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THREE LOWEST $^3\Pi_g$ AND THREE LOWEST $^3\Pi_u$ STATES OF THE HYDROGEN MOLECULE

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Abstract: Calculations of the Born-Oppenheimer (BO) potential energy curves and adiabatic corrections for three lowest $^3\Pi_g$ and three lowest $^3\Pi_u$, states of the hydrogen molecule have been performed using explicitly correlated wavefunctions in elliptic coordinates. The accuracy of the results obtained has been discussed. The adiabatic corrections as functions of R possess complex structure with one or more maxima illustrating changes in the character of the wavefunctions. It is shown that for the k state the adiabatic curve has huge maximum of the order of 50 000 cm^{-1}.

1. INTRODUCTION

For the $^3\Pi$ states of the hydrogen molecule very few accurate theoretical results are available. Only for the lowest states, $c\ ^3\Pi_u$ and $i\ ^3\Pi_g$, accurate potential energy curves have been computed in the Born-Oppenheimer (BO) approximation [1]. The agreement with experiment of the computed energies was, however, not satisfactory. The discrepancy, larger for the $i\ ^3\Pi_g$ state, was interpreted as caused by the Born-Oppenheimer approximation. Only for the $i\ ^3\Pi_g$ state the adiabatic corrections have been computed [2]. The theoretical potentials have also been used to interpret various experimental results (see, e. g., Ref. [3,4] and therefore it would be desirable to increase their accuracy, especially by computing the adiabatic corrections. The potential energy for the $i\ ^3\Pi_g$ state has a maximum resulting from an avoided crossing, and there are indications that the electronic wavefunction changes character at large vibrational amplitudes [3], Hence one may expect that the adiabatic correction to the BO potential is large in this region. Avoided crossings are also to be expected for higher states. Wolniewicz and Dressier have recently shown [6] that for some $^1\Sigma_g^+$ states of the hydrogen molecule avoided crossings result in huge maxima of the adiabatic corrections. It has been shown that such effects appear also for the pairs of triplet states naimly for the 3s and 3d as well as for the 4s and 4$d\ ^3\Sigma_g^+$ states of the hydrogen molecule [7-10].

In the present work we have computed adiabatic potential energy curves for three lowest $^3\Pi_u$ states (c, d, k) and for three lowest $^3\Pi_g$ states (i, r, w). Work on some higher states is in progress. The computed energies have been used to calculate the rovibrational levels, the results of these calculations will be published later. Recently, Staszewska and Wolniewicz have calculated BO energies and adiabatic corrections for five states considered, i. e. c, d and $k\ ^3\Pi_u$ and i and $r\ ^3\Pi_g$

states of the hydrogen molecule [5], Our results can serve as independent verification of then-data. In the case of the w $^3\Pi_g$ state our energies seem to be the first accurate potential curve.

Throughout this paper the energy is given in Hartree, the dissociation energy and all adiabatic corrections in cm^{-1} (1 Hartree = 219474.631 cm^{-1}), the internuclear distance in Bohr. For the nuclear masses we used M_p = 1836.1527 m_e and M_d = 3670.4831 m_e.

2. ADIABATIC POTENTIAL ENERGY CURVES

The standard nonrelativistic hamiltonian was used to calculate the Born-Oppenheimer energies. The electronic wavefunction was assumed in the form of the generalized James-Coolidge function [11]:

$$\Psi(1,2) = \sum_i c_i[\Phi_i(1,2)x_1 - \Phi_i(2,1)x_2]\,, \tag{1}$$

where the basis functions are expressed in elliptic coordinates ξ and η as

$$\Phi_i(1,2) = \exp(-\alpha\xi_1 - \bar{\alpha}\xi_2)\,\xi_1^{n_i}\eta_1^{k_i}\xi_2^{m_i}\eta_2^{l_i}(2r_{12}/R)^{\mu_i}\times$$
$$\times\exp(\beta\eta_1 + \bar{\beta}\eta_2) + (-1)^{k_i+l_i+1}\exp(-\beta\eta_1 - \bar{\beta}\eta_2)\,, \tag{2}$$

where α, β, $\bar{\alpha}$, $\bar{\beta}$ are variational parameters; n_i, k_i, m_i, l_i and μ_i are integers, and r_{12} and R denote the intereleetronic and internuclear distances, respectively.

The upper limits imposed on the powers of the variables were: $\mu \le 2$, $r, \bar{r}, s, \bar{s} \le 6$, $\mu + r$, $\mu + s$, $\mu + \bar{r}$, $\mu + \bar{s} \le 6$. The form of the wavefunction allows us to use both even and odd powers of η for g as well as for u states. We have found, however, that this creates problems with linearly dependent terms. Therefore only even powers of η have been used for the u states and odd powers of η for the g states. Several tests have been made showing that when e. g. terms with even powers of η have been added to the final wavefunction for a g state practically no improvement of the energy could be obtained.

The above limits generated wavefunctions with many linearly dependent terms. Therefore for each state a selection of terms had to be earned out. The procedure which has been used for lower states, was as follows: For three internuclear distances, usually R = 2, 4, 8 Bohr, the exponents have been optimized in an arbitrarily chosen short expansion ($\approx$ 40 terms or less). Next all terms have been tested for the three internuclear distances using a relatively large threshold for rejecting terms. In this way a somewhat longer expansion has been obtained in which again the optimization of exponents has been performed and followed by selection of all terms not included in the wavefunction. In the final selection the threshold was 0.002 cm^{-1}. The wavefunction selected in this way was used also for smaller and larger internuclear separations. Usually, however, for small and large distances some linearly dependent terms had to be rejected and new terms, not important for the intermediate R values, had to be introduced. This procedure failed, however, for higher states. The wavefunction for these states drastically changes its character with the change of R, and terms selected at large R create only numerical difficulties at small distances and *vice versa.* For some states the difficulties were quite serious, e. g., for the $1s4d\pi\ (r)$ state the wavefunction selected at $R = 2$ was found to be not applicable at $R = 1.95$. Hence, for higher states, the above procedure had to be modified and independent wavefunctions had to be selected for several internuclear distances. For each internuclear distance the exponents in the wavefunction have been optimized.

The electronic wavefunctions have been used to calculate the adiabatic corrections, given as expectation values of the operator

$$H' = H_1' + H_2' + H_3' , \tag{3}$$

where

$$H_1' = -(1/2\mu)\,\Delta_R , \tag{4}$$

$$H_2' = -(1/8\mu)(\Delta_1 + \Delta_2) , \tag{5}$$

$$H_3' = -(1/4\mu)\,\nabla_1\nabla_2 . \tag{6}$$

H_1' is the operator of the relative kinetic energy of the nuclei, H_2' is the correction to the kinetic energy of the electrons, H_3' is the mass polarization correction and μ denotes the reduced mass of the nuclei. The explicit expression for $H_1'(R)$ in terms of elliptic coordinates is given in Ref. [12]. In the present work essentially the same method of evaluation of the matrix elements of $H_1'(R)$ as in that reference is employed. While computing the derivatives of the wavefunction with respect to R, the R-dependence of the nonlinear variational parameters was ignored. This assumption simplifies the computation considerably and does not introduce significant errors, provided that the wavefunction is fairly accurate i. e. the expansion (1) is rather long.

