METHOD FOR DETERMINATION OF FUNDAMENTAL CHARACTERISTICS OF DIATOMIC MOLECULES FROM THEIR VIBRATIONAL-ROTATIONAL SPECTRA

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We propose a scheme for studying the effects of high-order corrections to the perturbation theory (PTH) on the solution of inverse spectroscopic problem. The effect of PTH-corrections is demonstrated for the case of diatomic molecules at different values of the vibrational and rotational quantum numbers, as an example. The effect that may produce truncating of the Danham series expansion of the potential function on the calculated results is analyzed.

INTRODUCTION

The problem arises, when applying the PTH to solution of spectroscopic problems, on correctly truncating the perturbation theory series expansion for the series residue to produce only weak effect on the result, being at least within the experimental errors. Taking the CO and HI molecules, as an example, we have attempted to assess the influence of such characteristics of the problem as quantum numbers, the view of the model potential, and the series truncation on the PTH applicability limits.

Naturally, similar analysis has already been undertaken earlier (see, for example, Ref. 1), but the difference of this paper is that it is based on the procedure that enables correct and quick computation of the corrections to energies using high orders (up to 100th) of the PTH on a computer. The approach used when developing this procedure may be found in Refs. 2 and 3 and its main idea is as follows. Using the harmonic oscillator approximation as a basis we have constructed the expressions that relate the vibrational-rotational energy of a molecule, that is being presented as a perturbation theory series expansion,

$$E_{vJ} = \sum_{n=0}^{N} E_{vJ}^{(n)}, \tag{1}$$

to the characteristics of a diatomic molecule like the harmonic frequency ω_e, rotational constant B_e, and parameters of the potential, $a_k (k > 0)$. The latter parameters are the coefficients of the potential function series expansion over the Danham parameter: $\xi = (r - r_e)/r_e$:

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

where

$a_0 = \omega_e^2/4B_e$.

To simplify the below description let us designate the set of parameters ω_e, B_e, and $a_k (k > 0)$ as $\{\alpha_k\}$.

Regardless of the fact that the below analysis is entirely performed in the harmonic oscillator basis the approach itself, used for studying high-order corrections, may be used for studies in other possible bases. As noted above, the HI and CO molecules have been selected for this study as most typical representatives of the diatomic molecules with a large (HI) and small (CO) rotational constant. Let us introduce the following designations: v and J are the vibrational and rotational quantum numbers, N is the maximum order of PTH considered, and M is the total number of the molecular parameters $\{\alpha_k\}$. Now we should like to explain the reasons why it was just these parameters the influence of which we have decided to investigate on the perturbation theory applicability.

(*M*) The parameter M itself implies that the series expansion, (Eq. (2)), of the potential function is truncated. That means that in calculations we shall use the model potential

$$V(\xi) = a_0\, \xi^2 \left(1 + \sum_{k=1}^{M-2} a_k\, \xi^k\right). \tag{3}$$

The necessity of representing the potential function in the form of a finite series expansion is connected with the following problem in solving the inverse spectroscopic (ISP) problem, that is, the task of reconstructing the potential parameters from the experimental data (for example from the RV-transition frequencies using the least squares method. When only limited bulk of experimental data is available, the "fitting" parameters $\{\alpha_k\}$ become to correlate with each other, that leads to inadequate and wrong results. That means that the lack of the experimental data, and specially of the number of vibrational bands available, imposes a restriction on the number of parameters that may be varied.

(*N*) The parameter N characterizes the truncation of the PTH series expansion, Eq. (1). Earlier the influence of increasing PTH order has been investigated (see Ref. 4) only to $N \leq 18$ ($M \to 14$) that is insufficient for making a correct analysis.

(*V*) The influence of the vibrational quantum number value on the convergence of equation (1) is essential in calculations, for the case of diatomic molecules, already at small v that strongly restricts the spectroscopic data that may be used for the ISP solution as "fitting" parameters and enables calculations of only lower part of the potential curve.

(*J*) The influence of rotational quantum number is, as shown below, qualitatively similar to that of v, although being not so strong.

ANALYSIS

(*M*) The parameter M is responsible for the truncation of the series (3) and can vary from 2 to $N + 2$, because the contributions of the higher orders to the potential V do not affect the PTH series expansion. The optimum in the M parameter value depends on the type of the problem (either the direct or the inverse one) to be solved.

