

Some properties of the generalized Euler transformation of series in application to molecular rovibrational energy levels

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Some properties of the generalized Euler transformation (GET), such as the possibility of obtaining exact sum of a series, the convergence of a transformed series, and its new representations, are considered. Certain criteria of convergence of transformed series are presented and conditions, under which the Euler method enables one to obtain a finite expression for the sum of a series, are established. The properties of a transformed series are analyzed for the case that the known Padé, Padé–Borel, or Padé–Hermite approximants are used as the zero approximation in GET. Different ways of parameterization of the coefficients of the transformed series are discussed. The method proposed is tested while applied to the exactly solvable quantum-mechanics problem of the Kratzer oscillator taken as an example.

Introduction

The calculations of energy levels of high-excited states by the method of effective rotational Hamiltonian need for application of the methods of series summation. As known,^{1–10} the series, representing the matrix elements of the effective rotational Hamiltonian, diverge at large quantum numbers of the angular momentum. Earlier, (see, for example, Refs. 1–22) various summation methods have been proposed to improve calculations in the case of high-excited states. However, new experimental data obtained on the levels of high-energy states of some molecules, for example, H₂O, H₂S, H₃⁺, and others, call for development and application of new computational methods, taking into account poor convergence of the series.

This paper considers some properties of the generalized Euler transformation (GET),^{23,24} such as the possibility of obtaining exact sum of a series, the convergence of the transformed series, and its new representations. The Euler transformation was successfully applied earlier to the series summation in some quantum-mechanics problems, for example, in calculating energy levels of an anharmonic oscillator, computation of the Stark and Zeeman effects in hydrogen atom, summation of the 1/*Z* expansion in the atomic theory (see, for example, Refs. 24 and 25). The GET method was also applied to calculation of the RV energy levels of H₂O molecule,¹⁵ CH₂ radical,¹⁶ and diatomic molecules.^{26,27} Brief description of the GET method is given in this paper.

One of the basic properties of the Euler method is that it is regular,²³ that is, the method gives correct sums of convergent series. This property is missing in other methods, for example, in the Padé method. It should be noted that the GET method gives no information about the convergence of the

transformed series. In any summation method, the convergence is of crucial importance, because in the case of divergence it is impossible to obtain a determinate result. Nevertheless, most papers, dealing with the application of methods for summation of divergent series in calculating rotational energy levels, present no arguments in favor of the series convergence. For this reason, in this paper, we give some criteria of convergence of the transformed series and establish conditions, under which the Euler method yields the finite value for the sum.

The properties of the transformed series are considered for the case when the known Padé, Padé–Borel, and Padé–Hermite approximants are used as zero approximation in the GET method. In addition, different methods of parameterization of the coefficients of the transformed series are presented along with the results of testing the method while applying it to the exactly solvable problem of Kratzer oscillator taken as an example.

1. Generalized Euler transformation

For convenience, this Section presents briefly the basic equations of the GET method.²⁴ Let the function $f(z)$ be expanded in the following series

$$f(z) = \sum_{n=0}^{\infty} f_n z^n, \quad (1)$$

and some its estimate (approximating function) is known:

$$g(z) = \sum_{n=0}^{\infty} g_n z^n = g_0 + g_1 z + g_2 z^2 + \dots \quad (2)$$

The approximating function can be used for the transformation of the series in the following way. Add the approximant to the right-hand side of

Eq. (1) and then subtract it, but in the form of a series. Then add $z \frac{dg(z)}{dz}$ and subtract it again, but in the form of a series. Repeating this procedure, we can exclude all power terms from the right-hand side of Eq. (1) and thus transform the series (1) into the functional one. The transformed series has the form

$$f(z) = \sum_{n=0}^{\infty} D_n \Phi_n(z); \quad \Phi_n(z) = (-1)^n \frac{z^n}{n!} \frac{d^n g(z)}{dz^n}; \quad (3)$$

$$D_n = \sum_{r=0}^n (-1)^r \binom{n}{r} a_r, \quad a_r = f_r/g_r.$$

The transformations presented here are formally identical, and the transformed expression restores the initial series (1) when expanded into the Taylor series. It is just this expression that is referred to as a “sum of the series.”

