Summation of divergent series by the Euler method in calculation of rotation energy levels of the H_3^+ molecule

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The series divergence in the perturbation theory should be taken into account in calculation of highly excited energy levels of light molecules by the effective rotation Hamiltonian method. For calculation of the rotation energy levels for the H_3^+ molecule in the ground vibration state, the well-known Euler method of series transformation is used. It is shown that the use of the elementary approximation function – the diagonal Pade approximant of the first order – allows calculating accurately the high energy levels.

Introduction

The research of rotation-vibration (RV) spectra of the H_3^+ molecular ion is of interest for several reasons. First, H_3^+ plays a certain part in formation of interstellar clouds and ionospheres of giant planets such as the Jupiter. As a consequence, molecular lines in spectra of various astrophysical objects are easily observed.[1] Second, H_3^+ is the elementary triatomic molecule, consisting of three protons and two electrons. It can be *ab initio* calculated with high accuracy. In turn, a comparison with the measured spectra allows improving the calculation, for example, of non-adiabatic or relativistic corrections.[2] Third, the H_3^+ molecule is a light symmetric top with strong non-hardness effects, and it has certain features of RV energy spectrum.[3] Therefore, the studying of IR-spectra of this molecule turns out to be useful also for improvement of calculation methods: the effective Hamiltonians or the variational one.

The H_3^+ molecule has a point group symmetry D_{3h}, the constant dipole moment is absent. As a consequence, spectra in the microwave region, caused by purely rotation transitions, are not observed. (Due to centrifugal effect, there are a low ~ 10^{-4} D dipole moment and a weak rotational spectrum). Moreover, the excited electronic states are decayed or weekly connected, perturbed by predissociation; the UV spectra are represented by the diffusive bands free of a clearly defined structure. Thus, a highly accurate experimental information about the molecule can be derived only from the analysis of its RV- spectra.

It is necessary to take into account that in calculations of RV energy spectrum of H_3^+ by the method of effective rotation Hamiltonian, the rotation leads to a strong perturbation of states and a bad convergence of series representing matrix elements of the effective Hamiltonian. The application of special summation methods, in particular, the Pade approximations method or Pade–Borel one allows taking into account these strong non-hardness effects (see, for example, Refs. 4–9). In this work, to solve the problem of series divergence for the lower vibration state of H_3^+, the well-known Euler generalized transformation method[10–15] is applied. Earlier, this method was successfully applied to solving various problems, in which the series of perturbation theory (PT) were diverged.[11,12]

1. Euler generalized transformation of PT series

Consider the application of the Euler method to the series summation.[10–12] Briefly, the basic relations of this method are reduced to the following. Let the expansion

$$f(\lambda) = \sum_{n=0} f_n \lambda^n \tag{1}$$

corresponds to function $f(\lambda)$ and a certain its estimate – approximating function – is known:

$$f(\lambda) \approx g(\lambda) = \sum_{n=0} g_n z^n = g_0 + g_1\lambda + g_2\lambda^2 + \ldots. \tag{2}$$

Then the initial series (1) can be transformed into the functional series of a kind

$$f(\lambda) = \sum_{n=0}^{\infty} (-1)^n D_n \Phi(\lambda);$$

$$\Phi_n(\lambda) = \frac{z^n}{n!}\frac{d^n g(\lambda)}{d\lambda^n}; \tag{3}$$

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

Here $\binom{n}{m} = \frac{n!}{m!(n-m!)}$ are binomial coefficients.

If the approximating function $g(\lambda)$ is chosen successfully, so that $a_n = f_n/g_n \to 1$ at $n \to \infty$ fast enough, then the transformed series converges even if the initial series is diverged. This is the advantage of the Euler method. The method allows using the PT expansions at a suitable choice of the approximating function including all physically significant moments of the solved problem even if these expansions are strongly divergent series.

Earlier, the Euler transformation was successfully applied to summation of the perturbation theory divergent series in some quantum-mechanical problems, for example, for calculation of energy levels of anharmonic oscillator, calculations of Stark and Zeeman effects for the hydrogen atom in strong fields, summation of $1/Z$-expansion in the atom theory (see, for example, Ref. 12). It is proved that the Euler generalized transformation is a regular summation method,[16] i.e., it yields correct sum values for the convergent series.

