Application of generalized Euler transformation to summation of Dunham series for diatomic molecules

T.V. Kruglova, A.D. Bykov, and O.V. Naumenko

Institute of Atmospheric Optics,
Siberian Branch of the Russian Academy of Sciences, Tomsk

Received August 23, 2001

The well known generalized Euler transformation of divergent series is applied to summation of Dunham series for diatomic molecules. The equation for the energy of a Kratzer oscillator, which is an exactly solvable problem of quantum mechanics, is used as an approximation function that is needed for series transformation. The transformed series consists of a main part, which is asymptotically correct for high values of vibrational and rotational quantum numbers, and an additional part depending on new variables, which are less than unity for all values of quantum numbers. New representation of the Dunham series may prove useful for calculation of highly excited rotational-vibrational states of diatomic molecules, for which only several first coefficients of the perturbation series are known.

To solve some problems of atmospheric spectroscopy, one has to calculate highly excited rotational-vibrational (RV) states of diatomic molecules and radicals. The frequencies of RV transitions of diatomic molecules are usually presented as power series over vibrational $(v + 1/2)$ and rotational $J(J + 1)$ quantum numbers – Dunham series. From the theoretical point of view, this representation is a result of applying perturbation theory (PT) to calculation of energy levels.

The observed values of line positions are usually used as input data for determination of the coefficients of the Dunham series by the method of least squares. Then the series obtained in such a way is used to predict the positions of lines with higher values of v and J or to reconstruct the potential-energy function of a molecule.[1] Obviously, the Dunham series determined in PT has a limited domain of convergence – it may diverge at high values of the quantum number of angular momentum J. So, it is necessary to apply special methods for summation of divergent series when calculating highly excited states of diatomic molecules.

Nowadays many papers (see, for example, Refs. 2–9) are devoted to application of different summation methods to calculation of RV spectra of diatomic molecules. In Ref. 2–6 a method was proposed for calculation of high energy levels of diatomic molecules. This method is based on "nonlinearization" and "$1/N$-expansion"; it provides for a good agreement with the experimental data for some molecules even for RV energy levels close to the dissociation threshold. In Refs. 7–9, a special version of PT was used, which gives rational approximations of RV energy levels of diatomic molecules. The calculations performed for H_2 and HBr molecules have demonstrated a marked progress in calculation of energy levels of highly excited states as compared to the traditional approach.

The aim of this work is to derive a new representation for the Dunham series using different approach – the so-called generalized Euler transformation.[10] As an approximating function needed in the Euler method, we use the well-known solution of the problem on the Kratzer oscillator.[11] This solution has a correct asymptotic dependence on the vibrational and rotational quantum numbers. It allows us to use some *a priori* information on the RV energy of diatomic molecules contained in the approximating function when summing up the Dunham series and to correctly simulate high terms of the Dunham series. The Euler transformation "separates out" the main part of RV energy and, therefore, the transformed series possesses better properties and converges at large values of the quantum number J.

The new representation of the PT series for two-particle systems may prove useful in the cases that only several first terms of the series are known and other summation methods have thus limited applicability. On the other hand, the new representation of the Dunham series can improve processing of RV spectra of diatomic molecules.

1. Generalized Euler transformation

For a convenience, we briefly present here the main equations of the Euler method.[10,12,13] Let the function $f(z)$ be expanded into a series as

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

and some its estimate – approximating function – be known:

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

Let also the following condition be fulfilled:

$$a_n = f_n / g_n \to 1 \qquad (3)$$

0235-6880/01/09 753-05 $02.00

at $n \to \infty$. Then the initial series (1), which may be divergent, can be transformed into a convergent one (or more rapidly convergent, if the series (1) converges slowly) in the following way:

$$f_0 + f_1 z + f_2 z^2 + \ldots = a_0 g(z) + (a_1 - a_0) g_1 z + \\ + (a_2 - a_0) g_2 z^2 + (a_3 - a_0) g_3 z^3 + \ldots . \quad (4)$$