$c\,^3\Pi_u\,(1s2p\pi)$ state

From parallel tests of terms at $R = 2, 4, 8$ a 185-term wavefunction has been constructed. For $R = 1.5$ additional tests have been made to check the accuracy of the wavefunction in this region. The additionally selected terms introduced, however, only negligible improvement (0.02 cm^{-1}), and therefore they were not included in the final computation. The 185-term wavefunction has been used for $1.0 \le R \le 7.5$. For $R = 8$ in the course of optimization of exponents linear dependencies have been encountered and the expansion had to be shortened to 168 terms. Further reduction of the expansion length was necessary for $R = 12$ (142 terms) and $R = 15$ (109 terms). The results are shown in Table I where R and E denote the internuclear distance and the BO energy in atomic units (Bohr and Hartree, respectively). The derivative dE/dR has been computed from the virial theorem. D denotes the dissociation energy and is given in cm^{-1}. $\langle H_i' \rangle$ are the adiabatic corrections defined in Eqs 3-6, and $\langle H' \rangle$ is their sum, all in cm^{-1}. For each value of the internuclear distance the exponents in the wavefunction have been optimized.

In comparison with the previous results the energy has been lowered by < 1 cm^{-1}. For the minimum of the BO energy (at $R = 1.960$) the lowering amounts to 0.5 cm^{-1}. As compared with the recent results by Staszewska and Wolniewicz [5] our BO energies are higher than theirs by no more than 0.1 cm^{-1} and at the equilibrium (R= 1.96 Bohr) the difference is 0.04 cm^{-1}.

The adiabatic correction has a minimum at $R \approx 3$ and increases the binding energy D_e by 13.2 cm^{-1}. The computed adiabatic corrections differ from those calculated by Staszewska and Wolniewicz by no more than 0.01 cm^{-1} and around equilibrium this difference amounts to 0.003 cm^{-1}.

$d\ ^{3}\Pi_{u}\,(1s3p\pi)$ state .

Parallel tests have been started for R = 1.5,2,4 and 8. It has been found, however, that terms important for short distances introduced linear dependencies at R = 8, and therefore for the latter distance independent tests have been made. This resulted in a 191-term expansion for smaller distances and 220-term expansion for larger ones. The 220-term wavefunction, selected at R = 8, even at R = 3 gave an energy that was still 0.001 cm^{-1} lower than the 191-term expansion. Therefore the latter has been used for $1.4 \le R \le 2.9$. For $R \le 1.3$ it has been shortened to avoid linear dependencies. The 220-term expansion has been used for $3.0 \le R \le 11.0$ and for larger R it has been shortened to 201 terms for R = 12 and 142 terms for R = 15. The results are shown in Table II. The minimum of the Born-Oppenheimer energy is at R = 1.9833. The BO energies for the d state calculated by Staszewska and Wolniewicz are lower than our energies by less than 0.22 cm^{-1} for $1.0 \le R < 1.5$ Bohr, less than 0.1 cm for $1.5 < R < 8.0$ Bohr and few tenths of cm^{-1} for larger R.

The adiabatic correction has a minimum at $R \approx 3.4$, i. e. in the same region as in the c state. Here, however, it has also a not very high maximum at $R \approx 7.5$ which is probably due to the interaction with the k state. The adiabatic correction increases the binding by ≈ 7 cm^{-1}.

$k\ ^{3}\Pi_{u}\,(1s4p\pi)$ state .

Parallel tests of terms in the wavefunction have been made for R = 2, 4 and 8 resulting in a 222-term expansion. Already for R = 1.9 one term in this wavefunction turned out to be linearly dependent and had to be rejected. For the same reason more terms have been removed for smaller distances. At R = 1.3 additional tests have been performed and the terms found to be important have been introduced also for neighboring distances. In consequence in the region of small R the wavefunction had from 220 terms (R = 1.7) to 103 terms (R = 1.0). Similarly as for small distances the 222-term expansion was found to contain superflous terms for $R > 10$ which had to be rejected. The calculated energy curve is lower than that obtained by Staszewska and Wolniewicz for $1.2 \le R \le 1.7$ and $2.4 \le R < 2.9$ otherwise it is higher than in [5], The computed values of the energy and of the adiabatic corrections are listed in Table III. In Fig. 1 we show the energies of the three $^{3}II_{u}$ states computed in the BO approximation, and in Fig. 2 the adiabatic corrections $\langle H' \rangle$ for these states.

Similarly as for the two lower states the BO energy has a minimum at $R \approx 2$ bohr. For this state it is located at R = 1.991. At R = 5.67 the energy reaches a maximum but the state is still bound by 185.89 cm^{-1}. At R = 6.96 a second minimum occurs which is 397.80 cm^{-1} deep.

The adiabatic correction $\langle H' \rangle$ has 3 maxima: a very sharp and high peak at $R = 2.86$ and two lower maxima at $R = 5.2$ and 7.5, respectively. The maximum at $R = 7.5$ indicates a strong interaction with the *d* state which also has a maximum of $\langle H' \rangle$ in the same region. The other two maxima are due to interaction with higher states.

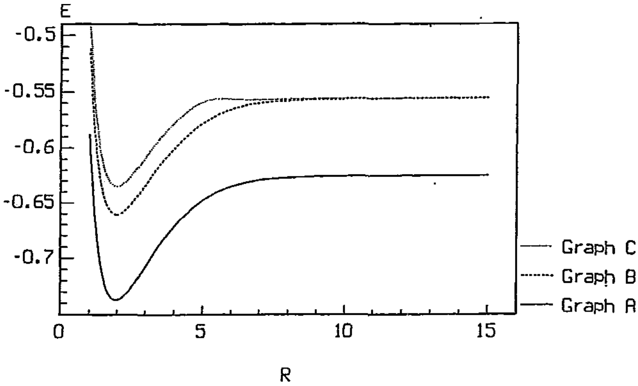

Fig. 1. Clamped nuclei energies for the c (graph *A*), *d* (graph *B*), *k* (graph *C*) states of the hydrogen molecule

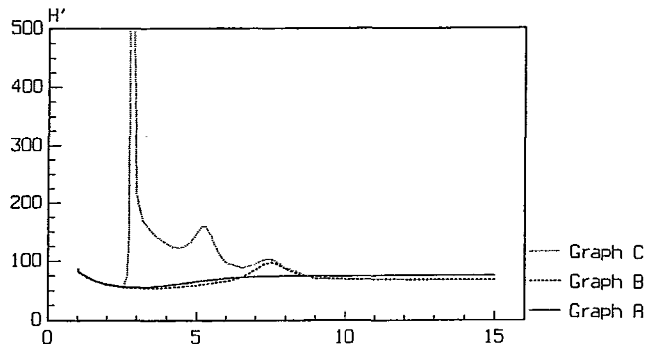

Fig. 2. Adiabatic corrections for the c (graph *A*), *d* (graph *B*), *k* (graph *C*) states of the hydrogen molecule

To check the reliability of the huge value of $\langle H' \rangle$ at $R = 2.86$ the expansion has been shortened from 222 to 117 terms. Without reoptimizing the exponents this resulted in $D = 12823.734$ cm^{-1} and $\langle H' \rangle = 50329$ cm^{-1}. Optimization of the exponents gave 12823.857 cm^{-1} and $\langle H' \rangle = 57268$ cm^{-1}. This shows that the computed value of $\langle H' \rangle$ is not very accurate, but it also very strongly indicates that the huge peak is not an artifact.