In the case of a direct spectroscopic problem (DSP) all the potential parameters α_k at any k value (some of them can be equal to zero) are assumed known. The parameter M can take any value up to the maximum one of $N + 2$. However, one may restrict the choice to the M value starting from which the energy corrections fall into the interval of experimental errors. Let us explain this by an example of calculations of the VR transitions using the Kratzer model potential. In so doing consider the dependence of the rms deviation, $D^{(M)}$, of the VR transition frequencies $\nu_{v'J'vJ}(v' \leq v)$

$$D^{(M)} = \frac{\sqrt{\sum_{J'J,v'v} (\nu^{\text{exp}}_{v'J'vJ} - \nu^{\text{calc}}_{v'J'vJ})^2}}{N_{\text{lines}}}$$

on M ($M \leq N + 2$; $N = 30$; $v' = 0$; $v \leq 4$, $J' = 0$; $J \leq 10$; ω_e and B_e are chosen close to those of CO molecule). Here the frequencies calculated by the formula

$$\nu^{\text{exp}}_{v'J',vJ} = E^{\text{Kratzer}}_{v'J'} - E^{\text{Kratzer}}_{vJ},$$

where

$$E^{\text{Kratzer}}_{vJ} = -\frac{a_0^2}{B_e}\,[(v + 1/2) +$$

$$+ \sqrt{J\,(J + 1) + 1/4 + a_0/B_e + a_0}]^{-2} + a_0.$$

are taken as the experimental values.

As seen from Fig. 1 at M above $M_0 = 15$ it becomes senseless to account for the higher-order corrections to the potential in Eq. (3) because the oscillations of $D^{(M)}$ are within the limits of conditional experimental error ε that in chosen to be 10^{-3}.

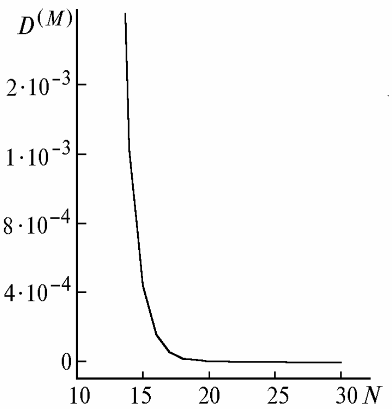

FIG. 1.

In the case of an ISP one must take into consideration, in addition to the condition $M \leq N + 2$, the above mentioned circumstance that correlation may appear among the "fitting" parameters at a lack of experimental data, namely, at an insufficiently large number of the vibrational bands, N_v, available when processing the spectrum.

Thus, one can state that at any given number of the vibrational bands available the number of fitting parameters, M, must be chosen such that the latter are independent.

The effect of correlation among the parameters itself may be expressed in terms of the standard confidence interval of the potential parameters, obtained from the ISP solution, at different M values.

The dependence of the mean relative confidence interval

$$\bar{\sigma} = \sum_{k=1}^{M} \frac{\sigma_k}{\alpha_k} \Big/ M$$

on the number of the fitting parameters for CO and HI molecules is shown in Fig. 2 (solid curves). For the clarity purpose the curve $D^{(M)}$ corresponding to the same values of M is also depicted in the figures (dotted curves). As can be seen from the curves plotted, at $M > M_b = 7$ for CO and $M > M_b = 9$ for HI the confidence intervals become comparable to the values of the parameters α_k varied. Note that the accuracy of estimations ($D^{(M)}$ value) changes significantly at $M \geq M_a = 6$ for CO and $M \geq M_a = 8$ for HI. It is obvious that most effective in the use are the values M_a, and we shall use them in calculations that follow.

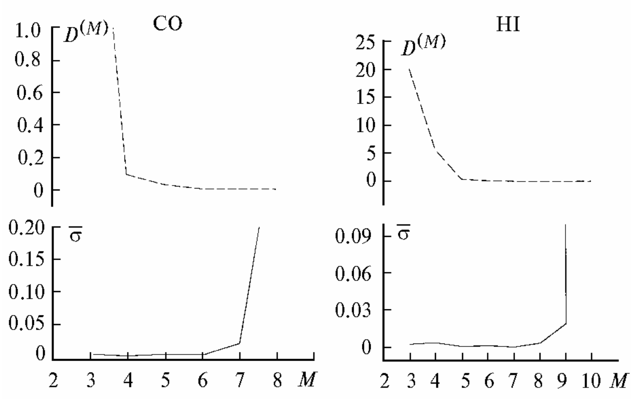

FIG. 2.

