

Improved Theoretical Ground-State Energy of the Hydrogen Molecule*

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The potential-energy curve for the electronic ground state of the hydrogen molecule has been calculated for $1 \leq R \leq 3.2$ a.u. in double precision and using a 100-term expansion for the electronic wavefunction. Accuracy of the previously computed diagonal corrections for nuclear motion has been tested. The vibrational equation has been solved for all isotopes of the hydrogen molecule and for the rotational quantum number $J \leq 10$. The calculated adiabatic dissociation energy of H_2 , corrected for relativistic and radiative effects, is by 3.8 cm^{-1} larger than the experimental value, hence the theoretical total energy is by the same amount lower than the experimental value. The calculated vibrational quanta for H_2 are by $0.5\text{--}0.9 \text{ cm}^{-1}$ larger than the experimental ones.

I. INTRODUCTION

Being a two-electron system the hydrogen molecule is, from the theoretical point of view, in an exceptional position. The Schrödinger equation for H_2 can be solved accurately and even the higher-order corrections can be calculated. Since for the hydrogen molecule accurate experimental data can also be obtained, a possibility exists, similarly as for the helium atom, to confront the basic theory with experiment.

The most accurate theoretical results obtained for the ground-state potential-energy curve of the hydrogen molecule are those given in Refs. 1 and 2 (referred to hereafter as I and II, respectively), and they result in a dissociation energy³ which corrected for the relativistic⁴ and radiative⁵ effects is $D_0 = 36\,117.3 \text{ cm}^{-1}$. This result is in disagreement with the experimental value $D_0 = 36\,113.6 \pm 0.3 \text{ cm}^{-1}$ obtained by Herzberg and Monfils.⁶ Since the theoretical result was obtained in the adiabatic approximation, the discrepancy presents a serious problem: A larger value of the dissociation energy means that the theoretical total energy of H_2 is lower than the experimental one. However, it is well known that the adiabatic approach gives an upper bound to the total energy and therefore the theoretical and experimental results are inconsistent.

Although the discrepancy is one order of magnitude larger than the experimental error, it appears only in the sixth significant figure of the total energy. Since the latter was calculated in single precision (eight significant figures) it was conceivable that part, if not all, of the discrepancy was due to rounding errors and numerical inaccuracies. To clarify this problem a double

precision calculation has been made and the results are reported below.

II. METHOD

The calculations were carried out in the adiabatic approximation.^{1,7} This corresponds to assuming the wavefunction in the form of the product

$$\Psi(\mathbf{r}, R) = \psi(\mathbf{r}; R)\chi(R), \quad (1)$$

where $\mathbf{r}$ denotes all electronic coordinates and R the internuclear distance. The function $\psi(\mathbf{r}; R)$, where R is treated as a parameter, is obtained by solving the electronic Schrödinger equation resulting from the complete equation if infinite nuclear masses are assumed. To solve this equation the variational method was employed, and $\psi(\mathbf{r}; R)$ was put forward as an expansion in terms of the elliptic coordinates and of the inter-electronic distance. The basis set was identical with that used in I. Assuming (1), one gets from the complete Schrödinger equation a second-order differential equation for the vibrational function $\chi(R)$. The corresponding eigenvalue can be shown⁸ to be identical with the expectation value of the complete four-particle Hamiltonian calculated with (1). Hence it represents an *upper bound* to the true eigenvalue of the Hamiltonian. In the present work the equation for $\chi(R)$ was solved numerically using the Cooley method.⁹ This method is known¹⁰ to give results accurate practically to as many figures as used in the computation. Therefore, it is not necessary to work in double precision when solving the vibrational equation. The only part of the computation that might be seriously affected by rounding errors is that leading to the potential-energy curve, and therefore only these calculations have been performed in double precision.

The calculation of the matrix elements was carried out in a way completely analogous to that used in I. First the $\phi_{n\bar{n}}^{Ml}$ integrals for $M=0$ were computed by numerical integration using Simpson's rule. For $M=1$,

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¹ W. Kołos and L. Wolniewicz, *J. Chem. Phys.* **41**, 3663 (1964).

² W. Kołos and L. Wolniewicz, *J. Chem. Phys.* **43**, 2429 (1965).

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⁴ W. Kołos and L. Wolniewicz, *J. Chem. Phys.* **41**, 3674 (1964).

⁵ J. D. Garcia, *Phys. Rev.* **147**, 66 (1966).

