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ITERATIVE PROCEDURE FOR DETERMINING HIGH-ORDER CORRECTIONS TO THE VIBRATION–ROTATION SPECTRA OF DIATOMIC MOLECULES

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The one-dimensional Schrödinger equation is reduced to a system of algebraic equations on the basis of the complex WKB method. As a result, recursion relations are obtained for the numerical calculation of high-order corrections to the vibration–rotation spectra of diatomic molecules. Various nonpolynomial representations of the potential are investigated.

INTRODUCTION

Diatomic molecules continue to draw the unabated interest of spectroscopists. First of all, a wealth of experimental and theoretical material makes diatomic molecules a kind of proving ground for new computational methods in molecular spectroscopy. Second, on their own merits these molecules still offer an abundant field of research.

Perturbation theory applied to the vibration–rotation (VR) Hamiltonian of a diatomic molecule, whose zeroth approximation is an exactly solvable model, has acquired a special reputation for the solution of many spectroscopic problems. There are many alternative modifications of perturbation theory, which differ in the technique used to break down the Hamiltonian in orders of smallness, in the choice of zeroth approximation, etc., but the most general approach is the method of contact transformations [1-3]. Several difficulties are encountered in the application of perturbation theory; for example, it is often necessary to include a large number of perturbation orders, particularly for nonrigid molecules, or to choose the zeroth approximation and the decomposition of the Hamiltonian in such a way that the VR spectrum is described by a small number of molecular parameters. Since the computational complexity increases with the order, computer engineering techniques are an essential tool for analytical calculations [4, 5]. Considerable progress has been made in this direction, both in the construction of perturbation series out to high-order energy corrections and in the solution of inverse problems, through reconstruction of the potential function of the molecule.

Even this situation, however, has its attendant difficulties: The amount of machine time required for each new correction has been found to exceed the entire preceding computational time. And, although studies have demonstrated the unsuitability of using high perturbation orders to solve inverse problems (the accuracy of the reconstructed spectrum decreases as each new order is included [6]), it would still be in our best interest to find a procedure that could be used with minimal effort to include very high perturbation orders. Such an achievement could be important, once it has passed the test for diatomic molecules, for further extension to the case of polyatomic molecules, where the inclusion of each new order exacts an enormous toll. Developments of this kind have been reported by Bender and Wu [7, 8], who have obtained 75 energy corrections for a special kind of anharmonic oscillator on the basis of an iterative procedure.

In the present article, on the basis of Rayleigh–Schrödinger perturbation theory and the complex Wentzel–Kramers–Brillouin (WKB) [9] method, we attempt to obviate the need for analytical calculations to obtain a perturbation series, using various nonpolynomial expansions (see, e.g., [6]) of the potential function. The energy is computed by an iterative procedure, which makes it possible to obtain very high perturbation orders at minimal time cost in order to solve the direct spectroscopic problem. The decomposition of the Hamiltonian is greatly facilitated by the simple form of the iteration series.

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The procedure used in this article is actually a special case of perturbation theory for the Riccati equation, to which the Schrödinger equation is reduced by the substitution of the wave function in the form $\Psi = \Phi \cdot \exp[\theta(x)]$. This approach has been implemented previously [10] for an exponent θ of general form. The present study differs from [10] in several ways: First, we use a different terminology; second, the form of θ is fixed at the outset and is not refined as new orders are added; third, the damping properties of the exponential function $\exp[\theta(x)]$ are taken into account; finally, as mentioned, the construction of the perturbation series does not required formidable analytical calculations.

