	3.20	
9	3.66		3.09	
10	3.08		2.50	
11	2.59		1.83	
12	-0.08			
13	-4.26			
14	-74			

(ii) From Energy Level Expansion

The expression for the Jth rotational level in a given vibrational state is

$$E_{v,J} = E_{v,o} + B_v J(J+1) - D_v J^2(J+1)^2 + H_v J^3(J+1)^3 - I_v J^4(J+1)^4 + \quad .....(19)$$

where B_v, D_v and H_v are functions of v.

The energy levels $E_{v,J}$ are listed in Ref 7. Since the J quantum numbers go from 0 to 10 (for the first 12 vibrational state), there are ten pieces of data available with which to solve for the coefficients B_v, D_v and H_v in the above formulas. The calculation of these constants was carried out on the IBM 360 computer using a double-precision least squares program.

Different orders of the least square polynomial fit have been tried. Only the resulting B_v, D_v and H_v coefficients from the least square five-term formula coincide with those determined from the Dunham's constant at low v. As a check on the order of the least square polynomial, these resulting B_v, D_v and H_v coefficients were then put into the right hand side of equation (19) to determine the residuals of $E_{v,J}$. The residuals are less than 0.01 cm^{-1} for the first seven J values; ($E_{v,o}$;---$E_{v,7}$) and less than 0.05 cm^{-1} for the remaining terms. This suggests that a satisfactory least square fit was made. The results are shown in Table 9 (a), 9 (b) and 9 (c).

For v=13 and v=14*, the number of $E_{v,J}$ values available is insufficient and the constants were determined from a 3rd order polynomial least square fit using 5 pieces of data. In both cases, the residuals of $E_{v,J}$ for the first 5 values of J are less than 0.01 cm^{-1}. Thus, it is believed that the numerical results of B_{13}, D_{13}, H_{13}, B_{14}, D_{14}, H_{14} are reliable, although with reduced accuracy.

As a further check on the proper order of the polynomial, the data between $0 \leq J \leq 7$ was fitted to a fifth order J(J+1) least square polynomial. The effect of the higher order approximation (which includes the unimportant term) was to cause wide oscillations in H_v values and to make them meaningless. (Table 10).

In addition, the coefficients B_v, D_v and H_v were solved from a 3rd order polynomial, using $0 \leq J \leq 10$. The terms in this polynomial fit are too few to represent the data in the given range. The resulting values of H_v are far below the corrected ones. (Table 10) The residues resulting from the use of this polynomial are much larger than the possible error of the individual $E_{v,J}$.

It was also noticed that the coefficients solved from the 4th order least square polynomial (using $0 \leq J \leq 10$) (Table 10) gave quite small residues of $E_{v,J}$ and are close to those determined from the 5th polynomial fit (differences in H_v are about ±0.2 x 10^{-5} a.u.). However, comparing with the constants determined from the Dunham's constants, we prefer the values from the 5th polynomial fit.

*For v=14, we use the data from Weach and Bernstein (Ref 12) which includes the levels below the rotational potential maximum but above the dissociation limit.

TABLE 10. H_v VALUES OBTAINED THROUGH LEAST SQUARES FIT TO POLYNOMIALS OF DIFFERENT ORDER

H_v $cm^{-1} \times 10^5$

v	$1 \leq J \leq 10$ 5TH POLYNOMIAL FIT	$1 \leq J \leq 7$ 5TH POLYNOMIAL FIT	$1 \leq J \leq 10$ 3RD POLYNOMIAL FIT	$1 \leq J \leq 10$ 4TH POLYNOMIAL FIT
0	4.96	4.41	3.72	4.75
1	4.70	6.90	3.62	4.65
2	4.90	6.11	3.51	4.5
3	4.80	2.16	3.42	4.4
4	4.55	3.08	3.30	4.3
5	4.35	4.77	3.17	4.2
6	4.39	5.20	3.03	4.1
7	4.17	4.02	2.86	3.9
8	3.56	0.24	2.64	3.6
9	3.66	4.03	2.35	3.4
10	3.08	3.56	1.83	3.0
11	2.59	0.62	0.80	2.7
12	-0.085	4.40	-2.58	
13		-3.67		

