

Summation of perturbation series by the Euler method. Rotation-vibration states of diatomic molecules

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Received July 9, 2002

Calculations of rovibrational energy levels of diatomic molecules by the perturbation method are considered. Perturbation series may diverge at large values of the angular momentum quantum number, and in this case the Euler method is used for series summation. The Kratzer oscillator, i.e., the exactly solvable quantum problem, is used as an approximant. The equation for the general term of a transformed series is derived and analyzed.

Introduction

Solution of various problems in atmospheric spectroscopy requires calculation of positions and strengths of spectral lines of diatomic molecules such as O₂, CO, OH, HCl, HI and some others for large values of the rotational quantum number J . As known, the energy levels of diatomic molecules can be presented by perturbation, or Dunham, series,¹ and these series are divergent at large values of J . The problem of divergence of the perturbation series becomes especially pressing for high-excited vibrational states, transitions to which form the spectra in the near IR and visible regions.

Several methods were proposed for solution of this problem (see, for example, Refs. 2–9). In Ref. 10, it was suggested that generalized Euler transform of the Dunham series to be used, a new representation of the perturbation series was obtained, and the conditions for convergence of the transformed series were established.

The aim of this work was to find the general term of the transformed series. As an approximating function, we used, as in Ref. 10, the equation for energy levels of the Kratzer oscillator – the exactly solvable quantum-mechanics problem. As known, the Kratzer potential rather well reproduces the characteristic features of a vibrating and rotating diatomic molecule. Therefore, its usage as an approximant in transformation of the perturbation series allows a large part of the rotational-vibrational energy to be taken into account already in the zero approximation. In Ref. 10, it was shown that at the Euler transform of the perturbation series (with the Kratzer potential as an approximant) at rather general assumptions concerning the coefficients of the initial series converges at any values of the vibrational and rotational quantum numbers. Reference 10 presents only some first terms of the transformed series, and this paper is aimed at performing this transformation in the general form.

Here, we consider briefly the Euler method and present equations for the Dunham series (which is the initial one here) for the problem with the Kratzer potential, as well as derive general equations for the transformed series. In the final section we give different presentations

of the transformed series and estimates of the coefficients of these series for the HI molecule.

1. Generalized Euler transformation

In this section, we present briefly the main equations of the Euler method.^{11,13,14} Let the function $f(z)$ be presented as

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

and some its estimate, the approximating function, be known

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

The Euler transform was earlier successfully applied to summation of divergent series in some problems of quantum mechanics, for example, for calculation of energy levels of an anharmonic oscillator, calculation of the Stark and Zeeman effects for the hydrogen atom in strong fields, summation of $1/Z$ -expansion in the atom theory (see, for example, Refs. 13 and 14). As known,¹⁵ the Euler method is regular, that is, it gives correct values of sums for convergent series.

The Euler transform of a series can be presented as

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

$$d_n = \sum_{r=0}^n (-1)^r \binom{n}{r} a_r, \quad a_i = f_i/g_i.$$

2. Dunham series and Kratzer oscillator

Application of the perturbation theory to calculation of the rotational-vibrational energy levels of diatomic molecules gives the following equation:

$$E(J, v) = \sum_{n,m} Y_{nm} (v + 1/2)^n [J(J + 1)]^m, \quad (4)$$

where v is the vibrational quantum number, and J is the angular momentum quantum number, and the series coefficients Y_{nm} are called the Dunham coefficients. These are related, in a certain way, to the coefficients of a power series expansion of the potential function over the displacements from the equilibrium position.¹ Equation (4) can be presented as

$$E(x, y) = \sum_m c_m(y) x^m, \quad (5)$$

where $c_m(y)$ are some functions that can be presented by the following series expansions:

$$c_m(y) = \sum_{n=0} Y_{nm} y^n \quad (6)$$

and

$$y = v + 1/2, \quad x = J(J + 1), \quad E(0, 0) = 0. \quad (7)$$

If the coefficients of the series (4) are known, then the functions $c_m(y)$ presented by the series in Eq. (5) can be determined by some methods, for example, by the Pade method.

