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SPECTROSCOPY OF ATOMS AND MOLECULES

On the Use of the Finite Difference Method in a Calculation of Vibration–Rotation Energies

R. I. Ovsyannikov[a, b], **P. Jensen**[b], **M. Yu. Tretyakov**[a], **and S. N. Yurchenko**[c]
[a] *Institute of Applied Physics, Russian Academy of Sciences, Nizhni Novgorod, 603950 Russia*
[b] *Bergische Universität Wuppertal, Wuppertal, D-42097 Germany*
[c] *Technische Universität Dresden, Dresden, D-01062 Germany*

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Abstract—The use of the finite difference method to obtain a Taylor series expansion of a potential energy function for a subsequent calculation of the rovibration energies of molecules is considered. A method is proposed that allows the stability of a finite-difference scheme to be increased against the computational inaccuracy upon numerical expansion of a multidimensional potential energy function into a high-order Taylor series. The method is based on the successive elimination of calculated expansion coefficients of a higher order in calculating the lower-order coefficients by the finite difference method. The approach is illustrated for the example of the CO and H_2S molecules.

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INTRODUCTION

The choice of a coordinate system plays an important role in calculations of the rovibration energy levels of molecules by solving the Schrödinger equation in the Born–Oppenheimer approximation [1, 2]. The necessity of using a moving coordinate system associated with the molecule gives rise to a significantly complicated form of the Schrödinger equation [1]. There are different methods of transforming the Hamiltonian operator from one coordinate system to another (see, e.g., [3] and the references therein). The theoretical rovibrational energies (TROVE) method [4] is fairly universal. In this method, the Hamiltonian is numerically transformed to a molecular coordinate system in that the kinetic energy operator and the potential function are represented as a Taylor series in internal coordinates. The TROVE method allows one to use arbitrary coordinates in such expansion. Expansion coefficients are calculated with the help of a difference scheme based on determining the derivatives of the function using the finite difference method (see, e.g., [5, 6]).

In this paper, a modification of the difference method used to determine the partial derivatives is proposed. The modification of the method takes into account the mutual influence of expansion coefficients by successively eliminating the higher-order terms. It is demonstrated that the proposed modification of the computational scheme decreases inaccuracy of the method and makes the calculated derivatives less sensitive to the finite difference step. The accuracy of the calculations can be increased by several orders of magnitude.

CONVENTIONAL SCHEME OF TRANSFORMATION OF A POTENTIAL ENERGY SURFACE

The TROVE method whose modification is presented in this paper is based on using linearized coordinates [1]. In many cases, the coordinates describing internal degrees of freedom (denoted here as $\mathbf{x} = \{x_i\}$) differ from the geometrically defined coordinates $\mathbf{r} = \{r_i\}$ in which the potential function $V(\mathbf{r})$ is usually represented. Therefore, it is necessary to transform the latter coordinates into the internal coordinates and, consequently, to represent the potential energy $V(\mathbf{r})$ as a function of $\mathbf{x}$. In the TROVE method, this transformation of the potential energy from the initial coordinates r_i to the internal coordinates x_i is performed numerically and implemented in the form of a compact recursive algorithm. In the initial method, which will be referred to as the nonmodified method or method A, the potential energy is described by a Taylor series expansion in the internal coordinates:

$$V(\mathbf{x}) \approx \sum_{l_1 l_2 \ldots l_n} V_{l_1 l_2 \ldots l_n} x_1^{l_1} x_2^{l_2} \ldots x_n^{l_n}, \quad l_1 + l_2 + \ldots + l_n \le m, \tag{1}$$

where m is the order of potential energy expansion and x_i are the coordinates describing the internal vibrations of a molecule. The expansion coefficients $V_{l_1 l_2 \ldots l_n}$ in