The maxima of $\langle H' \rangle$ occur in the region where the wavefunction rapidly changes its character. It is therefore not surprising, as we have found for some other states (to be published), that the values of $\langle H' \rangle$ at their maxima strongly depend on whether they are computed with a wavefunction selected at a smaller or at larger internuclear distance. For the state under consideration a single expansion resulting from tests at $R = 2, 4, 8$ has been used, and therefore there seems to be no reason to suspect that a differently selected wavefunction would produce significantly different results. Independent verification of the behavior of the adiabatic effects for the *k* state is given in [5].

$i\ ^3\Pi_g\,(1s3d\pi)$ state .

The previously computed wavefunction for this state [1] has been used as the starting point. Parallel tests of additional terms have been made at R = 2 and R = 4.5. They resulted in a 177-term wavefunction that has been used for $1.6 \le R \le 5.0$. Independent selection of terms has been made at R = 10. It produced a 157-term wavefunction that even for R = 5.5 gave a lower energy than the 177-term expansion. For R < 1.6 the number of terms in the 177-term wavefunction had to be reduced to 140-137 terms to remove the linearly dependent terms, and similarly the 157-term wavefunction for R= 12 and 15 has been shortened to 133 and 102 terms, respectively. The results of the computations are shown in Table IV. The improvement of the energy over the previous results amounts to 0.75 cm^{-1} at the equilibrium and reaches a maximum of about 2.1 cm^{-1} at R = 4. Our BO energy curve for the i state is lower than that obtained by Staszewska and Wolniewicz [5] for $1.6 \le R \le 3.6$ by at least 0.01 cm and otherwise is higher by 0.01 cm^{-1}.

The adiabatic correction $<H'(R)>$ has a minimum at R = 3.3, and a maximum at R = 4.2 cm^{-1}. This is very close to the maximum of the Born-Oppenheimer energy which is located at R = 4.35. The differences in the adiabatic corrections calculated by Staszewska and Wolniewicz [5] and by us are not higher than 0.01 cm^{-1}

$r\ ^3\Pi_g\,(1s4d\pi)$ state .

Attempts to produce a single expansions from wavefunctions selected at R = 2, 4 and 8 have failed. A 171-term expansion constructed at R = 2 has been used for $2.0 \le R \le 2.6$. For smaller distances some linearly dependent terms have been removed, but new terms selected at R = 1.2 have been added. For $2.7 \le R \le 10.0$ a 202 term expansion selected at R = 4 and 8 has been employed. For R =12 and 15 the expansion has been shortened to 180 and 183 terms, respectively. The results are listed in Table V. The calculated in this work energy curve for the r state is higher than that of [5] by 0.06 cm^{-1} for the equilibrium and by few tenths of cm^{-1} for larger R.

$<H'(R)>$ for the r state has a minimum at R = 3.2 and a maximum at R = 4.1. The latter is a clear effect of an avoided crossing with a repulsive potential resulting from the interaction of n = 1 and n = 2 hydrogen atoms. A very flat minimum of $<H'>$ appears also at $R \approx 7$. Its depth, relative to the maximum at $R \approx 8$ amounts to only 0.01 cm^{-1}. It is difficult to judge whether the minimum is real. We are inclined to believe that it is since a similar minimum appears also in the higher w state (see below).

$w\ ^3\Pi_g\,(1s5d\pi)$ state .

Independent tests of terms have been made at R = 2, 4, 8 and 138-, 218- and 205-term wavefunctions have been selected, respectively. Additional tests have been carried out for both smaller and larger separations. At R = 1.3 a 99-term wavefunction has been selected and used for $1.2 \le R \le 1.5$. For R = 1.1, however, 4 terms had to be removed from this expansion.

Table I. Clamped nuclei energies and adiabatic corrections for the $c\,^3\Pi_u$ state of the hydrogen molecule

R	E	D	dE/dR	$<H_1>$	$<H_2>$	$<H_3>$	$<H'>$	ΔD
1.000	-.588464493	-8018.617	-.522151173	22.516	66.376	-5.174	83.718	-9.004
1.100	-.633172934	1793.752	-.379909948	22.449	62.817	-5.235	80.031	-5.325
1.200	-.665748188	8943.193	-.276954073	22.371	59.651	-5.278	76.743	-2.037
1.300	-.689459967	14147.328	-.201022660	22.341	56.824	-5.307	73.818	0.888
1.400	-.706585726	17905.997	-.144165782	22.248	54.291	-5.321	71.219	3.487
1.500	-.718749958	20575.737	-.101067298	22.219	52.016	-5.323	68.913	5.793
1.600	-.727135021	22416.046	-.068078495	22.217	49.967	-5.314	66.870	7.836
1.700	-.732616497	23619.091	-.042637853	22.242	48.117	-5.296	65.063	9.643
1.800	-.735852581	24329.329	-.022912096	22.297	46.443	-5.271	63.469	11.237
1.900	-.737344562	24656.781	-.007566039	22.381	44.926	-5.239	62.068	12.638
1.950	-.737560822	24704.245	-.001216259	22.433	44.222	-5.221	61.434	13.272
1.960	-.737567074	24705.617	-.000038734	22.444	44.085	-5.217	61.312	13.394
2.000	-.737478627	24686.205	.004387514	22.492	43.551	-5.202	60.841	13.865
2.050	-.737133086	24610.368	.009330804	22.559	42.911	-5.181	60.289	14.417
2.100	-.736555321	24483.563	.013688029	22.632	42.302	-5.160	59.774	14.932
2.200	-.734810625	24100.646	.020896654	22.799	41.168	-5.116	58.852	15.854
2.300	-.732431306	23578.446	.026443324	22.994	40.139	-5.068	58.064	16.642
2.400	-.729566199	22949.628	.030661186	23.215	39.204	-5.019	57.400	17.306
2.500	-.726334657	22240.386	.033810405	23.462	38.358	-4.969	56.851	17.855
2.600	-.722832888	21471.837	.036095999	23.735	37.591	-4.917	56.408	18.298
2.700	-.719138812	20661.081	.037680662	24.033	36.899	-4.866	56.066	18.640
2.800	-.715315784	19822.023	.038694432	24.357	36.276	-4.815	55.817	18.889
2.900	-.711415470	18966.003	.039241932	24.705	35.716	-4.765	55.657	19.049
3.000	-.707480123	18102.294	.039407826	25.079	35.217	-4.716	55.580	19.126
3.200	-.699636430	16380.803	.038858359	25.897	34.382	-4.621	55.658	19.048
3.400	-.691992964	14703.256	.037462333	26.809	33.744	-4.534	56.020	18.686
3.600	-.684688786	13100.174	.035504901	27.810	33.281	-4.456	56.635	18.071
3.800	-.677815028	11591.559	.033186039	28.889	32.973	-4.388	57.474	17.232
4.000	-.671428831	10189.951	.030649711	30.036	32.801	-4.331	58.505	16.201
4.200	-.665562561	8902.453	.028002227	31.233	32.748	-4.287	59.694	15.012
4.400	-.660229926	7732.075	.025325139	32.456	32.799	-4.255	61.000	13.706
4.600	-.655430254	6678.669	.022682087	33.680	32.936	-4.236	62.380	12.326
4.800	-.651151430	5739.575	.020124201	34.872	33.143	-4.229	63.786	11.000
5.000	-.647372189	4910.128	.017692287	36.001	33.403	-4.233	65.172	9.534
5.500	-.639909387	3272.232	.012351758	38.378	34.184	-4.281	68.281	6.425
6.000	-.634813424	2153.798	.008241281	39.958	34.984	-4.361	70.581	4.125
6.500	-.631467395	1419.429	.005328545	40.870	35.670	-4.446	72.093	2.613
7.000	-.629322592	948.699	.003391544	41.350	36.192	-4.519	73.023	1.683
7.500	-.627959925	649.628	.002155613	41.602	36.564	-4.574	73.591	1.115
8.000	-.627090264	458.760	.001384110	41.738	36.816	-4.612	73.942	0.764
9.000	-.626154285	253.336	.000608918	41.875	37.094	-4.653	74.317	0.389
10.000	-.625721672	158.389	.000301366	41.934	37.216	-4.667	74.483	0.223
12.000	-.625361821	79.410	.000104984	41.979	37.299	-4.671	74.607	0.099
15.000	-.625173394	38.056	.000036678	42.001	37.330	-4.669	74.662	0.044

