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Adiabatic corrections for the $i\ ^3\Pi_g$ state of the hydrogen molecule*

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Summary. The adiabatic corrections of the $i\ ^3\Pi_g$ state of H_2 are calculated for a wide range of internuclear distances using an explicitly correlated wavefunction. The vibrational structure of this state is calculated in the adiabatic approximation. It is shown that for $N = 1$ levels of the "−" substate, for which the nonadiabatic corrections are negligible, the agreement between theory and experiment is excellent; the small mass independent discrepancy of the order of 0.5–3 cm^{-1} is due to the convergence error in the Born–Oppenheimer calculations. For higher N the discrepancy is much larger. However, it is mass and N-dependent and it is almost entirely due to the nonadiabatic effects caused by $^3\Pi_g$–$^3\Delta_g$ interactions. The still larger discrepancy for the "+" substate of the i state is evidently caused by additional interactions of the i state with close-lying states of $^3\Sigma_g^+$ symmetry.

Key words: H_2 (hydrogen molecule) – $i\ ^3\Pi_g$ state – Adiabatic corrections

1. Introduction

The $i\ ^3\Pi_g$ state of H_2 belongs to the $3s$, $d\,\Sigma\Pi\Delta$ complex of states which has been studied extensively in the recent years by experimental methods [1–12]. The states resulting from $3s$, d configurations which form this complex of states, i.e. $h(3s)\ ^3\Sigma_g^+$, $g(3d)\ ^3\Sigma_g^+$, $i(3d)\ ^2\Pi_g$ and $j(3d)\ ^3\Delta_g$ need special treatment since the electronic energy separations between the individual states are smaller than the rovibrational energy separations. Consequently, the rotation of the molecule induces a breakdown of the Born–Oppenheimer approximation. The only exceptions are the $N = 1$ levels of the $i\ ^3\Pi_g$ state for which the adiabatic approximation is adequate. Theoretically the $i\ ^3\Pi_g$ state of H_2 was studied in the Born–Oppenheimer approximation several years ago [13]. In that study a very

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* Dedicated to Prof. Klaus Ruedenberg on the occasion of his 70th birthday

** *Permanent address*: Department of Chemistry, A. Mickiewicz University, ul. Grunwaldzka 6, PL-60-780 Poznań, Poland flexible wavefunction depending explicitly on the interelectronic distance was used and an accurate potential energy curve was calculated. In this paper the previous study is extended to include adiabatic corrections.

2. Adiabatic calculations

The adiabatic corrections are given as expectation values of the operators:

$$H' = H'_1 + H'_2 + H'_3, \tag{1}$$

where

$$H'_1 = -(1/2\mu)\Delta_R, \tag{2}$$

$$H'_2 = -(1/8\mu)(\Delta_1 + \Delta_2), \tag{3}$$

$$H'_3 = -(1/4\mu)\nabla_1\nabla_2. \tag{4}$$

H'_1 is the operator of the relative kinetic energy of the nuclei, H'_2 is the correction operator to the kinetic energy of the electrons, H'_3 is the mass polarization operator and μ denotes the reduced mass of the nuclei. The explicit expression of $\langle\Lambda|H'_1|\Lambda\rangle$ in terms of elliptic coordinates is given in [14]. However, that general formula for $\Lambda = 0$ is quite inconvenient for numerical computations. Therefore we adopt here the simplified method developed by Wolniewicz [15, 16]. The electronic wavefunction for the $^3\Pi$ state is assumed in the form:

$$\Psi(1,2) = \sum_i c_i[\Phi_i(1,2)(x_1 + iy_1) - \Phi_i(2,1)(x_2 + iy_2)], \tag{5}$$

where x_i and y_i denote cartesian coordinates of ith electron and the basis functions $\Phi_i(1,2)$ which possess Σ symmetry are expressed in elliptic coordinates as:

