

$^1\Sigma_u$ and $^1\Pi_u$ states of the hydrogen molecule: Nonadiabatic couplings and vibrational levels

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Abstract

Nonadiabatic coupling matrix elements are computed for six lowest $^1\Sigma_u^+$ and four lowest $^1\Pi_u$ electronic states of H_2 in a wide range of internuclear distances. These matrix elements are used together with the adiabatic potentials to determine the bound ro-vibrational levels of the 10 electronic states for rotational quantum numbers $J \leq 10$. The computed energies agree quite well with existing experimental term values. However, some of the experimental levels should be assigned differently.

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1. Introduction

The outer well of the $B''\bar{B}^1\Sigma_u^+$ state was investigated experimentally very accurately several years ago, Ref. [1], and it has been established that the results obtained for higher vibrational levels differ markedly from the theoretical, adiabatic predictions. This is not very surprising as this state can interact strongly with the continua of the lower lying B and $B'^1\Sigma_u^+$ and $C^1\Pi_u^+$ states. Also, to a lesser extent, it is coupled with the higher lying bound $^1\Sigma_u^+$ and $^1\Pi_u^+$ states and also with the electronic continua. The latter couplings are very difficult to be taken into account for excited electronic states. The former, however, can be investigated in the framework of the close-coupling method.

The Born–Oppenheimer potentials and electronic wavefunctions of six lowest $^1\Sigma_u^+$ and four $^1\Pi_u$ states have been obtained before, Refs. [2,3]. In this work, we compute the nonadiabatic couplings between these electronic states and determine the ro-vibrational levels in the close-coupling

approximation. Thus, we get up to 10 coupled states and in effect, beside the $B''\bar{B}$ levels, a large number of ro-vibrational levels for all the remaining states. Together with the nonadiabatic coupling matrix elements this makes a large set of data and it would be unreasonable to publish it in print. Therefore, we present below only some characteristic result. The full set of the computed matrix elements and term values is deposited in the form of an ASCII file as [supplementary data](#) for this article and is also available from the authors in a zipped form through Internet Ref. [4].

Below, we use the notation $B, B', B''\bar{B}, 4B, 5B$ and $6B$ to denote the $n^1\Sigma_u$ states for $n = 1, \dots, 6$, respectively, and C, D, V, D' to denote the four Π_u states.

2. Nonadiabatic couplings

In the computation of nonadiabatic couplings we basically follow Ref. [5]. Here, we repeat the familiar formulas just for convenience.

The total Hamiltonian is written for the homonuclear case as

$$H = H^{\text{el}} + H' \quad (1)$$

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with H^{el} being the clamped nuclei Hamiltonian and H' the remainder:

$$H' = -\frac{1}{2\mu}A_R - \frac{1}{8\mu}(\nabla_1 + \nabla_2)^2. \quad (2)$$

Above 1 and 2 denote the coordinates of the two electrons, R the relative position of the nuclei and μ the nuclear reduced mass.

The approximate nonadiabatic function is assumed in the form of a finite expansion

$$\Psi(r, R) = \frac{1}{R} \sum_i \psi_i(r, R) f_i(R), \quad (3)$$

where ψ_i are the electronic Born–Oppenheimer functions of the coupled states and f_i the vibrational functions to be determined from the set of equations

$$\sum_k \left\{ -\frac{1}{2\mu} \left[\frac{d^2}{dR^2} - \frac{J(J+1)}{R^2} + C_{i,k} \right] + U_i^{\text{BO}} \delta_{i,k} - E \right\} f_k(R) = 0. \quad (4)$$

U_i^{BO} is the Born–Oppenheimer electronic energy,

$$U_i^{\text{BO}} = \langle \psi_i | H^{\text{el}} | \psi_i \rangle \quad (5)$$

and

$$C_{i,k} = \langle \psi_i | H' | \psi_k \rangle = D_{i,k} + G_{i,k} + B_{i,k} \frac{d}{dR}. \quad (6)$$

The form of the matrix elements $D_{i,k}$, $B_{i,k}$ and $G_{i,k}$ depends on the symmetry of the two states ψ_i and ψ_k . If both states have the same, Σ ($A=0$) or Π ($A=1$), symmetry we have

$$D_{i,k}^{A,A}(R) = \langle \psi_i | \frac{d^2}{dR^2} - \frac{L^+ L^- - A(A+1)}{R^2} | \psi_k \rangle, \quad (7)$$

$$B_{i,k}^{A,A}(R) = 2 \langle \psi_i | \frac{d}{dR} | \psi_k \rangle,$$

$$G_{i,k}^{A,A}(R) = \frac{1}{4} \langle \psi_i | (\nabla_1 + \nabla_2)^2 | \psi_k \rangle$$

with

$$L^\pm = L_x \pm iL_y \quad (8)$$

and L_i being the components of the electronic angular momentum in a molecule-fixed coordinate system with z -axis coinciding with the internuclear vector \vec{R} .