Table II. Clamped nuclei energies and adiabatic corrections for the $d^3[]_u$ state of the hydrogen molecule

R	E	D	dE/dB	$\langle H_1 \rangle$	$\langle H_2 \rangle$	$\langle H_3 \rangle$	$\langle H' \rangle$	ΔD
1.000	-.510714207	-9841.538	-.520995934	22.151	61.660	-1.241	82.570	-16.165
1.100	-.555332175	-49.026	-.379251161	21.980	58.122	-1.231	78.871	-12.466
1.200	-.587866322	7091.394	-.276779823	21.788	54.984	-1.218	75.553	-9.148
1.300	-.611583942	12296.810	-.201308164	21.689	52.192	-1.202	72.679	-6.274
1.400	-.628760205	16066.563	-.144883431	21.611	49.700	-1.183	70.128	-3.723
1.500	-.641016582	18756.527	-.102186857	21.562	47.471	-1.163	67.870	-1.465
1.600	-.649532276	20625.506	-.069566154	21.530	45.471	-1.141	65.860	0.545
1.700	-.655179548	21864.939	-.044460394	21.526	43.674	-1.119	64.081	2.324
1.800	-.658613203	22618.539	-.025035437	21.545	42.055	-1.096	62.504	3.901
1.900	-.660331153	22995.586	-.009956606	21.588	40.595	-1.073	61.111	5.294
1.950	-.660670008	23069.956	-.003728085	21.617	39.919	-1.061	60.476	5.929
1.980	-.660730560	23083.245	-.000350872	21.637	39.530	-1.054	60.113	6.292
1.983	-.660731127	23083.370	-.000027004	21.639	39.492	-1.053	60.078	6.327
2.000	-.660716270	23080.109	.001762451	21.652	39.277	-1.049	59.880	6.525
2.050	-.660504642	23033.662	.006600565	21.692	38.666	-1.038	59.320	7.085
2.100	-.660065853	22937.359	.010860428	21.737	38.086	-1.026	58.797	7.608
2.200	-.658612752	22618.440	.017896802	21.844	37.009	-1.003	57.849	8.556
2.300	-.656540775	22163.694	.023300808	21.966	36.035	-.981	57.020	9.385
2.400	-.653995876	21605.153	.027403859	22.106	35.155	-.959	56.302	10.103
2.500	-.651094678	20968.414	.030464854	22.262	34.361	-.938	55.685	10.720
2.600	-.647930798	20274.022	.032687347	22.435	33.644	-.917	55.162	11.243
2.700	-.644579726	19538.547	.034232775	22.621	32.999	-.897	54.723	11.682
2.800	-.641102488	18775.381	.035229817	22.821	32.420	-.878	54.363	12.042
2.900	-.637548595	17995.392	.035782023	23.032	31.901	-.860	54.073	12.332
3.000	-.633958179	17207.387	.035972338	23.259	31.439	-.842	53.856	12.549
3.200	-.626792334	15634.666	.035527228	23.746	30.666	-.810	53.602	12.803
3.400	-.619799112	14099.831	.034301286	24.279	30.072	-.781	53.570	12.835
3.600	-.613105313	12630.712	.032570696	24.852	29.634	-.756	53.731	12.674
3.800	-.606791669	11245.027	.030525994	25.462	29.332	-.734	54.060	12.345
4.000	-.600906931	9953.477	.028300298	26.109	29.148	-.717	54.540	11.865
4.200	-.595477213	8761.791	.025989074	26.791	29.065	-.704	55.152	11.253
4.400	-.590512399	7672.140	.023660971	27.506	29.070	-.696	55.881	10.524
4.600	-.586010583	6684.106	.021366289	28.258	29.149	-.693	56.714	9.691
4.800	-.581961161	5795.361	.019142278	29.045	29.289	-.695	57.639	8.766
5.000	-.578347118	5002.170	.017016543	29.873	29.480	-.704	58.648	7.757
5.500	-.571065350	3404.007	.012252213	32.168	30.102	-.756	61.515	4.890
6.000	-.565942960	2279.772	.008394228	35.212	30.813	-.851	65.175	1.230
6.500	-.562516871	1527.832	.005457018	41.018	31.499	-.983	71.534	-5.129
7.000	-.560351096	1052.500	.003328408	54.086	32.097	-1.123	85.059	-18.654
7.300	-.559499592	865.616	.002389876	63.212	32.396	-1.174	94.434	-28.029
7.500	-.559071943	771.758	.001905899	65.290	32.559	-1.174	96.674	-30.269
7.700	-.558729566	696.615	.001536433	62.602	32.685	-1.145	94.143	-27.738
8.000	-.558328593	608.612	.001169006	53.884	32.809	-1.059	85.635	-19.230
8.500	-.557831442	499.499	.000862119	42.936	32.901	-.882	74.955	-8.550
9.000	-.557442605	414.160	.000705447	38.784	32.936	-.730	70.991	-4.586
10.000	-.556846869	283.411	.000498056	36.638	32.982	-.529	69.091	-2.686
11.000	-.556429391	191.785	.000344567	36.053	33.028	-.422	68.658	-2.253
12.000	-.556143599	129.061	.000233368	35.718	33.070	-.369	68.419	-2.014
15.000	-.555735456	39.484	.000069341	35.068	33.151	-.360	67.859	-1.454

Table III. Clamped nuclei energies and adiabatic corrections for the $k\,^3\Pi_u$ state of the hydrogen molecule