(B) B_v, D_v, H_v CURVE

IN TABLE 9 (A), 9 (B) AND 9 (C) THE VALUES OF THE COEFFICIENTS OF THE ENERGY LEVEL EQUATION AS DETERMINED FROM THE 5TH ORDER POLYNOMIAL USING THE DATA $0 \leq J \leq 10$ ARE COMPARED WITH THE CONSTANTS DETERMINED FROM EQUATION (16), (17) AND (18), USING THE EXPERIMENTAL CONSTANTS OBTAINED BY HERZBERG AND HOWE (REF 6), AND BY FINK, WIGGINS AND RANK (REF 5). THE AGREEMENT OF B_v, D_v IS QUITE GOOD. HOWEVER, THERE IS A DISCREPANCY OF ABOUT 1×10^{-5} CM^{-1} BETWEEN THE THEORETICAL AND EXPERIMENTAL CONSTANT H_v. THIS DISCREPANCY IN THE H_v VALUES ARE BELIEVED TO BE MAINLY DUE TO THE EXPERIMENTAL ANALYSIS IN WHICH THE I_v VALUES ARE IGNORED (REF 8). IGNORING $I_v J^4 (J+1)^4$ IN THE ENERGY FIT COULD SYSTEMATICALLY UNDERESTIMATE H_v VALUES AS SEEN IN TABLE 10.

IN FIGURE 2(A), 2 (B) AND 2(C) ARE PLOTTED THE VALUES OF B_v, D_v AND H_v RESPECTIVELY. THE B_v VALUES ARE MUCH MORE ACCURATE THAN CAN BE REPRESENTED BY PLOTS LIKE THOSE IN FIGURE 2(A). THE B_v CURVE SHOWS A SLIGHTLY INCREASING NEGATIVE CURVATURE AT LOW V AND TOWARD THE END FALLS RAPIDLY TO ZERO. THE D_v CURVE RISES RAPIDLY AT HIGH V AFTER A MINIMUM AT ABOUT V=9. H_v CHANGES SIGN NEAR V=12 AND AT HIGH V SHOWS A RAPID DECREASE. THE ACCURACY CANNOT BE DETERMINED FROM LEAST SQUARE FIT. HOWEVER, THE FLUCTUATIONS FROM A SMOOTH CURVE OF H_v CAN BE USED AS AN ESTIMATE ON THE ERROR. INSPECTION OF THE H_v CURVE SHOWS THE FLUCTUATION TO BE ABOUT 0.2×10^{-5} CM^{-1}.