1. Change of Variables

We consider the vibration–rotation Schrödinger equation for a diatomic molecule [6]:

$$H\Psi_{vj}=E_{vj}\Psi_{vj}, \tag{1}$$

where

$$H=-\frac{h^2}{2}\frac{\partial^2}{\partial r^2}+V(r)+H^R,$$

$$H^R=\frac{BhJ(J+1)}{r^2},$$

h is a formal small parameter, and B is a constant (e.g.: $h = \sqrt{2B_e}$, $B = \sqrt{B_e/2}$); V(r) is the potential of the molecule. We represent V(r) by a certain nonpolynomial expansion

$$V(r)=\sum_{\kappa\geqslant 2} V_\kappa X(r)^\kappa,$$

for example (see [6]):

the Dunham (D) potential

$$X^{\mathrm{D}}=\frac{r-r_e}{r_e};$$

the Simons–Parr–Finlan (SPF) potential

$$X^{\mathrm{SPF}}=\frac{r-r_e}{r};$$

the Ogilvie–Tipping (OT) potential

$$X^{\mathrm{OT}}=\frac{r-r_e}{r+r_e}$$

etc.

For simplicity we assume that $X(r_e) = 0$.

Transforming to the variable x in Eq. (1), we obtain

$$H\Psi_{vj}=E_{vj}\Psi_{vj}, \tag{2}$$

$$H=-\frac{h^2}{2}\left(\alpha(x)\frac{\partial^2}{\partial x^2}+\beta(x)\frac{\partial}{\partial x}\right)+V(x)+H^R, \tag{3}$$

where $\alpha(x)$, $\beta(x)$, V(x), and $H^R(x)$ are expanded in Taylor series in x in the neighborhood of zero [we assume that the change of variable x = x(r) permits this to be done]:

$$\alpha(x)=\sum_{\kappa\geqslant 0}\alpha_\kappa x^\kappa;\quad \beta(x)=\sum_{\kappa\geqslant 0}\beta_\kappa x^\kappa,$$
$$V(x)=\frac{w^2x^2}{2}+\sum_{\kappa\geqslant 3}V_\kappa x^\kappa;\ H^R=\sum_{\kappa\geqslant 0}J(J+1)B_\kappa x^\kappa h. \tag{4}$$

We have therefore made the transition from Eq. (1) to Eq. (2), which is now the object of our investigation.

$$H_0=-\frac{h^2}{2}\alpha_0\frac{\partial^2}{\partial x^2}+\frac{w^2x^2}{2}$$

2. Inclusion of a Damping Exponent in the Estimation of the Orders of Smallness

We consider Eq. (2) from the viewpoint of Rayleigh–Schrödinger perturbation theory. We write the Hamiltonian (3) in the form $H = H_0 + H'$, where

is the zeroth approximation, and H' is an added perturbation.

We note that the perturbation solution of Eq. (2) has the form

$$\Psi = P(x) \exp\left(-\frac{cx^2}{h}\right), \tag{5}$$

where $P(x)$ is a certain polynomial in x, and c is a constant, which is determined by the zeroth approximation. An explanation of this important fact is given in [10]. Such a representation of the solution enables us to reduce the differential equation (2) to an arithmetic equation in the coefficients of the polynomial in (5). This approach was first used by Bender and Wu [7, 8].

Since the indicated form of the solution is the one used in the complex WKB method, the results of [9], in which this method is fully elaborated, are applicable to Eq. (2).

Following [9], we write the solution of Eq. (2) in the form

$$\Psi = \Phi(x) e^{iS/h}. \tag{6}$$

The complex WKB method differs from the WKB method in that it generalizes the Hamiltonian formalism to complex-valued S:

$$S = S_1 + iS_2, \quad S_2 \geqslant 0.$$

Equation (5) can be used to refine $\Psi(x)$: We seek the coefficient Φ of the exponential as a polynomial in x and let $S = iS_2 = icx^2$, where c is a certain positive constant.

We note that the substitution of Eq. (6) into (2) yields another expression in the form of a product of a polynomial and an exponential:

$$P(x) e^{iS/h} = 0. \tag{7}$$

Let us investigate the asymptotic properties of this construction. It is evident from the relation

$$\max(x^\kappa e^{-S_2/h}) \sim (h^{\kappa/2}) \tag{8}$$

that terms of the type $x^\kappa \exp(-cx^2/h)$ have the order of smallness $O(h^{\kappa/2})$.