Then make use of the fact that[10]

$$g_1 z = g'(z) z - 2g_2 z^2 - g_3 z^3 - \ldots - n g_n z^n + \ldots , \\ 2g_2 z^2 = g''(z) z^2 - 6g_3 z^3 - 12 g_4 z^4 - \ldots - \\ - n(n-1) g_n z^n + \ldots , \quad (15) \\ n! g_n z^n = g^{(n)}(z) z^n - g_{n+1} z^{n+1} - \ldots ,$$

and transform the series, excluding the coefficients g_n successively from the transformed series. We obtain

$$f(z) = a_0 g(z) + (a_1 - a_0) z g'(z) + \\ + (a_2 - 2a_1 + a_0) z^2 g''(z)/2! + \\ + (a_3 - 3a_2 + 3a_1 - a_0) z^3 g'''(z)/3! + \ldots + \\ + (a_n - n a_{n-1} + \ldots) z^n g^{(n)}(z)/n!. \quad (6)$$

If the condition (3) is fulfilled, then the coefficients of the transformed series tend to zero. If it also proves possible to introduce a new variable

$$Z = \sqrt[n]{z^n g^{(n)}(z)} \le 1, \quad (7)$$

weakly dependent on n, then the transformed series is a series over powers of Z and often turns out to be convergent.

The Euler transformation was earlier successfully used for summation of divergent PT series in some quantum-mechanics problems, for example, for calculation of energy levels of anharmonic oscillator, calculation of the Stark and Zeeman effects for hydrogen atoms in strong fields, summation of $1/Z$-series in theory of atoms (see, for example, Refs. 12 and 13). As known,[14] the Euler method is regular, that is, it gives correct values of sums for convergent series.

The series transformed by the Euler method can be represented in the form

$$f(z) = \sum_{n=0}^{\infty} (-1)^n D_n \frac{z^n}{n!} \frac{\mathrm{d}^n}{\mathrm{d}z^n} g(z); \\ D_n = \sum_{r=0}^{n} (-1)^r \binom{n}{r} a_r, \quad a_i = f_i / g_i . \quad (8)$$

Consider, as an example, the approximating function $g(z)$ of the form

$$g(z) = 1/(1+z) = 1 - z + z^2 - \ldots , \\ g_n = (-1)^n, \; z g'(z) = \frac{-z}{(1+z)^2},$$

$$\frac{z^2 g''(z)}{2!} = \frac{z^2}{(1+z)^3}, \ldots . \quad (9)$$

Then the initial series (1) transforms to the following form:

$$f(z) = \frac{1}{1+z} \times \\ \times \left[f_0 + (f_1 + f_0) \left(\frac{z}{1+z} \right) + (f_2 + 2f_1 + f_0) \left(\frac{z}{1+z} \right)^2 + \ldots \right]. \quad (10)$$

In Eq. (10) we can introduce a new variable, $Z = z/(1+z)$, which is obviously less than unity at $z > 0$. Transformation with the approximating function (9) and transition to a new variable often provide for better convergence of the initial series.[12]

2. Dunham series of diatomic molecules and Kratzer oscillator

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

$$E(J, v) = \sum_{n,m} Y_{nm} (v + 1/2)^n [J(J+1)]^m , \quad (11)$$

where v is the vibrational quantum number; J is the quantum number of angular momentum, and the series coefficients Y_{nm} are called the Dunham coefficients. They are related in a certain way to the coefficients of expansion of the potential function into series over powers of the displacement from the equilibrium position.[1] Equation (11) can also be presented as

$$E(x, y) = \sum_{m} c_m(y) x^m , \quad (12)$$

where $c_m(y)$ are some functions presented by the following series:

$$c_m(y) = \sum_{n=0} Y_{nm} y^n, \quad (13)$$

where

$$y = v + 1/2; \;\; x = J(J+1); \;\; E(0, 0) = 0. \quad (14)$$

If the coefficients of the series (11) are known, then the functions $c_m(y)$ represented as the series (13) can be determined using suitable methods, for example, Pade or Pade—Hermite method. Below we assume them to be given and we shall present them as sums (13) or finite equations determined by some summation method or values found from experimental data.

