Double-Minimum Potential-Energy Curve Resulting from the Adiabatic Effect: The h $^3\Sigma_g^+$ State of H_2

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Calculations of the adiabatic effects for the $h\,^3\Sigma_g^+$ state of the hydrogen molecule have been performed using an explicitly correlated wave function. It is shown that in contrast to the Born-Oppenheimer results the adiabatic potential-energy curve for the h state is characterized by a double-minimum function. The nature and consequences of this finding are discussed.

It has been well established that the $h(3s)\,^3\Sigma_g^+$ state of H_2 is nearly degenerate with the $g(3d)\,^3\Sigma_g^+$ state and, in the Born-Oppenheimer (BO) approximation, these two states are separated only by 162 cm^{-1} at equilibrium.[1] Wakefield and Davidson[1] have made extensive calculations of the mutual interactions of these two states in order to reach the best agreement with experimental data. They found good agreement except for the $J=0$ and 1 levels of the h state. Also Jost et al.,[2] in their studies of the g factor for the $3d$ triplet complex (including the h state) of H_2, found disagreement with experimental data for the lowest vibrational level of the h state, suggesting that the spectrum of this state is irregular.

Our recent calculations[3] on the BO potential-energy curve for the $h\,^3\Sigma_g^+$ state of the hydrogen molecule have revealed a relatively large discrepancy between theoretical and experimental vibrational levels. As it was pointed out in Ref. 3 this discrepancy cannot be caused by a convergence error in the BO calculations. Also, the adiabatic and nonadiabatic effects are unlikely to be responsible for the above-mentioned disagreement. Consequently, it has been suggested[2] that at least some levels of the h state had been misassigned.

To explore the disagreement between theory and experiment for the h state, calculations of the adiabatic corrections to the BO potential-energy curve for this state have been undertaken and the results are reported in this paper.

If the center-of-mass motion is separated out from the complete nonrelativistic Schrödinger equation for the hydrogen molecule, and the positions of the electrons are referred to the geometric center of the nuclei, the following Hamiltonian for the internal motion is obtained:

$$H = H_0 + H', \tag{1}$$

where H_0 is the clamped nuclei Hamiltonian and H' is the operator depending on the mass of the nuclei. The adiabatic correction is calculated as the expectation value of

$$H' = H_1 + H_2 + H_3, \tag{2}$$

with

$$H_1 = -(1/2\mu)\Delta_R, \tag{3}$$

$$H_2 = -(1/8\mu)(\Delta_1 + \Delta_2), \tag{4}$$

$$H_3 = -(1/4\mu)\nabla_1\nabla_2, \tag{5}$$

where μ denotes the rescued mass of the nuclei, the vector R describes the relative position of the nuclei, and the indices 1 and 2 label the electrons. An explicit expression for $\langle H' \rangle$ in terms of elliptic coordinates is given elsewhere (see, e.g., Ref. 4).

The wave function used was in the form of the generalized James-Coolidge expansion[5]

$$\Psi(1,2) = \sum_i c_i[\Phi_i(1,2) - \Phi_i(2,1)], \tag{6}$$

where

$$\Phi_i(1,2) = \exp(-\alpha\xi_1 - \bar{\alpha}\xi_2)\xi_1^{n_i}\eta_1^{k_i}\xi_2^{m_i}\eta_2^{l_i}(2r_{12}/R)^{u_i}[\exp(\beta\eta_1 + \bar{\beta}\eta_2) + (-1)^{k_i+l_i}\exp(-\beta\eta_1 - \bar{\beta}\eta_2)], \tag{7}$$

where ξ and η are elliptic coordinates, r_{12} and R denote the interelectronic and internuclear distances, respectively; α, $\bar{\alpha}$, β, $\bar{\beta}$, and c_i are variational parameters, and n_i, k_i, m_i, l_i, and u_i are integers.

To calculate the adiabatic corrections we used a 50-term wave function of this type. The computed corrections are listed in Table I and are shown graphically in Fig. 1. The R dependence of the total adiabatic correction $\langle H' \rangle$ in the vicinity of the equilibrium is dominated by the shape of $\langle H_1 \rangle$ which exhibits a maximum at $R = 1.95$ a.u. The term $\langle H_1 \rangle$ involves derivatives of the electronic wave function with respect to the internuclear distance R. Therefore, near the equilibrium where, due to avoided crossing, the wave function drastically changes its character, this correction may have a large value. The existence of the large adiabatic effect in the vicinity of the equilibrium very strongly influences the shape of the adiabatic potential-energy curve. In Fig. 2 the BO and adiabatic potential-energy curves are displayed. It is seen from this figure that, in contrast to the BO approximation in which the potential-energy

TABLE I. Adiabatic correction $\langle H' \rangle$ and its components for the $h\,^3\Sigma_g^+$ state in cm^{-1} [$\Delta D = \langle H'(\infty) \rangle - \langle H'(R) \rangle$ is the adiabatic correction to dissociation energy]. R is in a.u.

