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REVIEW PAPER

Studies on rovibrational energies in the ground state of nitrogen molecule using an algebraic approach

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Abstract: An Algebraic Method (AMr) is used to evaluate rotational spectrum constants and energies using a known accurate experimental/theoretical rovibrational energy subset of a given rovibrational band for a diatomic electronic state. The AMr has been applied to study the rovibrational energies up to $j = 40$ in vibrational bands from $v = 0$ to 8 of $X^1\Sigma_g^+$ electronic state of N_2 molecule. Calculations show that (i) the AMr not only reproduces the accurate experimental/theoretical energies, but also generates rotational constants and the E_{vj}'s of high-lying rovibtational excited states; (ii) The accuracies of the rotational spectrum constants and energies are uniquely determined by the quality of the input experimental/theoretical data.

Keywords: Algebraic method; Diatomic molecule; N_2 molecule; Rovibrational energy

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1. Introduction

Molecular rovibrational states and energies are indispensable for the understanding of spectrum structures and dynamical properties of a molecular system [1, 2]. Rotating molecules could cause molecular anisotropic phenomena, and molecular rovibrational states could strongly determine the collisional interactions and molecule–condensate couplings [3]. Accurate knowledge of complete rovibrational energies is vital for studying rovibrationally resolved reaction cross sections and reaction rates [4], is very useful for the assignment of molecular spectroscopic bands and possibly for investigating the nature of the resonances [5], and is the key for identifying abundant astronomical species. Highly excited rovibrational levels are essential for accurate quantitative studies of various processes, such as intramolecular vibrational redistribution, unimolecular reaction, and collision energy transfer [6].

Although there have been many experimental techniques such as resonance-enhanced multiphoton-ionization [7, 8], Fourier-transform spectroscopy [9], double resonance spectroscopy [10], and multistep laser excitation [11] spectroscopy etc., which are used to study the rovibrational states and energies for many diatomic molecules, most of the molecular rovibrational bands are incomplete, and particularly sparse data on the highly excited states.

Theoretically, many studies on rovibrational states have used a *variation-perturbation method* which been presented by Wolniewicz [12], although the theoretical data at low energies agree with the experimental values, the results at highly excited states are unreliable because of many approximations and corrections were considered incompletely such as nonadiabatic, relativistic, and radiative corrections. An expand *CSE* model has been performed on some electronic states of diatomic system [13, 14], which gives a good description of the experimental energies and line widths, but the precision of these characterizations has been limited by the quality of the existing experimental data, and there are weak rotational perturbations to be considered. Nowadays, many other different methods [15–18] are proposed for a diatomic system such as angular momentum insensitive quantum defect theory [15] and a hybrid computational technique combining discretization and basis set methods [16] etc. However, it is difficult to

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obtain accurate rovibrational energies and constants of the high-lying rotational excited states due to limitations of those theoretical methods.

In this study, an Algebraic Method (AMr) is provided to study the rotational spectrum constants and energies, just based on a group of known experimental rovibrational energy subsets of a vibrational band for a stable diatomic electronic state. Since an algebraic method (AM) has been proposed to generate accurate full vibrational spectrum $\{E_\upsilon\}$ for a stable diatomic electronic state in our previous studies [19, 20], we may call the above algebraic method used to generate accurate rovibrational energies $\{\varepsilon_{\upsilon j}\}_\upsilon$ as AMr, while the previous one [19, 20] for vibrational spectrum as AMv. Similarly, the AMr is also a hybrid method which makes use of the experimental accuracy and the theoretical advantages. The quality of the AMr rovibrational band is uniquely determined by the accuracy of the known experimental energy subset $[\varepsilon_{\upsilon j}]$. The lesser the error of the experimental subset $[\varepsilon_{\upsilon j}]$ is, the better the accuracy of the AMr rovibrational band $\{\varepsilon_{\upsilon j}\}_\upsilon$ will be.