$$\begin{aligned}\Phi_i(1,2) = {} & \exp(-\alpha\xi_1 - \bar{\alpha}\xi_2)\xi_1^{n_i}\eta_1^{k_i}\xi_2^{m_i}\eta_2^{l_i}[\exp(\beta\eta_1 + \bar{\beta}\eta_2) + (-1)^{k_i+l_i+1} \\ & \times \exp(-\beta\eta_1 - \bar{\beta}\eta_2)](2r_{12}/R)^{\mu_i},\end{aligned} \tag{6}$$

where α, β, $\bar{\alpha}$, $\bar{\beta}$ are nonlinear variational parameters, n_i, k_i, l_i, m_i and μ_i are integers greater or equal to zero; r_{12} and R describe the interelectronic and internuclear distances, respectively. According to Wolniewicz [15], in order to evaluate $\langle H'_1\rangle$ it is convenient to express basis functions in the form:

$$\Phi_i(1,2)(x_1 + iy_1) = 2^{1/2}\Phi_i(1,2)A_i\exp(i\psi), \tag{7}$$

where ψ is the Euler angle describing rotation around the molecular axis. Under this assumption the diagonal part of Δ_R has the form (we omit here the rotation term):

$$\begin{aligned}\langle 1|\Delta_R|1\rangle = \sum_{i,k}\Bigg[& \int A_i^* A_k \Phi_i^* [\langle 0|\Delta_R|0\rangle + \Lambda^2/(2\mu R^2)]\Phi_k\, dr \\ & + 2^{1/2}/R^2 \int A_i^* \Phi_i^* z_k \langle 1|L^+|0\rangle \Phi_k\, dr\Bigg],\end{aligned} \tag{8}$$

where integration is performed over all electronic coordinates. $L^+ = L_x + iL_y$, where L_x and L_y are the components of electronic angular momentum in the molecule fixed-frame and $\langle 1|L^+|0\rangle$ is an operator given explicitly in elliptic coordinates in [14]. The term $\langle 0|\Delta_R|0\rangle$ denotes the appropriate operator for Σ states [17].

Table 1. Adiabatic corrections $\langle H' \rangle$ of the $i\,^3\Pi_g$ state in cm^{-1}. $\Delta D = H'(\infty) - H'(R)$ is the adiabatic correction to the dissociation energy

R	$\langle H'_1 \rangle$	$\langle H'_2 \rangle$	$\langle H'_3 \rangle$	$\langle H' \rangle$	ΔD
1.0	499.953	61.514	0.018	561.485	−486.779
1.2	353.665	54.895	0.022	408.582	−333.876
1.4	265.366	49.684	0.026	315.076	−240.370
1.6	208.054	45.541	0.032	252.627	−178.921
1.8	168.822	42.223	0.039	211.084	−136.378
1.9	153.727	40.816	0.044	194.587	−119.881
2.0	140.877	39.554	0.047	180.478	−105.772
2.3	112.151	36.503	0.070	148.724	−74.018
2.5	98.795	34.979	0.091	133.865	−59.159
3.0	78.418	32.589	0.198	111.204	−36.498
3.5	74.990	32.088	0.516	107.594	−32.888
3.7	80.781	32.529	0.789	114.776	−40.070
4.0	95.337	34.245	1.468	130.848	−56.142
4.5	76.316	37.448	2.962	116.726	−42.020
5.0	44.440	38.801	3.811	87.052	−12.346
6.0	33.524	38.449	4.306	76.279	−1.573
7.0	32.756	37.869	4.469	75.094	−0.388
8.0	32.724	37.576	4.555	74.855	−0.149
10.0	32.746	37.409	4.627	74.783	−0.077
12.0	32.733	37.382	4.648	74.763	−0.057

