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Transition Moments between $w^3\Pi_g$ State and the First Three $^3\Sigma_u$ and $^3\Pi_u$ States of the Hydrogen Molecule[†]

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An explicitly correlated variational electronic wave function is obtained for the $w^3\Pi_g$ state of the hydrogen molecule and the Born−Oppenheimer potential energy curve as well as adiabatic corrections are given for internuclear distances $1 \leq R \leq 50$ au. The electronic dipole transition moments between $w^3\Pi_g$ and $b^3\Sigma_u$, $e^3\Sigma_u$, $f^3\Sigma_u$, $c^3\Pi_u$, $d^3\Pi_u$, and $k^3\Pi_u$ states for $0.6 \leq R \leq 20$ au are computed. These are the first accurate ab initio results for the above transitions. Also, the adiabatic vibrational levels are presented for $N = 1$.

Introduction

Recently, due to new sophisticated techniques the experimental investigation of excited states of the hydrogen molecule has shown considerable progress allowing the determination of energies of the rovibrational states with very high accuracy, often exceeding 0.05 cm^{-1} (see e.g. refs 1−13 and references therein). Hence, accurate theoretical description of the hydrogen molecule becomes more important and further systematic ab initio investigations are required. The determination of the electronic wave functions of the molecule and the Born−Oppenheimer (BO) energies is often necessary parts of such calculations (see e.g. refs 3, 14−20). As is well-known, for diatomic two-electron molecules the variational calculations in the confocal elliptical coordinates with explicitly correlated electrons allows one to achieve high accuracy (see e.g. refs 21−29). The data obtained in this way are also used to verify the accuracy of new methods developed for the description of larger molecular systems (see e.g. refs 30−33).

Recently, new accurate ab initio results for a number of triplet states have been published.[28,29] One of these papers[28] presents the Born−Oppenheimer potential energy curves and adiabatic corrections for three lowest $^3\Pi_u$ states (c, d, k) and three lowest $^3\Pi_g$ states (i, r, w); some of these data had been available before publication. In the second paper,[29] three lowest $^3\Sigma_g$ states (a, h, g), three lowest $^3\Sigma_u$ states (b, e, f), three lowest $^3\Pi_u$ states (c, d, k), and two lowest $^3\Pi_g$ states (i, r) were computed, or recomputed, and used to determine the potential energy curves, adiabatic corrections, and electronic dipole transition moments between these states with uniform accuracy in a wide range of internuclear distances.

The present work was undertaken in order to complete the calculations of the dipole transition moments by adding transitions from the third state of $^3\Pi_g$ symmetry, and these results seem to be the first accurate ab initio calculations of the transitions moments involving $w^3\Pi_g$ state. The computed transitions will be used in future in nonadiabatic calculations.

The method of computation of the wave function is briefly recalled in the following section. There the details of accurate calculations performed for the w state are given. In the following sections the results of the calculations of the Born−Oppenheimer potential, adiabatic corrections, and adiabatic vibrational energies for $N = 1$ are presented. The last section reports results of calculations of the electronic dipole transition moments between $w^3\Pi_g$ and $b^3\Sigma_u$, $e^3\Sigma_u$, $f^3\Sigma_u$, $c^3\Pi_u$, $d^3\Pi_u$, and $k^3\Pi_u$ states.

Atomic units are used throughout unless otherwise stated; the energy conversion factor to wavenumber is 1 hartree = 219 474.631 cm$-^1$, the reduced mass of the nuclei is μ = 918.0764.