(1) can be expressed in terms of derivatives with respect to the corresponding variables x_i ($i = 1, 2, \ldots, n$) at a point $x_i = 0$:

$$V_{l_1 l_2 \ldots l_n} = \frac{1}{l_1! l_2! \ldots l_n!} \frac{\partial^{l_1}}{\partial x_1^{l_1}} \frac{\partial^{l_2}}{\partial x_2^{l_2}} \ldots \frac{\partial^{l_n}}{\partial x_n^{l_n}} V(\mathbf{r}(\mathbf{x}))\bigg|_{0, \ldots, 0}, \quad (2)$$

assuming that the transformation $\mathbf{r}(\mathbf{x})$ is known. As already noted, in the TROVE method derivatives (2) are calculated by a recursive procedure using the finite difference method in the form of the central scheme

$$\partial V(x)/\partial x \approx [V(x+h) - V(x-h)]/2h, \quad (3)$$

where h is the difference step.[1] The higher order derivatives are calculated by recursively applying formula (3) whose iterative application allows one to dispense with analytic expressions. This is especially important with the use of special transformations of coordinates that cannot be expressed analytically.

THE PROBLEM OF CHOOSING AN OPTIMUM STEP

Let the initial (potential) function $V(x)$ be represented as the series

$$V(x) = a_0 x^0 + a_1 x^1 + a_2 x^2 + a_3 x^3 + a_4 x^4 + \ldots. \quad (4)$$

It can be shown that, upon numerical differentiation of $V(x)$ by the finite difference method (3), the mathematical error of determination of a coefficient a_k (i.e., the error δ of the method) is on the order of

$$\delta_{\text{method}}(a_k) \approx |a_{k+2}| h^2, \quad (5)$$

i.e., it decreases indefinitely for $h \longrightarrow 0$. In real calculations, a numerical error also exists in the calculation of the function $\varepsilon = \delta V(x)$, which we will call the round-off error. This error can be estimated as [5]

$$\delta_{\text{round}}(a_k) \approx \varepsilon \sum_{\lambda} |a_\lambda| / h^k \quad (6)$$

(where λ is the number of an expansion coefficient); i.e., $\delta_{\text{round}} \longrightarrow \infty$ for $h \longrightarrow 0$. It is customary to assume that the step size is optimum (h_{opt}) if the sum of errors (5) and (6) is minimum [6], which gives the estimate

$$h_{\text{opt}}(a_k) \approx \varepsilon^{1/(2+k)}, \quad (7)$$

where ε is the machine precision ($\varepsilon = 10^{-p}$, where p is the number of significant digits in decimal number representation). In calculations, the value of h is selected such that the energy values with maximum accuracy are obtained. Consequently, the choice of an optimum value of h is a complicated problem. The method proposed in this paper provides an easy solution of this problem.

A MODIFIED SCHEME OF TAYLOR SERIES EXPANSION OF A POTENTIAL ENERGY FUNCTION

The main disadvantage of the conventional difference scheme for calculating the higher-order derivatives is a decrease in the accuracy with increasing expansion order m (see, for example, [5]). One of the reasons for this is the finite accuracy of representation of real numbers in computers. As an example, let us consider a model (potential) function $V(x) = ax^4$. whose expansion into a Taylor series using the conventional recursive scheme (3) yields the following expression:

$$V_{r,4}(x) = ax^4 + (4ah^2)x^2.$$

Subscripts r and 4 are introduced to denote the reconstructed function and the fourth-degree polynomial, respectively. Consequently, the simplest model potential is reconstructed with the method error

$$\delta_{r,4} = (4ah^2)x^2.$$

Clearly, this error tends to zero for $h \longrightarrow 0$; however, in practice, this passage to the limit is impossible due to round-off errors [6]. The appearance of the term $(4ah^2)x^2$ can be interpreted as an attempt to describe a model function of any even power (in our example, $V(x) = ax^4$) in a certain region of the order h by a quadratic function V_2x^2. Thus, in expanding an arbitrary polynomial into a Taylor series, the higher-order terms of the polynomial introduce an error into calculated values of lower-order expansion coefficients because of the inaccuracy of the finite difference method. It will be shown below that this influence can be decreased significantly by successively eliminating the higher-order expansion terms in calculating the lower-order terms.

