

Extended Simons-Parr-Finlan approach to the analytical calculation of the rotational-vibrational energy of diatomic molecules

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An extension of the Simons-Parr-Finlan approach to the analytical calculation of the rotational-vibrational energy of diatomic molecules is proposed. The obtained eigenvalues are applied in the calculation of molecular constants as well as in assignment of rovibrational spectra of the $^1\Sigma$ state of $^{12}\text{C}^{32}\text{S}$ and of the $^1\Sigma_g$ state of $^{40}\text{Ar}_2$ molecules, giving quite satisfactory reproduction of the experimental data over a wide range of rotational states.

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In order to determine the possible energy states of rotating-vibrating diatomic molecules, we have to solve the Schrödinger equation

$$\left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial q^2} + \frac{\hbar^2 J(J+1)}{2mq^2} + U(q) - E_{vJ} \right] \psi_{vJ} = 0, \quad (1)$$

in which q denotes the internuclear separation, m the reduced mass, and $U(q)$ is the internuclear potential-energy function. The above equation can be solved analytically [1] for the harmonic [2] and Morse potential [3] using the parabolic expansion of the rotational term in (1), as well as the Kratzer potential [4,5] given in the slightly modified form [6–8] as

$$U(q) = D_0 \left[1 - \frac{q_0}{q} \right]^2, \quad (2)$$

where q_0 is an equilibrium distance and D_0 is a constant related to the dissociation energy of the molecule. Employing a quantum-mechanical equation of motion in the Heisenberg representation, as well as the explicit form of Hamilton's operator occurring in (1), one gets

$$\hat{p} = (i\hbar)^{-1} [\hat{p}, \hat{H}] = -\frac{2D_0 q_0 (q - q_0)}{q^3}, \quad (3)$$

$$D_J = D_0 [1 + BD_0^{-1} J(J+1)]^{-1}, \quad (4)$$

$$q_J = q_0 [1 + BD_0^{-1} J(J+1)],$$

where $B = \hbar^2 (2mq_0^2)^{-1}$. The right-hand side of (3) represents the quantum-mechanical force endowed with an effective potential

$$U(q)_{\text{eff}} = D_J \left[1 - \frac{q_J}{q} \right]^2, \quad (5)$$

whereas the quantities D_J and q_J are the modified dissociation constant and the changed equilibrium distance in the J rotational state, respectively. This is a simple consequence of the deformational action of the centrifugal force which acts upon systems with rotational degrees of freedom.

Introducing potential (5), the Schrödinger equation (1) may be rewritten into the equivalent formula

$$\left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial q^2} + D_J \left[1 - \frac{q_J}{q} \right]^2 + \frac{BJ(J+1)}{1 + BD_0^{-1} J(J+1)} - E_{vJ} \right] \psi_{vJ} = 0, \quad (6)$$

which can be analytically solved, leading to the energy eigenvalues and the corresponding wave functions

$$E_{vJ} = D_J \left[1 - \frac{C_J}{[1 + 2v + (1 + C_J)^{1/2}]^2} \right] + \frac{BJ(J+1)}{1 + BD_0^{-1} J(J+1)}, \quad (7)$$

$$C_J = 4D_0 B^{-1} [1 + BD_0^{-1} J(J+1)], \quad (8)$$

$$\psi_{vJ} = N_{vJ} (2\beta_{vJ}\rho)^{\alpha_J} \exp(-\beta_{vJ}\rho) L_v^{\gamma_J} (2\beta_{vJ}\rho), \quad (9)$$

$$L_v^{\gamma_J} (2\beta_{vJ}\rho) = \frac{\Gamma(1 + \gamma_J + v)}{v! \Gamma(1 + \gamma_J)} {}_1F_1(-v; 1 + \gamma_J; 2\beta_{vJ}\rho), \quad (10)$$

$$N_{vJ} = \left[\frac{v!}{2(\gamma_J + v) \Gamma(1 + \gamma_J + v)} \right]^{1/2}, \quad (11)$$

where $L_v^{\gamma_J} (2\beta_{vJ}\rho)$ is the generalized Laguerre polynomial, ${}_1F_1(-v; 1 + \gamma_J; 2\beta_{vJ}\rho)$ denotes the confluent hypergeometric (or Kummer) function, whereas

$$\rho = \frac{q}{q_J}, \quad \alpha_J = \frac{1 + \gamma_J}{2}, \quad (12)$$

$$\gamma_J = \sqrt{1 + C_J^{-1}}, \quad \beta_{vJ} = \frac{C_J}{4(v + \alpha_J)}. \quad (13)$$

The obtained results indicate that rovibrational energy of diatomic systems consists of an effective vibration energy described by the first term in (7), and an effective rotation energy given by the second one. It is easy to verify that

$$E_{\text{eff}}^{\text{rot}} = \frac{BJ(J+1)}{1 + BD_0^{-1} J(J+1)} = D_0 \left[1 - \frac{q_0}{q_J} \right]^2 + B_J J(J+1), \quad (14)$$

$$B_J = \hbar^2(2mq_J)^{-2} = B[1 + BD_0^{-1}J(J+1)]^{-2}, \quad (15)$$

i.e., the effective rotation energy is a result of a change of the equilibrium configuration $q_0 \rightarrow q_J$ caused by centrifugal force.