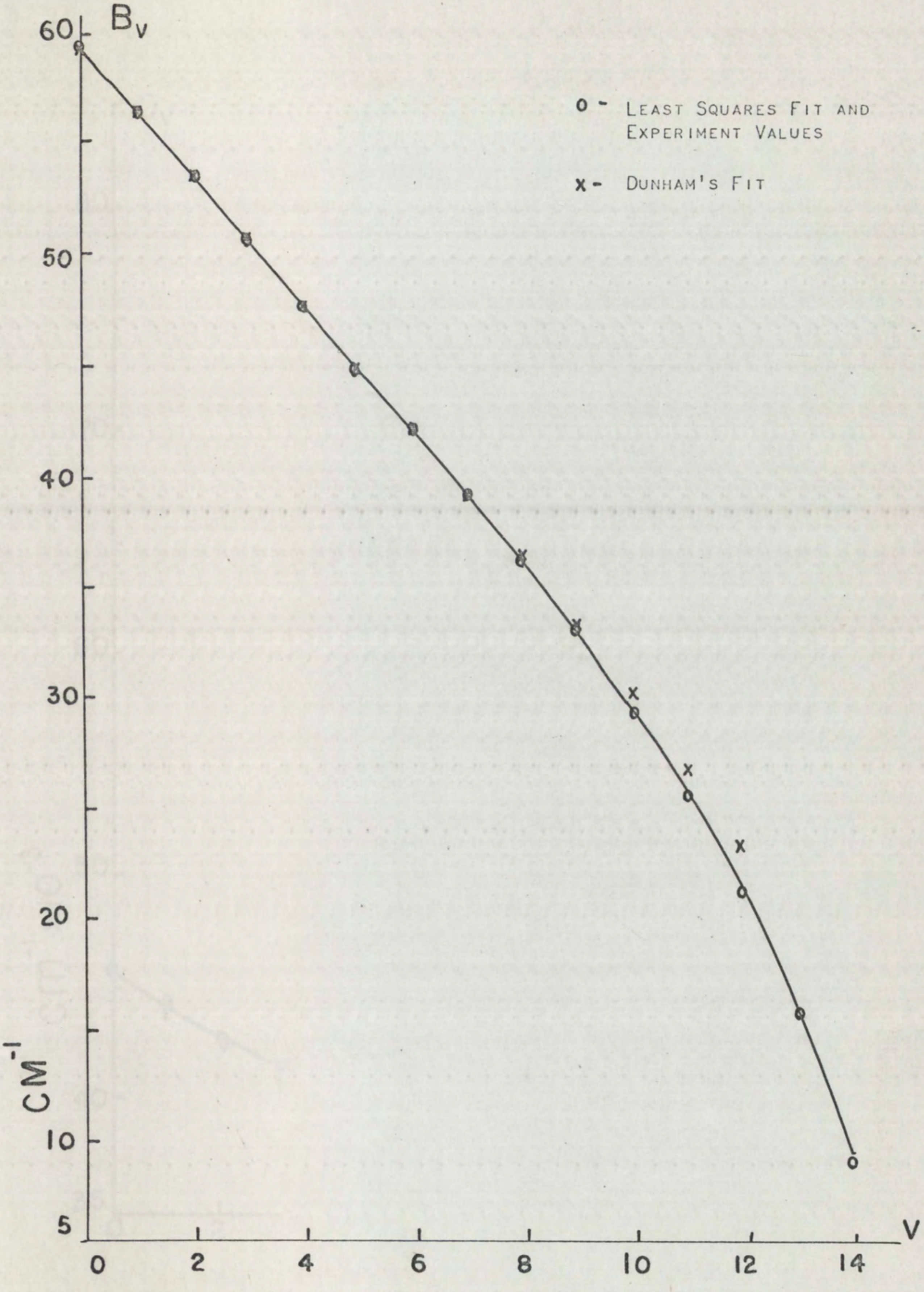

FIGURE 2 (A)