⁶ G. Herzberg and A. Monfils, *J. Mol. Spectry.* **5**, 482 (1960).

⁷ W. Kołos and L. Wolniewicz, *Rev. Mod. Phys.* **35**, 473 (1963).

⁸ See, e.g., Ref. 3.

⁹ J. W. Cooley, *Math. Computation* **15**, 363 (1961).

¹⁰ See, e.g., W. Kołos and L. Wolniewicz, "Vibrational and Rotational Energies for the $B^1\Sigma_u^+$, $C^1\Pi_u$, and $a^3\Sigma_g^+$ States of the Hydrogen Molecule," *J. Chem. Phys.* (to be published).

TABLE I. Clamped nuclei energy of H₂.^a

No. of terms	No. of integration points	R (a.u.)	E (a.u.)	D (cm ⁻¹)	$V/2E$
80	110	1.4011	-1.1744746	38 292.7	
80	150	1.4011	-1.174474657624	38 292.75903	
80	250	1.4011	-1.174474657935	38 292.75910	
80	350	1.4011	-1.174474657970	38 292.75911	
100	350	1.4011	-1.174474982924	38 292.830427	
100	500	1.4011	-1.177444982931	38 292.830428	
100	500	1.401075	-1.17447498301568	38 292.83044693	1.00000074423
100	500	1.401076	-1.17447498301674	38 292.83044717	1.00000052389
100	500	1.401077	-1.17447498301743	38 292.83044732	1.00000030355
100	500	1.401078	-1.17447498301776	38 292.83044739	1.00000008320
100	500	1.401079	-1.17447498301771	38 292.83044738	0.99999986286
100	500	1.401080	-1.17447498301730	38 292.83044729	0.99999964252

^a 1 a.u. of energy = 219 474.62 cm⁻¹.

2, 3 they were obtained by applying a recurrence relation. From the ϕ_{nn}^{Ml} integrals the $I_{rs\bar{r}\bar{s}}^{\mu}$ and $M_{rs\bar{r}\bar{s}}^{\mu}$ integrals were evaluated, and these were used in the calculation of the required matrix elements.

The numerical integration of ϕ_{nn}^{Ml} is the only approximation involved in the calculation of the expectation value of the Hamiltonian, since the rest of the calculation is purely algebraic. Therefore, to get insight into the dependence of the final energy on the accuracy of ϕ_{nn}^{Ml} , the program has been provided with an option to vary the number of integration points, up to 500, in the evaluation of ϕ_{nn}^{Ml} .

The matrix elements needed for the diagonal nuclear-motion corrections, when expressed in terms of the $I_{rs\bar{r}\bar{s}}^{\mu}$ and $M_{rs\bar{r}\bar{s}}^{\mu}$ integrals, are given by rather lengthy formulas. To double check the previous program, those matrices which were not symmetrical in I have been now symmetrized yielding different formulas for the matrix elements, and these formulas were used in the calculation.

III. RESULTS AND DISCUSSION

A. Potential-Energy Curve

Several test runs have been made to check the accuracy of the calculations and the most important results are given in Table I. In the first row we give, for comparison, the previous results obtained in single precision and with 110 integration points. The following three rows show the results obtained in double precision with the identical wavefunction and a varying number of integration points. In the next two rows we list the energies resulting from a more flexible 100-term wavefunction. The last six rows show the change in the energy caused by variation of the internuclear distance.

The results listed in Table I indicate that (1) the number of points used in the numerical integration was sufficient to yield accurate results; (2) not very significant, although not negligible, improvement of the energy is obtained by making the wavefunction more flexible.

Using the virial theorem and the values of $V/2E$ given in Table I one gets by linear interpolation the equilibrium internuclear distance $R_e = 1.4010784$ a.u. The accuracy of the diagonalization is illustrated by the fact that a direct quadratic interpolation of the energy, for which a 15-figure accuracy is needed, gives the same value of R_e .