A look into (7) reveals that the rotational term takes the continued-fraction form which suggests the possibility of introduction of some modification into the formula obtained. Namely, instead of Eq. (7) we propose to consider its simple extension given by the continued-fraction formula

$$E_{vJ} = D(J) \left[1 - \frac{C(J)}{[1 + 2v + (1 + C(J))^{1/2}]^2} \right] + \frac{BJ(J+1)}{1 + BD(J)^{-1}J(J+1)}, \quad (16)$$

$$D(J) = D_0 \{ 1 + xJ(J+1)/[1 + yJ(J+1)/(1 + \dots)] \}, \quad (17)$$

$$C(J) = 4D(J)B^{-1}[1 + BD(J)^{-1}J(J+1)], \quad (18)$$

to calculate the energy of rovibrational transitions and the molecular constants of diatomic systems. For our purpose the rigid molecule $^{12}\text{C}^{32}\text{S}$ and van der Waals molecule $^{40}\text{Ar}_2$ will be taken as examples.

The best values for the molecular parameters are determined by the linear least-square routine in which the statistical weights proportional to the inverse of experimental uncertainties are taken as equal to one (i.e., we use in the fit $1/\sigma_{\text{expt}}^2 = 1$ throughout). The calculated frequencies and the derived parameters are given with their standard errors at the bottom part of the tables and in parentheses, respectively. Tables I and II present the ob-

TABLE I. Energy of rovibrational transitions $\Delta E = E_{a_{\text{obs}}} - E_{\text{calc}}$ (cm^{-1}) for $R(J)$ band $v=0 \rightarrow 1$, of $^{12}\text{C}^{32}\text{S}$ molecule. E_{obs} is taken from Ref. [10].

J	ΔE^a	ΔE^b	ΔE^c	ΔE^d
0	-0.1378	0.0000	0.0013	-0.0474
1	-0.0859	0.0000	0.0002	-0.0121
2	-0.0401	-0.0001	-0.0006	0.0136
5	-0.0613	-0.0004	-0.0016	0.0439
6	0.0829	0.0022	-0.0017	0.0419
9	0.1148	0.0010	0.0019	0.0189
10	0.1110	0.0005	0.0010	0.0059
12	0.0874	-0.0029	0.0012	-0.0163
13	0.0633	-0.0010	-0.0020	-0.0275
14	0.0384	-0.0001	-0.0001	-0.0300
16	-0.0324	0.0009	0.0008	-0.0251
17	-0.0767	0.0010	0.0011	-0.0090
19	-0.1861	-0.0002	-0.0013	0.0406
σ	0.1039	0.0013	0.0015	0.0329

^a E_{calc} from (7).

^b E_{calc} from (16).

^c E_{calc} from Dunham formula $E_{vJ} = \omega(v+1/2) + [B - \alpha(v+1/2)]J(J+1)$.

^d E_{calc} from Dunham formula $E_{vJ} = \omega(v+1/2) + [B - DJ(J+1)]J(J+1)$.

TABLE II. Rotation-vibration energy $\Delta E = E_{\text{obs}} - E_{\text{calc}}$ (cm^{-1}) of $^{40}\text{Ar}_2$ molecule for $v=1$. E_{obs} is taken from Ref. [12].

J	ΔE^a	ΔE^b	ΔE^c	ΔE^d
0	-0.307	-0.002	-0.568	0.049
2	-0.298	-0.002	-0.551	0.046
4	-0.274	0.002	-0.508	0.042
6	-0.243	0.002	-0.449	0.030
8	-0.195	0.007	-0.365	0.022
10	-0.150	0.001	-0.274	0.000
12	-0.084	0.005	-0.158	-0.012
14	-0.017	0.004	-0.035	-0.029
16	-0.053	0.000	0.093	-0.046
18	0.130	-0.001	0.227	-0.057
20	0.205	-0.005	0.357	-0.064
22	0.272	-0.013	0.473	-0.070
24	0.354	0.000	0.595	-0.047
26	0.405	-0.004	0.673	-0.034
28	0.438	-0.006	0.716	-0.013
30	0.448	-0.002	0.716	0.019
32	0.418	-0.002	0.651	0.052
34	0.324	-0.003	0.493	0.070
36	0.171	-0.003	0.240	0.086
38	-0.067	-0.017	-0.138	0.083
40	-0.444	-0.013	-0.698	0.018
42	-1.005	-0.018	-1.493	-0.146
σ	0.369	0.008	0.593	0.061

^a E_{calc} from (7).

^b E_{calc} from (16).

^c E_{calc} from Dunham formula $E_{vJ} = \omega(v+1/2) + BJ(J+1)$.