B_V PLOTTED VERSUS V

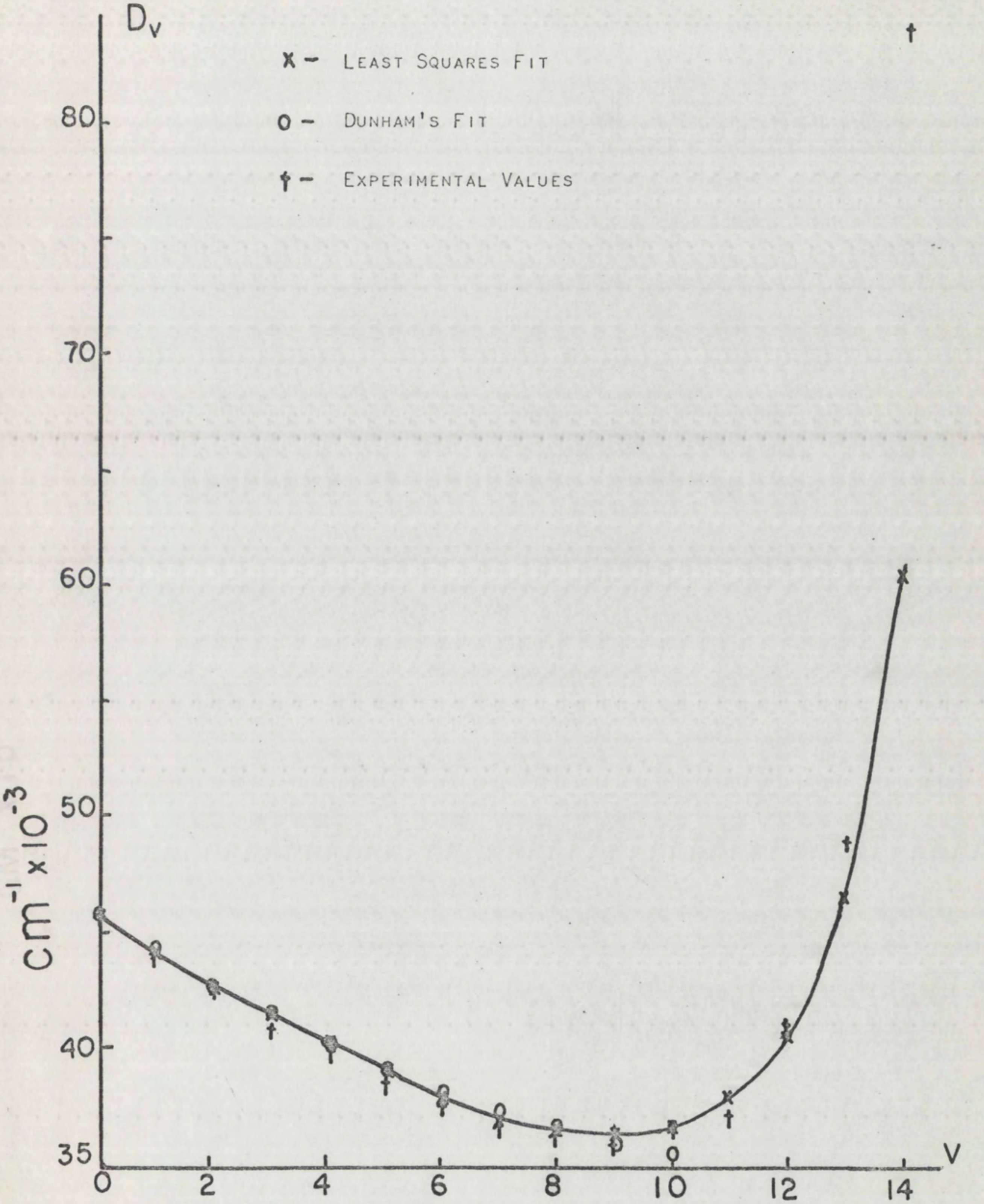

FIGURE 2 (B)