Let us consider a modification of the method of expansion of an arbitrary one-dimensional function $V(x)$ into a Taylor series of an mth order using the finite differences. We begin the calculation of derivatives with the highest power m, and introduce the notation $\tilde{V}^m(x) \equiv V(x)$. Let the expansion coefficient V_i be calculated at a certain iteration step i ($i = m, \ldots, 0$). We introduce the reduced function

$$\tilde{V}^{i-1}(x) = \tilde{V}^i(x) - V_i x^i, \quad (8)$$

which will be expanded at the following iteration step $i - 1$. Then, in a similar manner, we will eliminate the term obtained from this function using (8) to evaluate the $(i - 2)$th derivative, and so forth down to $i = 0$. It can be shown that, with the use of this scheme to expand an nth degree polynomial into a Taylor series, the expansion coefficients are reconstructed correctly

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[1] It should be noted that in the TROVE method and in this paper only uniform grids are used; i.e., the difference step along each coordinate is constant.

(to within the round-off error) if the calculation is performed starting with the power $m \geq n$. For any initial function $V(x)$ close to the expansion of the type (4), the considered computational procedure (described by Eq. (8)) allows one to efficiently exclude the influence of the term $a_i x^i$ on the calculation of lower-order terms. This is the main result of the study.

It can also be shown that with the use of scheme (8), which we will call the modified difference scheme or method B, the mathematical error (i.e., the error of the method) is estimated as

$$\delta_{\text{method}}(a_k) \approx a_{m+1} h^{m-k+1}, \tag{9}$$

where m is the maximum degree of the reconstructed potential. The value of m used in the calculations is maximum possible or sufficiently large in order for its further increase not to affect the final energy values. The round-off error will be determined by the same expression (6) as in the case of method A. The optimum step is again estimated from the condition for the minimum of a sum of the error of the method and the round-off error:

$$h_{\text{opt}}(a_k) \approx \varepsilon^{1/(m+1)}. \tag{10}$$

Thus, in method B, the optimum step value does not depend on k and is only governed by the value of a maximum power m. Therefore, estimate (10) allows us to select a single value of h optimum for the calculation of any expansion coefficients a_k. In addition, it will be shown below that method B is more stable, i.e., it imposes less rigid limitations on h, which can be used to reduce the round-off errors.

As is known [6], the procedure for calculating the derivatives by the finite difference method (by method A) is equivalent to solution of a system of linear equations, and each derivative corresponds to its own system of equations. The modified scheme (method B) represented by Eq. (8) is equivalent to solution of a single system of linear equations for all expansion coefficients of the same parity. The reconstructed function $V_{r,m}(x)$ coincides with the initial function to a maximum possible extent in the following sense. The even part of the reconstructed potential function coincides with the even part of the initial one at points $-mh$, $-(m-2)h$, ..., mh, while the odd part of the reconstructed potential function coincides with the odd part of the initial one at points $-(m-1)h$, $-(m-3)h$, ..., $(m-1)h$. Therefore, obtaining the expansion coefficients of a potential function by method B is equivalent to solving independent systems of linear equations for even and odd parts. The equivalence of method B to the solution of a system of linear equations means that this method is equivalent to fitting the polynomial to the set of points in the region $-mh$, ..., mh. Then, we can argue that, in the general case, the calculated coefficients V_i can differ from the coefficients a_i for $m < n$; however, the values of the initial function are to a maximum extent close to those of the reconstructed function within the interval $-mh$, ..., mh. According to its meaning, the reconstructed function gives an extrapolation of the initial one beyond the region $-mh$, ..., mh. In view of the above and taking into account the conclusions on the stability of method B against variation of the step h (9), we introduce an alternative estimate of the optimum step for calculating the finite differences by method B as follows:

$$2mh_{\text{opt}} \approx 2\Delta x, \tag{11}$$

where $2\Delta x$ is the region important in view of the specific features of the problem. The advantage of condition (11) over condition (10) is that Eq. (11) gives the condition for the best reconstruction of the potential within the entire region, while Eq. (10) gives the condition for only the most accurate reconstruction of $m+1$ expansion coefficients by this scheme. The advantage of using estimate (11) instead of (10) will be demonstrated below.

The method can be generalized to a multidimensional problem by combining calculations of coefficients $V_{l_1 l_2 \ldots l_n}$ with equal values of sums $L = l_1 + l_2 + \ldots + l_n$. The general calculations are performed according to the sequence $L = L_{\max}$, $L_{\max} - 1$, $L_{\max} - 2$, ...,1, 0.

