Calculation of H_2 vibrational-rotational energy levels. Testing of the Generalized Euler Transform (GET)

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The summation method of the divergent series, known as "Generalized Euler transform" is considered and applied to the simplest case: calculation of the perturbation theory series for two-atomic H_2 molecule. In calculations, the following kinds of approximants were used: the formula for energy levels of the Kratzer oscillator; Pade simplest approximants, Pade – Borel and Pade – Hermit approximants; effective characteristic polynomials. The computations were made for the ground state energy level. Comparisons of obtained results with the fitting data were conducted, and predictions were made for energy levels, which were not used in the fitting.

Introduction

For solution of many problems of spectroscopy, astrophysics, and flame physics, the determination of the levels of energy and wave functions of highly excited vibrational-rotational (VR) states of molecules is required. Nowadays it remains still impossible to conduct precise variation calculations for highly excited states of polyatomic molecules because of significant calculation difficulties. In its turn, the method of effective Hamiltonians uses an expansion in series, which diverge at a sufficient degree of vibrational or rotational excitation. Therefore, the using of special summation methods is necessary.[1]

At present there is quite extensive literature on the development and application of summation methods for calculation of VR spectra of molecule (see, for example Refs. 2–4).

In this paper the method of summation of divergent series, well-known as "Generalized Euler transform" (GET)[1] is used in the simplest case, i.e., in the calculation of summation of perturbation theory (PT) series of two-atomic H_2 molecule. As compared to other summation methods, the GET allows the use of additional information on VR-states from approximate solutions of the Schrödinger equation, that increases the series convergence. Therefore, this method can be very efficient means of calculation of energy levels of highly excited VR-states of molecules.

At the same time, for hydrogen molecule we had a full set of data (VR-energy levels for all bounded states and a part of resonances) obtained by highly accurate *ab initio* calculation.[5] These data present unique information about energy levels, convenient for development and testing of different summation methods.

Note that strong centrifugal distortion and high rotational energy (rotational constant $B \sim 60$ cm^{-1}, centrifugal constant $D \sim -0.05$ cm^{-1}) are characteristic of the H_2 molecule. Excitation of six or seven quanta produces the energy comparable with the energy of vibrations. Note that estimation of convergence radius for VR series,[13] yields $J \sim 25$ for the ground vibrational state. The convergence radius decreases for excited vibrational states.

The goal of this work is to test the GET method by calculation of the H_2 molecule energy levels as an example. The main point of this method is the choice of an approximant, i.e., a certain approximation for energy levels, describing their dependence on the perturbation parameter. At a proper choice of the approximant the series, transformed by GET method, converge quite fast. Since there is no universal way for finding the approximant, different approximation methods are used, in particularly, the formula for energy levels of Kratzer oscillator, i.e., an exactly solvable mathematical task,[7] the simplest Pade, Pade – Borel, and Pade – Hermitt approximants, effective characteristic polynomials. The task is solved in typical for VR-spectroscopy formulation, i.e., at a limited set of energy levels, from which the parameters of theoretical model are determined. Other levels, which are not present in this set, are predicted by the obtained model. Our task is to choose such approximant, which gives a satisfactory description of levels in the fitting and the most accurate prediction for higher energy levels.

In this paper, the ground vibrational state is considered, and it is shown that the most appropriate approximants, allowing us to properly represent H_2 molecule rotational energy levels, are the Kratzer and Pade – Borel approximants. Excited vibrational states will be discussed in future papers.

Note that the Euler series, i.e., a particular case of GET, were earlier used for solution of various tasks of quantum mechanics. They also were used for the calculation of energy levels of H_2O, HDO, D_2O and CH_2 molecules.[8–10]

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Generalized Euler transform

The use of perturbation theory for calculation of vibrational-rotational energy levels of two-atom molecules results in a series of the type

$$E(J,v) = \sum_{n,m} Y_{nm}(v+1/2)^n \left[J(J+1)\right]^m , \qquad (1)$$

where v is the vibrational quantum number; J is the quantum number of the angular momentum; Y_{nm} are the Dunham coefficients. They are connected in a certain way with the expansion coefficients of the potential function into a series in terms of degrees of shifting from the equilibrium state. Formally (not accounting for the convergence) for an individual vibrational state v the series (1) can be presented as

$$E(x,v) = \sum_{m=0} e_m(v) x^m, \qquad (2)$$

where $e_m(v)$ can also be written in the decomposition form:

$$e_m(v) = \sum_{n=0} Y_{nm}(v+1/2)^n. \qquad (3)$$

Here for brevity a variable is introduced

$$x = J(J+1). \qquad (4)$$

If decomposition coefficients (1) are known, then $e_m(v)$, presented as series in Eq. (3), can be found by the appropriate methods.

