PADE FORMS AND MOLECULAR POTENTIAL FUNCTION. REPRESENTATION BASED ON THE VIBRATIONAL QUANTUM NUMBERS IN DIATOMIC MOLECULES

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Received March 5, 1990

The relations between the Padé representations of the energies of the vibrational-rotational states of diatomic molecules on the one hand and the potential constants on the other are established. The advantage of this method for analyzing and extrapolating high excitation frequencies of vibrational-translational transitions over the traditional approach is demonstrated for the example of the molecule HBr. *Its anharmonic constants are calculated by solving the inverse problem.*

There now exist many works (see. for example. Refs. 1–8) on the construction of both fractional and Padé representations in perturbation theory or in the variational approach. In these works the advantages of this approach are pointed out in examples of calculations of the energies of the states of the simplest anharmonic oscillators and electrons in molecules. The power-series approximation is made in the small parameter λ. This approximation is developed explicitly in low orders.[4–8] Our interest in investigations of this type is dictated by several other presuppositions, for example, the striving to achieve the best description and predictions of the vibrational-rotational energies of the H_2O molecule, where the Padé approximants would be constructed for the most slowly converging Taylor series in power of the rotational operators J_z^2.[9,10] The analyses were performed at the phenomenological level by varying the spectroscopic parameters. At the same time, the physical meaning of Padé formations, i.e., the possibility of deriving them from the potential function of the molecule, remained unresolved. In this paper we take the first practical steps in this direction for the example of the simplest diatomic molecules on the basis of the perturbation theory. A detailed mathematical description of Padé approximants can be found in Ref. 11.

A VERSION OF THE PERTURBATION THEORY

There exists a quite general approach[12] that unifies the two versions of the perturbation theory — the Rayleigh–Schröedinger and the Brillouin–Wigner — by introducing an undetermined operator ε in the iteration equation. For example, after the ith iteration the wave function has the form

$$|\psi\rangle_s^{(i)} = |s\rangle + \frac{Q_s}{\varepsilon - H^{(0)}} (\varepsilon - E_s + H') |\psi\rangle_s^{(i-1)}, \quad (1)$$

where $H^{(0)}$ and H' are, respectively, the zeroth-order Hamiltonian and the perturbation potential. The orthogonal projection operator Q_s is such that $P_s + Q_s = I$, where I is the unit operator and P is the orthogonal projection on a selected subspace. In the case of the isolated states $|s\rangle = P_s|\psi\rangle_s$, where $|s\rangle$ are the eigenfunctions of the zeroth-order approximation. If in Eq. (1) ε is replaced by the energy of the zeroth-order approximation $E^{(0)}$ or its exact value E, then we obtain the Rayleigh–Schröedinger or the Brillouin–Wigner version.

Now, let $i = 1$ in Eq. (1) and assume that the initial wave function $|\psi\rangle_s^{(0)}$ for the first iteration has the form

$$|\psi\rangle_s^{(0)} = \sum_{k=0}^{i} \left\{ \frac{Q_s}{E_s^{(0)} - H^{(0)}} (E_s^{(0)} - E_s + H') \right\}^k |s\rangle. \quad (2)$$

The expression (2) is the zeroth-order approximation of the iteration equation (1), though in itself it is the wave function of the Rayleigh-Schröedinger version in the ith iteration. After substituting Eq. (2) into Eq. (1) we obtain an expression for the energy shift ΔE_s (Ref. 12)

$$\Delta E_s = \langle s|H'|s\rangle + H' \frac{Q_s}{\varepsilon - H^{(0)}} (\varepsilon - E_s + H') \times \times \sum_{k=0}^{i} \left\{ \frac{Q_s}{E_s^{(0)} - H^{(0)}} (E_s^{(0)} - E_s + H') \right\}^k |s\rangle. \quad (3)$$

0235-6880/90/06 562-06 $02.00

The operator ε in Eq. (3) commutes with $H^{(0)}$. Rational, with respect to the quantum numbers, ratios can be introduced in the expressions for ΔE_s in Eq. (3) by choosing a special from of the operator ε:

$$\varepsilon = E_s^{(0)} - (E_s^{(0)} - H^{(0)})b_s.$$

Here it is assumed that a unit operator I stands next to the scalar quantities. The specific Padé form depends on the quantities b_s and the values of l in Eqs. (2) and (3). The expression (3), determining the combined version of the perturbation theory, is the basic expression used to construct Padé forms.