The Kratzer equation[11] describes the rotational-vibrational energy levels of a diatomic molecule with the potential function

$$V(r) = \frac{A}{r^2} - \frac{B}{r} . \quad (15)$$

The Shrödinger equation for the radial part of the wave function with this potential has a correct solution and energy levels are values of the following function, which will be referred to as the Kratzer function,

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

$$a = B^2\mu/(2\hbar^2);\quad b = 1/4 + 2A\mu/\hbar^2. \qquad (16)$$

Here μ is the reduced mass; the energy is measured from the zero level $v = 0$, $J = 0$. The constants a and b can be expressed also 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 (16) 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 is asymptotically correct at large values of v and J.

The Kratzer equation gives the qualitatively correct asymptotic dependence – energy levels are concentrated in the interval determined by the depth of the potential well, at the same time the asymptotic behavior of the Dunham series at large values of $y = v + 1/2$ depends on the sign of the highest term kept in the series (13).

3. Transformed Dunham series

Using Eqs. (8) and (16) for transformation of the series (11), after some long, but simple transformations we can obtain the following equation:

$$E(x, y) = K(x, y)\, d_v(y) - [a/(y + \sqrt{x + b})^2]\, Z_1(x) \times \times Z_2(x, y) \sum_{n=0} d_n(y)\, \varphi_n(x, y)\, Z_1^n(x), \qquad (17)$$

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

$$\varphi_n(x, y) = \sum_{m=0}^{n} p_{nm}\, Z_2^m(x, y) \qquad (18)$$

are n-power polynomials of the variable $Z_2(x, y) = \sqrt{x + b}/(y + \sqrt{x + b})$. The general equation for $\varphi_n(x, y)$ looks rather bulky and therefore it is omitted here; several first terms are given below:

$$\varphi_0(x, y) = 1,$$

$$\varphi_1(x, y) = \frac{1}{4}\,[1 + 3Z_2(x, y)],$$

$$\varphi_2(x, y) = \frac{1}{8}\,[1 + 3Z_2(x, y) + 4Z_2^2(x, y)], \qquad (19)$$

$$\varphi_3(x, y) = \frac{1}{64}\,[5 + 15Z_2(x, y) + 24Z_2^2(x, y) + 5Z_2^3(x, y)],$$

$$\varphi_4(x, y) = \frac{1}{128}\,[7 + 21Z_2(x, y) + 36Z_2^2(x, y) + 40Z_2^3(x, y) + 24Z_2^4(x, y)].$$

Note that the coefficients of the polynomials are such that

$$\sum_{m=0}^{n} p_{nm} = 1.$$

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

$$d_n(y) = \sum_{i=0}^{n+1} (-1)^i \binom{n+1}{i} \frac{c_i(y)}{g_i(y)}, \qquad (20)$$

where

$$g_i(y) = \frac{1}{i!}\,\frac{\partial^i}{\partial x_i}\,K(x, y)\Big|_{x=0} \qquad (21)$$

are the coefficients of expansion of the Kratzer function into a Taylor series over the x variable. Several first functions $d_n(y)$ are given below:

$$d_v(y) = \frac{1}{a}\,\frac{c_0(y)}{a(y + \sqrt{b}) - (1/2 + \sqrt{b})}\,(y + \sqrt{b})(1/2 + \sqrt{b}),$$

$$d_0(y) = d_v(y) - \frac{1}{a}\,c_1(y)\,(y + \sqrt{b})^3\,\sqrt{b}, \qquad (22)$$

$$d_1(y) = d_0(y) - \frac{1}{a}\,c_1(y)\,(y + \sqrt{b})^3\,\sqrt{b} - \frac{4b^{3/2}}{a} \times \times \frac{c_2(y)\,(y + \sqrt{b})^4}{(y + 4\sqrt{b})}.$$

The general equation for $d_n(y)$ can be easily derived from Eq. (20). Note that since $c_0(1/2) = 0$, the term with $d_v(y)$ has no singularity at $v = 0$.