D_v PLOTTED VERSUS v

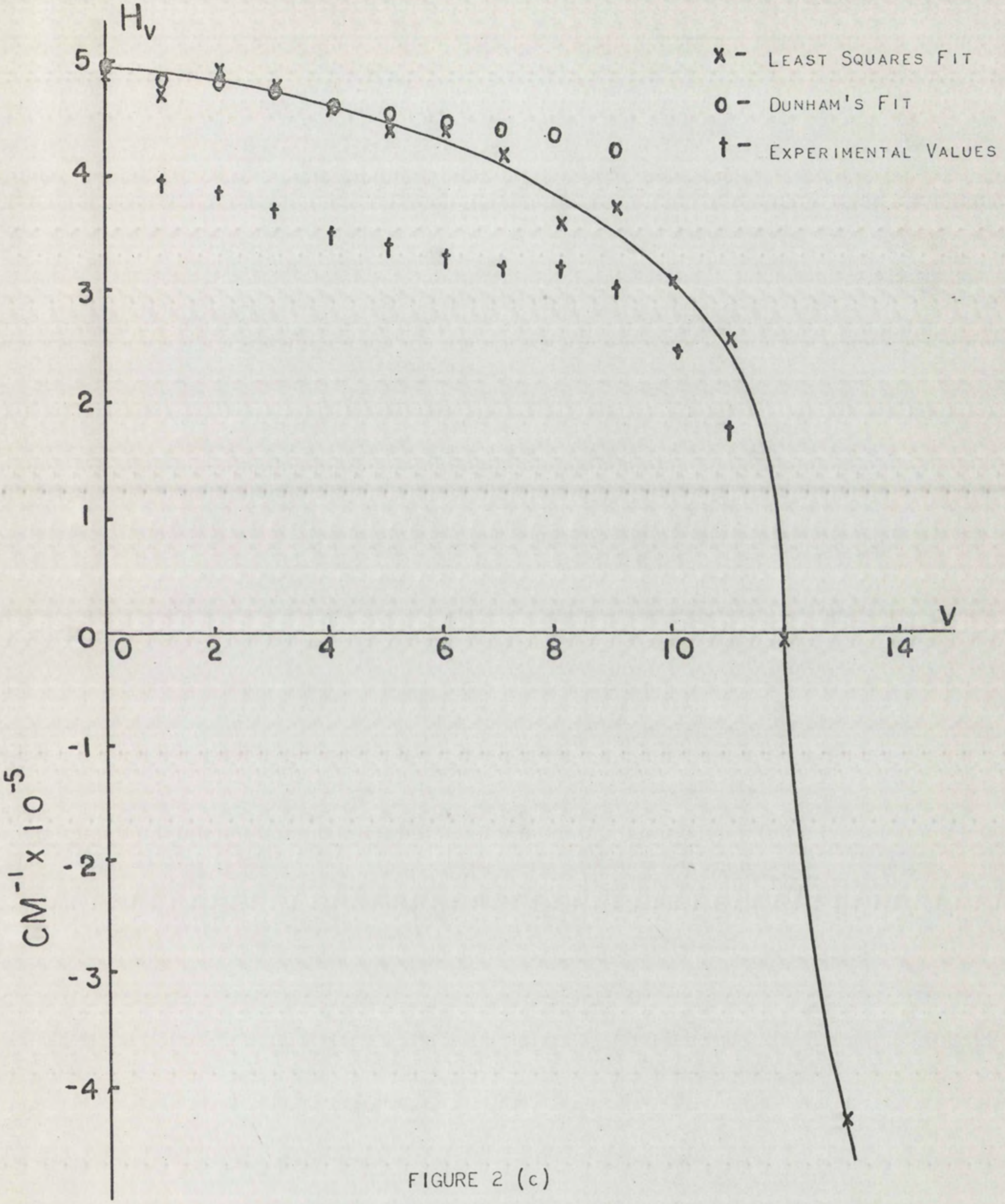

FIGURE 2 (c)

H_v PLOTTED VERSUS V

CHAPTER VIII

SUMMARY

THE PRESENT COMPUTATION BASED UPON THE KW POTENTIAL FOR THE GROUND ELECTRONIC STATE OF H_2 HAS INDICATED GOOD AGREEMENT BETWEEN THE CALCULATED AND OBSERVED SPECTROSCOPIC CONSTANTS. INDEED, THE DUNHAM CONSTANTS BASED ON THE PURE ELECTRONIC ENERGY $E-\frac{1}{R}$ ARE BETTER THAN THOSE BASED ON THE TOTAL POTENTIAL ENERGY E. THE PRESENT VALUES FOR THE SPECTROSCOPIC CONSTANTS CAN BE IMPROVED FURTHER BY DETERMINING THE NUCLEAR-ELECTRONIC AND RELATIVISTIC CORRECTIONS.

THE PRESENT VALUES OF B_V, D_V, BASED ON THE KW POTENTIAL FOR THE GROUND ELECTRONIC STATE OF H_2, ALSO HAVE INDICATED GOOD AGREEMENT BETWEEN THEORY AND EXPERIMENT. HOWEVER, IT IS SEEN THAT THERE IS A LARGE SYSTEMATIC DISCREPANCY OF ABOUT 1×10^{-5} CM-1 BETWEEN THE THEORETICAL AND EXPERIMENTAL H_V'S. THIS DISCREPANCY IN THE H_V VALUES IS BELIEVED TO BE DUE TO THE EXPERIMENTAL ANALYSIS IN WHICH THE I_V VALUES ARE IGNORED.