R	$\langle H_1 \rangle$	$\langle H_2 \rangle$	$\langle H_3 \rangle$	$\langle H' \rangle$	ΔD
1.0	32.151	61.493	0.140	93.784	−19.077
1.5	32.844	47.161	0.177	80.182	−5.475
1.8	245.056	41.735	0.184	286.975	−212.268
1.85	630.659	41.022	0.182	671.863	−597.156
1.9	1719.830	40.397	0.171	1760.398	−1685.691
1.925	2542.330	40.133	0.160	2582.623	−2507.916
1.95	3005.705	39.901	0.145	3045.751	−2971.044
1.96	2955.267	39.812	0.138	2995.217	−2920.510
1.97	2776.188	39.724	0.132	2816.044	−2741.337
1.98	2502.980	39.636	0.125	2542.741	−2468.034
2.0	1856.803	39.455	0.114	1896.372	−1821.665
2.05	745.377	38.987	0.097	784.461	−709.754
2.1	369.301	38.492	0.091	407.884	−333.177
2.25	202.307	36.902	0.120	239.329	−164.622
2.5	137.321	35.189	0.139	172.649	−97.942
3.0	104.032	33.071	0.318	137.421	−62.714
4.0	75.759	33.764	1.340	110.863	−36.156
5.0	57.123	36.633	2.688	96.444	−21.737
7.0	41.396	38.515	2.601	82.512	−7.805
10.0	39.721	37.736	1.047	78.504	−3.797

curve is characterized by a single minimum, in the adiabatic approximation this curve has a double minimum. To the author's knowledge this is the first example of the double-minimum potential-energy curve resulting exclusively from the adiabatic effect.

The rotation-vibration energy levels have been obtained by numerical solution of the one-dimensional Schrödinger equation for the nuclear motion

$$\left[-\frac{1}{2\mu}\frac{d^2}{dR^2} + U^{BO}(R) + \langle H'(R) \rangle \right.$$

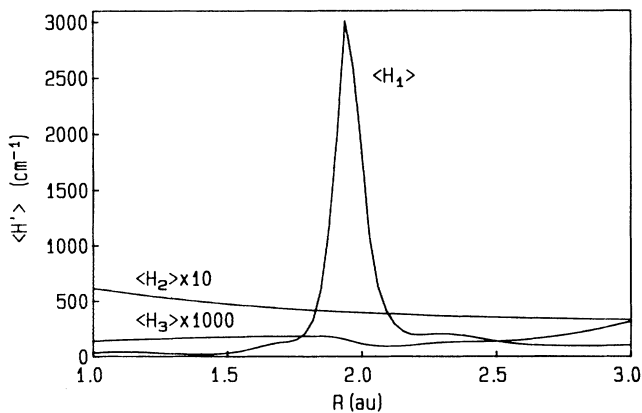$$\left. + \frac{J(J+1)}{2\mu R^2} - E_{vJ} \right] \chi_{vJ}(R) = 0. \quad (8)$$

FIG. 1. Components of the adiabatic correction for the $h\,^3\Sigma_g^+$ state of H_2.

TABLE II. Calculated adiabatic dissociation energies D_v and rotational constants B_v for the h state of H_2 and D_2 (all values in cm^{-1}).

v	H_2 D_v	B_v	D_2 D_v	B_v
0	6126.166	27.11	6395.200	13.30
1	4410.993	30.05	5239.461	16.03
2	2675.615	24.34	4001.526	12.53
3	872.543	21.55	2563.877	11.65
4			1358.155	12.71
5			316.901	11.88