It is necessary to take into account some moments connected with a specificity of the effective Hamiltonians method application to calculations of molecular RV-spectra. Usually, only a few first coefficients $f_0, f_1, \ldots, f_p$ are known in the initial PT expansion. In this case, the transformed series coefficients will be determined by the formula

$$D_n = \sum_{r=0}^{p} (-1)^r \binom{n}{r} a_r$$

for terms with $n > p$. It means, that values of the $f(\lambda) = \sum\limits_{n=0}^{p} f_n \lambda^n$ polynomial are described with the help of an infinite series. As n increases, the series coefficients (3) cancel out. In that case, it is desirable to introduce some additional *a priori* information about the coefficients $f_{p+1}, f_{p+2}, \ldots$ into the problem. Assume that for high PT orders the f_n coefficients are close to the approximant expansion coefficients, i.e.,

$$f_n \approx \alpha^n g_n, \quad n > p.$$

It is easy to show, that in this case

$$D_n = \sum_{r=0}^{p} (-1)^r \binom{n}{r} \left(\frac{f_r}{g_r} - \alpha^r \right) + (1 - \alpha)^n$$

for $n > p$. The parameter a should be chosen depending on a specificity of the problem.

2. Effective rotation Hamiltonian of the H_3^+ ground vibration state

The molecule H_3^+ in equilibrium configuration is an equilateral triangle, representing a flattened symmetric top with a point group symmetry D_{3h}. There exist two normal vibrations, ν_1 and ν_2, the latter is double degenerated. The vibration energy levels are determined by three quantum numbers $\nu_1 \nu_2^l$, the rotation energy levels – by two – J,G ($G = |k - l|$). The rotation energy levels of H_3^+ ground vibration state in view of symmetry properties are determined by the formula[3]

$$\begin{aligned} E(J,G) = &-E_{11} - \delta_{G,3n} E_{o-p} + BJ(J+1) + (C-B)G^2 - \\ &-D_{JJ} J^2 (J+1)^2 - D_{JG} J(J+1) G^2 - D_{GG} G^4 + \\ &+H_{JJJ} J^3 (J+1)^3 + H_{JJG} J^2 (J+1)^2 G^2 + \\ &+H_{JGG} J(J+1) G^4 + H_{GGG} G^6 + L_{JJJJ} J^4 (J+1)^4 + \\ &+L_{JJJG} J^3 (J+1)^3 G^2 + L_{JJGG} J^2 (J+1)^2 G^4 + \\ &+L_{JGGG} J(J+1) G^6 + L_{GGGG} G^8 - (-1)^J \delta_{G,3} h_3 \frac{(J+3)!}{(J-3)!} + \ldots . \end{aligned} \tag{4}$$

According to the Pauli principle, the $k = 0$, $J = 2n$ levels are forbidden, in particular, the level corresponding to the $|JK\rangle = |00\rangle$ state is absent, so the states $|10\rangle$ and $|11\rangle$ are the least in energy. Therefore, the first term in Eq. (4) is a lower level energy of the molecule's ortho-modification, and the second term determines the difference between lower levels of the ortho and para states. The subsequent terms represent the rotation energy and centrifugal corrections. The last term in Eq. (4) is connected with level splitting at $k = \pm 3$.

Rotational and centrifugal constants of H_3^+ were determined in several works, for example, in Ref. 3. It is marked in this work that the expression for rotation energy in the form of a standard series of the perturbation theory well describes rotation energy levels only in the range of quantum number values used in the fitting. The predictive calculations for great values of J or G do not give a satisfactory result because of the bad convergence of series (4).

Using the data from Ref. 3, it is possible to determine approximately the position of energy features considered as a function of rotation quantum numbers and to determine the convergence radius (if it is not zero) for series (4). For this purpose we use the so-called one-dimensional approximation of the effective Hamiltonian,[7] according to which series (4) can be written as:

$$E(J,G) = E_0 + a_0 + \lambda a_1 + \lambda^2 a_2 + \lambda^3 a_3 + \ldots, \tag{5}$$

where

$$\begin{aligned} E_0 &= -E_{11} - \delta_{G,3n} E_{o-p} - (-1)^J \delta_{G,3} h_3 \frac{(J+3)!}{(J-3)!}; \\ a_0 &= BJ(J+1) + (C-B)G^2, \\ a_1 &= -D_{JJ} J^2 (J+1)^2 - D_{JG} J(J+1) G^2 - D_{GG} G^4, \\ a_2 &= H_{JJJ} J^3 (J+1)^3 + H_{JJG} J^2 (J+1)^2 G^2 + \\ &\quad + H_{JGG} J(J+1) G^4 + H_{GGG} G^6, \\ a_3 &= L_{JJJJ} J^4 (J+1)^4 + L_{JJJG} J^3 (J+1)^3 G^2 + \\ &\quad + L_{JJGG} J^2 (J+1)^2 G^4 + L_{JGGG} J(J+1) G^6 + L_{GGGG} G^8 \end{aligned} \tag{6}$$