EXPANSION OF A ONE-DIMENSIONAL POTENTIAL FUNCTION OF THE CO MOLECULE

Let us consider an expansion of the one-dimensional potential function of the $^{12}C^{16}O$ molecule [7]

$$V = a_0 \xi^2 \left(1 + \sum_{k=1}^{11} a_k \xi^k\right),$$

where $\xi = (r - r_e)/r$ (r_e is the equilibrium value of the CO bond length), into a Taylor series of the mth order

$$V_r(x) = \sum_{k=0}^{m} V_k x^k, \tag{12}$$

where $x = (r - r_e)/r_e$. Note that this function with the values of constant coefficients a_i determined in [7] reproduces the experimental energy values to an accuracy of 0.001 cm^{-1}. Let us consider the closeness of potential (12) to the initial one in the range $x = -\Delta x \ldots \Delta x$ ($\Delta x = 0.25$) for different values of step h and expansion orders m. The derivatives will be calculated by methods A and B with the double precision representation of numbers and operations. The reconstruc-

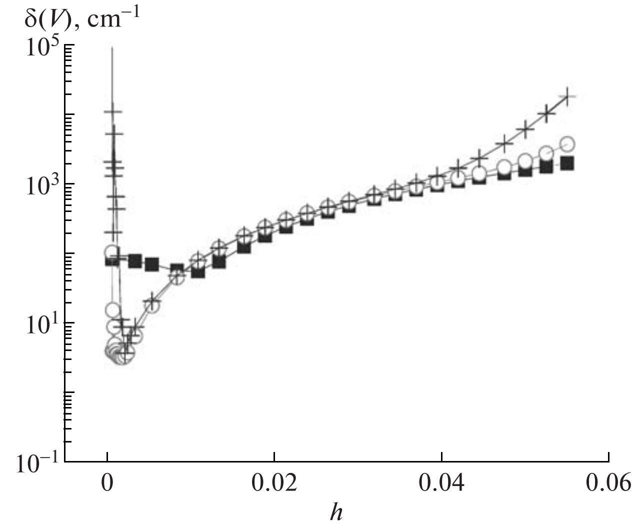

Fig. 1. Root-mean-square deviation δ(V) (13) for expansion of the potential function of the $^{12}C^{16}O$ molecule using the non-modified method. Squares correspond to the sixth-order polynomial, circles, to the eighth-degree polynomial, and crosses, to the tenth-degree polynomial.

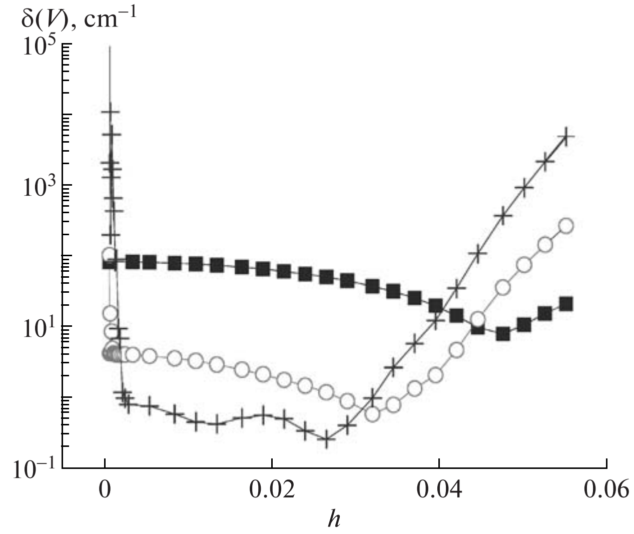

Fig. 2. Root-mean-square deviation δ(V) (13) for expansion of the potential function of the $^{12}C^{16}O$ molecule using the modified method. Squares correspond to the sixth-order polynomial, circles, to the eighth-degree polynomial, and crosses, to the tenth-degree polynomial.