APPENDIX 1(A) DIFFERENCE TABLE* OF KOLOS-WOLNIEWICZ 80-TERM PURE ELECTRONIC ENERGY

R	$E-\frac{1}{R}$	ΔE	$\Delta^2 E$	$\Delta^3 E$	$\Delta^4 E$	$\Delta^5 E$	$\Delta^6 E$	$\Delta^7 E$
0.6	-2.4363007							
		1662452						
0.8	-2.2700556		-207281					
		1455171		14819				
1.0	-2.1245385		-192461		10006			
		1262710		24826		-10486		
1.2	-1.9982675		-167636		-479		7713	
		1095074		24346		-2773		-5265
1.4	-1.8887601		-143289		-3252		2448	
		951785		21094		-324		
1.6	-1.7935816		-122195		-3576			
		829590		17518				
1.8	-1.7106226		-104677					
		724914						
2.0	-1.6381312							

R AND E ARE A.U.

THE DIFFERENCES ARE A.U. x 10^{-7}

*THE CALCULATIONS ARE DONE ON THE CUMPUTOR WITH DOUBLE-PRECISION.

APPENDIX 1(B) DIFFERENCE TABLE OF KOLOS-WOLNIEWICZ 54-TERM PURE ELECTRONIC ENERGY

R	$E - \frac{1}{R}$	Δ^1E	Δ^2E	Δ^3E	Δ^4E	Δ^5E	Δ^6E	Δ^7E	Δ^8E	Δ^9E	$\Delta^{10}E$
0.4	-2.6202028										
		1839108									
0.6	-2.4362970		-176676								
		1662433		-30601							
0.8	-2.2700487		-207277		45425						
		1455156		148243		-35430					
1.0	-2.1245331		-192452		9996		24959				
		1262704		248199		-10471		-17251			
1.2	-1.9982627		-167633		- 475		7708		11952		
		1095071		24344		-2763		-5298		-8316	
1.4	-1.8887556		-143288		-3338		2410		3637		5762
		951783		21106		-353		-1661		-2553	
1.6	-1.7935773		-122182		-3591		749		1084		
		829601		17516		396		- 577			
1.8	-1.7106172		-104666		-3194		171				
		0724936		14322		568					
2.0	-1.6381236		- 90344		-2626						
		0634592		11696							
2.2	-1.5746645		-78649								
		0555943									
2.4	-1.5190702										

R AND E ARE A.U.

THE DIFFERENCES ARE IN A.U. x 10^{-7}

*THE CALCULATION ARE DONE ON THE COMPUTOR WITH DOUBLE-PRECISION

APPENDIX II. THE USE OF THE STIRLING INTERPOLATION FORMULA TO EVALUATE THE POWER EXPANSION'S CONSTANTS

SUPPOSE THE FUNCTION E(R) IS ANALYTIC AND CAN THEREFORE BE EXPANDED IN THE NEIGHBORHOOD OF A POINT A_0 IN A TAYLOR SERIES OF THE FORM

$$E(R) - \sum_{J=0}^{\infty} \frac{(R-A_0)^J}{J!} \, F\,(J)\,(A_0)$$

$$= \sum_{J=0}^{\infty} c_J (R-A_0)^J$$

SUPPOSE THAT THE VALUES OF E(R) ARE GIVEN TO US FOR A SET OF DISCRETE VALUES OF ITS ARGUMENT -- LET US DENOTE SUCH ABSCISSAE BY $A_J = A_0 + JH$, $J = \pm 1, \pm 2, \ldots$