In this paper, we perform general analysis of the transformed series (17); the use of a new representation of the Dunham series for calculation of highly excited energy levels of diatomic molecules will be presented in our further papers.

The first term of the transformed series (17) contains the Kratzer function $K(x, y)$ and, consequently, has a correct asymptotic at large values of vibrational and rotational quantum numbers.* This term obviously gives the large part of rotational-vibrational energy. The factor $d_v(y)$ is the ratio of $c_0(y) \approx \omega\gamma$ and $g_0(y) = K(0, v + 1/2)$ – pure vibrational terms in the energy expansion into a power series over the parameter $x = J(J + 1)$. This factor can be considered as a "correction" accounting for inaccurate reconstruction of the vibrational energy of molecules by the approximant – the Kratzer function.**

* Under the condition of correct asymptotic behavior of $c_0(y)$ at $y \to \infty$.

** Recall that in our approach $c_n(y)$ are empiric parameters.

The second term in Eq. (17) is obviously a correction to the rotational energy of a molecule. The variables $Z_1(x)$ and $Z_2(x, y)$ are always less than unity at $x \geq 0$, $y > 1/2$. The dimensionless parameter $b \approx 2D\, r_e^2 \mu/\hbar^2$ is usually of the order of 10^3 (for example, $b = 3830.5$ for HI).

Thus, at $J \sim 100$ the variable $Z_1(x)$ has the value about 0.7. The variable $Z_2(x,y)$ is close to unity at practically significant values of x and y ($Z_2(x, y)$ varies within 0.99–0.86 for the HI molecule at $x = 0$ ... 10000, $y = 0.5$ ... 10.5), and it decreases for higher vibrational states. The transition to new variables at transformation of the series (17) provides for better convergence of the transformed series, unless the series coefficients increase catastrophically fast with the growth of n.

4. Convergence of the transformed series

Consider now conditions for the series (17) convergence. The radius of convergence of the transformed series obviously depends on how correctly the Kratzer function (16) reproduces the dependence of energy on the rotational quantum number. We can see that the functions $\varphi_n(x, y)$ are positive and less than unity at all values of J. Then the radius of convergence of the series

$$\sum_{n=0}^{\infty} | d_n(y) | Z_1^n(x) \qquad (23)$$

is a lower boundary of the radius of convergence of the series (17). According to Eq. (20), the coefficients $d_n(y)$ are combinations of the ratios $c_i(y)/g_i(y)$ – vibrational, rotational, and centrifugal terms in the power series over $J(J + 1)$. In the case that the Kratzer potential well reproduces the intramolecular potential, the Kratzer equation (16) also must reproduce the first derivatives of energy with respect to the variable $x = J(J+1)$ rather well, whereas the derivatives of high order are likely reproduced with a large error. It is reasonable to assume that the values of $d_n(y)$ increase with the growth of n no more rapidly than n^L do and we can introduce the estimate of the following form (valid, at least, for some set of vibrational states)

$$| d_n(y) | \leq n^L \varepsilon\,, \qquad (24)$$

where ε is some value. Then the series (23) is reduced to

$$\sum_{n=0}^{\infty} n^L Z_1^n(x)\,. \qquad (25)$$

As known, the series (25) converges at $Z_1(x) < 1$ and any integer L; consequently, the initial series (17) converges too.

Thus, if the derivative ratio $c_i(y)/g_i(y)$ is a limited value at all n or increases not very fast with the growth of n, then the transformed series converges at all $x = J(J + 1)$.

To illustrate the possibility of making estimates of the type (24), Fig. 1*a* shows the dependence of the parameters $d_n(y)$ of the HI molecule on the quantum number $y = v + 1/2$ and Fig. 1*b* shows the dependence of these values on n ($n = 1...3$) for $v = 1$ and $v = 6$. It can be seen that the dependence on the vibrational quantum number and the dependence on the index n is well approximated by linear functions; besides, all $d_n(y)$ are positive. All molecular and spectroscopic constants of the HI molecule that are used in calculations were borrowed from Ref. 15.