The Wave Function

In this work the generalized James−Coolidge wave function developed in refs 19, 23, and 34−36 is used to describe the electronic motion of the hydrogen molecule. It has a form of an expansion in elliptic coordinates of the two electrons

$$\psi = \sum_k c_k G_k(1,2) \qquad (1)$$

where

$$G_k(1,2) = (x_1 + iy_1)^\Lambda g_k(1,2) \pm (x_2 + iy_2)^\Lambda g_k(2,1) \qquad (2)$$

and

$$g_k(1,2) = \exp(-\alpha\xi_1 - \bar{\alpha}\xi_2)\varsigma^{\upsilon_k}\xi_1^{\,r_k}\eta_1^{\,s_k}\xi_2^{\,\bar{r}_k}\eta_2^{\,\bar{s}_k}\,\{\exp(\beta\eta_1 + \bar{\beta}\eta_2) + (-1)^{s_k+\bar{s}_k+\Lambda+p}\exp(-\beta\eta_1 - \bar{\beta}\eta_2)\} \qquad (3)$$

Assuming that the internuclear axis coincides with the z axis, in this expansion, ξ_j and η_j are elliptic coordinates of the two electrons, x_j and y_j their Cartesian coordinates, and $\varsigma = 2r_{12}/R$, where r_{12} and R denote the interelectronic and internuclear distances respectively; Λ denotes the angular momentum projection quantum number (equal to 0 for Σ states and 1 for Π states); $p = 0, 1$ for g and u symmetry respectively; $\pm$ in eq 2 refers to singlet and triplet states, respectively; c_k, α, $\bar{\alpha}$, β, $\bar{\beta}$ are variational parameters and the basis set is defined by the set of exponents υ_k, r_k, s_k, $\bar{r}_k$, $\bar{s}_k$.

For the w state, the terms in the expansions (1)−(3) were chosen from the set of exponents fulfilling the conditions: $\upsilon \leq 5$ and $\upsilon + r + s \leq 8$. The selection of terms was performed in the usual way.[26] First, for a short expansion, the nonlinear parameters were optimized for several values of R (1, 2, 5, 10, 15). Next, from the above set of exponents the individual terms were tested−terms which gave the biggest decrease of the

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energy were added to the expansion and nonlinear parameters were reoptimized. This procedure was repeated several times. When 300 terms were selected, the nonlinear parameters were optimized for 91 values of R from the interval between 1 and 50 au and next the selection of terms was continued. As a result, a 478-term wave function was generated. The phase of this function is chosen in agreement with the convention adopted earlier (see e.g. refs 25 and 29).

Born−Oppenheimer Energies and Adiabatic Corrections

The total nonrelativistic Hamiltonian of the molecule in the center of mass system is

$$H = H_0 + H' \tag{4}$$

where H_0 is the clamped nuclei Hamiltonian and H' is the operator depending on the mass of the nuclei. For homonuclear molecules H' can be expressed as a sum of two parts

$$H' = H'_1 + H'_2 \tag{5}$$

where

$$H'_1 = -\frac{1}{2\mu}\Delta_R \tag{6}$$

$$H'_2 = -\frac{1}{2\mu}(\nabla_1 + \nabla_2)^2 \tag{7}$$

and μ is the reduced mass of the nuclei.

Let the electronic wave function, ψ, be the approximate solution of the clamped nuclei Schrödinger equation. Then, in the adiabatic approximation, the total molecular wave function, Φ has the form of a product of a rotational function, ψ^{rot}, adiabatic vibrational function, $\chi(R)$, and the electronic wave function, ψ:

$$\Phi = \frac{1}{R}\chi(R)\psi^{rot}\psi \tag{8}$$

The use of this product in the Schrödinger equation with the total Hamiltonian (4) leads to the well-known one-dimensional equation for nuclear motion

$$\left\{-\frac{1}{2\mu}\frac{d^2}{dR^2} + U(R) - E_{v,N}\right\}\chi_{v,N} = 0 \tag{9}$$

where

$$U(R) = E^{BO}(R) + \langle \psi\psi_N^{rot}|H'|\psi\psi_N^{rot}\rangle \tag{10}$$