The same 80- and 100-term wavefunctions were used to calculate the energy for several other values of the internuclear distance. For the exponent α in the wavefunctions the values published in I were used (for $1 \leq R \leq 2$ from Table II and for $R > 2$ from Table III) and the numerical integrations were carried out with 350 points. The results are shown in Table II, where for each R the upper number gives the 100-term result and the lower one corresponds to 80 terms in the wavefunction. If, for a particular R , only one set of numbers is given, it represents the 100-term results. In the last two columns we give the improvement of the energy [$D(100) - D(80)$ in cm⁻¹] obtained by adding 20 terms to the 80-term wavefunction, and the improvement of the energy obtained in the present 100-term calculation over the best previous results [$D(100) - D_{old}$ in cm⁻¹]. It is seen that the previous results for $1 \leq R \leq 2$ were quite accurate except for $R = 1.6$ where apparently a machine error occurred in the previous calculation. This has already been pointed out by Beckel and Sattler.¹¹

In the previous single precision calculation reported in I and II the 80-term wavefunction was used only up to $R = 2.0$ a.u. since for larger values of the internuclear distance the energy seemed to be affected by rounding errors. For larger R , a wavefunction with a smaller number of terms but with an additional nonlinear parameter was used. In double precision, no problems connected with rounding have been encountered and up to $R = 2.8$ the single-exponent 80-term wavefunction was still better than the previous two-exponent 54-term wavefunction. However, at $R > 3.2$

¹¹ C. L. Beckel and J. P. Sattler, J. Mol. Spectry, **20**, 153 (1966).

TABLE II. Ground-state energies for H_2 calculated in double precision.^a

R	E	$V/2E$	D	$D(100)$ $-D(80)$	$D(100)$ $-D_{old}$
1.0	-1.12453881 -1.12453864	1.14337569 1.14337609	27 333.11 27 333.07	0.04	0.1
1.2	-1.16493435 -1.16493411	1.05517553 1.05517593	36 198.90 36 198.85	0.05	0
1.3	-1.17234623 -1.17234596	1.02477845 1.02477882	37 825.62 37 825.56	0.06	0
1.39	-1.17445199	1.00247242	38 287.78		0.1
1.4	-1.17447477	1.00023825	38 292.78		0.1
1.4011	-1.17447498 -1.17447466	0.99999523 0.99999562	38 292.83 38 292.76	0.07	0.1
1.41	-1.17446041	0.99804848	38 289.63		0.1
1.5	-1.17285408 -1.17285370	0.98017172 0.98017206	37 937.08 37 937.00	0.08	0.1
1.6	-1.16858212 -1.16858164	0.96363860 0.96363874	36 999.50 36 999.39	0.11	0.5
1.8	-1.15506752 -1.15506694	0.93870361 0.93870376	34 033.38 34 033.26	0.12	0.1
2.0	-1.13813155 -1.13813078	0.92198243 0.92198235	30 316.37 30 316.20	0.17	0.1
2.2	-1.12013035 -1.12012903	0.91150053 0.91150084	26 365.56 26 365.27	0.29	1.6
2.4	-1.10242011 -1.10241799	0.90601982 0.90602039	22 478.61 22 478.15	0.46	1.6
2.6	-1.08578740 -1.08578400	0.90468045 0.90468139	18 828.16 18 827.41	0.75	1.4
2.8	-1.07067758 -1.07067254	0.90679365 0.90679401	15 511.93 15 510.83	1.10	1.6
3.0	-1.05731738 -1.05730948	0.91172200 0.91172216	12 579.71 12 577.98	1.73	1.2
3.2	-1.04578647 -1.04577476	0.91880634 0.91880455	10 048.97 10 046.40	2.57	0.7

^a R and E in atomic units; D and the differences in cm^{-1} .

a.u. the latter becomes superior even to the 100-term single-exponent wavefunction.

It is seen from Table II, especially in connection with the previous results, that around the equilibrium the energy has almost converged and most probably an extension of the basis set would not give any significant improvement. However, it is also seen that at $R \approx 3$ a more extensive basis set, or a set carefully selected for this particular region, might improve the energy by at least a sizable fraction of a cm^{-1} .

As mentioned in the previous section, the diagonal corrections for nuclear motion have been recalculated in double precision and using an algorithm different from that employed in I. For $R=1.4011$ a.u., the previous results have been reproduced and by extending the expansion length from 54 to 66 terms the value of the corrections decreased by 0.013 cm^{-1} lowering the adiabatic potential-energy curve by the same amount. For $R=2.2$ a.u., the decrease amounted to 0.014 cm^{-1} . Since this is a smaller change than a possible inaccuracy in our clamped nuclei energy caused by incompleteness of the basis set, we concluded that the accuracy of the previously calculated corrections was satisfactory.