Generalized Euler transform allows series (2) to be presented in the following way

$$E(x,v) = \sum_{n=0}^{\infty} p_n(v)\chi_n(x,v);$$

$$\chi_n(x,v) = (-1)^n \frac{x^n}{n!}\frac{d^n g(x,v)}{dx^n}; \qquad (5)$$

$$p_n(v) = \sum_{r=0}^{n} (-1)^r \binom{n}{r} a_r;$$

$$a_i = e_i(v)/g_i(v);$$

$$\binom{n}{r} = C_n^r = \frac{n!}{r!(n-r)!},$$

where $g(x, v)$ is an approximant having the following decomposition

$$g(x,v) = g_0(v) + g_1(v)x + g_2(v)x^2 + \ldots .$$

Coefficients $p_n(v)$ in Eq. (5) can be considered as the fitting parameters.

The transformed series (5) in contrast to the initial series (2) is functional, i.e., GET is equivalent to partial summation of the initial series. The convergence of the transformed series depends on the degree of $E(x, v)$ proper description by approximant. Some conditions of the transformed series convergence were proposed in Ref. 11, where it was also shown that if the approximant is chosen properly, then the transformed series can be represented as a finite expression.

Thus, the use of GET depends on properties of the approximation function. In particular, different summation methods can be used as approximants, for example, Pade, Pade – Borel, and others. In this case, several first coefficients of PT series are used for building of the approximant (i.e., the simplest approximants of low order, e.g., Pade [0,1] or [1,1]), which give a certain approximation for the energy. This expression is further used in GET method for transformation of PT series according to Eq. (5).

It is useful to note that traditionally a semiempirical method is used for the calculation of VR-energy levels, in which parameters of the theoretical model (i.e., decomposition coefficients (1) or (2)) are defined by fitting to experimental energy levels by the least-squares method. Usually this provides for the most accurate calculated values of energy levels (at a measurement error level) at a small number of fitting parameters. The problem of empirical approach lies in the accuracy of predictive calculation: as a rule, the accuracy rapidly decreases at the transition to highly excited energy levels, which are not included into the fitting.

One of the reasons of poor predictability of the semi-empirical method is the series divergence. In case when series (1) or (2) are summed "properly," the quality of predictive calculations of energy levels significantly increases.

In the GET method the series representation in the form (5) is rather useful. First, in this case energy levels linearly depend on fitting parameters $p_n(v)$. Second, when using Pade, Pade – Borel, or other approximants, we need not calculations in high orders of PT; it is sufficient to take only several first coefficients.

Approximants and transformed PT series

In this paper, different equations are used as an approximation function.

1. Kratzer model[6] describes rotational-vibrational energy levels of a two-atom molecule with the potential function

$$V(r) = \frac{A_1}{r^2} - \frac{A_2}{r}. \qquad (6)$$

Schrödinger equation with this potential has an exact solution and the energy levels are presented by Kratzer function;

$$K(x,v) = -a\left[v + 1/2 + \sqrt{J(J+1)+b}\right]^{-2} + a\left[1/2 + \sqrt{b}\right]^{-2} =$$

$$= -a\left[v + 1/2 + \sqrt{x+b}\right]^{-2} + a\left[1/2 + \sqrt{b}\right]^{-2}; \qquad (7)$$

$$a = \frac{B^2\mu}{2\hbar^2}; \quad b = 1/4 + 2A\mu/\hbar^2.$$

Here μ is the reduced mass, and the energy is counted from zero level $v = 0$, $J = 0$. Constants a and b in Eq. (7) can also be expressed through the reduced mass μ, dissociation energy E_d, and the equilibrium distance r_e:

$$a = 2E_\mathrm{d}^2 r_\mathrm{e}^2 \mu/\hbar^2, \quad b = 1/4 + 2E_\mathrm{d} r_\mathrm{e}^2 \mu/\hbar^2. \tag{8}$$

Formula (7) can be used for the transformation of series (2). Apparently, the transformed series will have the proper asymptotic at high values of v and J, i.e., all energy levels will be concentrated in the interval defined by the depth of the potential well. At the same time, at $v, J \to \infty$ the initial series (2) at $E(x,v) \to \pm\infty$ has an asymptotic depending on the sign of the highest term.