The adiabatic calculations were performed using the previously constructed electronic wavefunction consisting of 70-terms in the expansion [13]. The adiabatic corrections were calculated for a wide range of internuclear distance: $1.0 \leqslant R \leqslant 12.0$ bohr. The results are presented in Table 1 where all values but R are given in units of cm^{-1}. ΔD denotes the adiabatic correction to the dissociation energy. The overall characteristic of the adiabatic corrections for the i state is similar to that found for the $I\,^1\Pi_g$ state [18]. It is characterized by a large value for small R which is a consequence of the fact that for small R the dominant contribution originates from the term $[L(L+1) - 2\Lambda^2]/2\mu R^2$ ($L = 2$ and $\Lambda = 1$ for the i state) which becomes very large for $R \rightarrow 0$. $\langle H'_1 \rangle$ possesses a maximum near $R = 4.0$ bohr. Therefore the adiabatic correction increases the hump on the Born–Oppenheimer potential energy curve appearing in this region [13].

3. Vibrational structure

The adiabatic wavefunctions $\chi_{vN}(R)$ and eigenvalues E_{vN} were obtained by numerical solution of the one-dimensional Schrödinger equation for nuclear motion:

$$\left[-\frac{1}{2\mu}\frac{d^2}{dR^2} + U^{\mathrm{BO}}(R) + \langle H'(R) \rangle + \frac{N(N+1)}{2\mu R^2} - E_{vN} \right] \chi_{vN}(R) = 0, \qquad (9)$$

with the BO potential energy curve taken from [13] and the adiabatic corrections $\langle H'(R) \rangle$ computed in this work. The numerical integration was carried out in

Table 2. Dissociation energies for the $i\,^3\Pi_g$ state of H_2, HD, and D_2 in the adiabatic approximation

v	$N=0$	$N=1$	$N=2$	$N=3$	$N=4$
			H_2		
0	6366.644	6309.671	6196.188	6027.111	5803.783
1	4250.420	4196.766	4089.903	3930.717	3720.504
2	2279.867	2229.566	2129.400	1980.232	1783.329
3	462.147	415.390	322.314	183.783	1.076
			HD		
0	6539.528	6496.543	6410.837	6282.928	6113.585
1	4688.237	4647.411	4566.015	4444.553	4283.767
2	2945.736	2907.078	2830.010	2715.024	2562.846
3	1315.242	1278.817	1206.213	1097.916	954.646
			D_2		
0	6740.932	6712.080	6654.492	6568.404	6454.161
1	5211.506	5183.832	5128.599	5046.034	4936.476
2	3754.408	3727.911	3675.029	3595.984	3491.108
3	2370.699	2345.394	2294.893	2219.416	2119.288
4	1062.958	1038.887	990.855	919.080	823.886

Table 3. Rotational constants B_v (in cm^{-1}) for the $i\,^3\Pi_g$ state of H_2, HD, and D_2

v	H_2	HD	D_2
0	28.525	21.514	14.436
1	26.865	20.434	13.846
2	25.187	19.350	13.258
3	23.415	18.233	12.662
4			12.045

the interval $R = 0$ to 12 bohr and the integration step was 0.01 bohr. For the nuclear masses we used $M_p = 1836.1515$ and $M_d = 3670.4907$ in units of m_e.

The final results of the computations of adiabatic rovibrational energies, D_v, are presented for the i state of H_2, HD, and D_2 in Table 2. In Table 3 the rotational constants B_v calculated in the adiabatic approximation are included. In Table 4 the calculated term values T_v are compared with the experimental data. The adiabatic T_v values were obtained by subtracting the computed vibrational energies D_v from the theoretical adiabatic dissociation limits. The latter values were taken from [16] and they are 118377.200, 118676.087, and 119029.841 cm^{-1} for H_2, HD, and D_2, respectively. The experimental term values listed in Table 4 are those for the "$-$" substate of the i state and were taken from [11] and [19] for H_2 and D_2, respectively. For HD the experimental term values were obtained by adding the experimental energy for the i state, measured in respect to the $v = 0$, $N = 1$ level of the $c\,^3\Pi_u^-$ state [9], to the theoretical adiabatic energy of this level of the c state [20]. It should be noted, however, that uncertainty in the latter value is of the order of 0.5 cm^{-1}

