

# PADE FORMS AND MOLECULAR POTENTIAL FUNCTION. REPRESENTATIONS BASED ON THE ROTATIONAL QUANTUM NUMBERS OF A DIATOMIC MOLECULE

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Received January 30, 1991*

*A technique for constructing the Pade representation is developed on the basis of the perturbation theory to describe vibrational–rotational spectra of diatomic molecules. The procedure provides fast summation of the series over the rotational quantum numbers. The physical meaning of Pade approximants becomes clear by examining the problem of the molecular potential function. The theoretical investigations are applied to calculations which show good prospects of the proposed approach in examples of solving the inverse problems on the force constants of the H<sub>2</sub> molecule. The values of the potential function obtained for the repulsive part of the potential up to the dissociation limit agree well with its "experimental" RKR–values.*

In our previous papers<sup>1,2</sup> we have described the possibility of representing Pade forms on the basis of the vibrational quantum numbers in terms of the potential constants. The technique developed has been brought to practical applications. It can be used for processing of the vibrational–rotational spectra in analogy with the Danham formulas<sup>3</sup> but with a considerably improved quality of the extrapolation of the calculated potential constants. At the same time it differs greatly from the first attempts to adapt the perturbation theory for the derivation of Pade forms for the representation of energy.<sup>4–6</sup>

## SERIES APPROXIMATION BASED ON THE ROTATIONAL QUANTUM NUMBERS

1. The aforementioned technique is not limited by the construction of Pade approximants to the energy series only on the basis of the vibrational quantum numbers. It also provides the possibility of their approximation on the basis of the rotational quantum numbers and, in the same way as in Refs. 4–6, in terms of the small parameter of the perturbation theory. Our preliminary calculations have shown, however, that the use of the "rotational" approximants, unlike their "vibrational" counterparts, improves but insignificantly the results for the HBr molecule.<sup>1</sup> At the same time there are light molecules for which the effect of nonrigidity on the molecular rotational spectrum is very strong, which is evident from the results of our calculations for H<sub>2</sub> (see Table I). In the same way as in Ref. 7 we employed phenomenological models in which the  $v$ –dependent quantities

$$c_j^v = \sum_{r=0}^{r_{\max}} Y_{rj}(v + 1/2)^r$$

were used instead of the  $J$ –dependent parameters  $c_j^J$ , where  $Y_{rj}$  are the well-known Danham spectroscopic parameters. The extrapolation of the energies  $E_{vJ}$  of the ground state with  $v = 0$  has been essentially improved (see Table I). The processing and comparison of the corresponding vibrational–rotational energies were performed using the

values calculated *ab initio*<sup>8</sup> because the experimental collection of frequencies is well-known to be less complete. The quality of processing of the energies  $E_{vJ}$  with  $J \leq 20$  can be judged by the values of the sum of the squared discrepancies  $\Sigma$  and by the maximum discrepancy  $\Delta E_{\max}$  (Table I). It is the H<sub>2</sub> molecule which is hereinafter used to test nonphenomenological Pade forms based on the rotational quantum numbers.

TABLE I. The quality of extrapolation of rotational energies (cm<sup>-1</sup>) of the H<sub>2</sub> molecule in the ground vibrational state ( $v = 0$ )  $\Delta E_{vJ} = E_{vJ}^{ab\ initio} - E_{vJ}^{calc}$  for the values of  $J$  satisfying the inequality  $21 \leq J \leq 31$  for Danham [6/0] and Pade [4/2] phenomenological models of the Hamiltonian.

$J$	$\Delta E_{vJ}$ [6/0]	$\Delta E_{vJ}$ [4/2]	$J$	$\Delta E_{vJ}$ [6/0]	$\Delta E_{vJ}$ [4/2]
21	0.87	0.02	26	198.63	0.71
22	4.25	0.06	27	404.45	1.02
23	14.04	0.13	28	779.05	1.30
24	38.08	0.26	29	1423.38	1.43
25	91.01	0.45	30	2537.18	1.16
—	—	—	31	4344.03	0.60
$\Sigma/\text{cm}^{-2}$ 5.7·10 <sup>-3</sup> 1.7·10 <sup>-5</sup>					
$\Delta E_{\max}/\text{cm}^{-1}$ 0.05 0.002					