Earlier the Euler transformation of series (2) with approximant (7) was conducted in Ref. 1 in general form. It was shown that the use of Kratzer function allows us to introduce new variables

$$Z_1(x) = x/(x+b)$$

$$\text{and } Z_2(x,v) = \sqrt{x+b}/(v + 1/2 + \sqrt{x+b}),$$

which are less than 1 for any value of vibrational v and rotational $x = J(J+1)$ quantum numbers. Transformed series is a power series with respect to these variables:

$$E(x,v) = K(x,v) + \sum_{i,j=1} p_{ij} Z_1^i(x) Z_2^j(x,v).$$

The transfer to new variables increases the quality of convergence. Expansion of the transformed expression into Taylor series returns a common exponential expression as a result. High centrifugal corrections, which usually are not defined in fitting, are "imitated" by the corresponding expansion terms. Thus, the Euler transformation allows one to "built in" an additional information in PT series and, as a result, obtain physically-based expression for energy.

2. The Euler method, a special case of GET, was used for the calculation of VR-energy levels of H_2O, HDO, D_2O, and CH_2 molecules.[8–10] This method corresponds to the use of the simplest Pade approximant [0,1] as an approximation function $g(x,v)$:

$$g(x,v) \equiv P^{[0,1]}(x,v) = \frac{e_0(v)}{1 - x e_1(v)/e_0(v)}. \tag{9}$$

The Euler transformation in this case results in a power series, which depends on a new variable X:

$$E(x,v) = P^{[0,1]}(x,v) + p_2 X^2 + p_3 X^3 + \ldots;$$
$$X = \frac{x}{1+\alpha x}, \quad \alpha = -e_1(v)/e_0(v). \tag{10}$$

The new variable is limited in magnitude at all values of rotational quantum number, that increases the series convergence. The use of an approximant of (9) type allows us to take into account the fact that the initial series (2) is alternating and centrifugal corrections in (2) can be approximately represented as exponential expressions. To calculate the approximant, only two summands of PT series are to be known. Note that when using Eq. (9), GET yields $p_0(v = 0) \equiv 1$ and $p_1(v = 0) \equiv 0$; these parameters were fixed in the fitting.

In this work we also used the Pade approximations for summing series. It is well-known that the Pade approximants $P^{[n,m]}(x)$ are the ratio of two polynomials, coefficients of which are selected in such a way that to accurately represent $n + m + 1$ coefficients of the initial series. In this case also $p_0(v = 0) \equiv 1$ and the following $n + m$ coefficients of the transformed series (5) are equal to zero. The series is the form

$$E(x,v) = P^{[n,m]}(x,v) + p_{n+m+1}\chi_{n+m+1}(x,v) + \ldots. \tag{11}$$

3. Other approximating functions, used in this work, are square Pade – Hermitt approximants.[7] In the general case they are presented as

$$PH^{[r,p,q]}(x,v) =$$
$$= \left\{-Q_q(x) \pm \sqrt{Q_q{}^2(x) - 4P_p(x)R_r(x)}\right\} \Big/ 2P_p(x), \tag{12}$$
$$P_p(0) = 1,$$

where $P_p(x)$, $Q_q(x)$, $R_r(x)$ are polynomials of p, q, r degrees, depending on coefficients of the summable series. It follows from Eq. (12) that this approximation method allows accounting for both the poles and points of $E(x,v)$ bifurcation; the approximants are determined by $r + p + q + 2$ first coefficients. The use of $PH^{[0,0,1]}(x,v)$ approximant (equivalent to generating function from Ref. 4) in the GET method also allows us to introduce a new variable bound in magnitude for all values of the rotational quantum number. The coefficients of the transformed series (5) are: $p_0(v = 0) \equiv 1$ and $p_n(v = 0) \equiv 0$, $n = 1 \ldots r + p + q + 1$. The series (5) has the form

$$E(x,v) = PH^{[r,p,q]}(x,v) + p_{r+p+q+2}\chi_{r+p+q+2}(x,v) + \ldots. \tag{13}$$