R	*E*	*D*	*dE/dR*	<H_1>	<H_2>	<H_3>	<*H*>	ΔD
1.000	-.484425998	-15611.133	-.520949275	28.812	60.086	-.474	88.424	-22.018
1.100	-.529051414	-5816.987	-.379314963	25.224	56.555	-.472	81.308	-14.902
1.200	-.561598600	1326.295	-.276975145	24.599	53.428	-.465	77.562	-11.156
1.300	-.585341820	6537.329	-.201616425	24.027	50.647	-.457	74.217	-7.811
1.400	-.602553419	10314.839	-.145293264	23.668	48.168	-.448	71.388	-4.982
1.500	-.614855611	13014.858	-.102690472	23.290	45.953	-.438	68.805	-2.399
1.600	-.623426512	14895.953	-.070153586	22.931	43.967	-.428	66.470	-0.064
1.700	-.629136310	16149.109	-.045121771	22.683	42.185	-.418	64.449	1.957
1.800	-.632640082	16918.098	-.025763046	22.478	40.581	-.409	62.650	3.756
1.900	-.634433752	17311.763	-.010741991	22.375	39.137	-.398	61.113	5.293
1.950	-.634812573	17394.905	-.004539306	22.334	38.468	-.393	60.409	5.997
1.990	-.634904103	17414.993	-.000111117	22.308	37.958	-.389	59.877	6.529
1.991	-.634904162	17415.006	-.000006139	22.310	37.946	-.389	59.866	6.540
2.000	-.634900003	17414.093	.000927553	22.305	37.834	-.388	59.751	6.655
2.050	-.634730700	17376.936	.005743167	22.303	37.231	-.383	59.150	7.256
2.100	-.634335298	17290.155	.009982807	22.301	36.658	-.378	58.580	7.826
2.200	-.632971819	16990.906	.016983742	22.341	35.596	-.369	57.568	8.838
2.300	-.630992659	16556.530	.022358846	22.440	34.638	-.359	56.719	9.687
2.400	-.628543167	16018.929	.026439016	22.668	33.772	-.350	56.090	10.316
2.500	-.625739384	15403.570	.029482560	23.270	32.992	-.341	55.921	10.485
2.600	-.622674411	14730.886	.031692676	25.560	32.289	-.333	57.516	8.890
2.700	-.619423306	14017.351	.033228644	42.557	31.658	-.324	73.890	-7.484
2.750	-.617747490	13649.552	.033782040	103.432	31.367	-.320	134.480	-68.074
2.800	-.616047323	13276.408	.034200776	713.717	31.095	-.312	744.500	-678.094
2.850	-.614331866	12899.909	.034299406	30510.287	30.873	-.258	30540.903	-30474.497
2.860	-.613989634	12824.798	.034128097	57981.497	30.862	-.202	58012.157	-57945.751
2.865	-.613819235	12787.399	.034008840	58297.918	30.862	-.165	58328.614	-58262.208
2.870	-.613649514	12750.150	.033905028	45777.343	30.859	-.132	45808.070	-45747.664
2.900	-.612636261	12527.767	.033733695	3033.225	30.767	-.053	3063.939	-2997.533
2.950	-.610947715	12157.174	.033810180	329.307	30.552	-.039	359.820	-293.414
3.000	-.609256019	11785.889	.033846252	183.290	30.344	-.038	213.595	-147.189
3.200	-.602519570	10307.410	.033362276	139.822	29.629	-.045	169.406	-103.000
3.400	-.595962459	8868.290	.032104388	126.508	29.094	-.058	155.544	-89.138
3.600	-.589711833	7496.436	.030332867	116.071	28.718	-.074	144.715	-78.309
3.800	-.583851839	6210.316	.028221095	107.626	28.485	-.097	136.014	-69.608
4.000	-.578438730	5022.276	.025877580	100.977	28.384	-.128	129.233	-62.827
4.200	-.573512477	3941.089	.023357636	96.239	28.413	-.171	124.480	-58.074
4.400	-.569107070	2974.214	.020665275	93.994	28.578	-.234	122.338	-55.932
4.600	-.565261365	2130.179	.017746166	95.630	28.904	-.326	124.208	-57.802
4.800	-.562033140	1421.666	.014481272	103.381	29.436	-.463	132.353	-65.947
5.000	-.559499992	865.704	.010774835	117.711	30.219	-.657	147.272	-80.866
5.200	-.557744586	480.437	.006768533	129.242	31.230	-.895	159.577	-93.171
5.300	-.557165192	353.274	.004843622	128.278	31.765	-1.013	159.030	-92.624
5.500	-.556531627	214.223	.001683957	110.799	32.707	-1.196	142.311	-75.905
5.600	-.556421398	190.031	.000575310	98.613	33.062	-1.249	130.426	-64.020
5.650	-.556403804	186.169	.000141284	92.719	33.206	-1.265	124.659	-58.253
5.670	-.556402523	185.888	-.000011204	90.462	33.257	-1.270	122.449	-56.043
5.700	-.556406031	186.658	-.000218483	87.212	33.328	-1.276	119.264	-52.858
5.800	-.556456038	197.633	-.000740963	77.712	33.513	-1.280	109.945	-43.539
5.900	-.556547028	217.603	-.001047523	70.348	33.631	-1.266	102.713	-36.307
6.000	-.556660143	242.429	-.001191844	64.901	33.696	-1.238	97.359	-30.953
6.500	-.557196412	360.126	-.000760597	55.529	33.596	-.988	88.138	-21.732
6.900	-.557365456	397.227	-.000090349	60.366	33.348	-.752	92.962	-26.556
6.960	-.557368063	397.799	.000002957	61.734	33.310	-.719	94.325	-27.919
7.000	-.557366735	397.508	.000063186	62.698	33.284	-.698	95.284	-28.878
7.300	-.557286625	379.926	.000449869	69.207	33.110	-.564	101.753	-35.347
7.500	-.557177747	356.030	.000626581	69.680	33.019	-.512	102.187	-35.781
7.700	-.557041079	326.035	.000727358	65.519	32.957	-.493	97.983	-31.577
8.000	-.556815978	276.631	.000751436	55.049	32.919	-.514	87.454	-21.048
9.000	-.556209739	143.577	.000435722	37.703	33.007	-.668	70.042	-3.636
10.000	-.555903776	76.425	.000204240	35.370	33.101	-.748	67.723	-1.317
12.000	-.555685573	28.535	.000053154	34.847	33.172	-.774	67.245	-0.839
15.000	-.555602909	10.393	.000013497	34.741	33.193	-.707	67.228	-0.822

Table IV. Clamped nuclei energies and adiabatic corrections for the $i\ ^3\Pi_g$ state of the hydrogen molecule