The Kratzer equation¹² describes the rotational-vibrational energy levels of a diatomic molecule with the potential function

$$V(r) = \frac{A}{r^2} - \frac{B}{r}. \quad (8)$$

The Schrödinger equation with this potential has an exact solution, and the energy levels are values of the following function, which will be referred to as the Kratzer function:

$$\begin{aligned} K(J, v) = & -a[v + 1/2 + \sqrt{J(J + 1) + b}]^{-2} + a[1/2 + \sqrt{b}]^{-2} = \\ & = -a[y + \sqrt{x + b}]^{-2} + a[1/2 + \sqrt{b}]^{-2}, \\ & a = \frac{B^2 \mu}{2\hbar^2}, \quad b = 1/4 + 2A\mu/\hbar^2. \end{aligned} \quad (9)$$

Here μ is the reduced mass of the diatomic molecule, and the energy is measured from zero level $v = 0, J = 0$. The constants a and b can also be expressed through the dissociation energy E_d and the equilibrium distance r_e :

$$a = 2E_d^2 r_e^2 \mu / \hbar^2, \quad b = 1/4 + 2E_d r_e^2 \mu / \hbar^2.$$

Equation (4) can be used for transformation of the Dunham series to a more convenient form so that the transformed series has better convergence and the function corresponding to it has correct asymptotic at large values of v and J . It should be noted that the Kratzer function gives qualitatively correct asymptotic dependence – the energy levels are concentrated in the interval determined by the depth of the potential well, while the asymptotic behavior of the Dunham series at

large values of $y = v + 1/2$ depends on the sign of the highest term in the series (4).

3. General term of transformed series

To determine the general term of the Euler transform of the Dunham series, we have to calculate the coefficients of Eq. (3). To do this, we have to find the n th-order derivative of the approximating function with respect to x . For this purpose, we can use the following equations

$$\begin{aligned} \frac{d^n}{du^n} F(\sqrt{u}) = & \frac{F^{(n)}(\sqrt{u})}{(2\sqrt{u})^n} - \frac{n(n-1)F^{(n-1)}(\sqrt{u})}{1!(2\sqrt{u})^{n+1}} + \\ & + \frac{(n+1)n(n-1)(n-2)F^{(n-2)}(\sqrt{u})}{2!(2\sqrt{u})^{n+2}} - \dots \end{aligned} \quad (10)$$

and

$$\frac{d^n}{du^n} (1 + a\sqrt{u})^{2n-1} = \frac{(2n-1)!!}{2^n} \frac{a}{\sqrt{u}} \left(a^2 - \frac{1}{u}\right)^{n-1} \quad (11)$$

from Ref. 16 [Eq. (0.433)] and the identity

$$\frac{d^n}{dx^n} K(x, y) = \frac{\partial}{\partial y} \frac{d^n}{dx^n} F(\sqrt{u}) + \delta_{n,0} \frac{a}{[1/2 + \sqrt{b}]^2}, \quad (12)$$

where

$$u = a + b; \quad \frac{d^n}{dx^n} F(\sqrt{u}) = \frac{d^n}{du^n} F(\sqrt{u}) \Big|_{u=x+b}.$$

Equation (10) can be written as follows

$$\frac{d^n}{du^n} F(\sqrt{u}) = \sum_{i=0}^n c_i(n) \frac{F^{(n-i)}(\sqrt{u})}{i!(2\sqrt{u})^{n+i}}, \quad (13)$$

where the coefficients $c_i(n)$ can be determined by the recursion equations:

$$c_i(n) = (n + i - 1) c_{i-1}(n) (n - i), \quad c_0 = 1, \quad c_n(n) = 0. \quad (14)$$

Using simple, though cumbersome, transformations, one can write Eq. (3) in the form

$$\begin{aligned} \sum_{n=0}^{\infty} (-1)^n d_n \frac{x^n}{n!} a \sum_{i=0}^{\infty} c_i(n) \frac{(-1)^{n+i} (n-i+1)!}{i! 2^{n+i}} \times \\ \times \frac{(y + \sqrt{x + b})^{-2}}{(\sqrt{x + b})^{n+i} (y + \sqrt{x + b})^{n-i}}. \end{aligned} \quad (15)$$

