Generalized Euler transformation for the series of two variables. Application to rovibrational energy levels of diatomic molecules

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The generalized Euler series transformation method is extended to the case of a series of two variables. It is applied to summation of the Dunham series for diatomic molecules. The Kratzer oscillator – the exactly solvable problem of quantum mechanics – is used as an approximating function. A new expression for the Dunham series is obtained, and the transformed series turns out to be a functional one, which corresponds to partial summation of the original series.

Introduction

For calculation of the atmospheric transmission function, it is necessary to know with high accuracy the positions and intensities of spectral lines of diatomic molecules and radicals, such as O_2, OH, CH, HCl, HF, and others. The energy levels of diatomic molecules can be represented as the Dunham power series (of the perturbation theory) in terms of the rotational $J(J+1)$ and vibrational $(V+1/2)$ quantum numbers.[1] However, the perturbation theory cannot be applied to highly excited rotational-vibrational (RV) states, because in this case the perturbation series are poorly convergent or even divergent. As a consequence, it is necessary to apply a specialized method for summation of the series.

In Refs. 2–9, various methods of summation of the series ($1/N$-expansion, rational approximation) were already used for calculation of the RV energy levels of diatomic molecules. The use of these methods significantly improved the calculations, but it seems useful and necessary to study the applicability of other methods for summation of the series. New methods for calculation within the framework of the perturbation theory, checked for diatomic molecules with relatively simple RV energy spectrum, may also be useful for more complex molecules, for example, triatomic H_2O, CH_2, H_3^+, and others. It is well-known that calculations by the perturbation method for such molecules face significant difficulties associated with quick divergence of the series.

The generalized Euler transformation is an efficient instrument for summation of the divergent series. Note that this transformation allows the summation of even rapidly divergent series of the quantum-mechanics perturbation series in the case of one-dimensional anharmonic oscillators.[10] It also allows one to use an additional information about the summed function in transformation of the series. Earlier,[11,12] the generalized Euler transformation was presented for the Dunham series of diatomic molecules, which were considered as the series of a single variable. In this paper, the Euler method is modified to be applied to summation of a series of two variables. The technique developed permits the Dunham power series to be presented as a functional series, which corresponds to its partial summation.

Generalized Euler transformation for the series of two variables

Let the function $f(x, y)$ of two variables x and y be expanded into the following series

$$f(x,y)=\sum_{i,j=0}^{\infty} f_{ij}x^i y^j=\sum_{n=0}^{\infty}\sum_{i=0}^{n} f_{i,n-i}x^i y^{n-i} \tag{1}$$

and some its estimate – an approximating function – be known

$$G(x,y)=\sum_{i,j=0}^{\infty} g_{ij}x^i y^j=\sum_{n=0}^{\infty}\sum_{i=0}^{n} g_{i,n-i}x^i y^{n-i}. \tag{2}$$

Let the condition

$$a_{ij}={f_{ij}}\Big/{g_{ij}}\to 1 \tag{3}$$

be fulfilled at $i, j\to\infty$. Then the initial series (1), which may be divergent, can be transformed into the convergent (or better convergent, if the series (1) converges slowly) in the following way:

$$f(x,y)=a_{00}G(x,y)+\sum_{n=0}^{\infty}\sum_{i=0}^{n}\left(a_{i,n-i}-a_{00}\right)g_{i,n-i}x^i y^{n-i}. \tag{4}$$

Then we use the relation

$$g_{i,n-i}x^i y^{n-i} = \frac{x^i y^{n-i}}{i!(n-i)!}\frac{\partial^n G(x,y)}{\partial x^i \partial y^{n-i}} -$$

$$-\sum_{m=n+1}^{\infty}\sum_{j=0}^{m}\frac{g_{j,m-j}}{i!(n-i)!}A(j,i)A(m-j,n-i)x^j y^{m-j}, \quad (5)$$

where

$$A(j,i) = j(j-1)\ldots(j-i+1) = \begin{cases} 0, \; i > j \\ \dfrac{j!}{(j-i)!}, \; i \le j \\ 1, \; i = 1 \\ 0, j = 0 \end{cases},$$

and transform the series, excluding sequentially the coefficients g_{ij} from the transformed series (4). We obtain (for the case $n = 3$)