^d E_{calc} from Dunham formula $E_{vJ} = \omega(v+1/2) + [B - DJ(J+1)]J(J+1)$.

served minus calculated frequencies obtained from (i) the modified continued-fraction formula (16) containing only one semiempirical parameter x , (ii) the starting equation (7) based on the Simons-Parr-Finlan potential, and (iii) the Dunham expansion [9]

$$E_{vJ} = \sum_{k,l} Y_{kl}(v+1/2)^k J^l(J+1)^l. \quad (19)$$

The continued-fraction parameters $\{q_0, D_0, x\}$, and the Dunham parameters

$$Y_{10} = \omega, \quad Y_{11} = \alpha, \quad Y_{01} = B, \quad Y_{02} = D, \quad (20)$$

evaluated by the fitting procedure and used for the calculation of the energy of rovibrational transitions, are collected in Table III. Moreover, the above table reports the molecular constant $\{\omega, B, D\}$ calculated from $\{q_0, D_0\}$ and the well-known formulas

$$\omega = \sqrt{2D_0(mq_0^2)^{-1}}, \quad B = \hbar^2(2mq_0^2)^{-1}, \quad D = 4B^3\omega^{-2}. \quad (21)$$

The performed calculations indicate that the modified fraction continued formula (16), including two molecular and one semiempirical parameters $\{q_0, D_0, x\}$, reproduces the observed rovibrational transitions and molecular constants very well over a wide range of rotational

TABLE III. Ground-state molecular constants (cm^{-1}) for molecules considered.

Source	σ (cm^{-1})	q_0 (\AA)	D_0	x^a (units of 10^6)	ω	B	D (units of 10^6)	α (units of 10^3)
$^{12}\text{C}^{32}\text{S}$								
Eq. (7)	0.1039	1.5675(26)	518546(1740)		1277.0683	0.786285	1.1922	
Eq. (16)	0.0013	1.53517(12)	497351(79)	-4.320(16)	1277.0726	0.819799	1.3512	
Dunham formula ^b	0.0015				1272.1653(12)	0.8207(15)		6.074(13)
Dunham formula ^c	0.0329				1272.261(23)	0.7880(18)	4.69(23)	
[11]		1.534941			1285.08	0.8200462	1.43	5.9224
$^{40}\text{Ar}_2$								
Eq. (7)	0.369	3.9981(64)	3291(39)		26.36	5.278×10^{-2}	0.846	
Eq. (16)	0.008	3.85028(47)	2988.0(12)	-192.3(11)	26.08	5.691×10^{-2}	1.084	
Dunham formula ^b	0.593				26.31(19)	$5.051(22) \times 10^{-2}$		
Dunham formula ^c	0.061				25.691(24)	$5.3853(80) \times 10^{-2}$	2.074(48)	
[11]		3.758			25.74	5.975×10^{-2}	1.13	

^aParameter x is dimensionless.

^b $E_{vJ} = \omega(v + 1/2) + [B - \alpha(v + 1/2)]J(J + 1)$.

^c $E_{vJ} = \omega(v + 1/2) + [B - DJ(J + 1)]J(J + 1)$.

states. Application of the third parameter x improves the standard deviation σ about two orders of magnitude relative to the equation based on the Simons-Parr-Finlan potential, and leads to the results better than these obtained from the two- and three-parameter Dunham expansions, respectively. The accuracy of calculations 0.0013 cm^{-1} for $^{12}\text{C}^{32}\text{S}$ and 0.008 cm^{-1} for $^{40}\text{Ar}_2$ molecules are of the order of experimental errors 0.001 and 0.01 quoted in Refs. [10] and [12]. It is worth mentioning here that the application of the second and following semiempirical parameters lowers the accuracy of calculations for the molecules considered, so only the modified formula containing one additional parameter x seems to be a physically well supported equation.

A look into (16) reveals that the proposed formula can be easily obtained by a formal substitution

$$D_0 \rightarrow D(J) = D_0[1 + xJ(J + 1)], \quad (22)$$

into the original equation (7), suggesting a rotational dependence of the dissociation energy. Because the semiempirical parameter x is negative for both the molecules considered, it is clear that the dissociation energy of rotating systems diminishes according to Eq. (22). This effect, for highly excited rotational states, leads to the possibility of *rotation-induced dissociation* of a molecule. Thus, the semiempirical parameter x may be viewed as an *indicator* of molecular susceptibility to rotational dissoci-

ation, which, according to our intuitive expectations, diminishes with rigidity of a molecule (see Table III).

The method presented in this work seems to have quite a lot in common with the method of summation of the divergent series arising from the perturbation approach to calculation of rovibrational energy of molecular systems. However, the main difference between our method and the other ones based for example on the Padé or Borel approximation [13–16] is that we start with the exact analytic solutions of the Schrödinger equation, which are next modified by continued-fraction expansion (17) of dissociation constant. So, our eigenvalues and eigenfunctions are not derived by summation of series obtained in the perturbation scheme. One of the most important advantages of the present approach is that it permits the wave function to be easily obtained by the substitution (22) into (9), so matrix elements of quantum-mechanical operators, the Franck-Condon factors and intensities of the rovibrational transitions, can be directly calculated [17]. The results of investigations of the aforementioned problems, as well as application of the method developed to molecules with octic and decadic molecular constants (for example, the HF molecule) will be presented in a separate paper.

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