Let us transform this equation, introducing new variables $Z_1(x) = x/(x + b), \quad Z_2(x, y) = \sqrt{x + b}/(y + \sqrt{x + b})$:

$$\begin{aligned} \sum_{n=0}^{\infty} d_n \frac{x^n}{(x + b)^n} a \sum_{i=0}^{\infty} c_i(n) \frac{(-1)^{n+i} (n-i+1)! (-1)^n}{i! 2^{n+i} n!} \times \\ \times \frac{(y + \sqrt{x + b})^{-2} (x + b)^n}{(\sqrt{x + b})^{n+i} (y + \sqrt{x + b})^{n-i}}. \end{aligned} \quad (16)$$

Then Eq. (15) takes the form:

$$\sum_{n=0}^{\infty} d_n Z_1^n(x) Z_2(x, y) (y + \sqrt{x+b})^{-2} a \times \\ \times \sum_{i=0}^{\infty} c_i(n) \frac{(n-i+1)!}{i! 2^{n+i} n!} \frac{(x+b)^n}{Z_2(x, y) (x+b)^2 (y + \sqrt{x+b})^{n-i}}. \quad (17)$$

Changing then the summation index, we obtain

$$d_0 K(x, y) - \frac{a Z_1(x) Z_2(x, y)}{(y + \sqrt{x+b})^2} \sum_{m=0}^{\infty} d_{m+1} Z_1^m(x) \varphi_m(x, y), \quad (18)$$

where

$$\varphi_m(x, y) = \sum_{i=0}^{m+1} c_i(m+1) \frac{(m-i+2)!}{i! 2^{m+1+i} (m+1)!} \times \\ \times \frac{(x+b)^{m+1}}{Z_2(x, y) (x+b)^2 (y + \sqrt{x+b})^{m+1-i}}. \quad (19)$$

Thus, the general equation for $\varphi_m(x, y)$ takes the form

$$\varphi_m(x, y) = \sum_{i=0}^{m+1} c_i(m+1) \frac{(m-i+2)!}{i! 2^{m+1+i} (m+1)!} Z_2^{m-i}(x, y). \quad (20)$$

Since $c_{m+1}(m+1) = 0$, Eq. (20) is the polynomial of m power in terms of $Z_2(x, y) = \sqrt{x+b}/(y + \sqrt{x+b})$.

The vibrationally dependent parameters $d_n(y)$ are calculated by the equation

$$d_n(y) = \sum_{i=0}^{n+1} (-1)^i \binom{n+1}{i} \frac{c_i(y)}{g_i(y)}, \quad (21)$$

where

$$g_i(y) = \frac{1}{i!} \frac{\partial^i}{\partial x^i} K(x, y) \Big|_{x=0} \quad (22)$$

are the coefficients of the Taylor series expansion of the Kratzer function over the variable x . Using Eq. (13), we obtain

$$g_i(y) = \frac{1}{i!} \times \\ \times \left(\sum_{j=0}^i c_j(i) \frac{(-1)^{i+1} (i-j+1)! (y + \sqrt{x+b})^{-(i-j)-2}}{j! 2^{i+j} i! (\sqrt{x+b})^{i+j}} + \right. \\ \left. + \delta_{i,0} \frac{a}{(1/2 + \sqrt{b})^2} \right) \Big|_{x=0}. \quad (23)$$

Thus, Eq. (12) for $d_n(y)$ with the allowance made for Eq. (14) has the same form as Eq. (21), where

$$g_i(y) = \frac{1}{i!} \left(\sum_{j=0}^n c_j(n) \frac{(-1)^{i+1} (i-j+1)! (y + \sqrt{b})^{-(i-j)-2}}{j! 2^{i+j} i! (\sqrt{b})^{i+j}} + \right. \\ \left. + \delta_{i,0} \frac{a}{(1/2 + \sqrt{b})^2} \right). \quad (24)$$

Conclusion

The general equations obtained suggest the following conclusions:

1. The Euler transformation (3) of the Dunham series (7) in the general form shows that the use of Kratzer function (9) as an approximation allows introduction of new variables $Z_1(x) = x/(x+b)$ and $Z_2(x, y) = \sqrt{x+b}/(y + \sqrt{x+b})$, which are smaller than unity for any values of the vibrational $y = v + 1/2$ and rotational $x = J(J+1)$ quantum numbers.