2. Conditions of convergence of the transformed series

It is intuitively clear that if the “proper” approximant is chosen, so that the coefficients of the Taylor series $f(z)$ and $g(z)$ are similar in some sense, then the “new” series (3) must have better properties than the initial one, that is, it must converge faster in view of the relation $\sum_{r=0}^n (-1)^r \binom{n}{r} b_r = 0$. However, it is desirable to have more definite conditions of convergence. We will specify two such necessary conditions

1) If at $z \leq z_0$

$$\left| D_n \frac{d^n g(z)}{dz^n} \right| \leq AB^n, \quad (4)$$

then the series (3) converges in the specified region. Indeed,

$$\sum_{n=0}^{\infty} (-1)^n D_n \frac{z^n}{n!} \frac{d^n g(z)}{dz^n} \leq \sum_{n=0}^{\infty} \left| D_n \frac{d^n g(z)}{dz^n} \right| \frac{z^n}{n!} \leq A \sum_{n=0}^{\infty} \frac{(Bz)^n}{n!} = A \exp(Bz). \quad (5)$$

Since the last series converges at any z , the transformed series, obviously, converges at $z \leq z_0$ too.

Thus, if the approximant derivatives and the coefficients $a_n = f_n/g_n$, considered as functions of the index n , increase with increasing n slower than by the exponential law, then the series transformed by the Euler method converges.

2) If at $z \leq z_0$

$$\left| D_n \frac{d^n g(z)}{dz^n} \right| \leq AB^n n!, \quad (6)$$

then the radius of convergence of the series (3) $z \leq \min\{z_0, 1/B\}$.

Let us prove this:

$$\sum_{n=0}^{\infty} (-1)^n D_n \frac{z^n}{n!} \frac{d^n g(z)}{dz^n} \leq \sum_{n=0}^{\infty} \left| D_n \frac{d^n g(z)}{dz^n} \right| \frac{z^n}{n!} \leq A \sum_{n=0}^{\infty} (Bz)^n = \frac{A}{1-Bz}. \quad (7)$$

Since the last series converges at $|z| \leq 1/B$, the above estimate follows from here.

The approximating function $g(z)$ can be chosen in different ways. As a consequence, the ratios $a_r = f_r/g_r$ can have different dependence on r . It is useful to introduce the estimates of the coefficients of the transformed series, assuming a certain dependence of the ratios $a_r = f_r/g_r$ on the index r . This will help one to establish some criteria, determining the “quality” of the approximant and to give a convenient parameterization of the transformed series. It should be noted here that the estimates of the coefficients f_r of the initial series of the perturbation theory (PT) can be obtained in the standard way, that is, based on the quasi-classical approach, described, for example, in Ref. 28. On the other hand, it is not difficult to obtain the coefficients of the approximant g_r expansion into the Taylor series. However, let us first establish the following fact.

3) If the approximating function $g(z)$ is chosen so that

$$f_r/g_r = a_r = \alpha_0 + \alpha_1 r + \alpha_2 r^2 + \dots + \alpha_K r^K, \quad (8)$$

then GET gives the finite expression for the sum of the series.

Indeed, in this case

$$D_n = \sum_{i=0}^K \alpha_i \sum_{r=0}^n (-1)^r r^i \binom{n}{r}. \quad (9)$$

Since

$$\sum_{r=0}^n (-1)^r r^m \binom{n}{r} = 0 \text{ at } m < n,$$

all the coefficients D_n , $n > K$ vanish. If the condition (8) is fulfilled, the generalized Euler transformation yields a finite expression for the sum of the series

$$f(z) = g(z)a_0 + \sum_{n=1}^K (-1)^n D_n \frac{z^n}{n!} \frac{d^n g(z)}{dz^n}, \quad (10)$$

where

$$D_n = \sum_{i=0}^{K-n} \alpha_{n+i} \sum_{r=0}^n (-1)^r r^{n+i} \binom{n}{r}, \quad (11)$$

and the series can be summed exactly. Thus, the approximant can be chosen so that it only

qualitatively reproduces the derivatives of the initial function f_r ; they should be approximately proportional, then GET yields the finite expression for the sum of the series. In this case, the difference between the initial function and the approximant can be arbitrary and quite large. This property of GET is very useful, since it allows rough approximations to be used, if only the ratio f_r/g_r does not change too quickly with the increasing index r .

3. Transformed series

In the method of effective Hamiltonians, we usually know only several first terms of the initial series (1) (that is, the coefficients f_r , $r = 0, \dots, N$), which are determined through the fitting to experimental energy levels or transition frequencies. Therefore, it is quite useful to consider different ways of approximation of the ratios $a_r = f_r/g_r$ in order to obtain new representations for matrix effective Hamiltonians, including new fitted parameters.