2. An algebraic method for diatomic rovibrational energies

An analytical nonrelativistic rovibrational energy expression for a diatomic molecular state can be written using second order perturbation theory as [19]

$$\begin{aligned} E_{\upsilon j} = {} & E_\upsilon + \{j(j+1) - \Lambda^2\} \\ & \times \left[B_e - \alpha_e\left(\upsilon + \frac{1}{2}\right) + \gamma_e\left(\upsilon + \frac{1}{2}\right)^2 - \sum_{i=3}^{7}\eta_{ei}\left(\upsilon + \frac{1}{2}\right)^i\right] \\ & - \{j(j+1) - \Lambda^2\}^2 \\ & \times \left[\tilde{D}_e + \beta_e\left(\upsilon + \frac{1}{2}\right) - \sum_{k=2}^{7}\delta_{ek}\left(\upsilon + \frac{1}{2}\right)^k\right] + \cdots \end{aligned} \quad (1)$$

$$\varepsilon_{\upsilon j} = B_\upsilon\{j(j+1) - \Lambda^2\} - D_\upsilon\{j(j+1) - \Lambda^2\}^2 + \cdots \quad (2)$$

where Λ is the eigenvalue of the z component, L_z of the electronic angular momentum L whose z axis coincides with the molecular axis, and $\varepsilon_{\upsilon j} = E_{\upsilon j} - E_\upsilon$. One may extend Eq. (2) as

$$\begin{aligned} \varepsilon_{\upsilon j} = {} & B_\upsilon\{j(j+1) - \Lambda^2\} - D_\upsilon\{j(j+1) - \Lambda^2\}^2 \\ & + H_\upsilon\{j(j+1) - \Lambda^2\}^3 + L_\upsilon\{j(j+1) - \Lambda^2\}^4 \\ & + P_\upsilon\{j(j+1) - \Lambda^2\}^5 + Q_\upsilon\{j(j+1) - \Lambda^2\}^6 \\ & + S_\upsilon\{j(j+1) - \Lambda^2\}^7 + \cdots \end{aligned} \quad (3)$$

where the vibrational-dependent rotational constants (VDRC) are

$$B_\upsilon = B_e - \alpha_e\left(\upsilon + \frac{1}{2}\right) + \gamma_e\left(\upsilon + \frac{1}{2}\right)^2 - \sum_{i=3}^{7}\eta_{ei}\left(\upsilon + \frac{1}{2}\right)^i \quad (4)$$

$$D_\upsilon = \tilde{D}_e + \beta_e\left(\upsilon + \frac{1}{2}\right) - \sum_{k=2}^{7}\delta_{ek}\left(\upsilon + \frac{1}{2}\right)^k \quad (5)$$

$$H_\upsilon = h_e + \sum_{k=1}^{7}h_{ek}\left(\upsilon + \frac{1}{2}\right)^k \quad (6)$$

$$L_\upsilon = l_e + \sum_{k=1}^{7}l_{ek}\left(\upsilon + \frac{1}{2}\right)^k \quad (7)$$

$$P_\upsilon = p_e + \sum_{k=1}^{7}p_{ek}\left(\upsilon + \frac{1}{2}\right)^k \quad (8)$$

$$Q_\upsilon = q_e + \sum_{k=1}^{7}q_{ek}\left(\upsilon + \frac{1}{2}\right)^k \quad (9)$$

$$S_\upsilon = s_e + \sum_{k=1}^{7}s_{ek}\left(\upsilon + \frac{1}{2}\right)^k \quad (10)$$

Eq. (3) may be rewritten as an matrix form of

$$AX_\upsilon = \varepsilon_\upsilon \quad (11)$$

where the column solution matrix, the VDRC matrix, X_υ and the energy matrix ε_υ are

$$X_\upsilon = \begin{pmatrix} B_\upsilon \\ D_\upsilon \\ H_\upsilon \\ L_\upsilon \\ P_\upsilon \\ Q_\upsilon \\ S_\upsilon \end{pmatrix}, \quad \varepsilon_\upsilon = \begin{pmatrix} \varepsilon_{\upsilon j} \\ \varepsilon_{\upsilon, j+k} \\ \varepsilon_{\upsilon, j+l} \\ \varepsilon_{\upsilon, j+m} \\ \vdots \\ \vdots \\ \varepsilon_{\upsilon, j+q} \end{pmatrix} \quad (12)$$

and the matrix element of coefficient matrix A is $A_{jk} = [j(j+1) - \Lambda^2]^k, \quad k = 1, 2, 3, 4, 5, 6, 7$