$E^{BO}(R)$ in eq 10 is the Born−Oppenheimer energy and the second term consists of the centrifugal potential as well as the adiabatic corrections. According to the convention adopted in ref 23, this splitting is written as

$$\langle \psi\psi_N^{rot}|H'|\psi\psi_N^{rot}\rangle = E'(R) + \frac{N(N+1)}{2\mu R^2} \tag{11}$$

and all N-independent parts of the expectation value of H' are included in the adiabatic correction $E'(R)$. The method of calculation of the adiabatic correction is given in, e.g., ref 23. Part of this correction connected with the operator H'_2 resolves itself into the form of the expectation value with electronic wave function only. For the states with $\Lambda \neq 0$, in the second part, coming from the operator H'_1, the expectation value must be evaluated over electronic and rotational coordinates.

TABLE 1: Born-Oppenheimer Energies and Adiabatic Corrections for the *w* State of H_2

R	E^{BO}	dE^{BO}/dR	D (cm^{-1})	E (cm^{-1})
1.00	−0.471 882 447 2	−0.521 102 919	−18364.125	559.328
1.20	−0.549 101 828 6	−0.277 338 725	−1416.429	406.426
1.40	−0.590 148 042 9	−0.145 837 911	7592.173	312.915
1.50	−0.602 508 751 1	−0.103 315 690	10305.035	279.202
1.60	−0.611 145 608 6	−0.070 855 614	12200.606	251.454
1.70	−0.616 929 269 5	−0.045 895 767	13469.973	228.342
1.80	−0.620 513 157 9	−0.026 603 166	14256.546	208.894
1.90	−0.622 394 060 1	−0.011 644 480	14669.356	192.387
2.00	−0.622 953 416 9	−0.000 033 729	14792.121	178.269
2.10	−0.622 487 787 3	0.008 965 328	14689.927	166.121
2.20	−0.621 228 799 1	0.015 912 327	14413.611	155.612
2.50	−0.614 343 164 6	0.028 244 717	12902.389	131.620
3.00	−0.598 414 220 0	0.033 327 900	9406.390	109.705
3.50	−0.582 446 661 1	0.029 418 572	5901.916	127.899
3.80	−0.574 493 577 7	0.022 829 342	4156.415	281.871
4.00	−0.570 553 405 4	0.016 772 735	3291.648	426.670
4.20	−0.567 482 978 3	0.014 833 988	2617.767	299.256
4.50	−0.562 867 224 5	0.015 776 261	1604.726	138.467
5.00	−0.555 522 989 5	0.012 734 163	−7.147	104.372
5.50	−0.550 907 644 8	0.004 885 277	−1020.099	181.463
5.59	−0.550 549 230 1	0.003 086 772	−1098.761	187.614
6.00	−0.550 590 215 9	−0.002 267 901	−1089.766	112.010
6.50	−0.552 022 638 7	−0.002 922 574	−775.386	74.451
7.00	−0.553 306 934 2	−0.002 171 560	−493.515	69.123
7.50	−0.554 201 364 4	−0.001 435 398	−297.211	68.167
7.80	−0.554 577 949 8	−0.001 087 363	−214.560	68.103
8.00	−0.554 775 646 0	−0.000 894 600	−171.170	68.144
8.50	−0.555 125 606 9	−0.000 531 184	−94.363	68.321
9.00	−0.555 328 941 5	−0.000 300 695	−49.736	68.375
9.50	−0.555 441 570 1	−0.000 162 189	−25.017	68.222
10.00	−0.555 500 977 7	−0.000 083 147	−11.979	67.951
10.50	−0.555 530 664 4	−0.000 040 113	−5.463	67.678
11.00	−0.555 544 482 5	−0.000 017 673	−2.430	67.459
11.50	−0.555 550 190 2	−0.000 006 505	−1.178	67.303
12.00	−0.555 551 963 8	−0.000 001 287	−0.788	67.193
12.50	−0.555 551 975 6	0.000 000 892	−0.786	67.115
13.00	−0.555 551 315 2	0.000 001 583	−0.931	67.056
14.00	−0.555 549 768 2	0.000 001 324	−1.270	66.969
15.00	−0.555 548 787 6	0.000 000 642	−1.485	66.901
16.00	−0.555 548 424 5	0.000 000 120	−1.565	66.844
17.00	−0.555 548 476 7	−0.000 000 195	−1.554	66.795
18.00	−0.555 548 763 1	−0.000 000 359	−1.491	66.754
20.00	−0.555 549 605 5	−0.000 000 448	−1.306	66.690
25.00	−0.555 551 589 7	−0.000 000 327	−0.870	66.575
30.00	−0.555 552 910 3	−0.000 000 209	−0.581	66.479
35.00	−0.555 553 751 7	−0.000 000 133	−0.396	66.435
40.00	−0.555 554 289 8	−0.000 000 086	−0.278	66.418
45.00	−0.555 554 640 9	−0.000 000 057	−0.201	66.412
50.00	−0.555 554 876 5	−0.000 000 039	−0.149	66.409