tion quality will be estimated by the root-mean-square deviation

$$\delta(V) = \sqrt{\frac{1}{2\Delta x}\int_{-\Delta x}^{\Delta x}(V - V_r)^2 dx} \qquad (13)$$

of the reconstructed function from the initial one in the specified range of x. The three curves in Fig. 1 describe the deviation δ(V) calculated by method A and correspond to $m = 6$, 8, and 10; similar results obtained by method B are shown in Fig. 2. On the whole, the accuracy of expansion of the initial potential becomes better by approximately an order of magnitude on passage from method A to method B. In addition, for method B (Fig. 2), an increase in the order of expansion (12) improves V_r for almost all h, unlike the case of method A (Fig. 1), for which the passage from $m = 8$ to $m = 10$ does not provide this effect. It is interesting to compare the predicted optimum step sizes of differentiation obtained from conditions (7), (10), and (11) with the real optimum values corresponding to minima of curves in Figs. 1 and 2. Assuming that the round-off error ε for double-precision calculations is about $\approx 10^{-12}$, we obtain from condition (7) the optimum step values for method A within the range of 0.0001–0.1 and, from condition (10), similar values for method B in the range 0.03–0.1. It can be seen in Fig. 1 that the optimum step values (0.011, 0.002, and 0.0023) lie in the predicted range and are close in order of magnitude to the estimates

$$h_{\text{opt}}(a_{k=2}) \approx \varepsilon^{1/4} = 10^{-3},$$

$$h_{\text{opt}}(a_{k=3}) \approx \varepsilon^{1/5} = 4 \times 10^{-3},$$

which correspond to the most important expansion coefficients a_2 and a_3. For method B, the estimates of an optimum step are also in qualitative agreement with the positions of minima (0.047, 0.032, and 0.026) in Fig. 2. However, estimate (10) predicts an increase in the optimum step with increasing m, which qualitatively differs from the real positions of minima. The discrepancy between the predictions (10) and the real positions of minima confirms the fact that the reconstruction of first several expansion coefficients of the function with the maximum accuracy does not correspond to the best reconstruction of the function itself in the considered interval $2\Delta x$. However, condition (11) allows the optimum step value for a particular interval $2\Delta x$ to be predicted with much higher accuracy. This is shown in Table 1 where the corresponding calculated optimal values are compared with the positions of minima of the curves in Fig. 2. This shows not only the advantage of estimate (11), which is only meaningful for method B, over estimates (7) and (10),

Table 1. Optimum values of the step obtained from condition (11) and the numerical experiment

m	h from (11)	h from Fig. 2
6	0.042	0.047
8	0.031	0.032
10	0.025	0.026

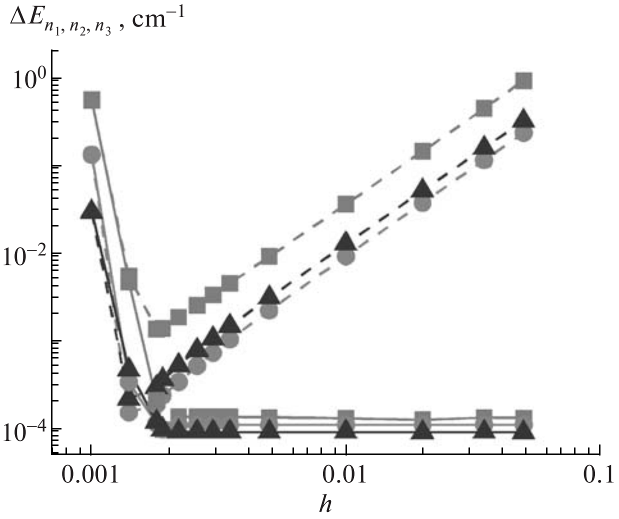

Fig. 3. Energy shifts $\Delta E_{n_1, n_2, n_3} = E_{n_1, n_2, n_3} - E^{\text{opt}}_{n_1, n_2, n_3}$ for the (0,2,0) (squares), (1,0,0) (circles), and (0,0,1) (triangles) vibrational states of the H_2S molecule in the ground electronic state as functions of the difference step h involved in expansion of the molecular potential function (see the text). The energy values are calculated by method A (dashed lines) and method B (solid lines).