4. We also used the effective characteristic polynomial $\Pi_2(x,v)$ (see Ref. 12) as an approximating function:

$$\Pi_2(x,v) = e(v)_0 + e(v)_1 + \frac{e_2^2(v)}{2}\frac{A}{B}\left\{1 \pm \sqrt{1 - \frac{4B}{A^2}}\right\}, \tag{14}$$

$$A = e(v)_2 - e(v)_3, \; B = e(v)_2 e(v)_4 - e_3^2(v).$$

Expression (14) takes into account that the initial series (2) is energy levels, which are roots of characteristic polynomial and, consequently, has both points of bifurcation and poles. To determine the approximant $\Pi_2(x,v)$, we need five first coefficients of the initial series. In this case GET method yields $p_0(v = 0) \equiv 1$ and $p_n(v = 0) \equiv 0$, $n = 1 \ldots 4$. Other coefficients of the transformed series are found by fitting. The series has the form

$$E(x,v) = \Pi_2(x,v) + p_5\chi_5(x,v) + \ldots. \tag{15}$$

5. In general case, Pade – Borel approximants have the form

$$PB^{[n,m]}(x,v) = \int\limits_0^\infty e^{-t} P^{[n,m]}(xt)\,\mathrm{d}t, \qquad (16)$$

where $P^{[n,m]}(x)$ are the Pade approximants of the orders n, m for the Borelean image of the initial series (2); they are determined from $n + m + 1$ first coefficients. In this case $p_0(v = 0) \equiv 1$, $p_n(v = 0) \equiv 0$, $n = 1...n + m$; and the transformed series is presented as

$$E(x,v) = PB^{[n,m]}(x,v) + p_{n+m+1}\chi_{n+m+1}(x,v) + \dots . \qquad (17)$$

Calculation of H_2 molecule vibrational-rotational energy levels

To validate the GET method applicability and predictability, the H_2 molecule rotational energy spectrum was calculated and compared with the results of highly accurate *ab initio* calculations,[5] in which the relativistic and adiabatic corrections were taken into account. Since in Ref. 5 energy levels for all bounded states of the molecule are presented, these data give us a rare possibility to test the summation method, using both lower and highly excited states up to the molecule dissociation energy, as an example.

The estimates of contribution of PT series summands to the molecule total energy in ground vibrational state are presented in Fig. 1. Rotational constant B and centrifugal ones D, H, L, ... were determined by fitting by the least squares method. Then rotational energy $BJ(J + 1)$ and centrifugal contributions $DJ^2(J + 1)^2$, $HJ^3(J + 1)^3$ etc... in the total energy were calculated with these values of spectroscopic constants. Figure 1 shows that at $J = 30$ centrifugal corrections are comparable with molecule dissociation energy. Rotational and centrifugal constants defined by this method were used further for the determination of approximating functions.

As it was mentioned above, different functions were used as approximants in this work, i.e., Pade $P^{[0,1]}(x, v)$ (model $P[0,1]$), Pade – Borel $PB^{[1,1]}(x, v)$ (model $PB[1,1]$), and Pade – Hermitt $PH^{[0,0,1]}(x, v)$ (model $PH[0,0,1]$), effective characteristic polynomial $\Pi_2(x, v)$ (model ECP), as well as Kratzer formula (7). In the last case, parameters a and b were determined by two methods: according to formula (8), using the known values of equilibrium state and dissociation energy (K-1 model), and by the method that reproduces rotational and first centrifugal constants (K-2 model).

In each case, an expression for transformed series (5) was obtained. After that the task has been solved by a traditional method of VR-spectroscopy. The parameters of the transformed series (7), $p_n(v = 0)$ were determined by fitting by the method of the least squares to rotational energy levels $J \le 22$ of the ground vibrational state. The initial data, i.e., calculated energy levels[5] were noised by a random error, which was uniformly distributed in interval –0.01–0.01 cm^{-1}. For each approximant the inverse problem was solved, and optimal set of parameters $p_n(v = 0)$ of the transformed series was selected. To do this, a 68% confidence interval was calculated for each determined parameters and a standard and maximal deviations of the calculated levels from the initial ones were found.