In making particular calculations, especially for light nonrigid molecules having small moments of inertia, the Padé² and Padé–Borel⁶ approximants or generating functions¹⁰ are used. These approximants are defined so that they reproduce accurately first N coefficients $f_0, f_1, f_2, \dots, f_N$ of the initial series (1). If these approximants are used as zero approximation in the Euler method, the transformed series becomes simpler. Indeed, if

$$g_0 = f_0, \quad g_1 = f_1, \quad \dots, \quad g_N = f_N,$$

then

$$D_n = \sum_{r=0}^n (-1)^r \binom{n}{r} \frac{f_r}{g_r} = \sum_{r=0}^n (-1)^r \binom{n}{r} = \delta_{n,0}, \quad n \leq N \quad (12)$$

and the transformed series (3) has the form

$$f(z) = g(z) + (-1)^{N+1} D_{N+1} \Phi_{N+1}(z) \times \left\{ 1 + \sum_{n=N+2}^{\infty} (-1)^{n-N-1} \tilde{D}_n \tilde{\Phi}_n(z) \right\}, \quad (13)$$

where

$$\begin{aligned} \tilde{D}_n &= D_n / D_{N+1}; \\ \tilde{\Phi}_n(z) &= \Phi_n(z) / \Phi_{N+1}(z) = \\ &= z^{n-N-1} \frac{(N+1)!}{n!} \frac{d^n g(z)}{dz^n} \Big/ \frac{d^{N+1} g(z)}{dz^{N+1}}. \end{aligned} \quad (14)$$

The expressions for the coefficients D_n of the transformed series also become simpler.

In Eq. (13) the first term $g(z)$ is an approximant, that is, the approximate expression for the rotational-vibrational energy. The second term is a correction to this approximation, following from the Euler transformation. The coefficients of the series in braces depend on the unknown parameters

$f_{N+1}/g_{N+1}, f_{N+2}/g_{N+2}, \dots$, and it is desirable to perform new parameterization of the transformed series, using certain estimates of these ratios and keeping in mind the fitting of the parameters of the new representation to experimental data. Obviously, this may improve the calculations of the rotational-vibrational energy levels.

Consider the following parameterization of the ratios $a_r = f_r/g_r$:

$$a_r = f_r/g_r = \omega(r) \sum_{i=0}^K \frac{\gamma_i}{(r+1)^i}. \quad (15)$$

Here $\omega(r)$ is the “main” part of the ratios between the coefficients of the summed series and the approximant (which is assumed to be known); γ_i are some coefficients. In this case, the coefficients D_n of the transformed series can be represented in the form

$$D_n = \sum_{r=0}^n (-1)^r \binom{n}{r} \omega(r) \sum_{i=0}^K \frac{\gamma_i}{(r+1)^i} = \sum_{i=0}^K \gamma_i T_i^n, \quad (16)$$

where

$$T_i^n = \sum_{r=0}^n (-1)^r \binom{n}{r} \frac{\omega(r)}{(r+1)^i}. \quad (17)$$

Now the transformed series can be represented as follows

$$f(z) = \sum_{i=0}^K \gamma_i \sum_n (-1)^n T_i^n \Phi_n(z). \quad (18)$$

Thus, we obtain the new representation of the transformed series, in which the new parameters γ_i are introduced. This approach is an analog of the summation method, known as a nonlinear sequence transformation.²⁹ In this method, the remainder in the estimates of the series sum is also represented in the form (12).

In the method of effective Hamiltonians, the summed series (that is, $f(z)$ in our case) are matrix elements. For example, for molecules like water molecule, the most significant part of the summed series is the so-called J_z -sequence,⁹ including the rotational constant A and the centrifugal distortion constants $\Delta_k, \Delta_{jk}, \Delta_j, H_k$, and so on. To determine $\omega(r)$ in this case, it is possible to take the r th term of the expansion of the generating function $G = (2/\alpha) \left\{ \sqrt{1 + \alpha J_z^2} - 1 \right\}$ into the Taylor series. The

parameters γ_i can be considered as values determined from the fitting to experimental energy levels. Thus, the use of the approximations of the form (15) introduces a new parameterization in the effective Hamiltonian.

Consider now some simplest cases.