As in [9], we introduce the class of asymptotic equivalence of functions. We denote by $G_f(h^\alpha)$ a function $\Phi(x, h) \in C^\infty(R \times (0, 1])$ such that

$$h^{\nu/2}\left(\frac{\partial^\nu}{\partial x^\nu} \Phi(x, h)\right) e^{-f/h} = O(h^\alpha). \tag{9}$$

The class $G_f(h^\alpha)$ has the obvious properties [9]

$$G_f(h^\alpha) \supset O(h^\alpha),$$
$$G_f(h^{\alpha_1}) G_f(h^{\alpha_2}) = G_f(h^{\alpha_1+\alpha_2}),$$
$$\sqrt{h}\frac{\partial}{\partial x} G_f(h^\alpha) \rightarrow G_f(h^\alpha).$$

We can now formulate the problem in specific terms. Let it be required to solve Eq. (2) to within $O(h^{M/2})$. In the notation (9) this is equivalent to solving the equation

$$P(x) = 0. \tag{10}$$

Here $P(x)$ is the coefficient of the exponential function in (7) to within $G_{S_2}(h^{M/2})$, where $S_2 = cx^2$.

It is important to note that Eq. (10) has two smallness parameters in the sense of (9), h and x, which are related by the equation

$$x^{\kappa} = G_{S_2}\,(h^{\kappa/2}).$$

2. Hamilton–Jacobi and Transport Equations

We now investigate Eq. (10). Substituting Eq. (6) in (2), we obtain

$$-\frac{h^2}{2}\left[\alpha(x)\left(\Phi_{,xx}+\frac{2i\Phi_{,x}S_{,x}}{h}+\frac{i\Phi S_{,xx}}{h}-\frac{\Phi S^2_{,x}}{h^2}\right)+\beta(x)\left(\Phi_{,x}+\frac{i\Phi S_{,x}}{h}\right)\right]$$
$$+\,(B(x)J(J+1)h+V(x)-E)\Phi = G_{S_2}\,(h^{M/2}), \tag{11}$$

where $S_{,x} = \partial S(x)/\partial x$, and $G_{S_2}(h^{M/2})$ on the right-hand side of Eq. (11) signifies that the solution Φ, when substituted into (11), must yield an identity to within terms $G_{S_2}(h^{M/2})$. We drop $G_{S_2}(h^{M/2})$ from now on with the tacit understanding that our operations will not alter the order of smallness of Eq. (11).

Using Eq. (4), we represent Eq. (11) by the expression

$$(H(S_{,x},\ x)-ih\hat{\Pi}+\hat{D}+B(x)J(J+1)h-E)\Phi=0, \tag{12}$$

in which H, $\hat{\Pi}$, $\hat{D}$, and B are expanded in orders of $G_{S_2}(h^{\kappa/2})$:

$$H(x)=\sum_{\kappa\geq 0}H_{\kappa}(x),$$

$$H_0=\frac{\alpha_0 S^2_{,x}}{2}+\frac{w^2x^2}{2},\ H_{\kappa}=\alpha_{\kappa}x^{\kappa}\frac{S^2_{,x}}{2}+V_{\kappa+2}x^{\kappa+2}; \tag{13}$$

$$\hat{\Pi}=\sum_{\kappa\geqslant 0}\hat{\Pi}_{\kappa},$$

$$\hat{\Pi}_{\kappa}=\alpha_{\kappa}x^{\kappa}\hat{\Pi}',\ \hat{\Pi}'\equiv S_{,x}\frac{\partial}{\partial x}+\frac{S_{,xx}}{2}-i\frac{h}{2}\frac{\partial^2}{\partial x^2}; \tag{14}$$

$$\hat{D}=\sum_{\kappa\geqslant 0}\hat{D}_{\kappa},\ \hat{D}_{\kappa}=\beta_{\kappa}x^{\kappa}\left(-\frac{h^2}{2}\frac{\partial}{\partial x}-\frac{ih}{2}S_{,x}\right); \tag{15}$$