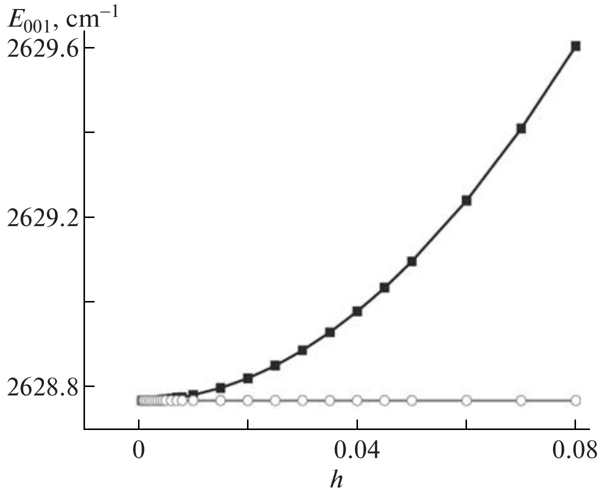

Fig. 4. Energy of the (0,0,1) vibrational state of the H_2S molecule in the ground electronic state as a function of the step h. The line with squares (method A) and the line with circles (method B) converge to $E_{0,0,1} = 2628.768$ cm^{-1}.

but also the advantage of method B over method A. Indeed, the minima in Fig. 2 (method B) lie lower than analogous minima in Fig. 1 (method A), which reflects the better reconstruction of the initial function with the use of method B.

CALCULATION OF VIBRATIONAL ENERGY LEVELS OF THE H_2S MOLECULE

To show the difference between the methods in expanding a multidimensional function, we carried out calculations of vibrational energy values of the H_2S molecule in the ground electronic state. The potential energy surface $V(r_1, r_2, \alpha)$ from [8] was used in the calculations. This surface allows the energy levels to be reproduced within 0.28 cm^{-1}. The calculations were performed by the TROVE method with expansion of the kinetic energy operator up to the eighth order and the potential function up to the 12th order. In the variational solution of the total Schrödinger equation the basis set consisted of the functions obtained from numerical solutions of one-dimensional Schrödinger equations for each degree of freedom and was limited by the polyad number

$$P_{\max} = 2n_1 + n_2 + 2n_3 \leq 22,$$

where n_1 and n_3 are the quantum numbers for the stretching vibrational modes and n_2 corresponds to excitation of the bending vibration. The rigid reference configuration was used in the calculations when the potential function was expanded in the internal coordinates in the vicinity of the minimum of the molecular potential energy surface. See [4] for the details of the method and the TROVE program.

Let us consider the influence of variation of the differentiation step h on the calculation of purely vibrational energy levels E_{n_1, n_2, n_3} (where n_i is the quantum number corresponding to the ith vibrational degree of freedom) of the H_2S molecule. The step size was chosen to be the same for all three degrees of freedom. As in the above examples, the vibrational energy $E_{n_1, n_2, n_3}(h)$ as a function of the differentiation step size exhibits a kink at a certain critical value $h_{\text{cr}} = h_{\text{opt}}$ corresponding to condition (7) or (10). The rounding error is dominant to the left of h_{cr} and the error of the method is dominant to the right of h_{cr}. The energies calculated by method B are more stable against variations in h. Changes in the energies with variation of h from 0.0005 to 0.08 are shown in Fig. 3 where the values of $\Delta E_{n_1, n_2, n_3} = E_{n_1, n_2, n_3} - E^{\text{opt}}_{n_1, n_2, n_3}$ are presented for three vibrational states with $(n_1, n_2, n_3) = (0,2,0)$, (1,0,0), and (0,0,1). Solid curves correspond to the energies calculated by method B and dashed curves correspond to the energies calculated by method A. For $E^{\text{opt}}_{n_1, n_2, n_3}$, we took energies that correspond to optimum h values, i.e., to the minima of $E_{n_1, n_2, n_3}(h)$, calculated by method B.