Table 4. Comparison of the theoretical adiabatic term values T_v (cm^{-1}) with experimental data for the $i\,^3\Pi_g^-$ state of H_2, HD, and D_2. Δ stands for $T_{adiab}-T_{exp}$

N	v	T_{adiab}	T_{exp}	Δ
		H_2		
1	0	112067.53	112066.96	0.53
1	1	114180.43	114177.96	2.47
1	2	116147.63	116144.82	2.81
1	3	117961.81	117961.06	0.75
2	0	112191.01	112141.19	39.82
2	1	114287.30	114259.30	28.00
2	2	116247.80	116227.03	20.77
-2	3	118054.89	118042.98	11.91
3	0	112350.09	112265.55	84.54
3	1	114446.48	114384.78	61.70
3	2	116396.97	116352.36	44.61
3	3	118193.42	118167.46	25.96
4	0	112573.42	112442.43	130.99
4	1	114656.70	114557.12	99.58
4	2	116593.87	116522.34	71.53
4	3	118376.12	118339.67	38.45
		HD		
1	0	112179.55	112179.39	0.16
1	1	114028.68	114028.24	0.44
1	2	115769.01	115768.09	0.92
1	3	117397.27	117295.75	1.52
2	0	112265.25	112243.81	21.44
2	1	114110.08	114094.27	15.81
2	2	115846.08	115834.28	11.80
2	3	117469.88	117461.22	8.66
3	0	112393.16	112344.59	48.57
3	1	114231.54	114195.10	35.44
3	2	115961.07	115934.42	26.65
3	3	117578.17	117559.61	18.56
4	0	112562.51	112483.65	78.86
4	1	114392.32	114332.07	60.25
4	2	116113.24	116068.83	44.41
4	3	117721.44	117690.94	30.50
		D_2		
1	0	112317.76	112317.13	0.63
1	1	113846.01	113845.27	0.74
1	2	115301.93	115301.01	0.92
1	3	116684.45	116683.29	1.16
1	4	117990.95	117975.17	15.78
2	0	112375.35	112365.66	9.69
2	1	113901.24	113893.63	7.61
2	2	115354.81	115348.78	6.03
2	3	116734.95	116739.18	4.77
2	4	118038.99	118038.20	0.79
3	0	112461.44	112439.25	22.19
3	1	113983.81	113966.40	17.41
3	2	115433.86	115420.39	13.47
3	3	116810.42	116800.31	10.11
3	4	118110.76	118103.67	7.09
4	0	112575.68	112538.45	37.23
4	1	114093.36	114063.94	29.42
4	2	115538.73	115516.05	22.68
4	3	116910.55	116893.90	16.65
4	4	118205.95	118194.84	11.11

In the adiabatic approximation the $i\,^3\Pi_g$ state is doubly degenerate. It is composed of two substrates, $i\,^3\Pi_g^-$ and $i\,^3\Pi_g^+$. If nonadiabatic effects are added, the above mentioned degeneracy is removed. The nonadiabatic effects for the i state, up to the second order in perturbation theory, are caused by the interaction between the i state and the close lying $h\,^3\Sigma_g^+$, $g\,^3\Sigma_g^+$, and $j\,^3\Delta_g$ states and are examples of so-called heterogeneous nonadiabatic effects. The homogeneous nonadiabatic effects caused by the interaction of the i state with higher states of this same symmetry are much smaller because of the relatively large energy gap between the i state and higher $^3\Pi_g$ states. For the "$-$" substate of the i state the heterogeneous nonadiabatic effects are caused entirely by the perturbation by the $j\,^3\Delta_g^-$ state. Therefore for $N=1$ levels of the $i\,^3\Pi_g^-$ state, for which there is no corresponding levels of the $j\,^3\Delta_g^-$ state, the nonadiabatic corrections should be negligible. As is seen from Table 4 the difference between theory and experiment for the $N=1$ levels is very small. For $v=0$ this is 0.53, 0.16, and 0.63 cm^{-1} for H_2, HD, and D_2, respectively. Since this discrepancy is almost mass-independent, except for HD for which there is uncertainty of the order of 0.5 cm^{-1}, it is clearly due to the convergence error in the Born–Oppenheimer potential energy curve. In vicinity of the equilibrium this error is of the order of 0.5 cm^{-1}. The slightly larger discrepancy for higher vibrational levels (but still for $N = 1$) means that the above mentioned convergence error is slightly larger for larger values of R.