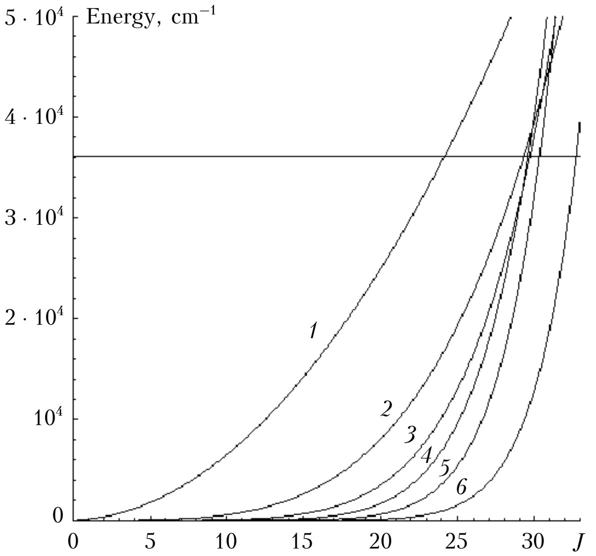

Fig. 1. Absolute values of contribution of centrifugal distortion constants to total energy rotational states H_2. Dissociation energy is marked by a horizontal straight line; *1–6* represent $BJ(J + 1)$; $-D[J(J + 1)]^2$; $H[J(J + 1)]^3$; $-L[J(J + 1)]^5$; $P[J(J + 1)]^5$; $-Q[J(J + 1)]^6$.

For $23 < J \le 32$ energy levels, the predictive calculations were conducted and standard and maximal deviations were determined. Analysis of these values allowed us to determine, which of calculation variants (depending on the number of fitting parameters) yields the best set of parameters, the best fitting and prediction for energy levels.

The choice of the optimal model was based on the following principle: if at a certain number of fitting parameters the minimal values of the root-mean-square error, maximal error, and mean standard deviation are the closest to each other, then the given model best describes the initial data set. The curves of these values for K-2 model are shown in Fig. 2 as an example. As is seen, using the given model, the most accurate results can be obtained at the number of fitting parameters $N = 3$.

Basic calculation data: parameters $p_n(v = 0)$ and error estimates, root-mean-square error and maximal deviation are presented in Table.

The calculations conducted revealed that rotational energy spectrum of the H_2 molecule up to $J = 22$ is described quite well by the power series (2), using six parameters. In this case, the root-mean-square error is equal to 0.019 cm^{-1} and the maximal deviation is 0.042 cm^{-1}. All the determined parameters are reliable. At the same time, the predictive calculation for higher energy levels gave a very poor result: deviations reached 809 cm^{-1} at a root-mean-square error of 314 cm^{-1}.

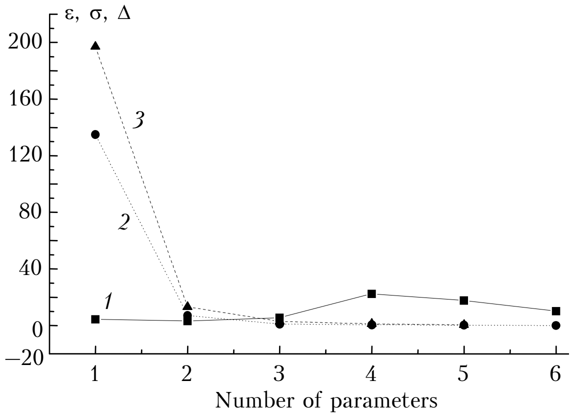

Fig. 2. Dependence of mean-root-square deviation ε (*1*), root-mean-square error σ (*2*), and maximal error Δ (*3*) on the number of fitting parameters (K-2 model).

The application of GET method with different approximating functions not always increases the quality of fitting, though in any case the predictive calculation is better by the order of magnitude.

Among all calculation variants, the best result for $J > 22$ levels is obtained with $PB[1,1]$ approximant (Eq. (16)). Although in this case the root-mean-square error for the fitted levels exceeds the "noise" by 4 times, maximal error is 0.082 cm^{-1} and the error in prediction of energy levels of higher states is the least. The K-1 approximant also gives quite acceptable values for higher state levels. In this case, parameters a and b are determined from dissociation energy and equilibrium bound length. Note that Pade – Borel approximant $PB[1,1]$ gives the best predicted levels but somewhat worse fitting result for $J \le 22$ levels. The predictive calculations of Pade – Hermitt $PH[0,0,1]$ approximants or effective characteristic polynomial (ECP) in the framework of GET method are quite inaccurate.

It was also found that K-2 model with three fitting parameters gives quite good results for levels with $J > 22$ ($\sigma = 3.35$ cm^{-1}, maximal error is 2.18 cm^{-1}). However, for levels with $J \le 22$ calculated levels significantly differ from the initial ones ($\sigma = 0.101$ cm^{-1}, maximal error us 0.169 cm^{-1}). Note, that this model was obtained from Kratzer approximant (7) by a specific selection of a and b parameters. Therefore, it is useful to modify Kratzer approximant in such a way that its parameters reproduce a larger number of terms of the PT series. Modified Kratzer formula can be presented in the following way (model K_m):

$$K_m(x) = \frac{a_0 + a_1x + a_2x^2 + \ldots}{V + 1/2 + \sqrt{b_0 + b_1x + b_2x^2 + \ldots}}. \tag{18}$$

In the process of calculation we revealed that with the help of a_0, b_0, b_1 parameters (Eq. (14)), determined in such a way that they reproduce rotational B and centrifugal D- and H-constants, we can obtain quite good calculation of levels with $J > 22$.