For every known rovibrational band, $\{\varepsilon_{\upsilon j}; [j, j+k, j+l, \ldots, j+q]\}_\upsilon$, of a diatomic system, one may solve for a solution $X_\upsilon \equiv \{B_\upsilon,\ D_\upsilon,\ H_\upsilon,\ L_\upsilon,\ P_\upsilon,\ Q_\upsilon,\ S_\upsilon\}$ of Eq. (11). There is different VDRC X_υ for different rovibrational band $\{\varepsilon_{\upsilon j}\}_\upsilon$. Eq. (11) can be solved using standard algebraic method. However, the coefficient matrix $A_{jk} = [j(j+1) - \Lambda^2]^k$ for $K > 7$ and $j > 20$ such that the algebraic calculations of these elements performed using computers with 32-digit precision may introduce notable numerical errors in rotational constants. Usually, one may obtain an energy subset $[\varepsilon_{\upsilon j}]$ of a given rovibrational band $\{\varepsilon_{\upsilon j}\}_\upsilon$ using modern spectroscopic method, and may chose 7 energies out of the m energies in the known subset $[\varepsilon_{\upsilon j}]$ at a time. Therefore, Eq. (11) can be solved C_m^7 times. One can find a solution X_υ out of C_m^7 VDRC vectors X_υ's, and this X_υ should best satisfy the following convergence requirements for the rovibrational band $\{\varepsilon_{\upsilon j}\}_\upsilon$,

$$\Delta B_\upsilon \%|_\upsilon = 100 \times |B_{\upsilon,inp} - B_{\upsilon,AMr}|_\upsilon / B_{\upsilon,inp} \to 0 \tag{13}$$

$$\overline{\Delta\varepsilon(\text{expt}, AMr)_\upsilon} = \sqrt{\left[\frac{1}{m}\sum_j^m \left|\varepsilon_{\upsilon j,\text{expt}} - \varepsilon_{\upsilon j,AMr}\right|^2\right]} \to 0 \tag{14}$$

$$Error\_j\%\left[= \left|E_{\upsilon j}^{\text{expt}} - E_{\upsilon j}^{AMr}\right| \Big/ E_{\upsilon j}^{\text{expt}} \times 100\%\right] \to 0 \tag{15}$$

where $B_{\upsilon,inp}$ is the experimentally determined rotational constant, $\varepsilon_{\upsilon j,\text{expt}}$ are the known experimental rovibrational energies of a subset $[\varepsilon_{\upsilon j}]$ of a given rovibrational band. Since accurate experimental energies $\varepsilon_{\upsilon j,\text{expt}}$ include all the quantum effects and rovibrational information, the so obtained converged $X_\upsilon \equiv \{B_\upsilon, D_\upsilon, H_\upsilon, L_\upsilon, P_\upsilon, Q_\upsilon, S_\upsilon\}$ will be the true physical representation of the VDRC constants, and the rovibrational band $\{\varepsilon_{\upsilon j}\}_\upsilon$ evaluated using the converged VDRC X_υ and Eq. (3) will be the correct physical energies include many high-lying energies $\varepsilon_{\upsilon j}$'s which may be difficult to obtain experimentally.

3. Application and discussion

In this section, the AMr is applied to study the rovibrational bands $\{\varepsilon_{\upsilon j}\}_\upsilon$ for different vibrational levels of the electronic state $X^1\sum_g^+$ of N_2 molecule. The unit of all energies and spectrum constants are in cm^{-1}.

The AMr and the literature rotational spectrum constants VDRC of corresponding vibrational levels which from $\upsilon = 0$ to 8 for the electronic state are given in Table 1 respectively. It is seen from Table 1 that the comparisons show that the high order rotational constants such as $\{L_\upsilon, P_\upsilon, Q_\upsilon, S_\upsilon\}$ are not given in the literature for every rovibrational band, and the present AMr rotational constants $B_{\upsilon,AMr}$ have good agreement with those of the reference $B_{\upsilon,inp}$. For example, in the vibrational band $\upsilon = 5$, the difference between $B_{5,AMr} = 1.9021831\,\text{cm}^{-1}$ and $B_{5,inp} = 1.90177\,\text{cm}^{-1}$ is only 0.0004131 cm^{-1}, which all satisfy requirement in Eq. (13), and that the second-order constants D_υ have much small relative error of the calculated AMr $D_{\upsilon,AMr}$ with the literature values $D_{\upsilon,inp}$. The differences in D_υ may be partly due to the fact that in the literature, the value might be generated using an energy expansion of fewer terms in an expression similar to Eq. (2). However, the AMr can gives reliable VDRC contain high order data which may be difficult to obtain experimentally or theoretically for a given rovibrational band.