The numerical integration was carried out in the interval $R = 0$ to 12 a.u. with BO energy $U^{BO}(r)$ from Ref. 3 and the integration step was 0.01 a.u. The resulting dissociation energy D_v and rotational constants B_v for the h state of H_2 and D_2 are listed in Table II. The calculated energies for the vibrational levels are also displayed in Fig. 2. In Fig. 3 the adiabatic and BO wave functions for the $v = 0$ and 1 levels are plotted. As is seen from Fig. 2, the lowest vibrational level lies below the barrier top, whereas the higher levels all lie above it. It is worthwhile to note that the amplitude of the adiabatic wave function for the $v = 0$ level is shifted to the right, so the maximum of the density is located in the outer minimum, which is wider and deeper than the inner one. It is also worthwhile to note that $R_1(\text{adiabatic}) < R_1(\text{BO})$. This suggests that the amplitude of the adiabatic wave function for the $v = 1$ level is shifted to the left. Figure 3 illustrates these effects. In Table III the calculated term values T_v are compared with the existing experimental data[6,7] and BO values.[3] The adiabatic T_v values were obtained by subtracting the computed vibrational energies, D_v, from the theoretical adiabatic dissociation limits (118377.7 and 119030.3
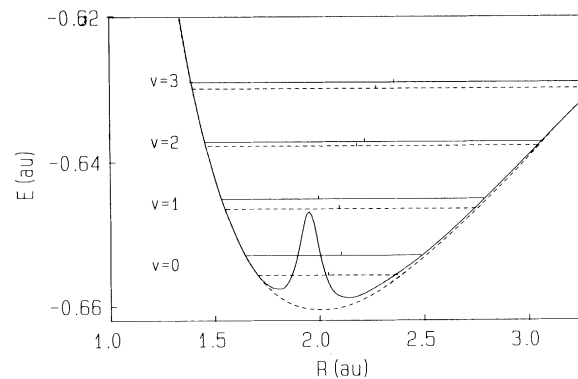

FIG. 2. The BO (dashed line) and adiabatic (solid line) potential-energy curves for the $h\,^3\Sigma_g^+$ state of H_2 in the vicinity of the equilibrium with the BO and adiabatic vibrational energies. The short vertical bar above each of the vibrational energy line marks the value $R_v = \langle R^{-2} \rangle^{-1/2}$.
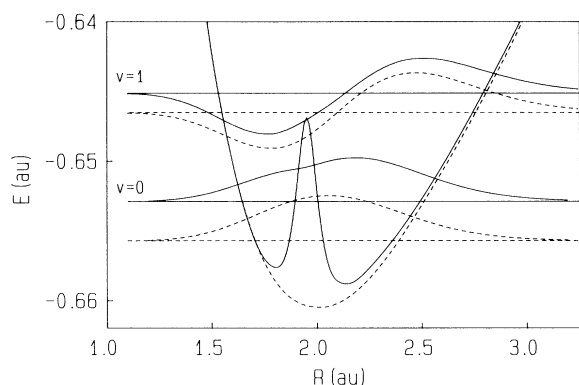
FIG. 3. The BO (dashed line) and adiabatic (solid line) vibrational wave functions for the $v=0$ and 1 levels of the $h\,^3\Sigma_g^+$ state of H_2.

TABLE III. Comparison of the theoretical adiabatic and BO term values T_v (in cm^{-1}) with the experimental ones for the h state of H_2 and D_2.

v	T_v^{adiab}	T_v^{expt}	Δ	T_v^{BO}	Δ
			H_2		
0	112 251.53	111 871.84	−379.69	111 675.52	196.32
1	113 966.71	114 140.57	173.86	113 704.16	436.41
			D_2		
2	115 028.77	115 420.15	391.38	114 937.55	483.10
3	116 466.42	116 936.51	470.09	116 320.19	616.32
4	117 672.15	118 390.50	718.35	117 538.52	851.98

cm^{-1} for H_2 and D_2, respectively). As is seen from this table, inclusion of the adiabatic correction leads to a larger discrepancy between theory and experiment for the lowest vibrational level and to only slight improvement over the BO results. This fact supports our previous conclusion[3] on an incorrect experimental assignment of the h state of the hydrogen molecule. The existence of the lowest vibrational level below the potential barrier leads to a different rotational constant for this level, which in turn may explain a difficulty with correct assignment of the spectrum for the h state.

Similar calculations performed for the $(1s\,3d)g\,^3\Sigma_g^+$ state[8] have shown that the potential-energy curve for this state is also characterized by a single minimum in the BO approximation and by a double minimum in the adiabatic approximation. The results will be published elsewhere. The strong interaction between the g and h states in the vicinity of the equilibrium may produce large effects in the off-diagonal terms; however, as was shown by Wakefield and Davidson,[1] these effects are not so dramatic as those produced by diagonal corrections.

In conclusion, the potential-energy curve for the $h\,^3\Sigma_g^+$ state of the hydrogen molecule is exceptional in that its double minimum (with the barrier located in the vicinity of the equilibrium) is caused exclusively by the adiabatic effect. A large value of the adiabatic correction results from drastic changes in the character of the wave function due to the mutual interactions between the close-lying h and g states.

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