$$E(x,y) = a_{00}G(x,y) + (a_{01} - a_{00})y\frac{\partial G(x,y)}{\partial y} +$$
$$+(a_{10} - a_{00})x\frac{\partial G(x,y)}{\partial x} + (a_{02} - 2a_{01} + a_{00})y^2\frac{\partial^2 G(x,y)}{\partial y^2} +$$
$$+(a_{11} - a_{01} - a_{10} + a_{00})xy\frac{\partial^2 G(x,y)}{\partial x \partial y} +$$
$$+\frac{1}{2}(a_{20} - 2a_{10} + a_{00})x^2\frac{\partial^2 G(x,y)}{\partial x^2} +$$
$$+\frac{1}{6}(a_{03} - 3a_{02} + 3a_{01} - a_{00})y^3\frac{\partial^3 G(x,y)}{\partial y^3} +$$
$$+\frac{1}{6}(a_{30} - 3a_{20} + 3a_{10} - a_{00})x^3\frac{\partial^3 G(x,y)}{\partial x^3} +$$
$$+\frac{1}{2}(a_{21} + 2a_{10} - 2a_{11} - a_{20} - a_{00} + a_{01})x^2 y\frac{\partial^3 G(x,y)}{\partial x^2 \partial y} +$$
$$+\frac{1}{2}(a_{12} + 2a_{01} - 2a_{11} - a_{02} - a_{00} + a_{10})xy^2\frac{\partial^3 G(x,y)}{\partial x \partial y^2}. \quad (6)$$

If the condition (3) is fulfilled, then the coefficients of the transformed series tend to zero with the growth of the total power of both x and y, and the series (6) must converge better than the initial one.

It should be noted here that the series (6), unlike (1), is a functional one, that is, the performed transformation with the use of the approximating function is equivalent to its partial summation.

The Dunham series and Kratzer oscillator

Application of the perturbation theory to calculation of rotational-vibrational energy levels of diatomic molecules leads to the series expansion depending on two parameters[1]:

$$E(J,v) = \sum_{n,m} Y_{nm}(v + 1/2)^n\left[J(J+1)\right]^m, \quad (7)$$

where v is the vibrational quantum number; J is the angular momentum quantum number, and the series coefficients Y_{nm} are called the Dunham coefficients. They are connected, in a certain way, with the coefficients of expansion of the potential function into a power series in terms of displacements from the equilibrium position.[1]

The Dunham series is a power series of two variables: vibrational $y = v + 1/2$ and rotational $x = J(J + 1)$ ones. It is convenient to represent it as

$$E(x,y) = \sum_{n,m} c_{nm}x^m y^n, \quad (8)$$

where the coefficients are re-grouped so that $E(0, 0) = 0$. This representation of the Dunham series corresponds to selection of the zero level as an energy reference.

The Kratzer equation describes the rotational-vibrational energy levels of diatomic molecules with the potential function

$$V(r) = \frac{A}{r^2} - \frac{B}{r}, \quad (9)$$

where A and B are the constants of the potential function. The Schrödinger equation with this potential has the exact solution, and the energy levels can be presented as the equation[13]:

$$K(J,v) = -a\left[v + 1/2 + \sqrt{J(J+1) + b}\right]^{-2} +$$
$$+a\left[1/2 + \sqrt{b}\right]^{-2} = -a\left[y + \sqrt{x + b}\right]^{-2} + a\left[1/2 + \sqrt{b}\right]^{-2}, \quad (10)$$
$$a = B^2\mu/(2\bar{h}^2), \quad b = 1/4 + 2A\mu/\bar{h}^2,$$

which will be called the Kratzer function. Here μ is the reduced mass of the diatomic molecules, the energy is measured from the zero level $v = 0$, $J = 0$, and the constants a and b can be expressed through the dissociation energy E_d and the equilibrium distance r_e:

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

Equation (10) can be used for transformation of the Dunham series to a more convenient form, so that the transformed series has better convergence properties and the corresponding function has a correct asymptotic at high values of v and J. Note that the Kratzer function gives the qualitatively correct asymptotic dependence: energy levels are concentrated in the interval determined by the depth of the potential well, while the asymptotic behavior of the Dunham series at high $y = v + 1/2$ depends on the sign of the highest term held in the expansion (7).