2. Pade approximants are constructed using the iterative procedure<sup>9</sup> with only one iteration.<sup>2</sup> The relation for the energy shift in the state  $s$  is written in the form:

$$\Delta E_s = \langle s | H' | s \rangle + \langle s | H' \frac{Q_s}{\epsilon - H^{(0)}} (\epsilon - E_s + H') \times \\ \times \sum_{k=0}^l \left\{ \frac{Q_s}{E_s^{(0)} - H^{(0)}} (E_s^{(0)} - E_s + H') \right\}^k | s \rangle.$$

Here  $Q_s = I + P_s$ ;  $|s\rangle$  is the eigenfunction of the zeroth-order approximation,  $|s\rangle = P_s |\Psi\rangle_s$ ,  $H'$  is the perturbation

potential, and  $H^{(0)}$  and  $E_s$  are the zeroth-order Hamiltonian and the exact energy, respectively. The form of the  $\varepsilon$  operator determines the version of the perturbation theory. For constructing Pade forms,  $\varepsilon$  is chosen as

$$\varepsilon = E_s - (E_s^{(0)} - H^{(0)})b_g. \quad (2)$$

The quantity  $b_g$  includes the functional dependence on the quantum numbers and in the present case it is the function of  $J$  or of  $g = J(J + 1)$ . The quantity  $b_g$  is defined by the specific Pade form  $[n/m]$  and is chosen so that the appropriate denominator of the length  $m$  is included in the Pade representation of the energies. Then it can be shown that for sufficiently large values of  $J$  the desired Pade numerator of the length  $n$  is obtained in Eq. (1). Detailed proofs are given elsewhere. The case of  $b_g = 0$  corresponds to the conventional Rayleigh-Schrodinger perturbation theory.

3. There are a number of procedures for treating rotational motions with the Hamiltonian describing the vibrational-rotation interaction.<sup>10</sup> For example, it is assumed that  $\beta^2 J(J + 1) \sim \lambda^0$ , where  $\lambda$  is the small parameter perturbation theory and  $\beta$  is the rotational constant. Then the dominant contributions to the spectroscopic parameters comes from the values of the following order of the perturbation theory:

$$Y_{(r,j)}^d \sim \lambda^{2(r+j-1)}. \quad (3)$$

The approach (3) is convenient for describing the states with large values of  $J$ , i. e.,  $J \sim 10$ . If  $J \sim 1$  then  $\beta^2 J(J + 1)$  is the term of the second order of the perturbation theory proportional to  $\lambda^2$ . It enters in the perturbation operator. Then the relations for the perturbation theory remain unchanged as compared to Eq. (3) but there occurs another order of perturbation theory proportional to the powers of  $\lambda$ .

$$Y_{(r,j)}^d \sim \lambda^{2(r+2j-1)}. \quad (4)$$

In analogy with Ref. 2, the formula for the vibrational-rotational energy can be written as

$$E_{vj} = \sum_{(r,j)} X_{rj}(v + 1/2)^r g^j + [n/m]_v. \quad (5)$$

The integers  $n$  and  $m$  denote the maximum degrees of polynomials in  $g$  in the numerator and denominator of the Pade approximant, respectively. The coefficients next to the powers of  $g$  in  $[n/m]_v$  are the combinations of the  $v$ -dependent spectroscopic parameters

$$c_j^v = \sum_{r=0}^{r_{\max}} Z_{r,j}(v + 1/2)^r,$$

where  $Z_{rj}$  are the spectroscopic constants which, unlike the Danham values of  $Y_{rj}$ , are constructed only on the basis of the terms of the Rayleigh-Schrodinger perturbation theory ( $\varepsilon = E_s^{(0)}$ ) incorporating resolvents.