(v, N) The scheme of analysis of the influence of v and N on the PTH applicability to solving spectroscopic problems can be as follows.

I. The potential parameters for different N and $v_{\max}$ values are determined from the ISP solution for VR transitions, where $v_{\max}$ is the maximum value of the vibrational number in the experimental data processed. In that way we obtain the series of potential parameter sets, corresponding to different N and $v_{\max}$. Each series enables reconstruction, with a certain accuracy, of the experimental values of the VR transitions, which can be evaluated by the control parameter $D_N^{(v_{\max})}$:

$$D_N^{(v_{\max})} = \frac{\sqrt{\sum_{J'J,v'v\le v_{\max}} (\nu^{\mathrm{exp}}_{v'J'vJ} - \nu^{\mathrm{calc}}_{v'J'vJ})^2}}{N_{\mathrm{lines}}} .$$

Here for each $D_N^{(v_{\max})}$ we obtain its own set of the potential parameters $\{\alpha_k\}$. Note that values M and J are within the limits that exclude their influence on the convergence of PTH series. By analyzing the behavior of $D_N^{(v_{\max})}$, one can estimate the PTH applicability limits regarding the N and $v_{\max}$ values.

II. Using the set of potential parameters $\{\alpha_k\}$, corresponding to the best N and $v_{\max}$ values from the series, obtained using the above analysis, the dependence of a new control parameter $D_N^{(v)}$,

$$D_N^{(v)} = \frac{\sqrt{\sum_{J'J} (\nu^{\mathrm{exp}}_{v'J'vJ} - \nu^{\mathrm{calc}}_{v'J'vJ})^2}}{N_{\mathrm{lines}}} \quad (v' \le v),$$

on v and N can be calculated. As one may see from the definition, the parameter $D_N^{(v)}$ differs from $D_N^{(v_{\max})}$. First, it is estimated for the fixed frequency rather than for the set of frequencies from the interval $v \le v_{\max}$. Second, the initial potentials are fixed as well. This allows one to find the PTH applicability limits regarding the v and N values more correctly.

Below we discuss the use of this scheme when analyzing the CO and HI molecules.

The stage *I* of the scheme gives the results that are presented in Fig. 3 from which we may draw the following conclusions.

1. The values $v_{\max}$ are low ($v_{\max}^{(\mathrm{CO})} = 8 - 12$ and $v^{(\mathrm{HI})}{}_{\max} = 4 - 5$). It is well seen that above certain N_a value the solution of the ISP is stabilizes and the rms deviation $D_N^{(v_{\max})}$ change only insignificantly. If in the case of HI molecule the value N_a is close to 24 ($v_{\max} = 4$), then for CO it approaches 16 ($v_{\max} = 12$). The same behavior have the "fitting" parameters. Thus at $N \ge N_a$ the changes in the parameters fall into the confidence intervals (see the data given in the Table I for values $=_1^{(\mathrm{HI})}$ at different N values).

TABLE I.

N	$=_1^{(\mathrm{HI})}$	$\pm\,\sigma \cdot 10^{-5}$
6	– 2.55352	38
8	– 2.54637	15
10	– 2.546666	6.5
12	– 2.547361	5.6
14	– 2.547379	5.7
16	– 2.547017	6.1
18	– 2.546594	6.7
20	– 2.546335	7.3
22	– 2.546210	7.8
24	– 2.546148	8.2
26	– 2.546114	8.5
28	– 2.546079	8.8

2. Higher values of $v_{\max}$ ($v_{\max}^{(\mathrm{CO})} = 13 - 16$, $v_{\max}^{(\mathrm{HI})} = 6 - 7$). The solution of ISP becomes significantly unstable and it does not stabilize with the increase in N.