B. Vibrational Levels

To calculate the vibrational levels the corresponding one-dimensional Schrödinger equation was solved nu-

merically using the Cooley method.⁹ For $1 \leq R \leq 3.2$ the new energies from Table II were used. For smaller and larger values of R the single precision results² were employed. The previously calculated¹ diagonal corrections for nuclear motion were also added to the clamped nuclei energies to yield the adiabatic potential. For $R > 3.6$ the corrections were extrapolated graphically which seems to give more realistic results than a linear extrapolation. The following values were assumed: $\Delta D_{\text{nuc}} = 5.5, 3.7, 1.5, 0.5$, and 0 cm^{-1} for $R = 3.8, 4.0, 4.3, 4.6$, and 5.0 a.u., respectively. Incidentally, it may be pointed out that any reasonable extrapolation of the corrections has been found not to affect the eigenvalues for $v \leq 9$.

Since for $1 \leq R \leq 3.2$ the double-precision calculation was carried out for only 17 values of R , and not for 29 as in single precision, an additional test has been made. It consisted in solving the vibrational equation with the old potential in which, however, the 12 values not calculated in double precision were omitted. The resulting eigenvalues differed from those calculated with the complete potential by not more than 2.10^{-7} a.u. ($= 0.4 \text{ cm}^{-1}$). This shows that the interpolation method employed in the calculation works quite satisfactorily.

The dissociation energies of H_2 for all bound vibrational levels are listed in Table III for several values of the rotational quantum number ($0 \leq J \leq 10$). For other isotopes the dissociation energies only for $J=0$

TABLE III. Dissociation energies (in cm⁻¹) of H₂ from various vibrational (*v*) and rotational (*J*) states.

<i>v</i> \ <i>J</i>	0	1	2	3	4	5	6	7	8	9	10
0	36 118.09	35 999.60	35 763.70	35 412.53	34 949.22	34 377.79	33 703.04	32 930.42	32 065.88	31 115.80	30 086.77
1	31 956.03	31 843.45	31 619.34	31 285.77	30 845.76	30 303.18	29 662.68	28 929.50	28 109.39	27 208.47	26 233.11
2	28 029.39	27 922.59	27 710.01	27 393.65	26 976.44	26 462.11	25 855.14	25 160.61	24 384.06	23 531.41	22 608.79
3	24 333.25	24 232.15	24 030.93	23 731.53	23 336.77	22 850.30	22 276.42	21 620.05	20 886.56	20 081.66	19 211.28
4	20 864.57	20 769.12	20 579.18	20 296.62	19 924.18	19 465.39	18 924.44	18 306.08	17 615.52	16 858.31	16 040.21
5	17 622.33	17 532.55	17 353.90	17 088.23	16 738.18	16 307.19	15 799.32	15 219.21	14 571.94	13 862.89	13 097.72
6	14 607.84	14 523.79	14 356.59	14 108.03	13 780.70	13 377.94	12 903.73	12 362.59	11 759.49	11 099.73	10 388.86
7	11 825.02	11 746.85	11 591.40	11 360.42	11 056.44	10 682.75	10 243.25	9 742.40	9 185.09	8 576.59	7 922.42
8	9 281.13	9 209.09	9 065.90	8 853.26	8 573.68	8 230.42	7 827.33	7 368.87	6 859.92	6 305.76	5 712.00
9	6 987.48	6 921.95	6 791.75	6 598.61	6 345.02	6 034.24	5 670.16	5 257.27	4 800.54	4 305.42	3 777.71
10	4 960.67	4 902.19	4 786.11	4 614.15	4 388.87	4 113.56	3 792.24	3 429.53	3 030.67	2 601.44	2 148.20
11	3 223.54	3 172.88	3 072.47	2 924.11	2 730.45	2 494.99	2 221.97	1 916.41	1 584.10	1 231.65	866.67
12	1 808.00	1 766.32	1 683.93	1 562.80	1 405.83	1 216.89	1 000.85	763.61	512.34	255.94	6.23
13	759.02	728.11	667.42	579.28	467.17	335.97	192.15	44.77			
14	138.86	121.81	89.38	45.21							

TABLE IV. Dissociation energies (in cm⁻¹) for nonrotational (*J*=0) states of various isotopes of the hydrogen molecule.*