Exponential approximation. If the approximating function is chosen so that

$$f_r/g_r = a_r = \beta^r \left\{ \gamma_0 + \frac{\gamma_1}{r+1} + \dots + \frac{\gamma_K}{(r+1)^K} \right\} = \beta^r \sum_{i=0}^K \frac{\gamma_i}{(r+1)^i}, \quad \omega(r) = \beta^r, \quad (19)$$

then the coefficients of the transformed series become simpler. It is assumed here that at large r the difference between the expansion coefficients of the approximant and the initial series becomes close to $\gamma_0\beta^r$ at the increase of r . Use the relation³¹:

$$\sum_{r=0}^n \binom{n}{r} (\pm x)^r = (1 \pm x)^n, \quad (20)$$

$$\sum_{r=0}^n \frac{(\pm 1)^r}{r+a} \binom{n}{r} x^r = x^{-a} \int_0^x t^{a-1} (1 \pm t)^n dt = Q(x, a, n), \quad (21)$$

$$a \neq 0, -1, -2, \dots$$

Then we obtain

$$\begin{aligned} T_0^n &= (1 - \beta)^n, \\ T_1^n &= Q(\beta, 1, n), \\ T_i^n &= \frac{(-1)^{i-1}}{(i-1)!} \left. \frac{d^{i-1}}{da^{i-1}} Q(\beta, a, n) \right|_{a=1}. \end{aligned} \quad (22)$$

Factorial approximation. Assume now that the difference between the coefficients of the approximant and the initial series is determined by the factorial function

$$f_r/g_r = a_r = \beta^r r! \left\{ \gamma_0 + \frac{\gamma_1}{r+1} + \dots + \frac{\gamma_K}{(r+1)^K} \right\} = \beta^r r! \sum_{i=0}^K \frac{\gamma_i}{(r+1)^i}. \quad (23)$$

The estimates of this kind are obtained for the terms of the PT series of the anharmonic oscillator. In this case, one fails to calculate exactly the sums (17), and T_i^n are to be determined through direct calculations. In the method of effective Hamiltonians, Eq. (23) gives a convenient parameterization of the transformed series in calculating the rotational-vibrational energy levels. The values of β , γ_i can be found through the fitting to experimental energy levels.

The results presented show that, regardless of the rate of divergence of the initial series, the Euler method can yield a correct result, if the approximating function is chosen properly, that is, either the condition (4) or (6) is fulfilled. This circumstance appears to be very important, and the problem can be thus reduced to the selection of the approximating function regardless of the divergence rate of the initial series of the perturbation theory.

4. Application to exactly solvable models

Consider now the application of GET to series summation in the exactly solvable problem of the Kratzer oscillator.

The Kratzer potential has the form

$$V(r) = \frac{A}{r^2} - \frac{B}{r}.$$

The solution of the Schrödinger equation with this potential can be found in the closed form; the equation for the energy levels has the form³⁰:

$$K(J, \nu) = -a \left[\nu + 1/2 + \sqrt{J(J+1) + b} \right]^{-2} + a \left[1/2 + \sqrt{b} \right]^{-2} = -a \left[y + \sqrt{x + b} \right]^{-2} + a \left[1/2 + \sqrt{b} \right]^{-2}, \quad (24)$$

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

Here μ is the reduced mass, and the energy is measured from the zero level $\nu = 0, J = 0$.

We use the problem of the Kratzer oscillator to test the GET method. The simplest Padé approximant [1/1] is used as an approximation. At $x = -b$ the Kratzer function (24) has a bifurcation point of the second-order, and the series diverges starting from $J = 23$ (Fig. 1).

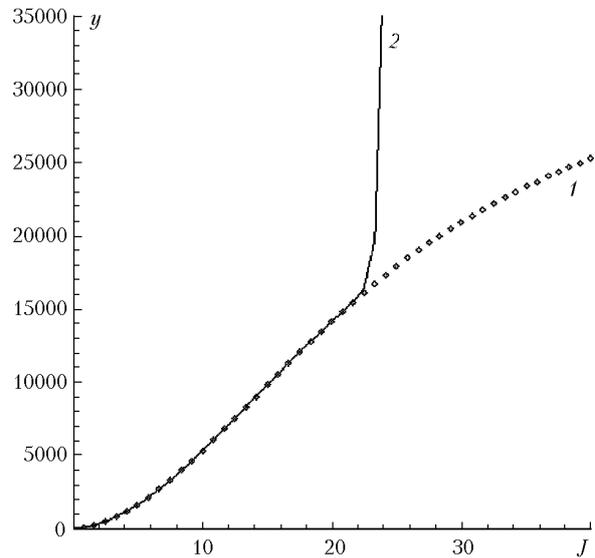


Fig. 1. Energy levels of the Kratzer oscillator (curve 1) and the sum of the series (1) (curve 2).