Based on data presented in Fig. 3 the assumption can be made that if the VR energy values (or the rms deviations) stabilize with the increasing order of the PTH, N, that is characterized by the plateau, then one may conclude that the corrections to energy, $E_{vJ}^{(n)}$, in the series expansion (1) can be considered decreasing monotonically with the increasing n, and the PTH series converging. If no plateau is observed and there is only a minimum in the dependence of $D_N^{(v)}$ on N, that is indicative of the absence of any stabilization in the behavior of PTH series. So, the series do not converge. It is evident that for a correct application of the PTH to calculations of the VR energy it is necessary to consider at least N_a (the beginning of the plateau) terms of the PTH series.

Thus, the preliminary conclusions are as follows. The PTH applicability limits regarding the v and N values for HI and CO molecules may be determined from the following expressions:

$$N^{(\mathrm{CO})} \le 16 \quad \text{for} \quad v \le 12;$$

$$N^{(\mathrm{HI})} \le 24 \quad \text{for} \quad v \le 5.$$

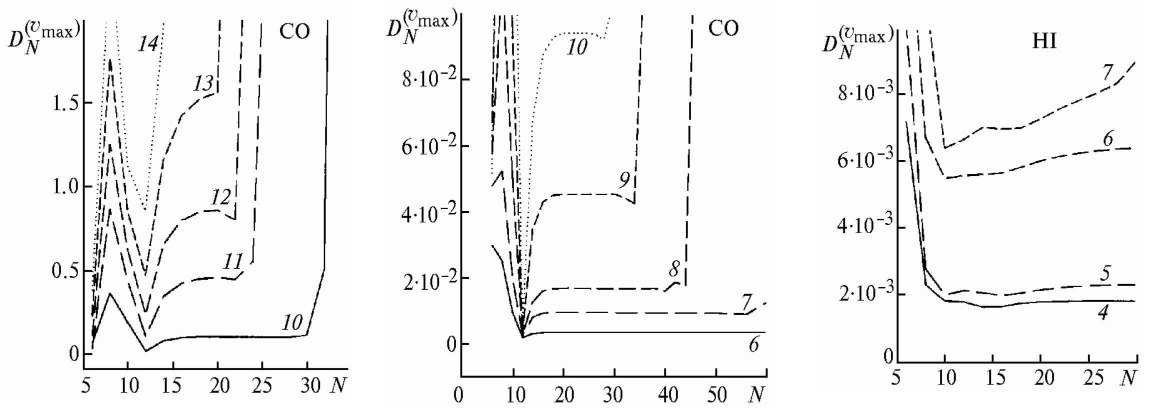

FIG. 3.

Following the steps from the stage II of the scheme proposed one can obtain from the parameters α_k calculated exactly for the above values of v and N, that is, determined most correctly, the VR transitions have been calculated and the dependences of $D_N^{(v)}$ on N at different v constructed. Set out in Fig. 4 (at the bottom) are the following results, obtained from the analysis made for the HI molecule.

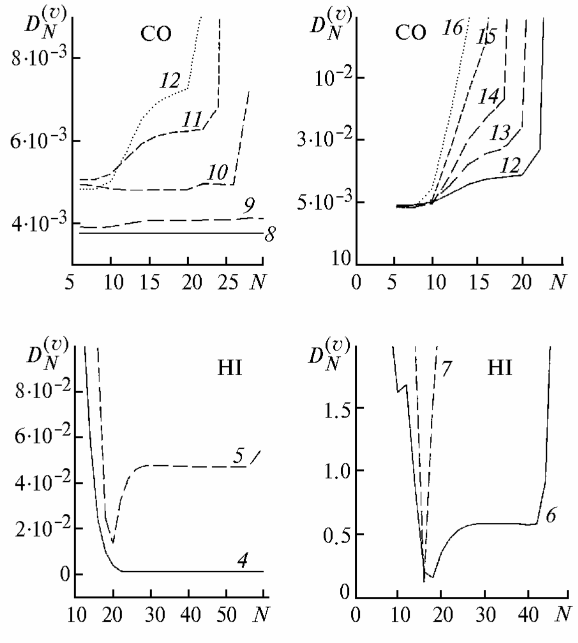

FIG. 4.

