Russian Physics Journal, Vol. 37, No. 12, 1994

OPTICS AND SPECTROSCOPY

NUMERICAL TEST FOR CORRECTNESS IN APPLYING AN ITERATIVE PROCEDURE TO CALCULATIONS IN DIRECT SPECTROSCOPIC PROBLEMS INVOLVING DIATOMIC MOLECULES

S. N. Yurchenko

UDC 539.19

On the basis of model potentials, the correctness in perturbation theory for diatomic molecules. The accuracy of the calculations, and the simplicity of use, allow this procedure to be applied to the solution of various spectroscopic problems requiring numerical calculations.

INTRODUCTION

In the study of molecular vibrational–rotational spectra, one is often obliged to consider higher orders in perturbation theory (PT), especially with loosely bonded molecules. Since the complexity of the calculations increases with order, the natural tend is towards the use of numerical algebraic methods [1]. A method was presented in [2] which makes it relatively easy to consider very high PT orders in vibrational–rotational spectroscopic problems of diatomic molecules, and avoids cumbersome analytical calculations. This method is an iterative procedure for numerically calculating energy from molecular parameters.

The present study introduces a test for the correctness of direct spectroscopic problems based on the proposed procedure, using Kreutzer and RKR models for the potential of CO molecules. Some questions about the application of the proposed method are also discussed.

1. ITERATIVE PROCEDURE

Let us briefly examine the results of [2]. In the vibrational–rotational Schrödinger equation for singlet states of diatomic molecules

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

$$H=-\frac{\hbar^2}{2}\frac{\partial^2}{\partial\xi^2}+V(\xi)+H^R(\xi), \tag{1}$$

$$H^R=\frac{B\cdot hJ(J+1)}{\xi^2}, \tag{2}$$

h is the formal small scale parameter, B is a constant, V(ξ) is assumed to be a polynomial, which, in the general case can be expanded into (see [3], for example);

$$V(\xi)=\sum_{\kappa\geq 2}V_\kappa X(\xi)^\kappa.$$

V. V. Kuibishev Tomsk State University. Translated from Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika, No. 12, pp. 43-47, December, 1994. Original article submitted January 21, 1994.

1064-8887/94/3712-1148$12.50

Transforming the variable x = X(ξ) in (2), we get

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

where $\alpha(x)$, $\beta(x)$, $V(x)$ and $H^R(x)$ are expanded, if possible, into a Taylor series in x about the equilibrium potential (considered for simplicity to be zero):

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

Asymptotically, with a precision of $O(h^{N/2})$, the solution to Eq. (1) with Hamiltonian (3) for the given vibrational number v takes the form:

$$\Psi = \Phi(x) e^{iS/h}, \quad S = S_1 + iS_2, \quad S_2 \geqslant 0,$$
$$\Phi = \sum_{j=0}^{N}\Phi_j, \quad \Phi_j = \sum_{\kappa=0}^{3j+v}\theta_\kappa^{(j)} x^\kappa h^{(j-\kappa)/2}, \quad E = \sum_{j=0}^{N} E_j h^{(j+2)/2}, \tag{4}$$

where j are the PT orders.

Substituting (4) and (3) into (1), the constants $\theta_\kappa^{(j)}$ and E_j can be found.

1. In the zero order approximation (j = 0), we have

$$S = \frac{iwx^2}{2\sqrt{\alpha_0}}, \quad \theta_\kappa^{(0)} = \frac{\alpha_0(\kappa+2)(\kappa+1)/2\cdot\theta_{\kappa+2}^{(0)}}{\sqrt{\alpha_0}\, w(\kappa - v)},$$
$$E_{0v} = w\sqrt{\alpha_0}(v+1/2) + B_0 J(J+1). \tag{5}$$