Transformed Dunham series

Using Eqs. (6) and (10), after some obvious transformations we can have the following equation for the transformed Dunham series:

$$
\begin{aligned}
E(x,y) = a_{00}&\left(-\frac{a}{\left(y+\sqrt{x+b}\right)^2}+\frac{a}{\left(1/2+\sqrt{b}\right)^2}\right)+\\
&+2(a_{01}-a_{00})\frac{ay}{\left(y+\sqrt{x+b}\right)^3}+\\
&+(a_{10}-a_{00})\frac{ax}{(y+\sqrt{x+b})^3\sqrt{x+b}}-\\
&-3(a_{02}-2a_{01}+a_{00})\frac{ay^2}{\left(y+\sqrt{x+b}\right)^4}-\\
&-3(a_{11}-a_{01}-a_{10}+a_{00})\frac{axy}{\left(y+\sqrt{x+b}\right)^4\sqrt{x+b}}+\\
&+\frac{1}{2}(a_{20}-2a_{10}+a_{00})x^2\times\\
&\times\left(-\frac{3}{2}\frac{a}{\left(y+\sqrt{x+b}\right)^4(x+b)}-\frac{1}{2}\frac{a}{\left(y+\sqrt{x+b}\right)^3(x+b)^{3/2}}\right)+\\
&+4(a_{03}-3a_{02}+3a_{01}-a_{00})\frac{ay^3}{\left(y+\sqrt{x+b}\right)^5}+\\
&+\frac{1}{6}(a_{30}-3a_{20}+3a_{10}-a_{00})x^3\times\\
&\times\left(3\frac{a}{\left(y+\sqrt{x+b}\right)^5(x+b)^{3/2}}+\frac{9}{4}\frac{a}{\left(y+\sqrt{x+b}\right)^4(x+b)^2}+\right.\\
&\left.+\frac{3}{4}\frac{a}{\left(y+\sqrt{x+b}\right)^3(x+b)^{5/2}}\right)+\\
&+\frac{1}{2}(a_{21}+2a_{10}-2a_{11}-a_{20}-a_{00}+a_{01})x^2y\times\\
&\times\left(6\frac{a}{\left(y+\sqrt{x+b}\right)^5(x+b)}+\frac{3}{2}\frac{a}{\left(y+\sqrt{x+b}\right)^4(x+b)^{3/2}}\right)+\\
&+6(a_{12}+2a_{01}-2a_{11}-a_{02}-a_{00}+a_{10})\times\\
&\times\frac{axy^2}{\left(y+\sqrt{x+b}\right)^5\sqrt{x+b}}. \qquad (11)
\end{aligned}
$$

The transformed series is presented here up to the third-order terms inclusive. In Eq. (11) it is convenient to introduce the following designations $Z_1(x) = 1/(x+b)$ and $Z_2(x, y) = 1/(y+\sqrt{x+b})$, then the transformed series is the power series in terms of $Z_1(x)$ and $Z_2(x, y)$:

$$
\begin{aligned}
E(x,y) = a_{00}&\left(-aZ_2^2(x,y)+\frac{a}{\left(1/2+\sqrt{b}\right)^2}\right)+\\
&+2(a_{01}-a_{00})ayZ_2^3(x,y)+\\
&+(a_{10}-a_{00})axZ_2^3(x,y)Z_1^{42}(x)-\\
&-3(a_{02}-2a_{01}+a_{00})ay^2Z_2^4(x,y)-\\
&-3(a_{11}-a_{01}-a_{10}+a_{00})axyZ_2^4(x,y)Z_1^{1/2}(x)+\\
&+\frac{1}{2}(a_{20}-2a_{10}+a_{00})x^2\times\\
&\times\left(-\frac{3}{2}aZ_2^4(x,y)Z_1(x)-\frac{1}{2}aZ_2^3(x,y)Z_1^{3/2}(x)\right)+\\
&+4(a_{03}-3a_{02}+3a_{01}-a_{00})ayZ_2^5(x,y)+\\
&+\frac{1}{6}(a_{30}-3a_{20}+3a_{10}-a_{00})x^3\times\\
&\times\left(3aZ_2^5(x,y)Z_1^{3/2}(x)+\frac{9}{4}aZ_2^4(x,y)Z_1^2(x)+\right.\\
&\left.+\frac{3}{4}aZ_2^3(x,y)Z_1^{5/2}(x)\right)+\\
&+\frac{1}{2}(a_{21}+2a_{10}-2a_{11}-a_{20}-a_{00}+a_{01})x^2y\times\\
&\times\left(6aZ_2^5(x,y)Z_1(x)+\frac{3}{2}aZ_2^4(x,y)Z_1^{3/2}(x)\right)+\\
&+6(a_{12}+2a_{01}-2a_{11}-a_{02}-a_{00}+a_{10})\times\\
&\times axy^2Z_2^5(x,y)Z_1^{1/2}(x). \qquad (12)
\end{aligned}
$$