$$B(x)J(J+1)h=\sum_{\kappa\geqslant 0}B_{\kappa}x^{\kappa}J(J+1)h; \tag{16}$$

$$E=\sum_{\kappa\geqslant 0}E_{\kappa}h^{(\kappa+2)/2}. \tag{17}$$

(It is evident from the definition of the class $G_{S_2}(h^{M/2})$ (9) that

$$H_{\kappa}=G_{S_2}\,(h^{(\kappa+2)/2}),$$
$$B_{\kappa}x^{\kappa}J(J+1)h=G_{S_2}\,(h^{(\kappa+2)/2}),$$
$$\hat{\Pi}_{\kappa}G_{S_2}\,(h^{M/2})\rightarrow G_{S_2}\,(h^{(\kappa+M)/2}),$$
$$\hat{D}_{\kappa}G_{S_2}\,(h^{M/2})\rightarrow G_{S_2}\,(h^{(\kappa+3+M)/2}).$$

It is now required to expand Φ in the orders of smallness. According to [9], we write Φ in the form

$$\Phi=\sum_{\kappa\geq 0}\Phi_{\kappa},\quad \Phi_{\kappa}=G_{S_2}\,(h^{\kappa/2}). \tag{18}$$

Substituting Eqs. (13)-(18) into (12) and changing to summation over identical orders of smallness, we have

$$\sum_{m=0}^{M-1}[H_0 - ih(\hat{\Pi}_0 + iB_0J(J+1) - iE_0)]\Phi_m$$
$$+\sum_{m=1}^{M-1}\sum_{\kappa=1}^{m}[H_\kappa - ih\hat{\Pi}_\kappa + B_\kappa x^\kappa J(J+1) + \hat{D}_{\kappa-1} - E_\kappa h^{(\kappa+2)/2}]\Phi_{m-\kappa} = 0. \tag{19}$$

We then set terms of different orders $G_f(h^\alpha)$ equal to zero.

1) For m = 0

$$H_0\Phi_0 = G_{S_2}(h^{3/2}) \quad \text{or} \quad H_0 = G_{S_2}(h^{3/2}) \tag{20}$$

[the Hamilton–Jacobi equation on the function S(x)],

$$(\hat{\Pi}_0 - iE_0 + iB_0J(J+1))\Phi_0 = G_{S_2}(h^{1/2}) \tag{21}$$

[the so-called transport equation, which is a Riccati-type equation, on $\Phi_0(x)$].

Before proceeding to the case m > 0, we examine the solutions (20) and (21):

a) The Hamilton–Jacobi equation

$$\frac{\alpha_0 S_{,x}^2}{2} + \frac{w^2 x^2}{2} = 0$$

has the solution [9]

$$S = \frac{iwx^2}{2\sqrt{\alpha_0}}. \tag{22}$$

b) The solution of the transport equation (21) can be written in the form [11]

$$\begin{gathered} E_{0\nu} = w\sqrt{\alpha_0}(\nu + \frac{1}{2}) + B_0J(J+1), \\ \Phi_{0\nu} = \chi_\nu \bar{\Lambda}^\nu 1, \\ \bar{\Lambda} = \left(\sqrt{h}\frac{\partial}{\partial x} - \frac{2wx}{\sqrt{h\alpha_0}}\right), \end{gathered} \tag{23}$$

where χ_ν is an arbitrary complex constant.

Clearly, $\Phi_{0\nu}$ is proportional to an Hermite polynomial, and $\Psi = \Phi_{0\nu}\exp(iS/h)$ is the solution of the Schrödinger equation in the harmonic approximation for $E_\nu = hE_{0\nu}$.

The ensuing discussion applies only to the vibrational quantum number ν, so that the subscript ν can be dropped.