<i>v</i>	D ₂	T ₂	HD	HT	DT
0	36 748.69	37 028.89	36 405.92	36 512.35	36 881.63
1	33 754.72	34 564.16	32 773.09	33 076.86	34 138.00
2	30 879.90	32 179.44	29 317.76	29 799.53	31 493.98
3	28 122.11	29 873.46	26 036.43	26 677.31	28 947.89
4	25 479.71	27 645.22	22 926.63	23 708.00	26 498.41
5	22 951.50	25 493.86	19 986.97	20 890.20	24 144.50
6	20 536.76	23 418.77	17 217.25	18 223.44	21 885.44
7	18 235.31	21 419.50	14 618.65	15 708.32	19 720.86
8	16 047.58	19 495.89	12 193.79	13 346.51	17 650.85
9	13 974.60	17 648.01	9 947.25	11 141.05	15 675.83
10	12 018.14	15 876.22	7 885.72	9 096.65	13 796.70
11	10 180.90	14 181.12	6 018.75	7 219.77	12 014.91
12	8 466.42	12 563.67	4 359.14	5 519.53	10 332.54
13	6 879.60	11 025.27	2 923.67	4 007.46	8 752.22
14	5 426.75	9 567.63	1 734.91	2 698.86	7 277.55
15	4 115.52	8 192.96	823.33	1 613.65	5 913.17
16	2 955.93	6 904.20	228.97	778.59	4 664.43
17	1 960.26	5 704.79		227.90	3 538.33
18	1 144.61	4 598.79			2 543.25
19	529.01	3 591.33			1 689.70
20	138.42	2 688.40			991.01
21		1 897.34			463.24
22		1 227.26			126.21
23		689.05			
24		295.51			
25		62.67			

* The following nuclear masses were used: $M_p = 1836.12$, $M_d = 3670.42$, $M_t = 5496.74$.

are given¹² in Table IV. In Table V the theoretical values of the vibrational quanta are presented and the discrepancies with the experimental results are also shown. Finally, in Table VI we give the expectation values of R^{-2} which are directly related to the rotational constants.

TABLE V. Calculated vibrational quanta (in cm⁻¹) and discrepancies with experiment ($\Delta = \Delta G_{\text{theoret}} - \Delta G_{\text{exptl}}$).

<i>v</i>	H ₂		HD		D ₂	
	$\Delta G(v)$	Δ	$\Delta G(v)$	Δ	$\Delta G(v)$	Δ
-1/2	2179.69	0.42	1890.62	0.2	1546.62	-0.4
0	4162.06	0.92	3632.84	0.6	2993.96	0.2
1	3926.65	0.67	3455.33	0.6	2874.82	1.2
2	3696.14	0.90	3281.33	1.5	2757.79	0.5
3	3468.68	0.67	3109.80	2.7	2642.40	0.9
4	3242.24	0.68	2939.66	0.3	2528.21	-0.5
5	3014.50	0.77	2769.72	0.0	2414.75	0.9
6	2782.82	0.64	2598.60	4.3	2301.45	0.3
7	2543.89	0.75	2424.86	-4.2	2187.72	1.3
8	2293.65	0.69	2246.54	-2.4	2072.98	0.2
9	2026.81	0.55	2061.53	4.6	1956.46	1.2
10	1737.14	0.48	1866.97	-1.9	1837.24	-0.3
11	1415.54	0.56	1659.61	2.2	1714.48	1.0
12	1048.98	-0.20	1435.47	-0.4	1586.83	-0.3
13	620.16	-1.80	1188.76	0.2	1452.84	0.0
14			911.57	-2.0	1311.23	-0.2
15			594.36		1159.59	0.4
16					995.67	1.0
17					815.66	0.2
18					615.60	-0.1
19					390.59	7.4

¹² The dissociation energies for isotopes other than H₂ and for $0 \leq J \leq 10$ will be published in the Technical Report (1967) of this Laboratory.

TABLE VI. Expectation values of R^{-2} (in atomic units) for various isotopes of the hydrogen molecule.