REPRESENTATION IN VIBRATIONAL QUANTUM NUMBERS

The vibrational energy of a one-dimensional anharmonic oscillator is traditionally written in terms of the spectroscopic parameters Y_r in powers of the quantity $h = (v + 1/2)$, where r is the power. To introduce rational ratios it is necessary to introduce into the denominators the expression (3) the required dependence on the quantum numbers v with the help of Eq. (4). In Eq. (3), however, there exist terms without denominators. For this reason, it can be assumed at the outset that

$$E_v = \sum_{r=0} X_r h^r + [n/m], \tag{5}$$

where $[n/m]$ is the Padé form,[11] which depends on the spectroscopic parameters Z_r. The values of n and m are the maximum powers of the polynomials in the numerator and denominator, respectively. In the case of Taylor series $m = 0$ and $Y_r = X_r + Z_r$. For $m > 0$, however, the last relation becomes meaningless. The parameters X_r follow from the first term on the right side of the relation (3).

It is well known that the values of Y_r are related with the molecular constants ω, β, and α_1, which appear in the Hamiltonian of a diatomic molecule

$$H = hc\left\{\frac{\omega}{2}\left[\frac{\beta^2 J(J+1)}{(1+\beta q)^2} + p^2\right] + V\right\},$$

where the perturbation potential has the form

$$V = \omega\left\{\frac{1}{2}q^2 + \sum_{i=1}^{\infty} \alpha_i q^{2+i}\right\}.$$

In this section $J = 0$.

The most complete collection of formulas for Y_r is given in Refs. 13 and 14. Every quantity Y_r is a sum of $Y_r^{(\eta)}$ in different orders η of the perturbation theory, so that with accuracy up to tenth order the vibrational energy can be written as

$$E_v = Y_0^{(0)} + \sum_{i=0}^{2} Y_0^{(a_i)} + \sum_{r=1}^{6}\sum_{i=0}^{d_r} Y_r^{(f_i)} h^r, \tag{6}$$

where $a_1 = 2 + 4i$, $d_r = (10 - 2(r - 1)$–:–4, $f_1 = 2(r - 1) + 4i$. Since the expression (6) is in the form of a Taylor series, i.e., a particular case of the formula (5), when $m = 0$, in Eq. (6) the relation $Y_r^{(\eta)} = X_r^{(\eta)} + Z_r^{(\eta)}$ is satisfied for every $Y_r^{(\eta)}$. It is obvious that $Y_0^{(0)}$ is the electronic energy; $Y_1^{(0)} = \omega$, where ω is the harmonic frequency of the vibrations; and, $Z_1^{(0)} = 0$. The specific Padé forms $[n/m]$ are constructed from the quantities $Z_r^{(\eta)}$. Thus the combined representation of the energy E_v in terms of the Taylor and Padé forms (5) immediately gives a relation between E_v and potential constants of the molecules, since the relation between $Z_r^{(\eta)}$ and the potential function is known.[13,14] It remains only to prove that the version (3) can be used consistently to construct the Padé forms (5).

SPECIFIC PADE FORMS

We start from the fact that the Padé relations approximate the Taylor series (6) in powers of h.

1. In the zeroth-order perturbation theory ($N = 0$) the only possible from is [1/0], identical to the zeroth-order harmonic approximation.

2. Let $N = 2$. The Danham form [2/0] is obvious. Like in the zeroth order, the form [1/1] is impossible.

3. $N = 4$. There is the Danham form [3/0] and the simplest of the possible Padé approximants [2/1] appears. It should approximate the series (6) to order $O(h^4)$ as follows:

$$[2/1] = Z_0^{(2)} + Z_1^{(4)}h + Z_2^{(2)}h^2 + Z_3^{(4)}h^3 + O(h^4),$$

or according to the relation

$$[2/1] = \left[Z_0^{(2)} + Z_1^{(4)}h + Z_2^{(2)}h^2 - Z_0^{(2)}Z_3^{(4)}h/Z_2^{(2)} - Z_3^{(4)}Z_1^{(4)}h^2/Z_2^{(2)}\right]\Big/\left[1 - Z_3^{(4)}h/Z_2^{(2)}\right]. \tag{7}$$