2) For m > 0, regrouping terms in Eq. (19) and dividing by −ih, we obtain

$$(\hat{\Pi}_0 + iB_0J(J+1) - iE_0)\Phi_m = F^{(m)} + iE_m h^{m/2}\Phi_0, \tag{24}$$

where

$$F^m = \sum_{\kappa=1}^{m}\left(-\frac{iH_\kappa}{h} - \hat{\Pi}_\kappa - \frac{i\hat{D}_{\kappa-1}}{h} - iB_\kappa x^\kappa J(J+1)\right)\Phi_{m-\kappa} + i\sum_{\kappa=1}^{m-1} E_m h^{\kappa/2}\Phi_{m-\kappa}.$$

Equation (24) is a transport equation with a right-hand side. We write Φ_m in the form

$$\Phi_m = h^{m/2}\theta^{(m)}, \tag{25}$$

where $\theta^{(m)} = G_{S_2}(h^0)$, and for $\theta^{(m)}$ we write the transport equation

$$(\hat{\Pi}_0 + iB_0J(J+1) - iE_0)\theta^{(m)} = \tilde{F}^{(m)} + iE_m h^{m/2}\Phi_0, \tag{26}$$

where

$$\tilde{F}^{(m)} = \frac{F^{(m)}}{h^{m/2}}. \tag{27}$$

By the definition of the class $G_f(h^{\alpha})$ we can write $\theta^{(m)}$ in the form

$$\theta^{(m)} = \sum_{n=0}^{N} \theta_n^{(m)} x^n h^{-n/2}. \tag{28}$$

It is readily perceived from Eqs. (25) and (27) that N = 3m + ν, i. e.,

$$\Phi_j = \sum_{\kappa=0}^{3j+\nu} \theta_\kappa^{(j)} x^\kappa h^{(j-\kappa)/2}. \tag{29}$$

To solve Eq. (26), we use the coefficients $\tilde{F}_p^{(j)}$ in the expansion

$$\tilde{F}^{(j)} = \sum_{p=0}^{3j+\nu} \tilde{F}_p^{(j)} \frac{x^p}{h^{p/2}}. \tag{30}$$

The coefficients $\theta_m^{(j)}$ are defined only on the set {j ∈ [0, ∞); m ∈ [0, 3j + ν]}. To evaluate $\tilde{F}_p^{(j)}$, we extend the domain of definition of $\theta_m^{(j)}$ to all integers m subject to the condition

$$\theta_m^{(j)} = 0 \quad \text{for} \quad m \notin [0, 3j+\nu]. \tag{31}$$

Substituting Eqs. (13)–(16), 29 into (26), changing the order of summation as needed, and invoking Eq. (31), we find

$$\tilde{F}_p^{(j)} = \sum_{\kappa=1}^{j} \Bigg[\left(\frac{\alpha_\kappa w^2}{2\alpha_0} - V_{\kappa+2} \right) \theta_{p-\kappa-2}^{(j-\kappa)} - \left((\alpha_\kappa (p-\kappa+1/2) + \beta_{\kappa-1}) \frac{w}{2\sqrt{\alpha_0}} - B_\kappa J(J+1) \right) \theta_{p-\kappa}^{(j-\kappa)}$$
$$+ \left(\frac{\alpha_\kappa}{2} (p-\kappa+2)(p-\kappa+1) + \frac{\beta_{\kappa-1}}{2} (p-\kappa+2) \right) \theta_{p-\kappa+2}^{(j-\kappa)} \Bigg] + \sum_{\kappa=1}^{j-1} E_\kappa \theta_p^{(j-\kappa)}.$$

If $\alpha(x) \equiv 1$ and $\beta(x) = 0$ (corresponding to the Dunham potential), we obtain the result in [11].

We return to Eq. (26) with the value obtained for $\tilde{F}_p^{(j)}$. Substituting Eqs. (28) and (30) into (26) and regrouping, we obtain a system of algebraic equations in $\theta_m^{(j)}$ and E_j:

$$w\sqrt{\alpha_0}(\kappa-\nu)\theta_\kappa^{(j)} = \alpha_0(\kappa+2)(\kappa+1)\theta_{\kappa+2}^{(j)}/2 + \tilde{F}_\kappa^{(j)} + E_j \theta_\kappa^{(0)}$$

for κ ∈ [0, 3j + ν]. It has the following solution (extending from κ = 3j + ν to κ = 0):