Table 2 gives these levels υ's input experimental rovibrational energies $E_{\upsilon j}^{\text{expt}}$, the present AMr rovibrational energies $E_{\upsilon j}^{AMr}$ those obtained using the AMr rotational spectrum constants listed in Table 1 respectively, and the relative percentage error $Error\_j\%$ in Eq. (15). Since the AMr generates a full set of rovibrational energies $\left\{E_{\upsilon j}^{AMr}\right\}$ from a subset of accurate experimental rovibrational energies $\left[E_{\upsilon j}^{\text{expt}}\right]$ which contains nearly all important quantum effects and rovibrational information for each vibrational band, and does not use any mathematical approximation and physical model in solving Eq (11)., the AMr vibrational energies $\left\{E_{\upsilon j}^{AMr}\right\}$ satisfy all convergence criteria described in Eqs. (13), (14) and (15). The results in Table 2 clearly demonstrate that every AMr energy $E_{\upsilon j}^{AMr}$ has agree with the corresponding experimental value. For all known rovibrational bands, the maximum percentage error is only 0.1993, and it's difference energy is 0.7207 cm^{-1} $(=|E_{0,13}^{\text{expt}} - E_{0,13}^{AMr}|)$ in $\upsilon = 0$, $J = 13$ state. All

Table 1 Molecular rotational constants for different vibrational states υ's of the $X^1\Sigma_g^+$ electronic state of N_2 molecule (unit: cm^{-1})

	B_υ		$D_\upsilon \cdot 10^6$	$D_\upsilon \cdot 10^5$	$H_\upsilon \cdot 10^{12}$	$H_\upsilon \cdot 10^7$	$L_\upsilon \cdot 10^{10}$	$P_\upsilon \cdot 10^{12}$	$Q_\upsilon \cdot 10^{16}$	$S_\upsilon \cdot 10^{19}$
υ	Ref [19]	AMr	Ref [19]	AMr	Ref [19]	AMr	AMr	AMr	AMr	AMr
0	1.9895776	2.01991	5.74137	39.4024	4.843	19.1315	−47.2062	6.10772	−38.7103	9.09998
1	1.9722073	1.96112	5.75094	−12.1756	4.621	−5.61496	12.0278	−1.33106	7.19910	−1.45307
2	1.9547829	1.94187	5.76152	−12.7032	4.400	−4.53016	4.94991	0.277110	−7.71940	2.88397
3	1.9373049	1.93220	5.77310	−2.51292	4.179	0.182260	−4.15701	0.890651	−6.83302	1.60633
4	1.9197723	1.91233	5.78569	−6.22785	3.957	−1.81731	0.501357	0.274265	−2.64617	0.614686
5	1.9021831	1.90177	5.79929	1.68652	3.736	1.69768	−7.06797	1.19704	−8.32929	1.87754
6	1.8845346	1.88129	5.81390	1.83874	3.515	1.96419	−6.22298	0.826569	−4.76301	0.926887
7	1.8668233	1.86926	5.82951	4.25499	3.293	2.53531	−8.51988	1.29975	−8.48177	1.83360
8	1.8490454	1.85186	5.84612	4.73640	3.072	2.43350	−6.73175	0.910250	−5.57073	1.15080

Table 2 Rovibrational energies of different vibrational states υ's of the $X^1\sum_g^+$ state of N_2 relative to $\upsilon = 0$, $J = 0$ (in cm^{-1})