The Born−Oppenheimer energies and the adiabatic corrections were computed for 361 internuclear distances. A complete set of results can be obtained through www.phys.uni.torun.pl/ftp/publications/ifiz/luwo/h2trans.00. Some of them are presented in Table 1, where besides the BO energies, $E^{BO}(R)$, and adiabatic corrections, E', (in cm^{-1}) the derivatives dE^{BO}/dR, obtained from the virial theorem, and the dissociation energies, D (in cm^{-1}), are also given. The accuracy of these calculations was tested by recomputing some points with real*16 arithmetic. The energy curve obtained in this work is generally slightly lower than that computed by Kołos and Rychlewski.[28]

The results are also displayed in Figures 1 and 2. It is seen in Figure 1 that besides the typical minimum at $R = 2.0$ the BO potential curve exhibits a very shallow second minimum at $R = 12.2$, located above the dissociation limit.

The total adiabatic corrections are plotted in Figure 2. One can observe the large corrections at about $R = 4.0$ and $R =$

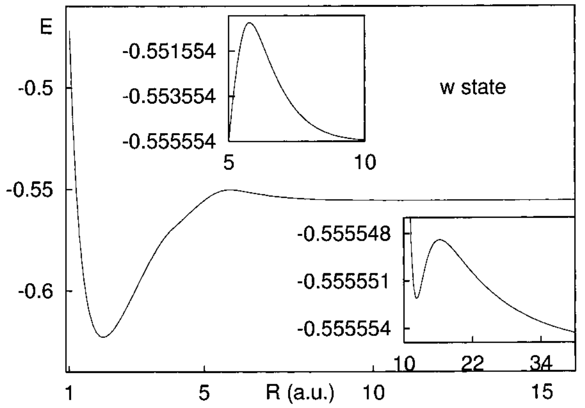

Figure 1. Born−Oppenheimer electronic energy curve of the $w^3\Pi_g$ state (in au).

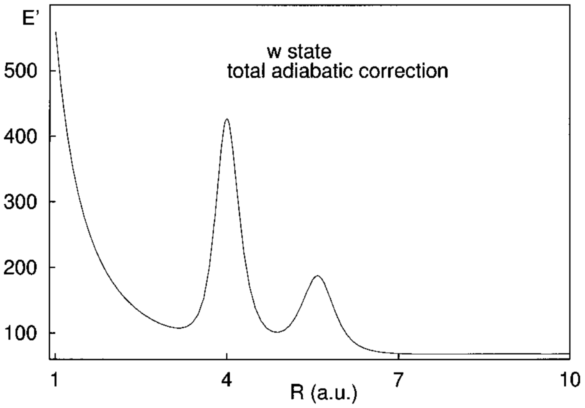

Figure 2. Total adiabatic corrections of the $w^3\Pi_g$ state (in cm^{-1}).