1) for $\kappa \neq \nu$

$$\theta_\kappa^{(j)} = \frac{\tilde{F}_\kappa^{(j)} + \alpha_0(\kappa+2)(\kappa+1)\theta_{\kappa+2}^{(j)}/2 + E_j\theta_\kappa^{(0)}}{w\sqrt{\alpha_0}(\kappa-\nu)} \tag{32}$$

(recalling that $\theta_\kappa^{(0)} = 0$ for $\kappa > \nu$);

2) for $\kappa = \nu$

$$E_j = -\frac{1}{\theta_\kappa^{(0)}} [\tilde{F}_\nu^{(j)} + \alpha_0(\nu+2)(\nu+1)\theta_{\nu+2}^{(j)}/2], \; \theta_\nu^{(j)} = r_\nu, \tag{33}$$

where r_ν is an arbitrary complex constant.

The elimination of $\theta_{\kappa+2}^{(j)}$ from (32) and (33) gives the final result obtained in [11].

It should be noted that the same solution of the transport equation (26) is obtained by the direct application of general equations in [9] (see p. 258).

CONCLUSIONS

We have thus reduced Eq. (1) to Eq. (2) and represented the solution of the latter by a product of a damping exponential and a power series $x^p h^{m/2}$ ($p \in N$, $m \in Z$). This substitution leads to the formulation of an iterative procedure for evaluating the coefficients $\theta_\kappa^{(j)}$ in Eq. (29). Since Eq. (2) has been solved using exactly the same expansions of the Hamiltonian in orders of smallness, the same estimates of the latter, and the same zeroth approximation as in Rayleigh–Schrödinger perturbation theory, the results should coincide. This conjecture has been confirmed by a comparative calculation for the Dunham potential representation. The advantage of the given method is that the energies can be plotted without laborious analytical calculations. Here the cost in machine time is not very great for the direct problem of calculating the energy from the molecular parameters. For example, computations up to the 30th correction require only a few seconds on a PC AT 286 personal computer.

The simplicity with which different types of expansions are interchanged in Eq. (2) means that the procedure is very flexible in application to the solution of inverse problems, where the potential curve is determined from the diatomic molecular spectrum.

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REFERENCES

1. M. R. Aliev and V. T. Aleksanyan, Opt. Spektrosk., **24**, No. 4, 520-530 (1968).
2. M. R. Aliev and V. T. Aleksanyan, Opt. Spektrosk., **24**, No. 5, 695-703 (1968).
3. Yu. S. Makushkin and Vl. G. Tyuterev, Perturbation Methods and Effective Hamiltonians in Molecular Spectroscopy [in Russian], Nauka, Novosibirsk (1984).
4. Yu. S. Makushkin and Vl. G. Tyuterev, IOA SO AN SSSR Preprint No. 12 [in Russian], Institute of Atmospheric Optics, Siberian Branch of the Academy of Sciences of the USSR, Tomsk (1975).
5. V. Ya. Galin, Yu. S. Makushkin, A. I. Petrova, and Vl. G. Tyuterev, in: Proceedings of the Third Seminar on the Application of Computers in Molecular Spectroscopy [in Russian], Novosibirsk (1975), pp. 111-112.
6. T. E. Velichko, V. Ya. Galin, Yu. S. Makushkin, and Vl. G. Tyuterev, Analytical Calculations on the Computer in Molecular Spectroscopy: A General Algorithm and Application to Diatomic Molecules [in Russian], Nauka, Novosibirsk (1986).
7. C. M. Bender and T. T. Wu, Phys. Rev., **184**, 1231 (1969).
8. C. M. Bender and T. T. Wu, Phys. Rev. D, **7**, No. 6, 1620 (1973).
9. V. P. Maslov, The Complex WKB Method in Nonlinear Equations [in Russian], Nauka, Moscow (1987).
10. A. V. Turbiner, Usp. Fiz. Nauk, **144**, 35 (1984).
11. S. N. Yurchenko, Izv. Vyssh. Uchebn. Zaved. Fiz., No. 8, 126-127 (1993).