From the form of the numerator in Eq. (7) we obtain the coefficient $b_h = b_v = b_s$ in accordance with the expression (4) as

$$b_h^{(2)} = \frac{Z_3^{(4)}}{Z_2^{(2)}}h. \tag{8}$$

Performing the required operations of the perturbation theory up to fourth order infinitesimals ($N = 4$), according to the expression (3) with $l = 3$, we obtain the corrections to the energy ΔE_h, following from the Padé form [2/1], in the form

$$\Delta E_h = \left[Z_0^{(2)} + Z_1^{(4)}h + Z_2^{(2)}h^2 + Z_3^{(4)}h^3 + D_h\right]/\left[1 - b_h^{(2)}\right]. \quad (9)$$

The numerator required for the Padé form [2/1] (7) can be constructed using the sixth-order perturbation theory, i.e., in Eq. (3) we can set $l = 5$. Then new terms are added to the numerator in Eq. (9), and the quantity D_h will have the form

$$D_h = - b_h^{(2)}\left[Z_0^{(2)} + Z_1^{(4)}h + Z_2^{(2)}h^2 + Z_3^{(4)}h^3\right]. \quad (10)$$

Substituting Eq. (10) into Eq. (9) we obtain $\Delta E_h = [2/1] + R^{(6)}$, where the remainder $R^{(6)}$ consists of terms from sixth-order perturbation theory

$$R^{(6)} = \left[Z_0^{(6)} + Z_2^{(6)}h^2 + Z_4^{(6)}h^4 - \frac{\left[Z_3^{(4)}\right]^2}{Z_2^{(2)}}h^4\right]/$$

$$/\left[1 - b_h^{(2)}\right],$$

which is what we were required to prove.

4. An analogous method for constructing the form [3/1], when the perturbation theory (3) is studied in eighth order but the theoretical Danham spectroscopic parameters of order no higher than sixth are employed. It is difficult to obtain the approximant [2/2] because the parameter b_h is more complicated.

5. The formulas derived in Refs. 13 and 14 make it possible to obtain a relationship between the energy and the potential function of the molecule in terms of the Padé form $[n/m]$, if the relations $3 \le n + m \le 6$ and $n \ge m$ are satisfied. On the basis of the approach studied above constructions for $n < m$ are also possible, but only if $n \ge 2$.

ANALYSIS OF INFRARED ABSORPTION SPECTRA

We introduce the J-dependent quantities $X_r^{(\eta)}(J)$ and $Z_r^{(\eta)}(J)$ according to the expressions

$$Z_r^{(\eta)}(J) = \sum_{j=0}^{j_{max}} Z_{r,j}^{(\eta)}\,[J(J+1)]^j.$$

The summation limit J_{max} is determined by the order N of the perturbation theory employed. Correspondingly, the energies of the vibrational-rotational states cam be represented in the form

$$E_{h,J} = \sum_{r=0} X_r(J)h^r + [n/m]_J. \quad (11)$$

The approximant $[n/m]_J$ is a function of $Z_r(J)$. The proof of the formula (11) is more complicated than that of Eq. (5), but the fundamental scheme of the proof is the same.

TABLE I.

Comparison of two sets of molecular constants calculated by analyzing the spectra of the molecule $H^{81}Br$ *using two models. The measurement units are* $[\omega] = cm^{-1}$, $[\beta] = 10^{-1}$, *and* $[\alpha_1] = 10^{-1}$.

Constants	Danham model [4/0]	Our model [4/0] + [3/1]
ω	2649.52950(152)	2649.41238(590)
β	0.79935732(296)	0.79937806(115)
α_1	-0.974188(108)	-0.97445568(498)
α_2	1.224132(431)	1.2294164(152)
α_3	-1.26498(194)	-1.275620(856)
α_4	1.1225(147)	1.00862(561)
α_5	-1.1567(462)	-0.4384(147)
α_6	2.3299(811)	0.6787(158)

TABLE II.

The computed values of the spectroscopic parameters of the molecule $H^{81}Br$ *in* cm^{-1}. *The Padé model* [4/0] + [3/1] *was used in analyzing the* $(0 - v)$ *band, where* $v = 1, \ldots, 7$.