v	H ₂	D ₂	T ₂	HD	HT	DT
0	0.4964227	0.5002768	0.5019664	0.4981907	0.4988406	0.5010802
1	0.4716615	0.4826216	0.4874864	0.4766667	0.4785161	0.4849296
2	0.4474458	0.4652762	0.4732231	0.4555773	0.4585850	0.4690441
3	0.4235996	0.4481799	0.4591457	0.4348099	0.4389576	0.4533780
4	0.3999337	0.4312728	0.4452206	0.4142480	0.4195333	0.4378849
5	0.3762253	0.4144857	0.4314131	0.3937579	0.4002042	0.4225140
6	0.3522131	0.3977507	0.4176872	0.3731860	0.3808482	0.4072160
7	0.3275902	0.3809793	0.4040055	0.3523634	0.3613262	0.3919291
8	0.3019336	0.3640856	0.3903203	0.3310808	0.3414832	0.3765874
9	0.2747283	0.3469714	0.3765872	0.3090726	0.3211117	0.3611246
10	0.2452425	0.3295036	0.3627562	0.2860317	0.2999835	0.3454623
11	0.2125416	0.3115419	0.3487750	0.2615020	0.2777843	0.3294901
12	0.1750356	0.2929242	0.3345614	0.2350059	0.2541232	0.3131118
13	0.1300893	0.2733959	0.3200492	0.2057448	0.2285495	0.2961996
14	0.0724396	0.2527331	0.3051596	0.1726324	0.2003232	0.2785627
15		0.2305967	0.2897750	0.1338081	0.1684446	0.2600316
16		0.2065337	0.2737433	0.0861109	0.1312751	0.2403933
17		0.1799327	0.2569845		0.0859912	0.2193026
18		0.1498389	0.2392775			0.1964155
19		0.1149466	0.2204012			0.1711123
20		0.0724753	0.2001135			0.1426350
21			0.1779678			0.1098310
22			0.1534741			0.0702327
23			0.1259076			
24			0.0940930			
25			0.0552815			

The constants have been measured¹³⁻¹⁶ for H₂, HD, and D₂. For H₂ the calculated values of $\langle R^{-2} \rangle$ agree with the experimental ones up to four decimal places or better. For HD and D₂ they agree up to three decimal places; however, the experimental values given by different authors also disagree among themselves in the third decimal figure.

For some of the isotopes, additional vibrational levels located just below the dissociation limit were also obtained. They are given separately in Table VII, since their accuracy and even their existence are not quite certain. To obtain these levels, the potential-energy curve was extended by calculating the energies and derivatives for $R=10.5$, 11.0 (1.0), 15.0 a.u. from the formula

$$E = -1 + b(B_6 R^{-6} + B_8 R^{-8} + B_{10} R^{-10}).$$

The B_n constants were taken from a perturbation calculation¹⁷ and b was adjusted to give for $R=10$ the energy coinciding with the variational result. To check how sensitive the vibrational energies are to the form of the potential assumed for $R>10$, a calculation was also made in which the interaction energy was represented by a single term $B_{10}' R^{-10}$. The resulting energies did not differ by more than 0.1 cm^{-1} from those given in Table VII.

By extrapolating the experimental results, Takezawa *et al.*¹⁴ concluded that for D₂ the highest vibrational

state should be $v=21$; for HD the existence of the $v=17$ state, although less certain, could not be excluded.

It is likely that the nonadiabatic effects would make the levels listed in Table VII significantly more stable. However, on the other hand, the location of these states is determined mainly by the outer section of the potential-energy curve which is less accurate than in the vicinity of the equilibrium and for which the nuclear-motion corrections have not been computed. Therefore, the existence of these states, although very probable, does not seem to be conclusively established.

The most important conclusion of the present work concerns the ground-state dissociation energy of H₂. For $1 \leq R \leq 3.2$ the potential used in the calculation was (a) free from rounding errors; (b) improved by the use of 100- rather than 80-term wavefunction. The region $1 \leq R \leq 3.2$ is sufficient to determine unambiguously the energies of the seven lowest vibrational levels. Therefore, the energies of the seven lowest vibrational levels would not be affected by any change of the potential for $R>3.2$, and in consequence they also do not depend on the extrapolation method assumed for the diagonal nuclear-motion corrections.

TABLE VII. Highest vibrational levels for some isotopes of the hydrogen molecule.

Molecule	v	E (a.u.)	D_v (cm ⁻¹)	$\langle R \rangle$ (a.u.)	$\langle R^{-2} \rangle$ (a.u.)
D ₂	21	-1.0000051	1.12	9.768	0.0153
HD	17	-1.0000117	2.57	9.008	0.0194
HT	18	-1.0000230	5.05	8.272	0.0235
DT	23	-1.0000090	1.98	9.205	0.0175

¹³ G. Herzberg and L. I. Howe, Can. J. Phys. **37**, 636 (1959).

¹⁴ S. Takezawa, F. R. Innes, and Y. Tanaka, J. Chem. Phys. **46**, 4555 (1967).

¹⁵ K. Mie, Z. Physik **91**, 475 (1934).

¹⁶ C. K. Jeppesen, Phys. Rev. **49**, 797 (1936).

¹⁷ W. Kolos, Intern. J. Quantum Chem. **1**, 169 (1967).