R	E	D	dE/dR	$<H_1>$	$<H_2>$	$<H_3>$	$<H'>$	ΔD
1.100	-.552430676	-15927.126	-.380106872	416.902	58.005	.010	474.917	-400.213
1.200	-.585063600	-8765.027	-.277904615	353.688	54.897	.011	408.596	-333.892
1.300	-.608906670	-3532.078	-.202691800	304.463	52.139	.013	356.615	-281.911
1.400	-.626233628	270.750	-.146513563	265.391	49.686	.015	315.091	-240.387
1.500	-.638664863	2999.091	-.104051791	233.869	47.498	.016	281.383	-206.679
1.600	-.647378406	4911.492	-.071655434	208.076	45.542	.019	253.638	-178.934
1.700	-.653245440	6199.157	-.046764446	186.718	43.792	.022	230.532	-155.828
1.800	-.656919934	7005.616	-.027546518	168.844	42.224	.025	211.093	-136.389
1.900	-.658899077	7439.987	-.012668354	153.748	40.818	.029	194.594	-119.890
1.950	-.659376005	7544.661	-.006538803	147.070	40.170	.031	187.270	-112.566
2.000	-.659565253	7586.196	-.001146366	140.898	39.556	.033	180.487	-105.783
2.010	-.659571706	7587.612	-.000148523	139.719	39.437	.034	179.190	-104.486
2.050	-.659501508	7572.206	.003594074	135.182	38.975	.036	174.193	-99.489
2.100	-.659215491	7509.432	.007756084	129.884	38.424	.038	168.347	-93.643
2.200	-.658082655	7260.804	.014595843	120.390	37.411	.045	157.846	-83.142
2.300	-.656350820	6880.710	.019798141	112.170	36.505	.053	148.728	-74.024
2.400	-.654166622	6401.334	.023690982	105.029	35.69$	.062	140.789	-66.085
2.500	-.651647756	5848.507	.026528732	98.815	34.982	.074	133.870	-59.166
2.600	-.648889421	5243.122	.028509510	93.409	34.351	.087	127.84'7	-53.143
2.700	-.645969243	4602.217	.029788228	88.721	33.799	.104	122.625	-47.921
2.800	-.642951140	3939.820	.030485644	84.688	33.324	.125	118.138	-43.434
2.900	-.639888372	3267.620	.030695167	81.271	32.923	.151	114.344	-39.640
3.000	-.636825987	2595.504	.030488175	78.455	32.593	.182	111.231	-36.527
3.100	-.633802868	1932.006	.029917189	76.257	32.336	.222	108.815	-34.111
3.200	-.630853472	1284.689	.029018600	74.723	32.153	.271	107.147	-32.443
3.300	-.628009337	660.473	.027814567	73.940	32.047	.333	106.320	-31.616
3.400	-.625300436	65.938	.026314532	74.035	32.024	.411	106.470	-31.766
3.500	-.622756357	-492.423	.024517120	75.165	32.091	.509	107.765	-33.061
3.600	-.620407231	-1007.996	.022413577	77.490	32.256	.633	110.379	-35.675
3.800	-.616419099	-1883.290	.017256741	85.815	32.921	.978	119.715	-45.011
4.000	-.613581048	-2506.170	.010976063	95.804	34.047	1.476	131.326	-56.622
4.200	-.612052695	-2841.605	.004361151	97.602	35.485	2.093	135.18	-60.476
4.300	-.611769378	-2903.786	.001365410	93.000	36.211	2.411	131.623	-56.919
4.350	-.611735199	-2911.287	.000021201	89.501	36.555	2.565	128.621	-53.917
4.400	-.611765225	-2904.697	-.001200956	85.442	36.878	2.713	125.033	-50.329
4.500	-.611992262	-2854.868	-.003250522	76.482	37.450	2.985	116.917	-42.213
4.700	-.612930820	-2648.879	-.005815653	59.766	38.265	3.420	101.452	-26.748
5.000	-.614895888	-2217.596	-.006868760	44.451	38.802	3.831	87.084	-12.380
5.500	-.618084983	-1517.671	-.005604392	35.681	38.782	4.161	78.624	-3.920
6.000	-.620430203	-1002.955	-.003816269	33.518	38.448	4.317	76.283	-1.579
6.500	-.621973965	-664.138	-.002441327	32.919	38.121	4.411	75.450	-0.746
7.000	-.622948456	-450.262	-.001524229	32.753	37.868	4.475	75.096	-0.392
7.500	-.623554955	-317.151	-.000948089	32.719	37.692	4.523	74.934	-0.230
8.000	-.623933992	-233.962	-.000597381	32.724	37.575	4.558	74.857	-0.153
8.500	-.624175737	-180.905	-.000387315	32.735	3?.501	4.584	74.820	-0.116
9.000	-.624335439	-145.854	-.000261970	32.743	37.454	4.603	74.801	-0.097
10.000	-.624526683	-103.881	-.000139746	32.748	37.408	4.628	74.783	-0.079
12.000	-.624713600	-62.858	-.000063997	32.733	37.382	4.648	74.763	-0.059
15.000	-.624844595	-34.107	-.000029204	32.713	37.370	4.657	74.740	-0.036

Table III. Clamped nuclei energies and adiabatic corrections for the r $^3\Pi_g$ state of the hydrogen molecule