For the levels with $N > 1$ the discrepancy is much larger and it is strongly N-dependent. Since these levels are perturbed by the j state the discrepancy might be attributed to the heterogeneous nonadiabatic effects. These effects for the $\Delta-\Pi$ interaction depend on N like $(N+2)(N-1)$ [21], so the nonadiabatic effects for $N = 2, 3, 4$ levels should be of ratios $4:10:18 = 2:5:9$. The corresponding ratios can be found from Table 4 and they amount to $2:4.3:6.6$, $2:4.4:7.1$, and $2:4.3:7$ for $v = 0, 1, 2$ levels of H_2, respectively. The corresponding ratios for D_2 are $2:4.6:7.7$, $2:4.6:7.7$, and $2:4.5:7.5$ for $v = 0, 1, 2$, respectively. It is seen that despite a small error in the BO calculation the discrepancy between theoretical and experimental term values for the $i\,^3\Pi_g^-$ state can be attributed almost entirely to nonadiabatic effects and these effects can be estimated from Table 4.

In Table 5 we compare the theoretical and experimental term values for the $i\,^3\Pi_g^+$ state of H_2. As is seen from this table the discrepancies are much larger and have opposite sign. For the "+" substate of the i state, in addition to perturbation by the $j\,^3\Delta_g^+$ state, the perturbation by the close lying $h\,^3\Sigma_g^+$ and $g\,^3\Sigma_g^+$ states appears. It is evident that the latter interaction leads to much larger nonadiabatic corrections and these corrections have opposite sign to the corrections caused by $\Pi-\Delta$ interactions. Treating both corrections as additive it is possible to estimate the nonadiabatic effects caused by the $^3\Pi_g$–$^3\Sigma_g$ interaction.[1]

Table 5. Comparison of the theoretical adiabatic term values (cm^{-1}) with experimental data for the $i\,^3\Pi_g^+$ state of H_2. Δ stands for $T_{\mathrm{adiab}}-T_{\mathrm{exp}}$

N	v	T_{adiab}	T_{exp}	Δ
1	0	112067.53	112153.71	−86.18
1	1	114180.43	114269.15	−88.72
1	2	116147.63	116182.28	−34.65
1	3	117961.81	117983.74	−21.93
2	0	112191.01	112311.08	−120.07
2	1	114287.30	114419.48	−132.18
2	2	116247.80	116319.29	−71.40
2	3	118054.89	118106.95	−52.06
3	0	112350.09	112503.79	−153.70
3	1	114446.48	114614.27	−167.74
3	2	116396.97	116504.17	−107.20
3	3	118193.42	118278.96	−85.54

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[1] As one of the referees pointed out, the unperturbed term values for the i state calculated from L-uncoupled parameters for $3s$, $3d$ complex of states listed in Table VII of [11] for H_2 and in Table VII of [9] for HD are far from the observed term values, but in agreement with the calculated ones given in this paper

4. Conclusion

We have presented in this paper adiabatic corrections for the $i\,^3\Pi_g$ state which improve agreement between theory and experiment for this state. The convergence error in the BO calculations has been estimated as 0.5 cm^{-1} in the vicinity of the equilibrium internuclear distance. The remaining discrepancy is clearly due to the nonadiabatic effects originating from $\Pi-\Delta$ and $\Sigma-\Pi$ interactions. Comparison between theoretical and experimental term values allows one to estimate these corrections.

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