2. In higher order approximation (j > 0), the following is obtained:

a) $\kappa \in [0, 3j + v]$, $\kappa \neq v$:

$$\theta_\kappa^{(j)} = \frac{F_\kappa^{(j)} + \alpha_0(\kappa+2)(\kappa+1)/2\cdot\theta_{\kappa+2}^{(j)} + E_j\theta_\kappa^{(0)}}{w\sqrt{\alpha_0}(\kappa - v)}; \tag{6}$$

b) $\kappa = v$:

$$E_j = -\frac{1}{\theta_v^{(0)}}[F_v^{(j)} + \alpha_0(v+2)(v+1)/2\cdot\theta_{v+2}^{(j)}], \tag{7}$$

$\theta_v^{(j)} = r_v$, where r_v is an arbitrary constant,

$$F_\kappa^{(j)} = \sum_{m=0}^{j}\left[\left(\frac{\alpha_m w^2}{2\alpha_0} - V_{m+2}\right)\theta_{\kappa-m-2}^{(j-m)} - \right.$$
$$- \left((2\alpha_m(\kappa - m + 1/2) + \beta_{m-1})\frac{w}{2\sqrt{\alpha_0}} + B_m J(J+1)\right)\theta_{\kappa-m}^{(j-m)} +$$
$$\left. + \left(\frac{\alpha_m}{2}(\kappa - m + 2)(\kappa - m + 1) + \frac{\beta_{m-1}}{2}(\kappa - m + 2)\right)\theta_{\kappa-m+2}^{(j-m)}\right] +$$
$$+ \sum_{m=1}^{j-1} E_m\theta_\kappa^{(j-m)};$$

c) $\kappa \notin [0, 3j + v]$:

$$\theta_\kappa^{(j)} = 0. \tag{8}$$

TABLE 1

α, β	D	OT	SPF
α_0	1	1/4	1
β_0	0	—1/2	—2
α_1	0	—1	—4
β^1	0	3/2	6
α_2	0	3/2	6
β_2	0	—3/2	—6
α_3	0	—1	—4
β_3	0	1/2	2
α_4	0	1/4	1
β_4	0	0	0
α_5	0	0	0
β_5	0	0	0
...	...	...	...
...	...	...	...

TABLE 2

V	J	D	OT	SPF	V	J	D	OT	SPF
0	0	6,0 (—14)*	6,0 (—14)	6,0 (—14)	0	0	6,0 (—14)	6,0 (—14)	6,0 (—14)
1	0	9,6 (—14)	9,6 (—14)	9,6 (—14)	0	1	2,8 (—14)	2,8 (—14)	2,8 (—14)
2	0	2,1 (—14)	2,1 (—14)	2,1 (—14)	0	2	3,4 (—14)	3,4 (—14)	3,4 (—14)
3	0	6,1 (—14)	6,1 (—14)	6,1 (—14)	0	3	—2,1 (—14)	—2,1 (—14)	—2,1 (—14)
4	0	5,0 (—14)	5,0 (—14)	4,9 (—14)	0	4	—6,5 (—15)	—6,5 (—15)	—6,5 (—15)
5	0	3,3 (—14)	3,3 (—14)	3,4 (—14)	0	5	—2,9 (—15)	—2,9 (—15)	—2,9 (—15)
6	0	3,5 (—14)	3,4 (—14)	4,0 (—14)	0	6	8,9 (—14)	8,9 (—14)	8,9 (—14)
7	0	3,5 (—14)	3,5 (—14)	4,0 (—13)	0	7	9,5 (—14)	9,5 (—14)	9,5 (—14)
8	0	6,8 (—14)	—2,9 (—13)	2,4 (—11)	0	8	1,4 (—14)	1,4 (—14)	1,4 (—14)
9	0	9,1 (—14)	3,6 (—12)	2,7 (—9)	0	9	3,8 (—14)	3,8 (—14)	3,8 (—14)
10	0	1,2 (—13)	—1,9 (—11)	1,0 (—9)	0	10	3,8 (—14)	3,8 (—14)	3,8 (—14)
11	0	2,7 (—13)	—3,1 (—9)	—1,1 (—6)	0	11	—3,6 (—14)	—3,6 (—14)	—3,6 (—14)
12	0	3,2 (—13)	—7,8 (—8)	5,8 (—5)	0	12	1,0 (—14)	1,0 (—14)	1,0 (—14)
13	0	1,1 (—12)	—5,4 (—7)	—1,9 (—3)	0	13	5,2 (—14)	5,2 (—14)	5,2 (—14)
14	0	8,4 (—13)	—3,3 (—7)	—2,2 (—2)	0	14	4,4 (—14)	4,4(—14)	4,4 (—14)

*(6,0(−14) represents $6.0 \cdot 10^{-14}$).