TABLE 2: Vibrational Energies, Dissociation Energies,Vibrational Quanta, and Rotational Constants for Vibrational Levels in the *w* State of H$_2$

v	E_v	D_v	$\Delta G(v + {}^1/_2)$	$\langle R_2 \rangle$
0	−0.616 687 03	13483.178	2167.372	0.2411
1	−0.606 811 76	11315.806	2036.659	0.2281
2	−0.597 532 06	9279.147	1908.055	0.2155
3	−0.588 838 32	7371.092	1779.916	0.2030
4	−0.580 728 43	5591.176	1646.717	0.1905
5	−0.573 225 43	3944.459	1465.758	0.1770
6	−0.566 546 94	2478.701	1170.484	0.1561
7	−0.561 213 83	1308.216	1055.018	0.1315
8	−0.556 406 81	253.198		0.1288

5.59 and a very small maximum at $R = 8.9$. Large corrections indicate changes in the character of the molecular states due to avoided crossings and strong nonadiabatic interactions.[21−23,29] As was pointed out in ref 28, the maximum at $R = 4.0$ is due to an avoided crossing with a repulsive diabatic curve and the maximum at $R = 5.59$ arises from interaction with a higher state. The third small maximum at $R = 8.9$ can indicate an avoided crossing with the $r^3\Pi_g$ state for which the adiabatic corrections have a maximum in the same region (at $R = 7.8$).

Adiabatic Vibrational Levels

The adiabatic potential (10) obtained in this work was used in the equation for nuclear motion (9) to calculate the rovibrational energies. The results for $N = 1$ are listed in Table 2. In the first column the vibrational energies, E_v, are given, next, the dissociation energies, D_v, further, vibrational quanta denoted as ΔG and in the last column the expectation values of R^{-2}. The latter are proportional to the rotational constants: $B_v = \langle v|R^{-2}|v\rangle/2\mu$. All vibrational states are localized within inner potential well, the outer well is too shallow to support a bound state. The presented vibrational energies are calculated in the adiabatic approximation, in order to compare them with experimental data (if available) the nonadiabatic calculations are necessary.

TABLE 3: Dipole Transition Moments Involving *w* State of H$_2$

R	$w \rightarrow b$	$w \rightarrow e$	$w \rightarrow f$	$w \rightarrow c$	$w \rightarrow d$	$w \rightarrow k$
0.60	−0.4155	−1.0498	2.9981	−0.4292	−1.1773	3.8117
0.80	−0.3956	−0.9206	2.3540	−0.4280	−1.1766	3.7998
1.00	−0.3648	−0.7635	1.6774	−0.4269	−1.1814	3.8287
1.25	−0.3160	−0.5663	0.9446	−0.4254	−1.2138	4.0733
1.75	−0.2320	−0.3058	0.1179	−0.4190	−1.2344	4.2649
2.00	−0.2084	−0.2467	−0.0530	−0.4121	−1.2622	4.5103
2.25	−0.1957	−0.2160	−0.1295	−0.4009	−1.2895	4.8064
2.50	−0.1917	−0.2084	−0.1423	−0.3828	−1.3116	5.1549
2.75	−0.1957	−0.2185	−0.1038	−0.3535	−1.3270	5.6043
3.00	−0.2082	−0.2450	−0.0145	−0.3052	−1.3314	1.7941
3.25	−0.2321	−0.2918	0.1452	−0.2215	−1.3140	1.7038
3.50	−0.2743	−0.3715	0.4426	−0.0622	−1.2417	1.9485
3.75	−0.3434	−0.5100	1.0795	0.2784	−0.9850	2.5428
4.00	−0.3887	−0.6687	2.3751	0.9016	−0.1461	3.7549
4.50	−0.1434	−0.4601	3.9015	1.4049	2.1697	5.8097
5.00	0.0483	−0.1288	−0.0370	1.3225	2.9228	5.8241
5.50	0.2353	0.3730	−1.4924	1.1851	2.4656	4.9467
6.00	0.3789	0.9358	−1.6405	0.8175	0.9554	4.4064
6.50	0.4161	1.1993	−1.4138	0.5115	−0.0766	4.2455
7.00	0.4253	1.3429	−1.1985	0.3014	−0.9059	4.1460
7.50	0.4275	1.4496	−1.0140	0.1279	−1.8132	3.8889
8.00	0.4267	1.5432	−0.8389	−0.0347	−2.5408	3.5181
8.50	0.4236	1.6280	−0.6587	−0.1936	−2.8999	3.2814
9.00	0.4187	1.7005	−0.4683	−0.3456	−3.0124	3.2190
9.50	0.4126	1.7550	−0.2698	−0.4838	−3.0003	3.2601
10.00	0.4059	1.7874	−0.0682	−0.6025	−2.9298	3.3458
10.50	0.3993	1.7967	0.1307	−0.7002	−2.8350	3.4433
11.00	0.3934	1.7842	0.3203	−0.7784	−2.7329	3.5382
11.50	0.3882	1.7544	0.4931	−0.8401	−2.6310	3.6248
12.00	0.3838	1.7140	0.6422	−0.8886	−2.5325	3.7024
13.00	0.3771	1.6292	0.8602	−0.9568	−2.3478	3.8331
15.00	0.3700	1.5302	1.0485	−1.0234	−2.0172	4.0269
20.00	0.3741	1.5491	1.0108	−0.9829	−1.0428	4.3854