$v = 4$. The curve reaches the plateau with the increase in the PTH order within the limits of experimental error ε, which is equal to 10^{-3} cm^{-1} for HI (see, for example, Ref. 5). Assumption can be made that PTH series converges quite well at any N. Here we should like to attract attention to the threshold value of N ($N_a^{(4)} \approx 22$) above which the higher-order corrections fall into the interval ε.

$v = 5$. Now one cannot state that $E_{vJ}^{(n)} \ll E_{vJ}^{(n-1)}$ in Eq. (1) and the more so, the corrections $E_{vJ}^{(n)}$ can not be considered monotonically decreasing with the infinitely increasing order n. In this case the values 26 and 46, between which the curve $v = 5$ reaches its the plateau within the limits ε, may be considered as the lower $N_a^{(5)}$ and the upper $N_b^{(5)}$ limits of the PTH applicability at this vibrational quantum number used in calculations. In this interval of the PTH corrections no influence of the series residue $\delta E_{vJ} = E_{vJ} - \sum_n E_{vJ}^{(n)}$ is already observed, but the influence of the errors of calculations does not yet reach the level, as that when $N > N_b^{(v)}$.

$v = 6$. Although the curve behavior in the range $28 < N < 36$ still has certain stability, its oscillations already do not fall into the ε corridor, that means that the lower boundary $N_a^{(6)}$ tends to approach the upper one at $N_b^{(6)} = 36$.

$v = 7$. The use of PTH at this value v is already incorrect for each the succeeding correction essentially contributes to the value δE_{vJ}.

Thus, when solving the ISP for HI molecule only the VR energies can be used that correspond to $v \le 5$ and at least $N = 24$ terms of the series (1) must be taken into account ($N = 22$ for $v \le 4$).

Similar curves calculated for the CO molecule are presented in Fig. 4. The optimal values of N and v are respectively equal to 16 and 10.

This statement in no ways means that it is senseless to use higher values of the vibrational quantum number in the fitting. It may happen so that thus retrieved parameters will provide for quite a good reconstruction of the whole VR spectrum involved into the processing, but in this case one may not be sure at certain that the parameters sought are those of the potential, rather they are the "fitting" parameters.

(J) In contrast to the parameters M, N, and v the influence of high values of the rotational quantum numbers on the spectroscopic solution achieved by the PTH method is not so strong. Moreover, there are no experimental data available that could enable one to reveal that influence. For these reasons one may assess this influence by analyzing the behavior of the PTH energy corrections, $E_{vJ}^{(n)}$ in the series expansion (1), calculated using the potential parameters obtained from the previous analysis at the optimum values of M and v, with increasing n. The analysis of such a dependence shows that for CO and HI molecules the influence of the rotational quantum number on the PTH series expansion convergence becomes noticeable only at its values close to $J_a = 80$ at $n > 60$. This means that the divergence of the series (1) for these molecules may be controlled by the parameters N, M and v, as well as by their joint effect. In practical calculations the parameter J does not show any significant influence on this process.

CONCLUSION

The data presented in this paper concerning the limits of the perturbation theory applicability to treatment of HI and CO molecules show its applicability to any calculation scheme of retrieving the spectroscopic data on the diatomic molecules from the potential parameters constructed using the PTH, with the harmonic approximation being used as the initial approach (harmonic basis of wave functions). The scheme of the applicability limits estimation itself can be used for the PTH series expansions, in other bases, as well.

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REFERENCES

1. T.I. Velichko, V.Ya. Galin, Yu.S. Makushkin, and Vl.G. Tyuterev, *Analytic Computer Calculations in Molecular Spectra. General Algorithm and Application to Diatomic Molecules* (Nauka, Novosibirsk, 1986), 286 pp.
2. I.R. Sorokin and S.N. Yurchenko, Izv. Vyssh. Uchebn. Zaved., Ser. Fizika, No. 6, 9–16 (1994).
3. S.N. Yurchenko, Izv. Vyssh. Uchebn. Zaved. Ser. Fizika, No. 12, 43–47 (1994).
4. V.Ya. Galin, V.F. Golovko, Yu.S. Makushkin, and Vl.G. Tyuterev, Opt. Spektrosk. **57**, No. 4, 582–587 (1984).
5. G. Guelashvili, P. Niay, and P. Bernage, J. Mol. Spectrosc. **85**, No. 2, 253–270 (1981).