J	$\upsilon = 0$			$\upsilon = 1$			$\upsilon = 2$		
	$E_{\upsilon j}^{\mathrm{expt}\,\mathrm{a}}$	$E_{\upsilon j}^{AMr\,\mathrm{b}}$	$Error\_j\,\%^{\mathrm{c}}$	$E_{\upsilon j}^{\mathrm{expt}t}$	$E_{\upsilon j}^{AMr}$	$Error\_j\,\%$	$E_{\upsilon j}^{\mathrm{expt}}$	$E_{\upsilon j}^{AMr}$	$Error\_j\,\%$
0		0.25		2329.95	2329.9500	0.000E+00	4631.19	4631.1900	0.000E+00
1		4.2883		2333.91	2333.8727	1.597E−03	4635.16	4635.0743	1.850E−03
2		12.3557		2341.75	2341.7210	1.240E−03	4642.85	4642.8457	9.227E−05
3		24.4354		$\underline{2353.50}$	2353.5000	0.000E+00	$\underline{4654.51}$	4654.5100	0.000E+00
4		40.5051		2369.27	2369.2168	2.247E−03	4670.22	4670.0747	3.110E−03
5		60.5406		2389.03	2388.8789	6.325E−03	4689.78	4689.5487	4.932E−03
6		84.5189		2412.68	2412.4937	7.722E−03	4713.26	4712.9408	6.773E−03
7		112.4220		2440.27	2440.0669	8.322E−03	4740.56	4740.2587	6.355E−03
8		144.2393		2471.77	2471.6019	6.800E−03	4771.82	4771.5081	6.537E−03
9		179.9692		2507.31	2507.0989	8.419E−03	4807.04	4806.6910	7.260E−03
10		219.6191		2546.77	2546.5548	8.452E−03	4846.06	4845.8058	5.245E−03
11		263.2043		2590.15	2589.9631	7.215E−03	4889.04	4888.8463	3.963E−03
12		310.7446		2637.43	2637.3151	4.355E−03	4935.94	4935.8021	2.793E−03
13	361.54	362.2607	1.993E−01	2688.64	2688.6005	1.468E−03	$\underline{4986.66}$	4986.6600	0.000E+00
14	$\underline{417.77}$	417.7700	2.278E−14	2743.79	2743.8088	6.855E−04	5041.36	5041.4049	8.915E−04
15	477.32	477.2829	7.772E−03	2802.92	2802.9308	3.859E−04	5099.91	5100.0228	2.211E−03
16	$\underline{540.80}$	540.8000	5.280E−14	$\underline{2865.96}$	2865.9600	0.000E+00	5162.43	5162.5027	1.407E−03
17	608.37	608.3118	9.573E−03	2932.78	2932.8934	3.866E−03	$\underline{5228.84}$	5228.8400	2.913E−14
18	679.71	679.8005	1.332E−02	3003.70	3003.7319	1.061E−03	5299.04	5299.0383	3.145E−05
19	754.91	755.2451	4.439E−02	$\underline{3078.48}$	3078.4800	1.237E−14	$\underline{5373.11}$	5373.1100	7.086E−14
20	834.66	834.6276	3.888E−03	3157.14	3157.1445	1.439E−04	5451.07	5451.0740	7.405E−05
21	$\underline{917.94}$	917.9400	3.940E−13	3239.84	3239.7327	3.313E−03	$\underline{5532.95}$	5532.9500	1.927E−13
22	$\underline{1005.19}$	1005.1900	5.871E−13	3326.27	3326.2495	6.152E−04	5618.79	5618.7461	7.812E−04
23	$\underline{1096.40}$	1096.4000	8.508E−13	3416.81	3416.6958	3.342E−03	$\underline{5708.44}$	5708.4400	4.802E−13
24	1191.52	1191.5970	6.461E−03	3511.02	3511.0663	1.318E−03	5801.99	5801.9506	6.790E−04
25	1290.54	1290.7870	1.914E−02	$\underline{3609.35}$	3609.3500	1.055E−13	$\underline{5899.10}$	5899.1000	1.136E−12
26	$\underline{1393.91}$	1393.9100	2.117E−12	3711.58	3711.5338	1.245E−03		5999.5651	
27	$\underline{1500.77}$	1500.7700	2.791E−12	$\underline{3817.61}$	3817.6100	1.795E−13		6102.8206	
28		1610.9410		$\underline{3927.59}$	3927.5900	2.326E−13		6208.0770	
29		1723.6509			4041.5244			6314.2204	
30		1837.6553		$\underline{4159.53}$	4159.5300	4.027E−13		6419.7681	
31		1951.1259			4281.8231			6522.8569	
32		2061.5932			4408.7554			6621.2940	
33		2166.0096			4540.8473			6712.7104	
34		2261.0302			4678.8093			6794.8726	
35		2343.6522			4823.5346			6866.2280	
36		2412.4110			4976.0423			6926.7846	
37		2469.3997			5137.3377			6979.4568	
38		2523.4732			5308.1449			7032.0451	
39		2595.1075			5488.4536			7100.0676	
40		2723.5266			5676.7972			7210.7143	
J	$\upsilon = 3$			$\upsilon = 4$			$\upsilon = 5$		
	$E_{\upsilon j}^{\mathrm{expt}}$	$E_{\upsilon j}^{AMr}$	$Error\_j\,\%$	$E_{\upsilon j}^{\mathrm{expt}}$	$E_{\upsilon j}^{AMr}$	$Error\_j\,\%$	$E_{\upsilon j}^{\mathrm{expt}}$	$E_{\upsilon j}^{AMr}$	$Error\_j\,\%$
0	6903.78	6903.7800	0.000E+00	9147.61	9147.6100	0.000E+00	11362.55	11362.550	0.000E+00
1	6907.60	6907.6445	6.441E−04	9151.42	9151.4349	1.628E−04	11366.38	11366.353	2.333E−04