Figure 2 demonstrates the relative error $E^{Kr}[J(J+1)]/E^{Padé}[J(J+1)]$ in the calculation of rotational energy levels at $V = 0$ and 10 of the Kratzer oscillator by the GET method (curves 1–4) and the calculation with the Padé approximant [1/1] (5).

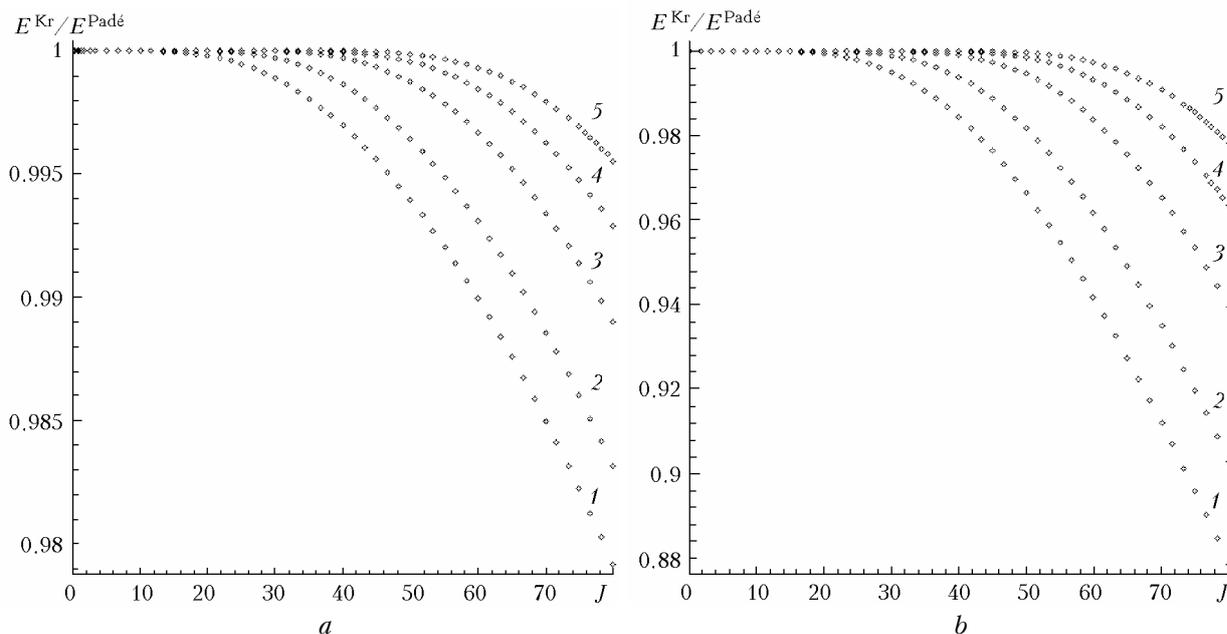


Fig. 2. Relative error $E^{\text{Kr}}[J(J+1)]/E^{\text{Padé}}[J(J+1)]$ in the calculation of rotational energy levels for $V=0$ (a) and $V=10$ (b).

The dependence of the rotational energy levels of the vibrational state $V=10$ on the quantum number J is shown in Fig. 3.

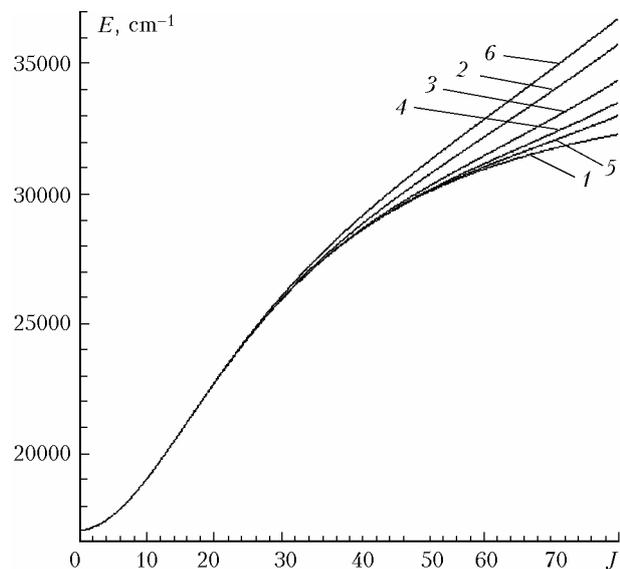


Fig. 3. Dependence of the rotational energy levels of the vibrational state $V=10$ on the quantum number J : exact equation (1); calculation by the GET method, $N=5, 10, 15, 20$ (2–5); calculation with the Padé approximant $[1/1]$ (6).

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