#### EXAMPLES OF CONSTRUCTION OF PADE FORMS

1. Let us consider the approximant  $[0/1]$  for an example of peculiarities of representations of the vibrational-rotational energies on the basis of Eq. (1), namely,

$$[0/1]_v = \frac{c_0^v}{1 - (c_1^v/c_0^v)g}.$$

On account of Eq. (1) the quantity  $b_g^v$  in Eq. (2) should be assumed to be equal to  $(c_1^v/c_0^v)$ . The quantities  $c_1^v$  appear in a definite order  $N$  of the perturbation theory. Let us examine first distribution (4).

a) In the second order of the perturbation theory, according to Eqs. (4) and (5), the parameters  $Y_{0,0}^{(2)}$  and  $Y_{2,0}^{(2)}$  are separated into two constants  $X_{0,0}^{(2)}$ ,  $X_{2,0}^{(2)}$  and  $Z_{0,0}^{(2)}$ ,  $Z_{0,0}^{(2)}$ . An ordinary meaning of the parameters  $Y_{0,0}^{(0)}$ ,  $Y_{1,0}^{(0)}$ , and  $Y_{0,1}^{(2)}$  is retained. Here the superscript denotes the order of the perturbation theory, in which the given parameter appears. Thus, the constant  $c_0^v$  can be written as

$$c_0^v = Z_{(0,0)}^{(2)} + Z_{(2,0)}^{(2)}(v + 1/2)^2, \quad (6)$$

while the constant  $c_1^v$  is absent in this order.

b) The quantity  $c_1^v$  appears in the fourth order of the perturbation theory  $c_1^v = Z_{1,1}^{(4)}(v + 1/2)$ , and in this very order the terms incorporating  $Z_{1,0}^{(4)}$  and  $Z_{3,0}^{(0)}$  are added to the right side of Eq. (6).

2. The approximant  $[1/1]$ . Its construction requires the constants  $c_0^v$ ,  $c_{10}^v$  and  $c_2^v$  to be wellknown. According to Eq. (4) the quantity  $c_2^v$  appears in the sixth order of the perturbation theory. In the case of Eq. (3) the quantities  $c_0^v$ ,  $c_1^v$  and  $c_2^v$  have the same order of the perturbation theory. Therefore, in processing the rotational states with large  $J$  according to Eq. (3) by means of  $[1/1]$  the expansion terms have different orders of the perturbation theory.

3. The approximant  $[2/1]$ . This is the simplest Pade form which is consistent with distribution (3), and the constant  $b_g = (c_3^v/c_2^v)g$  in Eq. (2) is proportional to  $\lambda^2$ .

According to distribution (4) the coefficient  $c_3^v$  appears in the tenth order of the perturbation theory.

4. An advantage of the procedure developed here is in the fact that the simple version (1) which is most close to the Rayleigh-Schrodinger perturbation theory, exactly results in the classical Pade constructions with the parameters  $Z_{rj}$ . This procedure makes it possible to use all the well-known formulas relating the Danham spectroscopic parameters  $Y_{rj}$  and the molecular constants of diatomic molecules: the harmonic frequency  $\omega$ , the rotational constant  $\beta$ , imposed and the anharmonic constant  $\alpha_i$ . The restrictions on the variety of Pade forms  $[n/m]$  are, in fact, determined by the number of the parameters  $Y_{rj}$  for which these formulas are wellknown. According to Refs. 11 and 12 they have been derived for all  $r$  and  $j$  satisfying the conditions  $r + j = 10$  and  $r \leq 6$ . In addition to Pade representations mentioned above, those currently realized in practice are Pade forms  $[n/m]$  with  $n + m = j_{\max} = 10$ . They can be used directly for solving the inverse problems of the determining the potential function.

#### RESULTS OF COMPUTATIONS AND DISCUSSIONS

To describe the vibrational-rotational states of  $H_2$  in terms of the potential constants we have chosen theoretically the form  $[4/2]$  (Table I), which proved to be a good

approximant which, on account of Eq. (5), represents schematically the energies  $E_{vJ}$  as  $[6/0] + [4/2]$ . We have used the results of the *ab initio* calculations<sup>8</sup> of the ground electronic state as the "observed" processed energies of a hydrogen molecule.

We have calculated the states with large  $J$  numbers ( $J > 10$ ). Therefore, distribution (3) over the orders of the perturbation theory has been taken into account. The form  $[4/2]$  requires the tenth order of the perturbation theory to be considered. This makes it possible to determine 12 molecular constants by solving the inverse problem.