Table. Values of $p_n(v = 0)$ parameters in Eq. (5), root-mean-square error and maximal difference between calculated and initial values of levels

N	$PB[1,1]$	K-1	K-2	K_m	$P[0,1]$	$PH[0,0,1]$	ECP
0	1	2.5843(14)	1	1	1	1	1
1	0	1.5444(13)	0	0	0	0	0
2	0	0.9918(17)	0.000971(65)	0	0.3642(24)	0–	0
3	0.2887(38)	0.58114(82)	−0.3793(10)	0.0200(21)	−0.088(21)	−0.319(68)	0
4	0.263(10)	0.4332(54)	−0.1714(57)	−0.488(40)	−0.170(46)	9.39(58)	0
5	–	–	−0.3403(97)	2.98(24)	–	−26.1(14)	0.065(58)
6	–	–	–	−7.29(62)	–	30.9(11)	0.71(33)
7	–	–	–	8.83(55)	–	–	1.08(54)
				Root-mean-square and maximal errors *Fitting up to $J = 22$*			
σ	0.042	0.024	0.012	0.009	0.036	0.074	0.015
Δ	0.082	0.042	0.026	0.018	0.071	0.137	0.32
				Predictive calculation $J > 22$			
σ	2.3	7.3	9.4	14.0	15.8	63	49
Δ	6.3	18.8	22.8	33.9	38	139	116
				Fitting to all energy levels up to $J = 30$			
N_p	5	8	7	7	5	7	5
σ	0.091	0.32	0.036	0.068	0.024	0.093	1.18
Δ	0.34	0.57	0.063	0.13	0.056	0.15	4.59

Note. N is the order of summand (5), the estimation error in determination of the parameter is presented in units of the last significant digits is given in brackets; σ is root-mean-square error; Δ is the maximal error; N_p is the number of fitting parameters. The parameters, free of error estimate, are fixed.

The GET method and the approximants mentioned above were used for fitting to all energy levels of the ground vibrational state of H_2. We have selected a theoretical model, the parameters of which were statistically reliable. Polynomial representation, as expected, does not give a satisfactory result, because in this case the same quantity of parameters, as initial data, is required to reproduce the levels. At the same time, the use of Euler method with any approximant gives energy levels, which agree with the initial ones much better at a small number of parameters. The best fitting is when using K-2 Kratzer approximant and $P[0,1]$ Pade approximant. Maximal deviations for these models are 0.063 and 0.056 cm^{-1}, respectively, and standard deviations σ are of 0.036 and 0.025 cm^{-1} when using five and seven fitting parameters, respectively. For other approximants the fitting is worse (the data are presented in the Table).

In this paper we considered the simplest case, i.e., rotational energy spectrum of the H_2 molecule, which was used as an example in testing the GET method. The results of application of different approximating functions were analyzed. The calculations were conducted in a typical spectroscopic way, i.e., some levels were used for fitting model parameters. The model was further used for calculation of higher rotational states up to dissociation energy. The complete set of levels, obtained as a result of highly accurate *ab initio* calculations, was used as the initial data. These energy levels were “noised” with 0.01 cm^{-1} random error, typical for such measurements.

Conclusion

Analysis of results, presented in this paper, allows us to draw two conclusions. First, in the framework of traditional semiempirical approach of the theory of VR-spectra of molecules, the generalized Euler transform allows us to use the simplest approximants in calculations of molecule rotational energy levels, which do not require high orders of PT calculations. Second, provided the approximant is selected correctly, the application of this method allows quite satisfactory predictions for the levels, which were not used in fitting parameters of the theoretical model.

It should be noted that the range of energy levels, used in calculations, is quite wide: from 0 to 34000 cm^{-1}; and the whole energy range is described only by two parameters (in case of Pade – Borel approximant) with a maximal error of 6.3 cm^{-1} for $J = 31$ state close to dissociation energy. Such accuracy is comparable with results of “global” variation calculations. Apparently, the theoretical model parameters, determined by the fitting, include large inharmonic additions, centrifugal distortion, and some more fine effects, caused by non-adiabatic interactions and relativistic corrections.

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