Table 2 continued

J	$\upsilon = 3$			$\upsilon = 4$			$\upsilon = 5$		
	$E_{\upsilon j}^{\mathrm{expt}}$	$E_{\upsilon j}^{AMr}$	$Error\_j\,\%$	$E_{\upsilon j}^{\mathrm{expt}}$	$E_{\upsilon j}^{AMr}$	$Error\_j\,\%$	$E_{\upsilon j}^{\mathrm{expt}}$	$E_{\upsilon j}^{AMr}$	$Error\_j\,\%$
2	6915.24	6915.3741	1.939E−03	9158.98	9159.0862	1.159E−03	11373.95	11373.960	8.860E−05
3	6926.97	6926.9700	0.000E+00	9170.48	9170.5666	9.441E−04	11385.33	11385.369	3.439E−04
4	6942.46	6942.4341	3.736E−04	9185.88	9185.8800	0.000E+00	11400.58	11400.580	0.000E+00
5	6961.79	6961.7687	3.061E−04	9205.05	9205.0310	2.065E−04	11419.63	11419.592	3.318E−04
6	6985.04	6984.9768	9.055E−04	9228.12	9228.0243	1.037E−03	11442.50	11442.405	8.274E−04
7	7012.18	7012.0614	1.691E−03	9254.96	9254.8643	1.034E−03	11469.02	11469.020	0.000E+00
8	7043.15	7043.0257	1.765E−03	9285.64	9285.5544	9.220E−04	11499.52	11499.437	7.223E−04
9	7078.02	7077.8722	2.089E−03	9320.20	9320.0961	1.114E−03	11533.69	11533.657	2.848E−04
10	7116.76	7116.6022	2.217E−03	9358.54	9358.4889	5.458E−04	11571.73	11571.681	4.193E−04
11	7159.26	7159.2157	6.188E−04	9400.81	9400.7291	8.601E−04	11613.51	11613.510	0.000E+00
12	7205.71	7205.7100	0.000E+00	9446.81	9446.8100	0.000E+00	11659.19	11659.141	4.170E−04
13	7256.08	7256.0800	0.000E+00	9496.76	9496.7214	4.069E−04	11708.52	11708.572	4.471E−04
14	7310.22	7310.3178	1.338E−03	9550.45	9550.4500	0.000E+00	11761.73	11761.797	5.733E−04
15	7368.35	7368.4133	8.597E−04	9607.94	9607.9804	4.201E−04	11818.73	11818.809	6.686E−04
16	7430.20	7430.3550	2.086E−03	9669.31	9669.2957	1.475E−04	11879.46	11879.598	1.163E−03
17	7495.86	7496.1315	3.623E−03	9734.38	9734.3800	0.000E+00	11944.06	11944.156	8.051E−04
18	7565.53	7565.7341	2.698E−03	9803.36	9803.2198	1.430E−03	12012.37	12012.477	8.876E−04
19	7638.88	7639.1590	3.652E−03	9876.21	9875.8073	4.077E−03	12084.53	12084.559	2.372E−04
20	7716.41	7716.4100	1.974E−14	9952.77	9952.1427	6.303E−03	12160.41	12160.410	6.262E−14
21	7797.46	7797.5006	5.210E−04	10033.17	10032.237	9.300E−03	12240.05	12240.050	9.954E−14
22	7882.50	7882.4545	5.770E−04	10117.43	10116.114	1.301E−02	12323.51	12323.511	1.193E−05
23	7971.26	7971.3033	5.428E−04	10205.37	10203.809	1.530E−02	12410.84	12410.840	2.454E−13
24	8064.08	8064.0800	9.443E−14	10297.14	10295.372	1.717E−02	12501.76	12502.089	2.634E−03
25	8160.45	8160.8071	4.376E−03	10392.87	10390.856	1.938E−02	12596.74	12597.310	4.527E−03
26	8260.49	8261.4759	1.194E−02	10492.29	10490.313	1.884E−02	12694.95	12696.532	1.247E−02
27	8365.17	8366.0174	1.013E−02	10595.36	10593.781	1.491E−02	12797.12	12799.735	2.043E−02
28	8472.96	8474.2606	1.535E−02	10702.56	10701.255	1.219E−02	12902.74	12906.805	3.150E−02
29	8585.88	8585.8800	7.272E−13	10813.12	10812.669	4.173E−03	13013.16	13017.481	3.321E−02
30	8700.33	8700.3300	1.050E−12	10927.85	10927.850	1.533E−12	13126.59	13131.290	3.581E−02
31		8816.7706		11046.48	11046.480	2.192E−12	13243.66	13247.461	2.870E−02
32		8933.9880		11168.04	11168.040	3.123E−12	13364.84	13364.840	8.854E−12
33		9050.3187			11291.754			13481.811	
34		9163.5937			11416.531			13596.224	
35		9271.1216			11540.913			13705.378	
36		9369.7440			11663.039			13806.066	
37		9456.0058			11780.640			13894.760	
38		9526.4994			11891.086			13967.971	
39		9578.4627			11991.515			14022.897	
40		9610.7317			12079.072			14058.459	