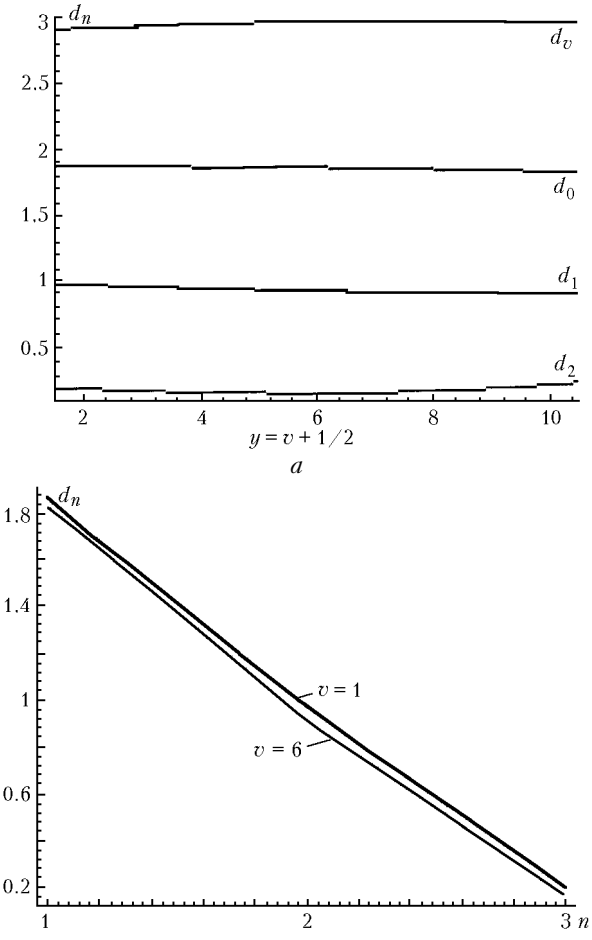

Fig. 1.

The series (17) can be summed up approximately in the following way. Since the variable $Z_2(x, y)$ is close to unity, we assume $Z_2(x, y) = 1$ and $\varphi_n(x, y) = 1$ in Eq. (17) and represent $d_n(y)$ by the following polynomials:

$$d_n(y) = \varepsilon_0(y) + n\varepsilon_1(y) + n^2\varepsilon_2(y) + \ldots + n^L\varepsilon_L(y). \qquad (26)$$

Thus we obtain

$$E(x, y) \approx K(x, y)\, d_v(y) - [a/(y + \sqrt{x + b})^2]\, Z_1(x) \times$$

$$\times \sum_{i=0}^{L} \varepsilon_i(y) \sum_{n=0}^{\infty} n^i\, Z_1^n(x). \qquad (27)$$

The sum of the series in the right-hand side of Eq. (27) can be easily calculated by the equation

$$\sum_{n=0}^{\infty} n^L Z_1^n(x) = \left(\mu \frac{\mathrm{d}}{\mathrm{d}\mu}\right)^L \frac{1}{1-\mu}\bigg|_{\mu=Z_1(x)}. \qquad (28)$$

Thus, the RV energy of a diatomic molecule can be represented by a finite expression. For example, at $L = 2$:

$$E(x, y) \approx K(x, y)\, d_v(y) - [a/(y + \sqrt{x+b})^2]\, Z_1(x) \times$$
$$\times \left\{ \frac{\varepsilon_0(y)}{1-Z_1(x)} + \frac{\varepsilon_1(y)\, Z_1(x)}{[1-Z_1(x)]^2} + \frac{\varepsilon_2(y)\, Z_1(x)\, [1+Z_1(x)]}{[1-Z_1(x)]^3} \right\}. \qquad (29)$$

In deriving Eq. (29), it was also assumed that the derivatives of the approximating function $\partial^n / \partial^n K(x, y)\,|_{x=0}$ correctly reproduce the signs of derivatives of energy with respect to the variable $x = J(J + 1)$. In particular calculations, $d_v(y)$ or $\varepsilon_l(y)$ can be considered as some vibration-dependent parameters that are determined from solution of inverse problems. For this purpose, it is sufficient to represent them as power series with the coefficients determined from fitting to measured line positions.