The Dunham series transformed by the Euler method includes the Kratzer function as an approximant [the first term in Eq. (18)] with the correction factor d_0 depending only on the vibrational quantum number and the rotational-vibrational addition represented by the functional series – the second term in Eq. (18). The use of the approximant for calculation of the sum of perturbation series allows a large part of the RV energy of a molecule to be taken into account already in the zero-order approximation, what facilitates summation of the remaining part of the series.

2. It can be shown that the functions $\varphi_m(x, y) \leq 1$ for all possible values of x and y , what relatively easily gives the convergence conditions of the transformed series (see Ref. 10).

Assume that the series (6) converge or, in other words, they can be summed up by some method, and they are bounded above by functions $d_n(y)$ of the vibrational variable y . Then we can show that the correction term in Eq. (18) is also a bounded function, and the addition in Eq. (18) tends to zero at $y \rightarrow \infty$. Thus, the asymptotic of the transformed series is determined by the first term in Eq. (18) – the Kratzer function $K(x, y)$.

3. Besides, the general equations for the transformed series allow the vibrational dependence of the rotational and centrifugal distortion constants to be analyzed. Equations (9) and (12) show that at $y = -\sqrt{b}$ the vibrational energy has a second-order pole, the rotational constant (coefficient $c_1(y)$) has a third-order pole, and the centrifugal distortion constants are determined by Eq. (26) at $i > 1$. These constants considered as functions of the vibrational variable y have poles of the $(i+2)$ th order at $y = -\sqrt{b}$, what allows the summation method used in calculation of Eq. (6) to be justified. In particular, it can be noted that the centrifugal distortion constants are presented by a part of the series over inverse powers of $(y + \sqrt{b})$.

4. The transformed series can be presented in different forms, what is convenient from the computational point of view. For example, the

correction term in Eq. (18) can be presented as an ordinary power series by expanding the factors $\varphi_m(x, y)$ into a power series of $Z_1(x)$ or $U(x) = \sqrt{1 - Z_1(x)}$, because

$$Z_2(x, y) = \frac{1}{1 + b^{-1/2} y U(x)}.$$

Acknowledgments

The author is thankful to Prof. S.D. Tvorogov, Corresponding Member of RAS, for his interest in this work and Prof. A.D. Bykov for useful consultations.

This work was partly supported by the Russian Foundation for Basic Research Grant No. 00-15-98589 "School."

References

1. T.I. Velichko, V.Ya. Galin, Yu.S. Makushkin, and V.I.G. Tyuterev, *Analytical Computation in Molecular Spectroscopy. General Algorithm and Application 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 with allowance for asymptotic properties of the nuclei interaction potential," Cand. Phys.-Math. Sci. Dissert., Nizhnii Novgorod (1999), 159 pp.
7. V.F. Golovko, S.N. Mikhailenko, and V.I.G. Tyuterev, *J. Mol. Struct.* **218**, 291–296 (1990).
8. V.F. Golovko and V.I.G. Tyuterev, *Atm. Opt.* **3**, No. 6, 562–567 (1990).
9. V.F. Golovko, S.N. Mikhailenko, and V.I.G. Tyuterev, *Atm. Opt.* **4**, No. 5, 367–370 (1991).
10. T.V. Kruglova, A.D. Bykov, and O.V. Naumenko, *Atmos. Oceanic Opt.* **14**, No. 9, 748–752 (2001).
11. P.M. Morse and H. Feshbach, *Methods in Theoretical Physics* (McGraw-Hill, 1953).
12. L. Landau and E. Lifshitz, *Quantum Mechanics: Nonrelativistic Theory* (Oxford, 1991).
13. K. Bhattacharyya, *Int. J. Quantum Chem.* **XXII**, 307–330 (1982).
14. J.N. Silverman, *Phys. Rev. A* **28**, No. 1, 498–501 (1983).
15. G.H. Hardy, *Divergent Series* (Oxford University Press, New York, 1949).
16. I.S. Gradshteyn and I.M. Ryzhik, *Tables of Integrals, Series, and Products* (Academic Press, New York, 1965), 1108 pp.