J	$\upsilon = 6$			$\upsilon = 7$			$\upsilon = 8$		
	$E_{\upsilon j}^{\mathrm{expt}}$	$E_{\upsilon j}^{AMr}$	$Error\_j\,\%$	$E_{\upsilon j}^{\mathrm{expt}}$	$E_{\upsilon j}^{AMr}$	$Error\_j\,\%$	$E_{\upsilon j}^{\mathrm{expt}}$	$E_{\upsilon j}^{AMr}$	$Error\_j\,\%$
0	13548.74	13548.740	0.000E+00	15706.08	15706.080	0.000E+00	17834.49	17834.490	0.000E+00
1	13552.64	13552.503 1014E	1.014E−03	15709.88	15709.818	3.925E−04	17838.27	17838.194	4.287E−04
2	13560.04	13560.027 9481E	9.481E−05	15717.35	15717.294	3.559E−04	17845.67	17845.599	3.952E−04
3	13571.34	13571.313	1.974E−04	15728.49	15728.505	9.771E−05	17856.75	17856.706	2.473E−04

Table 2 continued

J	$\upsilon = 6$			$\upsilon = 7$			$\upsilon = 8$		
	$E_{\upsilon j}^{\mathrm{expt}}$	$E_{\upsilon j}^{AMr}$	$Error\_j\,\%$	$E_{\upsilon j}^{\mathrm{expt}}$	$E_{\upsilon j}^{AMr}$	$Error\_j\,\%$	$E_{\upsilon j}^{\mathrm{expt}}$	$E_{\upsilon j}^{AMr}$	$Error\_j\,\%$
4	13586.36	13586.360	0.000E+00	15743.45	15743.450	0.000E+00	17871.51	17871.510	0.000E+00
5	13605.33	13605.167	1.197E−03	15762.19	15762.126	4.087E−04	17890.06	17890.009	2.847E−04
6	13627.94	13627.735	1.507E−03	15784.53	15784.530	0.000E+00	17912.21	17912.200	5.349E−05
7	13654.26	13654.064	1.438E−03	15810.62	15810.662	2.640E−04	17938.13	17938.082	2.678E−04
8	13684.47	13684.156	2.295E−03	15840.52	15840.520	0.000E+00	17967.67	17967.652	9.761E−05
9	13718.27	13718.015	1.862E−03	15874.10	15874.105	2.874E−05	18000.96	18000.912	2.687E−04
10	13755.99	13755.643	2.525E−03	15911.41	15911.416	3.459E−05	18037.86	18037.860	0.000E+00
11	13797.49	13797.044	3.233E−03	15952.44	15952.453	7.905E−05	18078.58	18078.499	4.505E−04
12	13842.63	13842.221	2.953E−03	15997.26	15997.215	2.833E−04	18122.87	18122.828	2.303E−04
13	13891.62	13891.176	3.195E−03	16045.72	16045.699	1.323E−04	18170.90	18170.849	2.780E−04
14	13944.28	13943.908	2.667E−03	16097.90	16097.900	1.628E−06	18222.62	18222.561	3.218E−04
15	14000.72	14000.414	2.189E−03	16153.81	16153.810	0.000E+00	18278.01	18277.961	2.663E−04
16	14060.90	14060.686	1.522E−03	16213.42	16213.420	0.000E+00	18337.08	18337.045	1.903E−04
17	14124.88	14124.716	1.162E−03	16276.83	16276.719	6.795E−04	18399.80	18399.807	3.706E−05
18	14192.59	14192.491	6.942E−04	16343.90	16343.699	1.229E−03	18466.24	18466.240	1.649E−14
19	14264.00	14264.000	0.000E+00	16414.62	16414.354	1.618E−03	18536.35	18536.339	6.025E−05
20	14339.23	14339.230	0.000E+00	16489.12	16488.688	2.621E−03	18610.10	18610.100	1.637E−14
21	14418.15	14418.174	1.648E−04	16567.24	16566.713	3.180E−03	18687.50	18687.525	1.319E−04
22	14500.83	14500.830	0.000E+00	16649.17	16648.458	4.274E−03	18768.62	18768.620	3.246E−14
23	14587.25	14587.206	2.999E−04	16734.78	16733.966	4.866E−03	18853.40	18853.400	4.847E−14
24	14677.32	14677.320	2.075E−14	16824.13	16823.290	4.995E−03	18941.84	18941.884	2.318E−04
25	14771.17	14771.198	1.870E−04	16917.15	16916.489	3.908E−03	19033.87	19034.092	1.165E−03
26	14868.87	14868.870	2.048E−14	17013.61	17013.610	1.432E−13	19129.62	19130.035	2.168E−03
27	14970.26	14970.363	6.885E−04	17113.98	17114.663	3.991E−03	19229.02	19229.701	3.540E−03
28	15075.16	15075.682	3.463E−03	17218.04	17219.583	8.962E−03	19332.08	19333.029	4.911E−03
29	15183.91	15184.788	5.780E−03	17325.72	17328.180	1.420E−02	19438.67	19439.881	6.230E−03
30	15296.27	15297.563	8.453E−03	17436.97	17440.071	1.778E−02	19548.95	19549.994	5.339E−03
31	15412.53	15413.771	8.049E−03	17552.26	17554.605	1.336E−02	19662.93	19662.930	1.239E−13
32	15533.00	15533.000	2.157E−13	17670.77	17670.770	9.256E−12		19778.017	
33		15654.607			17787.107			19894.280	
34		15777.649			17901.628			20010.380	
35		15900.826			18011.773			20124.564	
36		16022.431			18114.422			20234.646	
37		16140.340			18206.022			20338.046	
38		16252.052			18282.872			20431.915	
39		16354.819			18341.661			20513.405	
40		16445.921			18380.358			20580.130	