The formulae (4)-(8) are results from [2].

It is not difficult to see that the formal small parameter h, through which the asymptotic expansion is generated, does not reflect the real geometry of the problem. Actually, varying in the scale x can make h as large or as small as desired. Nevertheless, we can formally consider h to be the expansion parameter, since the energy correction $E_j h^{(j+2)/2}$ does not depend on the scale x, but rather the finite expansion does not depend on the absolute value of h. As a result, the solution turns out to be an expansion in the real small parameter of the problem, which can be determined using regular techniques (see, for example [4], p. 23).

2. NUMERICAL TEST

As in [7], the test for correctness is applying the given procedure to the calculation of a straight spectroscopic problem was carried out using the Kreutzer and RKR potential models for CO.

1. The Kreutzer potential

$$V(\xi) = D_e \left(1 - \frac{1}{\xi}\right)^2$$

TABLE 3

v	D	OT	SPF	v	D	OT	SPF
0	−1,4 (−3)	−1,4 (−3)	−1,4 (−3)	15	−5,2 (−1)	−5,1 (−1)	−5,1 (−1)
1	−2,3 (−3)	−2,3 (−3)	−2,3 (−3)	16	−5,9 (−1)	−5,9 (−1)	−5,8 (−1)
2	−2,0 (−3)	−2,0 (−3)	−2,0 (−3)	17	−8,0 (−1)	−8,0 (−1)	−8,0 (−1)
3	−2,0 (−3)	−1,9 (−3)	−2,0 (−3)	18	−9,7 (−1)	−9,6 (−1)	−9,6 (−1)
4	−3,6 (−3)	−3,5 (−3)	−3,5 (−3)	19	−1,2	−1,1	−1,1
5	−8,0 (−3)	−7,8 (−3)	−7,8 (−3)	20	−1,4	−1,3	−1,3
6	−1,6 (−2)	−1,6 (−2)	−1,6 (−2)	21	−1,6	−1,5	−1,5
7	−3,0 (−2)	−2,9 (−2)	−2,9 (−2)	22	−1,7	−1,7	−1,7
8	−5,0 (−2)	−4,9 (−2)	−4,9 (−2)	23	−1,9	−1,9	−1,9
9	−7,8 (−2)	−7,7 (−2)	−7,7 (−2)	24	−2,1	−2,1	−2,1
10	−1,2 (−1)	−1,2 (−1)	−1,2 (−1)	25	−2,2	−2,2	−2,2
11	−1,7 (−1)	−1,6 (−1)	−1,6 (−1)	26	−2,2	−2,2	−2,2
12	−2,3 (−1)	−2,3 (−1)	−2,3 (−1)	27	−2,1	−2,1	−2,1
13	−3,1 (−1)	−3,1 (−1)	−3,1 (−1)	28	−1,9	−1,9	−1,9
14	−4,0 (−1)	−4,0 (−1)	−4,0 (−1)				

is convenient for carrying out the test when the exact spectral solution to the Schrödinger equation (1) is known

$$E_{vj} = -\frac{2D_e^2}{h^2}\left[(v+1/2)+\sqrt{J(J+1)\frac{2B}{h}+0{,}25+\frac{2D_e}{h^2}}\right]^{-2}+D_e. \tag{9}$$

The parameters of the Hamiltonian (3) are selected to be z:

$$h=\sqrt{2B_e},\quad B=\sqrt{B_e/2},\quad D_e=\frac{w_e^2}{4B_e},$$

which corresponds to the dimension less coordinate $\xi = r/r_e$.