Here

$$
\begin{aligned}
&a_{01}=\frac{Y_{01}}{2a/b^{3/2}},\quad a_{10}=\frac{Y_{10}}{a/b^2},\quad a_{11}=\frac{Y_{11}}{-3a/b^{5/2}},\\
&a_{20}=\frac{Y_{11}}{-a/b^3},\quad a_{02}=\frac{Y_{02}}{-3a/b^2},\quad a_{12}=\frac{Y_{12}}{6a/b^3}, \qquad (13)\\
&a_{21}=\frac{Y_{21}}{15a/4b^{7/2}},\quad a_{03}=\frac{Y_{03}}{4a/b^{5/2}},\quad a_{30}=\frac{Y_{30}}{a/b^4}.
\end{aligned}
$$

Thus, using Eqs. (5) and (6) derived above for the generalized Euler transformation of the series of two variables, we can obtain a new representation of the perturbation series for RV energy levels of diatomic molecules. The transformation procedure presented by Eqs. (5) and (6) is an extension of the well-known method[10] for the series of two variables. It can be readily seen that this procedure can be also applied for the series of three and more variables.

The transformed Dunham series (12), unlike the initial one (8), is a part of the functional series. It is obvious that expansion of Eq. (12) into the Taylor power series in terms of x and y returns the initial equation with the Dunham coefficients Y_{ij} up to the total power $n = i + j = 3$. Higher terms of the expansion $n > 3$ estimate the higher-order Dunham coefficients. In contrast to the finite part of the Dunham series, which is used in practice for description of experimental data, these estimates meet a certain asymptotic condition caused by the inequality

$$K(J,v) < a/\left[\frac{1}{2}a+\sqrt{b}\right]^2.$$

At the same time, the asymptotic behavior of the initial perturbation series is incorrect at high values of v and J, and the function determined by it takes the values ± ∞ depending on the sign of the last term held in Eq. (7).

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References

1. T.I. Velichko, V.Ya. Galin, Yu.S. Makushkin, and Vl.G. Tyuterev, *Analytical Calculations in Molecular Spectroscopy on Computer. General Algorithm as Applied to Diatomic Molecules* (Nauka, Novosibirsk, 1986), 189 pp.
2. A.V. Burenin and M.Yu. Ryabikin, J. Mol. Spectrosc. **136**, No. 1, 140–150 (1989).
3. A.V. Burenin and M.Yu. Ryabikin, Opt. Spektrosk. **68**, No. 5, 1037–1042 (1990).
4. A.V. Burenin and M.Yu. Ryabikin, Opt. Spektrosk. **78**, No. 5, 742–748 (1995).
5. A.V. Burenin and M.Yu. Ryabikin, Opt. Spektrosk. **79**, No. 2, 223–225 (1995).
6. M.Yu. Ryabikin, "*Methods for description of rotational-vibrational states of diatomic molecules taking into account asymptotic properties of the nuclei interaction potential,*" Cand. Phys.-Math. Sci. Dissert., Institute of Applied Mathematics RAS, Nizhny Novgorod (1999), 159 pp.
7. V.F. Golovko, S.N. Mikhailenko, and Vl.G. Tyuterev, J. Mol. Struct. **218**, 291–296 (1990).
8. V.F. Golovko and Vl.G. Tyuterev, Atm. Opt. **3**, No. 6, 562–567 (1990).
9. V.F. Golovko, S.N. Mikhailenko, and Vl.G. Tyuterev, Atm. Opt. **4**, No. 5, 367–370 (1991).
10. K. Bhattacharyya, Int. J. Quantum Chem. **XXII**, 307–330 (1982).
11. T.V. Kruglova, A.D. Bykov, and O.V. Naumenko, Atmos. Oceanic Opt. **14**, No. 9, 748–752 (2001).
12. T.V. Kruglova, Atmos. Oceanic Opt. **15**, No. 9, 730–733 (2002).
13. L.D. Landau and E.M. Lifshitz, *Course of Theoretical Physics.* Vol. 3. *Quantum Mechanics. Non-Relativistic Theory* (Pergamon Press, 1958).