[a] Experimental rovibrational energies from Ref [20]

[b] Calculated using the algebraic method (AMr)

[c] The percent error $Error\_j\,\%$ in Eq. (15)

AMr energies in each band satisfy the requirement in Eq. (14).

Since Table 2 shows that the measured data and the theoretical energies agree with each other perfectly, the predicted unknown or high-lying rovibrational energies (up to j = 40) bear the true physical nature of the band. For example, the rotational states of j = 0–12 in $\upsilon = 0$ are not available experimentally, but the AMr predicts that these energies. If, under the same conditions as those in [21], the energies are measured, the relative percentage error $Error\_j\,\%$ should be less than 0.03 unless there are notable errors in the experimental energies used to predict the $E_{\upsilon j}^{AMr}$.

Table 2 also indicates that there are 7 energies with underline in every rovibrational band, the fact is that these energies are the best set which would be good to list important quantum effects and rovibrational information for calculating the best solution $\{B_\upsilon, D_\upsilon, H_\upsilon, L_\upsilon, P_\upsilon, Q_\upsilon, S_\upsilon\}$. Since there are no mathematical approximation and physical model used in the algebraic approach, the AMr study not only can reproduces accurate experimental energies but also may gives accurate energies of high rovibrational states which might be difficult to obtain experimentally or theoretically. Table 2 clearly shows that the AMr energies have excellent agreement with the known experimental rovibrational energies, and gives the high-lying rovibrational energies for each vibrational band.

4. Conclusions

In this study, an algebraic approach (AMr) is proposed to study diatomic molecular rotational constants and rovibrational energies based on a set of reliable physical criterion and a subset of accurate limited experimental/theoretical rovibrational energies which contain important quantum effects and rovibrational information for a given rovibrational band of a diatomic system. The accuracy of the AMr constants and energies is uniquely dependent on the quality of the literature experimental/theoretical data. The AMr generates accurate rotational constants and energies using a standard algebraic approach, and it not only reproduces the input energies but also generates high-lying rovibrational energies. The study of the ground state $X^1\Sigma_g^+$ of N_2 molecule shows that the AMr low-order constants have excellent agreement with limited experimental constants, and the AMr study can give the correct high-lying rovibrational spectrum which, in addition to reproducing all input data, includes those energies of more excited rotational states that may not be easily determined experimentally or theoretically. Therefore, as long as a subset of accurate rovibrational energies of a given rovibrational band can be obtained using modern experimental technique or popular quantum method, one may easily generate reliable corresponding constants and spectrum by using the AMr approach as a quick and simple method. The AMr approach can be taken as a useful alternative to evaluate reliable rovibrational energies particularly for those of high excited rotational states which may be difficult to obtain experimentally or theoretically.

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