We consider three different expansions which reduce (2) to (3);

(D) the Dunham expansion $x^D = \xi - 1$ [5];

(OT) the Ogilvy–Tipping expansion $x^{OT} = (\xi - 1)/(\xi + 1)$ [3];

(SPF) the Simons–Parr–Finlan expansion $x^{SPF} = (\xi - 1)/\xi$ [6].

It is easy to find the coefficients of the series expansion $V^K(x)$ for this variable:

$$V(x)=a_0(1+a_1x+a_2x^2\ldots),\quad w^2/2=a_0,$$
$$V_\kappa=a_0\cdot a_{\kappa-2},\quad \kappa>2,$$

(D) $a_0^D = De$, $a_\kappa^D = (-1)^j(\kappa + 1)$, $\kappa > 0$;

(OT) $a_0^{OT} = 4De$, $a_\kappa^{OT} = (-1)^\kappa(\kappa + 1)$, $\kappa > 0$;

(SPF) $a_0^{SPF} = De$, $a_\kappa^{SPF} = 0$, $\kappa > 0$;

The coefficients α_κ, β_κ are given in Table 1, and for B_κ, we have

(D) $B_0^D = B$, $B_\kappa^D = B(-1)^\kappa(\kappa + 1)$, $\kappa > 0$;

(OT) $B_0^{OT} = B$, $B_\kappa^{OT} = 4\cdot B(-1)^j\kappa$, $\kappa > 0$;

(SPF) $B_0^{SPF} = B$, $B_\kappa^{SPF} = B$, $B_\kappa^{SPF} = 0$, $\kappa > 0$;

Note that α_κ, β_κ and B_j do not depend on the form of the potential.

By substituting the values for the coefficients shown into formulae (4)-(8), the energy (4) can be calculated for several N and compared against the exact values (9). The results of this test (the difference between the calculated and exact values for energy in cm^{-1}) for $B_e = 0.5\ cm^{-1}$, $w_e = 1000\ cm^{-1}$, N = 16 and various values of v, J are shown in Table 2.

2. Analogous tests were carried out for the RKR-potential for the ground state of molecular CO. The parameters of the potential for the same three expansions (N = 6) were taken from (8), and the energy used for comparison with the values calculated from formulae (4)-(8), from [9].

The results of the numerical test (the difference between the calculated values for energy in cm^{-1} and those taken from [9]) are shown in Table 3.

CONCLUSION

Tests of the calculations using the iterative procedure show good agreement with (from the standpoint of a vibrational model) with the direct solutions to the problem. In short, the possibility of finding cumbersome analytical solutions in order to construct PT series, as well as its great calculational speed makes this method useful for solving various spectroscopic problems (the construction of potential curves, intensity calculations, etc.) involving singlet states of diatomic molecules.

In conclusion, the author thanks Yu. S. Makushkin for helpful discussions.

REFERENCES

1. Yu. S. Makushkin and V. G. Tyuterev, Siberian Branch of the USSR Academy of Sciences, Institute of Atmospheric Optics, No. 12, Tomsk (1975).
2. I. R. Sorokin and S. N. Yurchenko, Izv. Vyzov. Fiz, No. 6, 9-16 (1994).
3. R. Engelke, J. Chem. Phys., **68**, No. 8, 3514-3521 (1978).
4. T. E. Velichko, V. Ya. Galin, Yu. S. Makushkin, and V G. Tyuterev, Analytical Calculations using Computers in Molecular Spectroscopy, Nauka, Novosibirsk (1986).
5. J. L. Dunham, Phys. Rev. **41**, 721-731 (1932).
6. G. Simons, R. G. Parr, and J. M. Finlan, J. Chem. Phys. **59**, No. 6, 3229-3234 (1973).
7. Yu. S. Makushkin and V. G. Tyuterev, Perturbation Methods and Effective Hamiltonians in Molecular Spectroscopy [in Russian], Nauka, Novosibirsk (1984).
8. T. I. Velichko, V. F. Golovko, and V. G. Tyuterev, Izv. Vysshikh Ucheb. Zaved. Fiz., No. 5, 98-101 (1984).\
9. A. W. Mantz, J. K. G. Watson, and K. N. Rao, J. Mol. Spectrosc., **39**, 180-184 (1971).