A comparison of the values of molecular constants (Table II) is in favour of the combined model  $[6/0] + [4/2]$ . Indeed, the value of the harmonic frequency  $\omega$  differs but slightly (by  $\sim 2 \text{ cm}^{-1}$ ) from the values obtained in processing of low excited states,<sup>13</sup> while in the second column the difference is  $> 30 \text{ cm}^{-1}$ . The constants given in the third column are less distorted. Presented in Table II are only the stable values of anharmonic coefficients, namely,  $\{\alpha\}_{i=1}^5$ . The sum  $\Sigma$  of squared deviations of energies in Pade computations is much smaller (Table II) than that found in the computations according to the Danham procedure. The potential function has been obtained as a result of processing of the first seven vibrational bands including *ab initio* values  $E_{vJ}$  ( $v = 0, 1, 2, \dots, 6$  with  $J \leq 20, 18, 16, 13, 10, 5, 3$ ), respectively) given in Ref. 8.

TABLE II. The values of potential constants of the  $\text{H}_2$  molecule calculated using the conventional Danham procedure  $[6/0]$  and our technique based on Pade forms  $[6/0] + [4/2]$ ; units of measurement are  $[\omega] = \text{cm}^{-1}$ ,  $[\beta] = 10$ , and  $\alpha_i = 10$ .

Constant	Danham model [6/0]	Pade from model [6/0]+[4/2]
$\omega$	4368.8400	4402.981(129)
$\beta$	1.669796(301)	1.6625524(253)
$\alpha_1$	-1.33869(651)	-1.329299(182)
$\alpha_2$	3.1264(186)	2.55973(220)
$\alpha_3$	-8.1656(241)	-4.6142(114)
$\alpha_4$	16.745(274)	8.5278(177)
$\alpha_5$	-20.18(158)	-16.183(105)
$\Sigma/\text{cm}^{-2}$	684.2	0.56

It is worth noting, when comparing the capabilities of the two approaches, that the ratio  $E_D/E_P$  of the values of energies extrapolated using the calculated constants presented in Table II for Danham and Pade models in the ground vibrational state  $v = 0$  of the  $\text{H}_2$  molecule is represented by a smooth function of  $J$  and ranges from 40 at  $J = 21$  to 453 at  $J = 31$ .

Our results (Table III) show that the procedure developed here for constructing the potential functions of light molecules gives practically the same internuclear spacing at the turning point for the repulsive part of the potential energy curve up to the dissociation limit as the "experimental" values obtained by the *RKR*-method (see Ref. 14). At the same time, using the Danham procedure we have obtained starting from  $v = 10$  (Table I) quantitatively incorrect behavior of the potential energy curve.

TABLE III. The internuclear spacing  $r_{\min}$  ( $\text{\AA}$ ) in the  $\text{H}_2$  molecule for the repulsive part of the potential energy curve at turning points of the vibrational states  $v$ .

$v$	$r_{\min}$		
	<i>KRR</i> [14]	Danham model [6/0]	Pade from model [6/0]+[4/2]
-0.5	0.7416	0.7416	0.7416
0	0.6333	0.6330	0.6332
1	0.5706	0.5716	0.5707
2	0.5345	0.5363	0.5346
3	0.5087	0.5109	0.5088
4	0.4886	0.4908	0.4890
5	0.4726	0.4738	0.4730
6	0.4594	0.4589	0.4599
7	0.4485	0.4450	0.4489
8	0.4390	0.4314	0.4396
9	0.4315	0.4155	0.4318
10	0.4250	—	0.4253
11	0.4197	—	0.4200
12	0.4160	—	0.4159
13	0.4128	—	0.4129

Specific calculations performed in this paper confirm that Pade approximations on the basis of the rotational quantum numbers according to the formulas of the perturbation theory have good prospects. Together with a successful representation of the state energies on the basis of the vibrational quantum numbers,<sup>1,2</sup> as applied to the anharmonicity problem, the technique proposed can, on the whole, be useful in practice for describing high excitation vibrational-rotational states of light nonrigid molecules. In addition, it provides an accurate reconstruction of the repulsive part of the potential energy curve in agreement with the "experimental" *RKR*-values. However, the *RKR*-values are obtained using experimental vibrational energies which, as a rule, are not available near the dissociation limit for most diatomic molecules. The procedure proposed here is more advantageous in this respect.

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