The dependence of energies calculated by method B on the step size is negligible in the region $h > h_{\text{cr}}$ which corresponds to a larger region of allowable values of h. Figure 4 shows the dependence of energy of the (0,0,1) vibrational state on the step h for method A (curve with squares) and method B (curve with cir-

Table 2. Energy values of vibrational states of the H_2S molecule calculated in this work by method B with the optimum step size and the potential function from [8], the experimental values from [9–15], and the energy values calculated in [8], as well as the derivatives of vibrational state energies with respect to the difference step h for the H_2S molecule obtained with the use of non-modified (A) and modified (B) methods

Vibrational state	Energy, cm^{-1}			dE/dh, cm^{-1}	
	E_{calc} method B	E_{obs} [9–15]	E_{calc} [8]	Method A	Method B
010	1182.9	1182.57	1182.90	7×10^{-1}	3×10^{-3}
020	2354.1	2353.96	2354.15	1	2×10^{-2}
100	2614.4	2614.41	2614.39	9×10^{-2}	6×10^{-4}
001	2628.8	2628.45	2628.79	2×10^{-1}	3×10^{-4}
030	3513.8	3513.79	3513.84	1	5×10^{-2}
110	3779.0	3779.17	3779.04	4×10^{-1}	9×10^{-3}
011	3789.1	3789.26	3789.18	1×10^{-1}	4×10^{-3}
040	4661.6	4661.68	4661.57	2	9×10^{-2}
120	4932.4	4932.70	4932.45	7×10^{-1}	6×10^{-2}
021	4938.6	4939.10	4938.66	3×10^{-1}	3×10^{-2}
200	5145.3	5144.99	5145.30	4×10^{-1}	4×10^{-4}
101	5147.3	5147.22	5147.27	4×10^{-1}	4×10^{-4}
002	5243.5	5243.10	5243.53	4×10^{-1}	3×10^{-4}
050	5796.8	5797.24	5796.63	2	7×10^{-3}
130	6074.6	6074.58	6074.69	1	3×10^{-1}
031	6077.2	6077.60	6077.26	5×10^{-1}	1×10^{-3}
210	6287.9	6288.15	6287.90	9×10^{-2}	8×10^{-3}
111	6288.7	6289.17	6288.70	1×10^{-1}	8×10^{-3}
121	7419.6	7420.09	7419.64	6×10^{-2}	6×10^{-2}
102	7576.5	7576.38	7576.42	7×10^{-1}	7×10^{-5}
201	7576.6	7576.54	7576.48	7×10^{-1}	4×10^{-5}
300	7752.6	7752.26	7752.65	6×10^{-1}	1×10^{-3}
003	7779.8	7779.32	7779.80	8×10^{-1}	4×10^{-4}
112	8696.9	8697.14	8696.75	6×10^{-1}	5×10^{-3}
211	8696.9	8697.15	8696.71	6×10^{-1}	5×10^{-3}
202	9911.1	9911.02	9910.70	1	8×10^{-4}
301	9911.1	9911.02	9910.69	1	8×10^{-4}

cles). It is clear that both energies monotonically tend to the same limit when $h \longrightarrow h_{\mathrm{opt}}$. The energy calculated by method B weakly depends on the differentiation step and is very close to this limit even for large values of h. For example, for $h = 0.06$ this difference amounts to 0.8 cm^{-1} in the case of method A, but is as small as 10^{-5} cm^{-1} for method B. This effect is clearly demonstrated by analysis of the calculated derivatives $dE_{n_1, n_2, n_3}/dh$ presented in Table 2 for a set of energy states of H_2S obtained by both methods. The values of derivatives were estimated by the finite difference method. One can see that the derivatives $dE_{n_1, n_2, n_3}/dh$ obtained by method B are several orders of magnitude smaller than the corresponding values obtained by the conventional finite difference method. The energies calculated by method B that are also listed in Table 2 are in good agreement with the calculated results of [8]. It was discussed above that, for $h_{\mathrm{opt}} \sim h_{\mathrm{cr}}$, i.e., when condition (7) or (10) are satisfied, the expansion coefficients should be calculated with the maximum accuracy and the expanded potential function should be closest to the initial function in a certain vicinity of the equilibrium position. In this case, the lower-lying energy levels are calculated most accurately. In the other case, when condition (11) is satisfied, $h_{\mathrm{opt}} \sim h_{\max}$ and the reconstructed function is close to the initial one over the entire interval considered, which is especially important in calculating the higher lying energy levels of molecules. We emphasize that, due to the stability of the method proposed, we can use expansions of the potential energy up to 20–30 orders in the variational calculation of vibrational energies of the H_2S molecule, which allows potentials of a complicated form to be well described and is rather inefficient with the use of the conventional method. Even for $L_{\max} \approx 28$, the value of h_{cr} (determined in a manner similar to that used in the calculation of CO) is estimated to be 0.008 which is fairly small compared to the estimate $h_{\max} = 0.03$ from (11). Thus, calculations by method B are possible with a step size varying in a wide range, while method A allows one to perform a calculation only in a small vicinity of h_{cr} and its error becomes appreciably greater than that of method B for higher expansion orders.