THEN WE ESTABLISH THE FOLLOWING FORMULAS (REF 8)

$$c_1 = \frac{1}{H}\left(\Delta_0 - \frac{1}{6}\Delta_0^3 + \frac{1}{30}\Delta_0^5 - \frac{1}{140}\Delta_0^7 + \frac{1}{630}\Delta_0^9 - \frac{1}{2772}\Delta_0^{11} + \ldots\right)$$

$$c_2 = \frac{1}{H^2 2!}\left(\Delta_0^2 - \frac{1}{12}\Delta_0^4 + \frac{1}{90}\Delta_0^6 - \frac{1}{560}\Delta_0^8 + \frac{1}{3151}\Delta_0^{10} - \frac{1}{16632}\Delta_0^{12} \ldots\right)$$

$$c_3 = \frac{1}{H^3 3!}\left(\Delta_0^3 - \frac{1}{4}\Delta_0^5 + \frac{7}{120}\Delta_0^7 - \frac{41}{3024}\Delta_0^9 + \frac{479}{151200}\Delta_0^{11} + \ldots\ldots\right)$$

$$c_4 = \frac{1}{H^4 4!}\left(\Delta_0^4 - \frac{1}{6}\Delta_0^6 + \frac{7}{240}\Delta_0^8 - \frac{41}{7560}\Delta_0^{10} + \frac{479}{453600}\Delta_0^{12} + \ldots\ldots\right)$$

$$c_5 = \frac{1}{H^5 5!}\left(\Delta_0^5 - \frac{1}{3}\Delta_0^7 + \frac{13}{144}\Delta_0^9 - \frac{139}{6048}\Delta_0^{11} + \ldots\ldots\right)$$

$$c_6 = \frac{1}{H^6 6!}\left(\Delta_0^6 - \frac{1}{4}\Delta_0^8 + \frac{13}{240}\Delta_0^{10} - \frac{139}{12096}\Delta_0^{12} + \ldots\ldots\right)$$

$$c_7 = \frac{1}{H^7 7!}\left(\Delta_0^7 - \frac{5}{12}\Delta_0^9 + \frac{31}{240}\Delta_0^{11} - \ldots\ldots\right)$$

$$c_8 = \frac{1}{H^8 8!}\left(\Delta_0^8 - \frac{1}{3}\Delta_0^{10} + \frac{31}{360}\Delta_0^{12} - \ldots\ldots\right)$$

$$c_9 = \frac{1}{H^9 9!}\left(\Delta_0^9 - \frac{1}{2}\Delta_0^{11} + \ldots\ldots\right)$$

$$c_{10} = \frac{1}{H^{10} 10!}\left(\Delta_0^{10} - \frac{5}{12}\Delta_0^{12} + \ldots\ldots\right)$$

Where the Δ^{N}_{J}'s denote tabular differences of a given function, abbreviated in accordance with the following scheme:

Function	Differences			
E_{-2}				
	$\Delta^{1}_{-1.5}$			
E_{-1}		Δ^{2}_{-1}		
	$\Delta^{1}_{-0.5}$		$\Delta^{3}_{-0.5}$	
E_{0}		Δ^{2}_{0}		Δ^{4}_{0}
	$\Delta^{1}_{0.5}$		$\Delta^{3}_{0.5}$	
E_{1}		Δ^{2}_{1}		
	$\Delta^{1}_{1.5}$			
E_{2}				

and $\Delta^{2J-1}_{0} = \frac{1}{2}\left\{\Delta^{(2J-1)}_{-0.5} + \Delta^{(2J-1)}_{0.5}\right\}$, where

$E_J = E(A_J)$ The superscripts indicate the order of the respective differences, while the subscripts describe their position with respect to A_J.