R	E	D	dE/dR	$\langle H_1 \rangle$	$\langle H_2 \rangle$	$\langle H_3 \rangle$	$\langle H \rangle$	ΔD
1.100	-.527871059	-6076.045	-.379734303	416.921	56.512	0.013	473.446	-409.040
1.200	-.560465387	1077.584	-.277494751	353.707	53.397	.014	407.119	-342.713
1.300	-.584265205	6301.040	-.202242650	304.504	50.632	.016	355.151	-290.745
1.400	-.601545536	10093.634	-.146023066	265.425	48.169	.017	313.612	-249.206
1.500	-.613925530	12810.729	-.103516960	233.925	45.971	.019	279.916	-215.510
1.600	-.622583417	14710.915	-.071074130	208.120	44.005	.021	252.146	-187.740
1.700	-.628389831	15985.276	-.046132630	186.773	42.243	.023	229.039	-164.633
1.800	-.631998403	16777.266	-.026859519	168.903	40.661	.026	209.590	-145.184
1.900	-.633905948	17195.923	-.011922133	153.817	39.239	.030	193.086	-128.680
1.950	-.634344977	17292.279	-.005761207	147.150	38.583	.031	185.763	-121.357
2.000	-.634494540	17325.105	-.000335533	140.982	37.961	.033	178.976	-114.570
2.003	-.634495065	17325.220	-.000031309	140.623	37.924	.033	178.580	-114.174
2.010	-.634492853	17324.734	.000668979	139.805	37.840	.033	177.678	-113.272
2.050	-.634389397	17302.028	.004439671	135.273	37.370	.035	172.678	-108.272
2.100	-.634060206	17229.779	.008638120	129.981	36.810	.037	166.828	-102.422
2.200	-.632835331	16960.95	0.01555628	120.503	35.776	.042	156.321	-91.915
2.300	-.631003185	16558.841	.020845726	112.303	34.846	.048	147.197	-82.791
2.400	-.628709469	16055.428	.024835864	105.188	34.012	.055	139.256	-74.850
2.500	-.626070788	15476.305	.027782597	99.010	33.266	.063	132.339	-67.933
2.600	-.623181038	14842.078	.029886579	93.658	32.600	.073	126.332	-61.926
2.700	-.620116311	14169.448	.031303921	89.033	32.010	.086	121.129	-56.723
2.800	-.616938954	13472.099	.032159159	85.115	31.490	.100	116.705	-52.299
2.900	-.613700078	12761.248	.032548294	81.884	31.036	.119	113.039	-48.633
3.000	-.610442438	12046.278	.032545229	79.375	30.648	.141	110.164	-45.758
3.100	-.607202364	11335.164	.032204529	77.688	30.323	.170	108.181	-43.775
3.200	-.604011529	10634.857	.031565432	77.067	30.062	.206	107.335	-42.949
3.300	-.600898793	9951.690	.030645825	77.858	29.869	.253	107.980	-43.574
3.400	-.597891824	9291.737	.029448587	80.752	29.749	.315	110.816	-46.410
3.500	-.595019009	8661.227	.027956511	86.838	29.713	.396	116.948	-52.542
3.600	-.592311947	8067.095	0.02612875	97.775	29.778	.503	128.056	-63.650
3.700	-.589806338	7517.178	.023915728	115.689	29.961	.641	146.291	-81.885
3.800	-.587543176	7020.471	.021278978	142.010	30.282	.816	173.107	-108.701
3.900	-.585563684	6586.023	0.01826392	173.941	30.739	1.020	205.700	-141.294
4.000	-.583895512	6219.902	.015112442	200.679	31.284	1.229	233.191	-168.785
4.100	-.582530452	5920.305	0.01228951	207.703	31.803	1.395	240.901	-176.495
4.200	-.581410534	5674.512	.010272611	191.016	32.169	1.473	224.658	-160.252
4.300	-.580442932	5462.148	.009240160	161.131	32.315	1.450	194.896	-130.490
4.400	-.579535559	5263.002	.009014950	130.826	32.265	1.347	164.438	-100.032
4.500	-.578624571	5063.064	.009255180	105.934	32.092	1.198	139.224	-74.818
4.600	-.577679365	4855.615	.009657755	87.272	31.870	1.034	120.175	-55.769
4.800	-.575677119	4416.173	.010286218	64.327	31.454	.728	96.509	-32.103
5.000	-.573603302	3961.022	.010358038	52.972	31.186	.487	84.645	-20.239
5.500	-.568740531	2893.768	.008821112	43.680	31.091	.119	74.891	-10.485
6.000	-.564892416	2049.204	.006567317	41.811	31.406	-.071	73.145	-8.739
6.500	-.562126304	1442.113	.004572528	41.253	31.819	-.179	72.893	-8.487
7.000	-.560235732	1027.180	.003074295	40.918	32.196	-.239	72.876	-8.470
7.500	-.558973926	750.246	.002042406	40.661	32.491	-.264	72.888	-8.482
8.000	-.558133969	565.896	.001367256	40.450	32.703	-.264	72.889	-8.483
8.500	-.557565766	441.190	.000938813	40.151	32.846	-.242	72.754	-8.348
9.000	-.557168582	354.018	.000671284	39.615	32.938	-.203	72.350	-7.944
10.000	-.556654370	241.162	.000397618	38.000	33.031	-.097	70.934	-6.528
12.000	-.556092182	117.776	.000193579	35.728	33.096	.095	68.919	-4.513
15.000	-.555729533	38.184	0.00067088	34.533	33.153	.219	67.905	-3.499

Table VI. Clamped nuclei energies and adiabatic corrections for the $w\ ^3\Pi_g$ state of the hydrogen molecule

R	E	D	dE/dR	$\langle H_1 \rangle$	$\langle H_2 \rangle$	$\langle H_3 \rangle$	$\langle .H \rangle$	ΔD
1.100	-.516517805	-8567.796	-.379602726	423.165	55.825	.011	479.001	-412.595
1.200	-.549098354	-1417.192	-.277368946	353.783	52.709	.011	406.502	-340.096
1.300	-.572883752	3803.100	-.202073887	304.407	49.938	.011	354.356	-287.950
1.400	-.590145472	7591.609	-.145826353	265.271	47.471	.012	312.754	-246.348
1.500	-.602505438	10304.308	-.103308420	233.754	45.270	.013	279.037	-212.631
1.600	-.611142301	12199.881	-.070849621	208.716	43.300	.013	252.029	-185.623
1.700	-.616928290	13469.758	-.045895110	186.811	41.534	.015	228.359	-161.953
1.800	-.620512468	14256.394	-.026602687	168.926	39.947	.016	208.888	-142.482
1.900	-.622393317	14669.193	-.011643670	153.837	38.519	.018	192.375	-125.969
1.950	-.622817960	14762.392	-.005471277	147.169	37.860	.019	185.049	-118.643
2.000	-.622952736	14791.971	-.000034172	141.009	37.235	.020	178.264	-111.858
2.050	-.622832220	14765.521	.004753307	135.301	36.641	.022	171.964	-105.558
2.100	-.622487019	14689.758	.008964552	130.015	36.078	.023	166.115	-99.709
2.200	-.621228083	14413.454	.015911276	120.530	35.036	.026	155.591	-89.185
2.300	-.619358890	14003.213	.021232385	112.322	34.097	.029	146.449	-80.043
2.400	-.617024777	13490.935	.025258237	105.201	33.253	.034	138.487	-72.081
2.500	-.614341894	12902.110	.028245640	99.014	32.496	.038	131.548	-65.142
2.600	-.611403846	12257.283	.030394717	93.727	31.817	.045	125.589	-59.183
2.700	-.608286038	11573.003	.031865915	89.148	31.212	.052	120.413	-54.007
2.800	-.605049442	10862.653	.032783416	85.267	30.675	.061	116.003	-49.597
2.900	-.601744572	10137.317	.033246548	82.113	30.201	.072	112.386	-45.980
3.000	-.598413137	9406.152	.033328815	79.746	29.788	.086	109.620	-43.214
3.200	-.591804712	7955.770	.032569925	78.308	29.140	.128	107.576	-41.170
3.400	-.585455497	6562.279	.030749424	86.017	28.741	.201	114.960	-48.554
3.600	-.579583548	5273.535	.027731157	122.802	28.672	.340	151.815	-85.409
3.700	-.576914088	4687.656	.025569748	169.744	28.825	.452	199.021	-132.615
3.800	-.574489089	4155.430	.022834102	248.851	29.148	.594	278.594	-212.188
3.900	-.572362746	3688.752	.019660807	344.498	29.625	.740	374.862	-308.456
4.000	-.570548171	3290.499	.016768396	391.254	30.090	.817	422.161	-355.755
4.100	-.568966812	2943.431	.015113501	349.161	30.301	.761	380.223	-313.817
4.200	-.567478980	2616.889	.014824349	266.225	30.194	.595	297.015	-230.609
4.300	-.565979682	2287.832	.015209540	192.340	29.917	.400	222.656	-156.250
4.400	-.564436693	1949.185	.015620924	140.890	29.626	.227	170.743	-104.337
4.600	-.561292338	1259.078	.015619383	89.356	29.251	-.005	118.603	-52.197
4.800	-.558260782	593.729	.014550951	73.379	29.190	-.127	102.443	-36.037
5.000	-.555521231	-7.533	.012731632	75.107	29.396	-.188	104.315	-37.909
5.200	-.553214340	-513.837	.010209805	94.237	29.890	-.197	123.930	-57.524
5.400	-.551494089	-891.389	.006846225	132.519	30.750	-.129	163.140	-96.734
5.500	-.550906605	-1020.327	.004884282	150.128	31.319	-.053	181.394	-174.988
5.700	-.550322987	-1148.416	.001062091	144.151	32.528	.174	176.853	-110.447
5.770	-.550287825	-1156.133	-.000026482	129.125	32.897	.263	162.285	-95.879
5.800	-.550294838	-1154.594	-.000434616	121.848	33.039	.301	155.188	-88.782
6.000	-.550589582	-1089.905	-.002268359	77.729	33.719	.522	111.971	-45.565
6.500	-.552022212	-775.479	-.002922694	39.496	34.127	.819	74.442	-8.036
7.000	-.553306412	-493.630	-.002171768	34.205	33.977	.934	69.115	-2.709
7.500	-.554200919	-297.308	-.001435391	33.413	33.765	.987	68.165	-1.759
8.000	-.554775230	-171.262	-.000894543	33.547	33.584	1.012	68.142	-1.736
9.000	-.555328554	-49.821	-.000300596	34.013	33.351	1.011	68.375	-1.969
10.000	-.555500593	-12.063	-.000083073	33.740	33.249	.966	67.954	-1.548
11.000	-.555544074	-2.520	-.000017605	33.337	33.214	.913	67.464	-1.058
12.000	-.555551484	-.894	-.000001312	33.123	33.203	.871	67.198	-0.792
13.000	-.555550704	-1.065	.000001418	33.099	33.201	.844	67.144	-0.738
14.000	-.555549273	-1.379	.000001162	33.007	33.201	.824	67.033	-0.627
15.000	-.555548418	-1.567	.000000491	32.930	33.202	.813	66.945	-0.539
16.000	-.555548163	-1.623	.000000005	32.859	33.202	.808	66.869	-0.463
17.000	-.555548299	-1.593	-.000000274	32.793	33.203	.807	66.803	-0.397
20.000	-.555549545	-1.319	-.000000473	32.621	33.203	.832	66.656	-0.250
25.000	-.555551573	-.874	-.000000346	32.392	33.203	.917	66.512	-0.106