$X_{r,j}$	Meaning	$Z_{r,j}$	Meaning
$X_{1,0}$	2650.247462	$Z_{1,0}$	-1.026019
$X_{0,1}$	8.4655906	$Z_{0,1}$	-0.0007631060
$X_{2,0}$	48.885929	$Z_{2,0}$	-94.333549
$X_{1,1}$	0.1623226	$Z_{1,1}$	-0.3957105
$X_{0,2}$	0.0	$Z_{0,2}$	-0.0003457190
$X_{3,0}$	0.668061	$Z_{3,0}$	-0.593480
$X_{2,1}$	0.00259235	$Z_{2,1}$	-0.00157994
$X_{1,2}$	0.0	$Z_{1,2}$	$3.59751\cdot10^{-6}$
$X_{0,3}$	0.0	$Z_{0,3}$	$7.93143\cdot10^{-9}$
$X_{0,4}$	0.00786660	$Z_{4,0}$	-0.01501608
$X_{3,1}$	$3.86523\cdot10^{-5}$	$Z_{3,1}$	$-1.904090\cdot10^{-4}$
$X_{2,2}$	0.0	$Z_{2,2}$	$-3.50149\cdot10^{-7}$
$X_{1,3}$	0.0	$Z_{1,3}$	$-2.08020\cdot10^{-10}$
$X_{0,4}$	0.0	$Z_{0,4}$	$-3.36450\cdot10^{-13}$

The frequencies of the vibrational-rotational transitions[15] of seven vibrational bands of the molecule $H^{81}Br$ were analyzed using the formula (11). The values of the computed molecular constants are compared in Table I using the form [3/1] (11) with the results of our calculation using the Danham formulas, i.e., $[n/m]$ in (11) is expressed as [4/0]. The quantities

inverse to $2 \cdot 10^{-7}\,\nu_1$ in cm^{-1} for each ith frequency ν of the two R and P-branches were chosen as the weights. Judging from the sum of the squared deviations the quality of the analysis of the frequencies is at least three times better when the Padé forms are employed. The values of the constants of the high anharmonicity for the two calculations differ appreciably from one another. Table II gives the values of the spectroscopic constants $X_{r,j}$ and $Z_{r,j}$. Some values of $X_{r,j}$ are equal to zero, since for given indices r and j there are no contributions from terms without resolvents in the perturbation series (3). Just like for the water molecule,[10] the advantage of the Padé models was noticeable when extrapolating the frequencies. In Table III the deviation of their values from the experimental values is mainly an order of magnitude better than in the case of the Danham representation.

TABLE III.

Comparison of the errors in the extrapolation of $\Delta\nu = \nu_{exp} - \nu_{calc}$ *, in* cm^{-1} *for the band* $(0 - v = 7)$*, calculated based on force fields obtained in two models in the analysts of the first six bands of the molecule* HBr.

J	R-band			P-band		
	Our model [4/0] + [3/1]		Danham [4/0]	Our model [4/0] + [3/1]		Danham [4/0]
	ν	Δν	Δν	ν	Δν	Δν
0	16010.5508	0.0892	-0.396			
1	16020.6938	0.0862	-0.393	15980.4323	—	—
2	16027.5484	0.1016	-0.369	15960.4730	0.0870	-0.399
3	16031.1068	0.0932	-0.366	15937.2583	0.0417	-0.438
4	16031.3611	0.0489	-0.398	15910.7965	0.0535	-0.417
5	16028.3035	0.0065	-0.429	15881.0962	—	—
6	16021.9266	-0.0566	-0.482	15848.1658	—	—

In conclusion we note that the possibility of deriving rational expressions for the vibrational-rotational energies or effective Hamiltonians by the methods of perturbation theory has been discussed on a formal level in the literature (see, for example. Refs. 16 and 17). This possibility in itself does not guarantee that the convergence of the expansions or the accuracy of the calculations will be improved, since the class of rational expressions is very large. To evaluate the prospects of each version of the calculations it is necessary to perform a quantitative analysis that includes reconstruction of the parameters used in inverse problems and determined uniquely from the experimental data. In this paper a nonpolynomial mathematical model (11) was constructed and investigated quantitatively. This model is a representation of the Padé type, but it is not identical to it, since the relations between it and the Taylor constants are somewhat different from the Jacobi relations.[11] It makes it possible to increase the accuracy of the description and the prediction of the spectra of diatomic molecules based on the calculation of the potential function of the molecule. The accuracy of the extrapolation for high overtones of HBr is close to the experimental accuracy, and this indicates that in the future such models could replace the standard Danham model for analyzing the energies of highly excited vibrational states, especially since they are at least as versatile as the Danham model and the well-known relations between the spectroscopic constants and the force field can be employed.

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