If the states have different Π/Σ symmetry

$$D_{i,k}^{A+1,A}(R) = [J(J+1) - A(A+1)]^{1/2} \frac{\langle \psi_i | L^+ | \psi_k \rangle}{R^2} \quad (9)$$

and the $B_{i,k}$, $G_{i,k}$ matrix elements vanish.

The diagonal matrix elements of B vanish in any case, $B_{i,i} = 0$, and $\Delta E_i(R) = -C_{i,i}/2\mu$ is the adiabatic correction to the Born–Oppenheimer potential U_i^{BO} .

Obviously, Π^- and Σ^+ states do not couple and the mixed matrix elements are

$$\begin{aligned} \langle \Pi_i^\pm | H' | \Sigma_k^\pm \rangle &= \sqrt{2} D_{i,k}^{1,0}(R), \\ \langle \Pi_i^\pm | H' | \Sigma_k^\mp \rangle &= 0. \end{aligned} \quad (10)$$

3. Numerical computations

3.1. Coupling matrix elements

In this work, we use the Born–Oppenheimer wavefunctions of the six lowest $^1\Sigma_u^+$ states determined in Ref. [2] and the four $^1\Pi_u$ state functions from Ref. [3]. The couplings were computed in the interval $0.5 \leq R \leq 80.0$ a.u. Here, in Tables 1–3 we give just a sample for illustration and for comparison with earlier results, Ref. [5]. The latter were obtained with considerably shorter wavefunction expansions. Still the differences amount to a few percents only. It should be noted in this connection that the present definition of the $B_{i,k}$ matrix elements is different from that of Ref. [5]: the present $B_{i,k}$ being twice the old value.

3.2. Vibrational levels

The computed couplings together with the adiabatic corrections and Born–Oppenheimer electronic energies of Refs. [2,3] were used in Eq. (4) to determine the ro-vibrational energy levels. Since all levels above the $(1s, 2l)$ disso-

Table 1
 B' – B coupling matrix elements

R	D_{12}^{a}	B_{12}	G_{12}	D_{12}^{b}
1.00	0.0808635	0.1717331	−0.0582439	−0.0137795
2.00	−0.0430529	0.2885653	−0.0823444	−0.0416542
3.00	−0.0955891	0.2008620	−0.0761860	−0.0386272
4.00	−0.0595290	0.1211224	−0.0434741	−0.0359993
5.00	−0.0320170	0.0868612	−0.0129487	−0.0181060
10.00	−0.0152731	−0.0039690	0.0127397	−0.0054849

^a The indices 1 and 2 correspond to B' and B , respectively.

^b $D_{12}^{\text{b}} = (D_{12} + D_{21})/2$.

Table 2
 D – C coupling matrix elements

R	D_{12}^{a}	B_{12}	G_{12}	D_{12}^{b}
1.00	−0.0170713	−0.0763703	−0.0456933	−0.0034475
2.00	0.0037781	−0.0778595	−0.0456213	−0.0059895
3.00	0.0149814	−0.0428930	−0.0461337	−0.0091980
4.00	0.0122291	0.0130099	−0.0487235	−0.0171484
5.00	−0.0114315	0.0624530	−0.0522371	−0.0287165
10.00	−0.0306531	0.1015134	−0.0375083	−0.0399229

^a The indices 1 and 2 correspond to D and C , respectively.

Table 3
 $\langle \Pi | L^+ | \Sigma \rangle$ coupling matrix elements

R	C – B	C – B'	D – B	D – B'
2.00	−1.3341973	0.3722856	−0.2555989	−1.2852862
3.00	−1.2058269	0.6587941	−0.3477744	−1.0249546
4.00	−1.1157000	0.7857248	−0.3504441	−0.7134630
5.00	−1.0415478	0.7841848	−0.2876443	−0.4949155
10.00	−0.8431736	0.8783574	−0.1608942	−0.0630072

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