Conclusion

The Euler transformation with the approximating Kratzer function yields a new representation of the perturbation series for diatomic molecules. The transformed series depends on the variables $Z_1(x)$ and $Z_2(x, y)$, which are less than unity by definition for all values of vibrational and rotational quantum numbers. The series converges if the estimate (24) is valid.

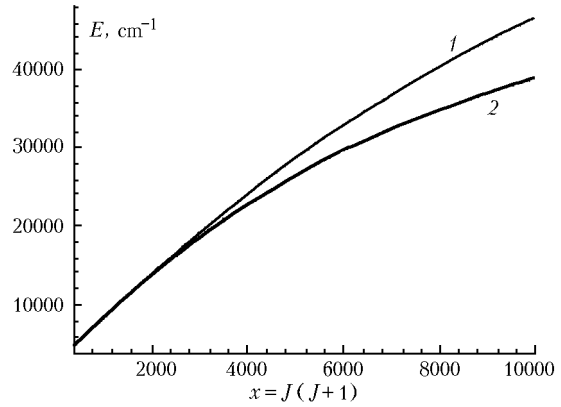

Fig. 2. Rotational energy levels of the first excited vibrational state of the HI molecule (in cm^{-1}): calculation by the Dunham equation (curve *1*), calculation with the transformed series (17) (curve *2*).

The test calculations for the first excited vibrational state ($v = 1$) of the HI molecule showed that the transformed series (17) gives the rotational levels with $J \le 10$ almost coinciding with those calculated by Eq. (11). For higher rotational levels $10 \le J \le 20$, the difference between these two sets of calculated levels achieves 0.8 cm^{-1}, at $20 \le J \le 30$ it grows up to 16 cm^{-1}, and at $30 \le J \le 100$ it is as high as 6000 cm^{-1}. Equation (17) predicts lower energies than the Dunham series does (see Fig. 2).

In practice of using the transformed Dunham series (17), the coefficients $d_n(y)$ (for individual vibrational state) can be determined through fitting to measured frequencies of the transitions. Another parameterization of the vibrational dependence represented by Eq. (26) is also possible. The new parameterization consists in description of the vibrational dependence of the ratio of the Kratzer estimate of derivatives on the RV energy with respect to the variable $J(J + 1)$ to the "true" values of derivatives. This problem is likely simpler than the problem of reconstruction of the derivatives $c_n(y)$ from the coefficients of the divergent series (11).

Acknowledgments

The authors are thankful to Professor S.D. Tvorogov, Corresponding Member of the Russian Academy of Sciences, for support of this work within the framework of the Russian Foundation for Basic Research Grant No. 00–15–98589.

References

1. T.I. Velichko, V.Ya. Galin, Yu.S. Makushkin, and Vl.G. Tyuterev, *Analytical Computer Calculations 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 nuclear interaction potential*," Cand. Phys.-Math. Sci. Dissert, Institute of Applied Physics RAS, Nizhnii Novgorod (1999), 159 pp.
7. V.F. Golovko, S.N. Mikhailenko, and Vl.G. Tyuterev, J. Mol. Structure **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. P.M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953).
11. L.D. Landau and E.M. Lifshitz, *Quantum Mechanics: Nonrelativistic Theory* (Pergamon Press, Oxford, 1965).
12. K. Bhattacharyya, Int. J. Quantum Chemistry **XXII**, 307–330 (1982).
13. J.N. Silverman, Phys. Rev. A **28**, No. 1, 498–501 (1983).
14. G.H. Hardy, *Divergent Series* (Oxford University Press, London, 1949).
15. K.P. Hubert and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand, New York, 1979).