and the formal parameter λ, assumed equal to unity in finite formula, is introduced. A direct calculation with the parameters taken from Ref. 3, shows that the expression (5) (except for the first term) is sign-alternating up to the term proportional to λ^2. As is generally known,[17] this is due to the fact that centrifugal constants $D_{JJ}, D_{JG},\ldots$ are determined by expansion of tensor elements of the inertia inverse moments with some additives connected with the Coriolis forces and anharmonicity of vibrations. It is possible to assume, that the centrifugal effect is the strongest for the lower vibration state of the light molecule H_3^+, and the whole PT series (5) is sign-alternating.

To estimate the convergence radius, we use the Pade approximant [1/1] and determine (for each value of J) the G^2 values, at which the approximant denominator vanishes. The results are given in Fig. 1.

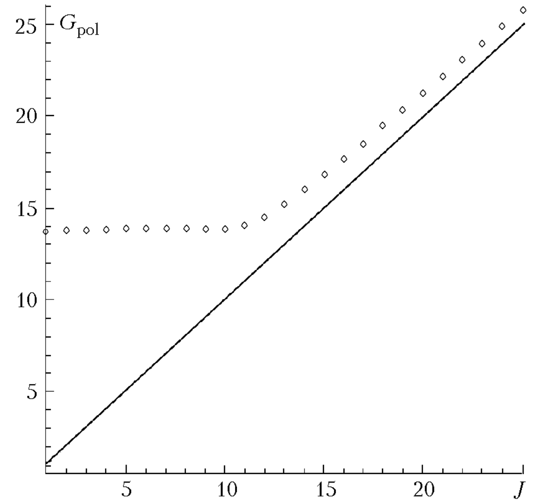

Fig. 1. Positions of poles (circles) of Pade approximant [1/1] for the series (5). A continuous line corresponds to $G = J$ quantum number.

It is seen, that for small J values the poles are at $G \approx 14$, for high values they are rather close to the levels $G = J$. Just this circumstance determines the series (5) divergence.

3. Summation of the effective Hamiltonian series

As it was earlier shown,[18] application of the Pade approximants for calculation of rotation-vibration energy levels of the H_3^+ molecule gives much better results than the use of expansions (5) and (6). Therefore, we apply the diagonal Pade approximant of the first order $P_{[1/1]}(\lambda)$ over λ as an approximating function. The transformed, according to relations (3), series (5) with approximant

$$P_{[1/1]}(\lambda) \equiv g(\lambda) = \frac{a_2 a_0 - a_1^2}{a_2} + \frac{a_1^3}{a_2}\frac{1}{a_1 - a_2\lambda} \qquad (7)$$

can be transformed to

$$E(J,G) = g(\lambda) + Z_0 Z^3\left\{p_0 + p_1 Z + p_2 Z^2 + p_3 Z^3 + \ldots\right\}, \qquad (8)$$

where a new variable is introduced

$$Z = a_2\lambda/(a_1 - a_2\lambda) \qquad (9)$$

and

$$Z_0 = \frac{a_1^3}{a_2(a_1 - a_2\lambda)}.$$

Using Eq. (3), it is also possible to receive easily a general expression for the coefficients of the transformed series (8):

$$F_n = (-1)^n \frac{a_1^3 a_2^{n-1}}{(a_1 - a_2\lambda)^{n+1}} \times$$
$$\times\left(1 - n + \frac{(n-1)n}{2} - \frac{(n-2)(n-1)n\, a_1\, a_3}{6a_2^2}\right)\lambda^n.$$

Since centrifugal corrections $a_1 < 0$ and $a_2 > 0$, the denominator in Eq. (9) does not vanish at $\lambda > 0$. The new variable Z has a sign-alternating expansion in Taylor's series by λ degrees and the poles at the same values of G, as in the above estimations, thus "simulating" peculiarities of the function $E(J, G)$. It is obvious, that the transformed series has no longer peculiarities accounted for by the new variable. This circumstance together with $|Z| < 1$ provide for a better convergence of the transformed series as compared to the initial series (5). The power series in the right part of equality (8) can also be summarized by some method, for example, the Levin rational approximations,[19] many-valued Pade–Hermite approximations,[20] etc.