As mentioned above, it does not seem very probable that in the close vicinity of the equilibrium internuclear distance the clamped nuclei energy could be significantly improved by using a more flexible wavefunction. On the other hand, there is not much doubt that, e.g., at $2.5 \leq R \leq 3.0$, an extension of the expansion length could lower the clamped nuclei energy by a sizable fraction of a cm^{-1} . However, the energies of the two lowest vibrational levels of H_2 are not affected by any changes of the potential for $R > 2.2$. Therefore, any improvement of the electronic wavefunction is not likely to change the energies of the two lowest vibrational levels by more than a small fraction of a cm^{-1} .

The calculated energies of H_2 disagree with the experimental results in two respects: (1) The theoretical ground-state dissociation energy is larger than the experimental value; (2) the theoretical vibrational quanta are larger than the experimental ones. We think that the nature of the disagreement is quite different in these two cases.

Let us first discuss the ground-state dissociation energy. The adiabatic ground-state energy represents an upper bound to the exact lowest eigenvalue of the complete four-particle Hamiltonian. Therefore, if by making the electronic wavefunction still more flexible the energy could be improved, it would lower the total energy and hence it would still increase the dissociation energy. If we went beyond the adiabatic approximation, this would correspond to introducing more freedom into the wavefunction, and hence it would also lower the total energy, the lowering being of the order of $(m/\mu)^2$. For instance, in the case of the H_2^+ ion the nonadiabatic ground-state energy has been found to be about 0.1 cm^{-1} lower than the adiabatic value.¹⁸ The fact that in a previous nonadiabatic calculation⁴ a higher value of the total energy was obtained than in the adiabatic approach indicates only that the nonadiabatic energy had not yet converged to the proper eigenvalue.

The energies given in Tables III–V are the non-relativistic values; however, they can be readily corrected for the relativistic and radiative effects. The relativistic corrections, calculated in the Pauli approximation, when averaged over the zero-point vibrations,⁴ change the dissociation energy by $\Delta D_{\text{rel}} = -0.5 \text{ cm}^{-1}$. The radiative corrections contribute⁵ to the dissociation energy $\Delta D_{\text{rad}} = -0.2 \text{ cm}^{-1}$. The latter is not a value averaged over the zero-point vibrations; however, the effect of averaging would be probably negligible, although it might be not completely negligible for higher vibrational states. It may be worth mentioning that the exact upper limit to the radiative corrections has also been calculated,³ and by using it one gets $\Delta D_{\text{rad}} > -0.36 \text{ cm}^{-1}$. If the nonrelativistic adiabatic dissociation energy from Table III, $D_0 = 36\,118.1 \text{ cm}^{-1}$, is corrected for the relativistic and radiative effects,

one gets the final theoretical value $D_0 = 36\,117.4 \text{ cm}^{-1}$ which is by 3.8 cm^{-1} larger than the experimental value. Hence, the theoretical total energy is by the same amount *lower* than the experimental one.

The experimental dissociation energy was obtained⁶ by measuring the far ultraviolet absorption edges corresponding to dissociation of the molecule from the electronic ground state via the $B' \, ^1\Sigma^+$ excited state; the dissociation occurring with different rotational quantum numbers. Although an extrapolation is needed to $J=0$ for the upper state to get the dissociation energy, it has been shown¹⁷ that for H_2 the extrapolation does not throw any shadow on the experimental results.

Let us now discuss the second type of discrepancy between the theoretical and experimental energies, viz., the fact that the theoretical vibrational quanta are larger than the experimental ones. Our 100-term wavefunction has been selected from a larger basis set. The selection was made for the equilibrium internuclear distance and using the energy criterion for retaining or discarding certain terms. Therefore, the outer sections of the potential calculated with this wavefunction have a larger error than the region close to the equilibrium. This kind of error, obviously, raises the vibrational levels and also the values of the vibrational quanta. Hence, it may account for part of the discussed discrepancy. However, we have mentioned before that any improvement of the wavefunction is not likely to change appreciably the potential for $R < 2.2$. Hence it is also not likely to change the theoretical value of $\Delta G(0)$ and a different reason for the discrepancy with experiment must exist.