At $R =$ 12 a 182-term wavefunction has been constructed but already at $R =$ 13 the expansion had to be shortened to 110 terms, and to 88 terms for $R = 25$. The results are shown in Table VI. The BO energy has a minimum at $R = 2.0$, a maximum at $R = 5.77$, again a minimum at $R = 12.5$, which is located about 0.9 cm^{-1} above the dissociation limit, and a small maximum at $R = 16$. In Fig. 3 we show the BO energies of the three $^3\Pi_g$ states, and in Fig. 4 the adiabatic corrections for these states.

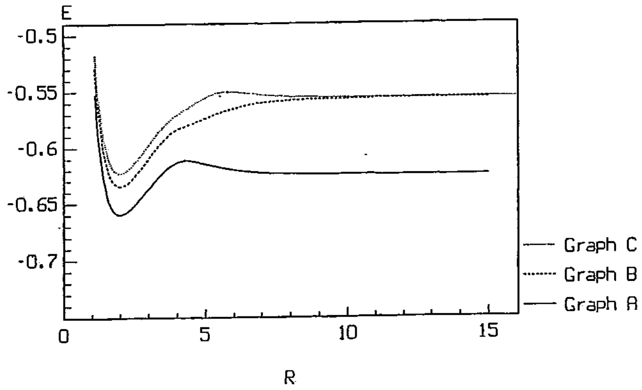

Fig. 4. Clamped nuclei energies for the *i* (graph *A*), *r* (graph *B*), *w* (graph *C*) states of the hydrogen molecule

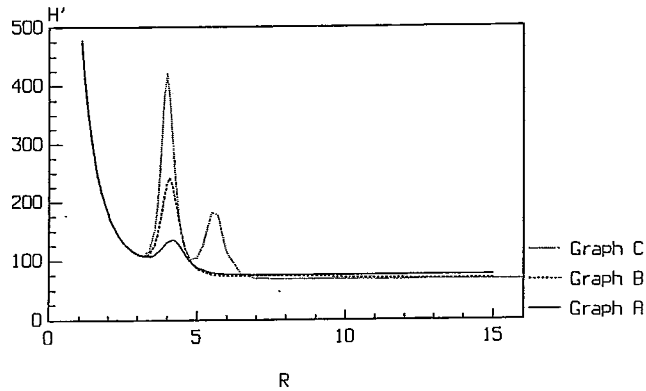

Fig. 5. Adiabatic corrections for the *i* (graph *A*), *r* (graph *B*), *w* (graph *C*) states of the hydrogen molecule

The adiabatic correction has the usual minimum for the 1*snp* and 1*snd* states located at the internuclear separation somewhat larger than $R = 3$. In the w state, under consideration, the minimum appears at $R = 3.2$. The maximum at $R = 4$, similarly as the maxima in this region for the *i* and *r* states, is due to an avoided crossing with a repulsive diabatic curve. The very small maximum at $R = 9$ seems to indicate an avoided crossing with the *r* state which has a maximum of $\langle H' \rangle$ at $R = 8$. The maximum at $R = 5.5$ arises from interaction with a higher state.

The asymptotic form of the angular contribution to the adiabatic correction H_1' for $R \to 0$ is $[L(L+1) - 2\Lambda^2]/2\mu R^2$ where L and Λ denote the quantum numbers of the united atom angular momentum and of the projection of the electronic angular momentum on the molecular axis, respectively. For the 1*snd*π states this contribution does not vanish and therefore for the *i*, *r* and *w* states $<H_1^{'}>$ for small *R* has much larger values than for the *c, d* and *k* states which are of the $1sn p\pi$ type.

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References

[1] W. Kołos and J. Rychlewski, J. Mol. Spectrosc. **66**, 428 (1977).
[2] J. Rychlewski, Theor. Chim. Acta **83**, 249 (1992).
[3] S. R. Keiding and N. Bjerre, J. Chem. Phys. **87**, 3321 (1987).
[4] W. Koot, W. J. van der Zande, J. Los, S. R. Keiding, N. Bjerre, Phys. Rev. **A39**, 590 (1989).
[5] G. Staszewska and L. Wolniewicz, J. Mol. Spectrosc, (1999) in press.
[6] L. Wolniewicz and K. Dressier, J. Chem. Phys. **100**, 444 (1994).
[7] J. Rychlewski, Phys. Rev. Letters **63**,1223 (1989).
[8] W. Kołos and J. Rychlewski, J. Mol. Spectrosc. **143**, 212 (1990).
[9] J. Rychlewski, Phys. Rev. **A45**, 5270 (1992).
[10] W. Kołos and J. Rychlewski, J. Mol. Spectrosc. **177**,146 (1996).
[11] W. Kołos and L. Wolniewicz, J. Chem. Phys. **43**, 2429 (1965).
[12] W. Kłos and L. Wolniewicz, J. Chem. Phys. **41**, 3663 (1964).