Now we want to expand the potential energy about R_E instead of A_0, i.e.,

$$E(R) = E_E + A_0(R-R_E)^2 + A_1(R-R_E)^3 + \ldots \qquad (2.2)$$

By comparing the coefficients of R between equation (2.1) and equation (2.2), we can establish the following relations:

$$A_0 = \frac{1}{H^2}\,(c_2 + 3c_2 s + 6c_4 s^2 + 10c_5 s^3 + 15c_6 s^4 + 21c_7 s^5 + 28c_8 s^6 + 36c_9 s^7 + 45c_{10} s^8 + \ldots)$$

$$A_1 = -\frac{1}{H^3}\,(c_3 + 4c_4 s + 10c_5 s^2 + 20c_6 s^3 + 35c_7 s^4 + 56c_8 s^5 + 84c_9 s^6 + 120c_{10} s^7 + \ldots\ldots)$$

$$A_2 = \frac{1}{H^4}\left(c_4 + 5c_5 s + 15c_6 s^2 + 35c_7 s^3 + 70c_8 s^4 + 126c_9 s^5 + 210c_{10} s^6 + \ldots\ldots\ldots\ldots\right)$$

$$A_3 = \frac{1}{H^5}\left(c_5 + 6c_6 s + 21c_7 s^2 + 56c_8 s^3 + \ldots\ldots\ldots\ldots\right)$$

$$A_4 = \frac{1}{H^6}\left(c_6 + 7c_7 s + 28c_8 s^2 + \ldots\ldots\ldots\ldots\right)$$

$$A_5 = \frac{1}{H^7}\left(c_7 + 8c_8 s + 36c_9 s^2 + \ldots\ldots\ldots\ldots\right)$$

$$A_6 = \frac{1}{H^8}\left(c_8 + 9c_9 s + \ldots\ldots\ldots\ldots\right)$$

WITH $s = \frac{R_E - A_0}{H}$

APPENDIX III. Virial Theorem

The virial theorem states (Ref 11),

$$(K.E.)_{AV} = -\frac{1}{2}\left(\Sigma_i x_i F_i \right) AV$$

Here the average is taken over the wave function for the stationary state of any system, and K. E. is the Kinetic energy. The coordinates of the system are denoted by x_i and F_i is the component of force arising both from internal and external sources.

Consider a molecular system acting under the internal coulomb forces and external applied forces, Fexx.. The virial theorem gives

$$(K.E.)_{AV} = -\frac{1}{2}(P.E.)_{AV} - \frac{1}{2}\left(x_i F_{EXT_i}\right)_{AV} \qquad (3.1)$$

In the Born-Oppenheimer method, the external forces act only on the nuclei, not directly on the electrons; it is only the nuclei which must be held constant. Hence the summation in equation (3.1) has to be extended only over the nuclear coordinates.

We let the capital letters Z_i, according to Born-Oppenheimer approximation, is $\partial E/\partial X_i$. If there is to be an external force balancing this and thereby holding the nuclei fixed, it must be given by $F_{EXT_i} = \partial E/\partial X_i$

Then in place of equation (3.1) we have

$$(K.E.)_{AV} = -\frac{1}{2}(P.E.) - \frac{1}{2}\left(\sum_i X_i\,\partial E/\partial X\right)_{AV} \ldots \qquad (3.2)$$

Applying this result to the case of the diatomic molecule, the summation in equation (3.2) must be over the coordinates of the two nuclei. The energy E is a function of the internuclear distance

$$R = ((X_A - X_B)^2 + (Y_A - Y_B)^2 + (Z_A - Z_B)^2)^{1/2}$$

where X_A, Y_A, Z_A are the coordinates of the first nucleus, and X_B, Y_B, Z_B of the second. We have

$$\frac{\partial E}{\partial X_A} = \frac{X_A - X_B}{R}\,\frac{dE_P}{dR} \qquad \frac{\partial E}{\partial X_B} = -\frac{X_A - X_B}{R}\,\frac{dE_P}{dR}$$

with the corresponding equation for the Y and Z components.

Equation (3.2) becomes

$$(K.E.)_{AV} = -\frac{1}{2}(P.E.)_{AV} - \frac{1}{2}R\,dE/dR$$

and since

$$(K.E.)_{AV} + (P.E.)_{AV} = E,$$

we have, at last

$$(P.E.)_{AV} = 2E + R\,\frac{dE}{dR},$$

or

$$\frac{dE}{dR} = \left(\frac{V}{2E} - 1\right)\frac{2E}{R}.$$

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