General arguments and numerical results obtained for the H_2^+ ion strongly suggest that at least part of the discrepancy is due to the adiabatic approximation. In the case of the nonrotational Σ state the nonadiabatic effects are caused by interaction with other, in this case excited, Σ states. The energy difference between the interacting states decreases with increasing vibrational excitation in the ground electronic state. Hence the interaction energy is likely to increase and the lowering of the higher vibrational states caused by the nonadiabatic effects may be larger than that in the lower states. If this is the case, a nonadiabatic calculation should yield smaller vibrational quanta than the adiabatic one. This general conclusion is confirmed by the numerical results obtained recently¹⁸ for the H_2^+ ion. For this system, the lowering of the energy due to the nonadiabatic effects for the three lowest vibrational states was 0.12 , 0.21 , and 0.35 cm^{-1} , respectively. Hence, the two lowest nonadiabatic vibrational quanta were by 0.09 and 0.14 cm^{-1} , respectively, smaller than their adiabatic counterparts. The conclusion is also supported by estimation of the nonadiabatic effects made by Poll and Karl.¹⁹

There is also no doubt that part of the discrepancy

¹⁸ W. Kołos and L. Wolniewicz (unpublished); G. Hunter and H. O. Pritchard, *J. Chem. Phys.* **46**, 2153 (1967).

¹⁹ J. D. Poll and G. Karl, *Can. J. Phys.* **44**, 1467 (1966).

between the theoretical and experimental values of the vibrational quanta can be removed at least for some states by taking into account the relativistic effects. For $R < R_e$ the relativistic corrections decrease quite rapidly¹ and therefore their averaged value decreases for excited vibrational states. It has been found⁴ that for the two lowest vibrational states of H_2 the relativistic corrections to the dissociation energy are $\Delta D_{rel} = -0.48$ and -0.34 cm^{-1} , respectively. Hence, they decrease the theoretical value of $\Delta G(0)$ by 0.14 cm^{-1} .

In Table V we also compare with experiment the theoretical vibrational quanta calculated for HD and D_2 . In contradistinction to H_2 , the errors for these two isotopes are quite random. In all three cases the theoretical values were obtained from the same clamped nuclei potential by applying only a different mass factor to the nuclear-motion correction. Therefore, the rather

consistent discrepancy obtained for H_2 seems to suggest that for the two other isotopes the experimental results are responsible for the inconsistency.

Summarizing the preceding discussion we may say that the nonadiabatic and relativistic effects are likely to remove at least part of the discrepancy between the experimental and theoretical values of the vibrational quanta. However, the authors do not know any effect which when taken into account might bring the theoretical and experimental dissociation energies into agreement.

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Fourth-Order Vibration-Rotation Hamiltonian of the Nonlinear XYX Molecule*

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Detailed expressions in terms of fundamental molecular parameters are given for the fourth-order centrifugal distortion constants of the nonlinear XYX molecule. It is shown how these expressions can be used for the determination of the cubic potential constants of the XYX molecule if they are considered in conjunction with the reduced-Hamiltonian theory of Watson. Three reduced Hamiltonians are treated in detail, and a generalization of Watson's theory is presented, and its need is justified.

I. INTRODUCTION

In a study¹ appearing in this journal in 1963, Chung and Parker (CP-I) developed the general form of the molecular asymmetric-top vibration-rotation Hamiltonian in the Nielsen-Amat-Goldsmith formulation for all possible equilibrium configuration point-group symmetries. Olson and Allen² (OA) subsequently produced an important simplification of the Hamiltonian for the orthorhombic point groups through judicious use of angular-momentum commutation relations. Chung and Parker extended their previous work by publishing a study³ (CP-II) of the fourth-order centrifugal distortion effect, and by specifically applying their considerations to the nonlinear XYX (H_2O -type)

molecule⁴ (CP-III). It was then shown by Kneizys, Freedman, and Clough⁵ (KFC) that the Hamiltonian for the orthorhombic point groups in general, and for XYX in particular, could be given in much simplified form through extensive rearrangement, again based on angular-momentum commutation relations. The form of the resulting Hamiltonian is, for a given vibrational state, a power series in the angular-momentum components which needs for its specification, to fourth order of approximation, three coefficients, A , B , and C , of terms of the second power in the body-fixed angular-momentum components (these being the three effective rotational constants); six coefficients T_i of fourth-power angular-momentum terms (these being the second-order centrifugal distortion constants τ_i plus fourth-order corrections to them); and 10 coefficients of sixth-power angular-momentum terms (these being the fourth-order centrifugal distortion coefficients Φ_i).

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² W. B. Olson and H. C. Allen, Jr., *J. Res. Natl. Bur. Std.* **A67**, 359 (1963).

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⁴ K. T. Chung and P. M. Parker, *J. Chem. Phys.* **43**, 3869 (1965).

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