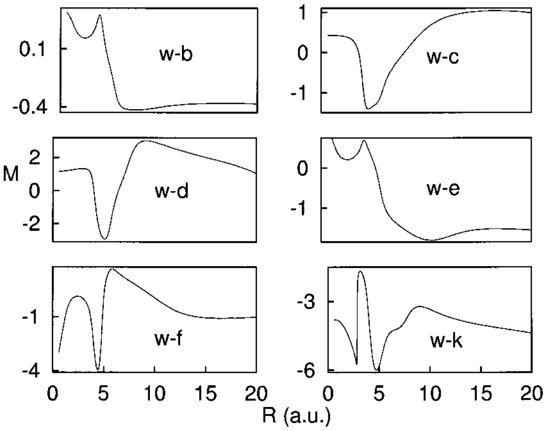

Figure 3. Transition moments involving the $w^3\Pi_g$ state (in au).

Transition Moments

Dipole transition moments have been computed in several recent studies.[5,16,21,25,29] It was shown in ref 25 that the dipole formula is more suitable for numerical calculations than the velocity formula. So, here, as in a previous paper,[29] the transition moments, **M**, between states ψ_1 and ψ_2 were computed from the dipole formula

$$\mathbf{M} = \langle \psi_1 | \mathbf{r}_1 + \mathbf{r}_2 | \psi_2 \rangle \tag{12}$$

For $\Sigma \rightarrow \Pi$ transitions, the wave function of the Π state is inserted on the left side of eq 12 so the nonvanishing components of the transition moments are $M_+ = (M_x + iM_y)/\sqrt{2}$ for the $\Sigma \rightarrow \Pi$ transitions and M_z for the $\Pi \rightarrow \Pi$ transitions. All transitions are computed for internuclear distances from the interval [0.6−20]. Some of the results are given in Table 3 and in Figure 3. Full tables are available under file name www.phys.uni.torun.pl/ftp/publications/ifiz/luwo/h2trans.00.

The transition moments presented in this work have not been investigated before; together with those considered in ref 29, they correspond to all possible transitions between three lowest states of $^3\Sigma_g$, $^3\Sigma_u$, $^3\Pi_g$, and $^3\Pi_u$ symmetries. In all those cases, one can observe an irregular behavior of the moments, in particular, in the regions where the adiabatic corrections of the involved states are large. Experience with previously investigated transitions (where the comparison with experimental data was possible) shows that nonadiabatic interactions are important. The investigation of these effects is in preparation in this laboratory.

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