RESULTS AND CONCLUSIONS

In this paper, we propose a modification of the method of expansion of molecular potential functions into a Taylor series using the finite differences. The modification allows one to increase the accuracy of calculations with the use of higher expansion orders. The method is tested in the problems of expansion of potential functions in calculations of the vibration–rotation energies of molecules and can be used in other areas of mathematical physics involving a series expansion of functions.

The modification proposed requires an insignificant change in the calculation algorithm and has hardly any effect on the computation time. The modified method allows one to perform expansions with considerably lower errors as compared to the conventional method. The proposed method is more stable against variations in the step size and, consequently, provides a larger region of variation of coordinates where the reconstructed potential is well determined. Thus, good accuracy is achieved even far from the equilibrium position, which is especially important in calculations of higher lying energy levels. Stability of the method makes it possible to achieve an acceptable accuracy using potentials with complicated forms that are characteristic of molecules with nonrigid internal vibrations.

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REFERENCES

1. R. R. Bunker and R. Jensen, *Molecular Symmetry and Spectroscopy* (NRC Research Press, Ottawa, 1998).
2. D. Papoušek and M. R. Aliev, *Molecular Rotational-Vibrational Spectra* (Elsevier, Amsterdam, 1982).
3. D. Lauvergnat and A. Nauts, J. Chem. Phys. **116**, 8560 (2002).
4. S. N. Yurchenko, W. Thiel, and P. Jensen, J. Mol. Spectrosc. **245** (2), 126 (2007).
5. N. N. Kalitkin, *Numerical Methods* (Nauka, Moscow, 1978) [in Russian].
6. N. S. Bakhvalov, N. P. Zhidkov, and G. M. Kobel'kov, *Numerical Methods* (Nauka, Moscow, 2001) [in Russian].
7. K. Nakagawa and M. Akiyama, Chem. Phys. Lett. **190**, 91 (1992).
8. O. L. Polyansky, P. Jensen, and J. Tennyson, J. Mol. Spectrosc. **178** (2), 184 (1996).
9. L. E. Snyder and T. H. Edwards, J. Mol. Spectrosc. **31**, 347 (1969).
10. J.-M. Flaud, C. Camy-Peyret, and J. W. C. Johns, Can. J. Phys. **61**, 1462 (1983).
11. L. Lechuga-Fossat, J.-M. Flaud, C. Camy-Peyret, and J. W. C. Johns, Can. J. Phys. **62**, 1889 (1984).
12. W. C. Lane, T. H. Edwards, J. R. Gillis, F. S. Bonomo, and F. J. Murcray, J. Mol. Spectrosc. **111** (2), 320 (1985).
13. L. Lechuga-Fossat, J.-M. Flaud, C. Camy-Peyret, P. Arcas, and M. Cuisenier, Mol. Phys. **61** (1), 23 (1987).
14. S. P. Belov, K. M. T. Yamada, G. Winnewisser, L. Poteau, R. Bocquet, J. Demaison, O. L. Polyansky, and M. Yu. Tretyakov, J. Mol. Spectrosc. **173** (2), 380 (1995).
15. A. D. Bykov, O. V. Naumenko, M. A. Smirnov, L. N. Sinitsa, L. R. Brown, J. Crisp, and D. Crisp, Can. J. Phys. **72**, 989 (1994).