The performed calculations have shown that the transformed series (8) gives approximately the same values as the initial one (5) for energy levels, from which the rotation and centrifugal constants were determined. For energy levels with great values of J and G, the expression (8) gives the values close to the results of variational calculations. The calculation results on energy levels at $G = 1$ and $G = J$ in comparison with the data from Refs. 3 and 21 are presented in Figs. 2 and 3.

As is seen in Fig. 3*b*, the transformed series gives quite satisfactory values for high rotational energy levels. At the same time, the formula (5) considerably overestimates values of energy for the states with $G = J > 11$.

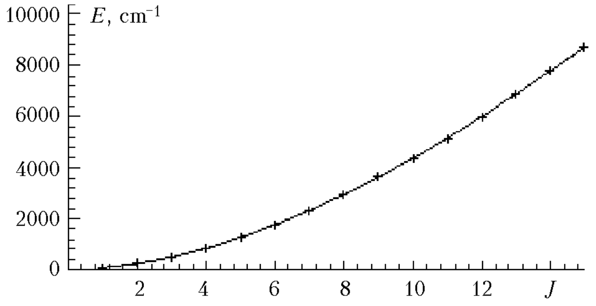

Fig. 2. $G = 1$ energy levels of the H_3^+ molecule. Variational calculation (daggers), calculation with the transformed series (8) (continuous line), calculation with initial series (5) (dashed line (almost completely coincides with continuous line)).

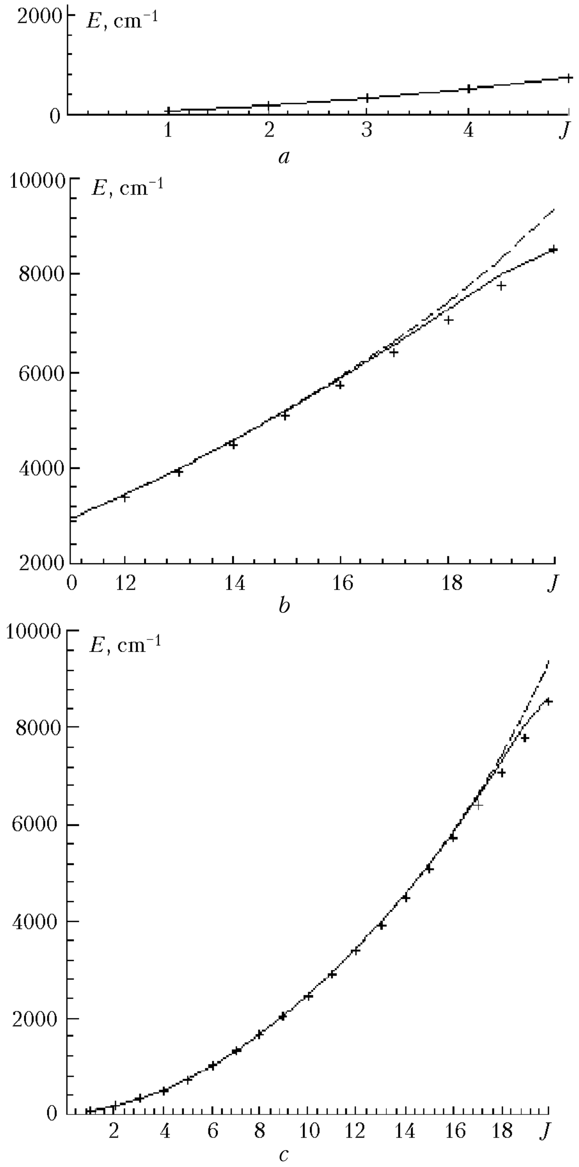

Fig. 3. $G = J$ energy levels of the H_3^+ molecule. Variational calculation (daggers), calculation with the transformed series (8) (continuous line), calculation with initial series (5), $\alpha = 2.26$ (dashed line).

It is useful to note, that a minimum of experimental information was used here for the series transformation: the values of rotation and centrifugal constants, received in traditional model (5) by fitting to the levels with $J < 11$.

Conclusion

With the help of the Euler generalized transformation, a new representation for the energy of ground vibration state of the H_3^+ molecule in the form of a functional series is obtained, that corresponds to the partial summation of initial series in the perturbation theory. The calculations show that the transformed series gives more exact predictions of energy levels for great values of rotation quantum numbers, than traditional representation of energy in the form of power series, even without usage of fitting parameters.

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