LETTER TO THE EDITOR

SU$_q$(1, 1) description of vibrational molecular spectra

Dennis Bonatsos†, E N Argyres† and P P Raychev‡

† Institute of Nuclear Physics, NCSR 'Demokritos', GR-15310 Aghia Paraskevi, Attiki, Greece
‡ Institute for Nuclear Research and Nuclear Energy, 1784 Sofia, Bulgaria

Abstract. The SU$_q$(1, 1) quantum algebra is used for the description of vibrational spectra of diatomic molecules, for which SU(1, 1) is used in the classical approach. While in the classical case only the first two terms of the empirical Dunham expansion occur, in the quantum case all terms are obtained. The improved description of the empirical data is obtained with q being a phase (and not a real number), in agreement with the situation occurring in the q-rotor (having the symmetry SU$_q$(2)), used for the description of rotational spectra of molecules and nuclei.

Quantum algebras [1–5], which mathematically are Hopf algebras [6], have been introduced with the aim of solving the quantum Yang–Baxter equation [7]. More recently, the realization of the quantum algebra SU$_q$(2) in terms of the q-analogue of the quantum harmonic oscillator [8–10] has initiated much work in this field [11–13]. The SO$_q$(3) quantum algebra has been found useful in describing the q-deformed spin-1 Heisenberg chain [14], while the q-rotor (the Hamiltonian of which is proportional to the second-order Casimir operator of SU$_q$(2)) has been found suitable for the description of rotational spectra of deformed nuclei [15, 16], superdeformed nuclei [17] and diatomic molecules [18]. The success of the q-rotor in describing rotational spectra has been understood [16] to be due to its equivalence to the variable moment of inertia (VMI) model [19].

On the other hand, the Morse potential [20], which offers a widely accepted description of vibrational spectra of diatomic molecules [21], has been known to have the symmetry SU(1, 1) [22–28]. Vibrational spectra are then described by a Hamiltonian which is proportional to the second-order Casimir operator of SU(1, 1). It is therefore of interest to check the consequences and the physical content of generalizing SU(1, 1) into the quantum algebra SU$_q$(1, 1), which is already known [29, 30].

In the classical case [28] the SO(2, 1) generators satisfy the commutation relations

$$[K_1, K_2] = -iK_3 \qquad [K_2, K_3] = iK_1 \qquad [K_3, K_1] = iK_2. \qquad (1)$$

Defining

$$K_+ = K_1 + iK_2 \qquad K_- = K_1 - iK_2 \qquad K_3 = K_z \qquad (2)$$

one obtains the SU(1, 1) commutation relations

$$[K_z, K_\pm] = \pm K_\pm \qquad [K_+, K_-] = -2K_z. \qquad (3)$$

The generators of SU(1, 1) accept the following boson representation [24]

$$K_+ = a_1^+ a_2^+ \qquad K_- = a_1 a_2 \qquad K_z = \tfrac{1}{2}(a_1^+ a_1 + a_2^+ a_2 + 1) \tag{4}$$

where a_1^+, a_1, a_2^+, a_2 satisfy usual boson commutation relations.

The second-order Casimir operator of SO(2, 1) is [28]

$$C_2[SO(2, 1)] = -(K_1^2 + K_2^2 - K_3^2). \tag{5}$$

If N is the number of excitation quanta given to the system (which is equal to the total number of bosons in the case of the boson representation) and v is the vibrational quantum number, the eigenvalues of the Casimir operator are given

$$C_2[SO(2, 1)]|N\omega\rangle = \tfrac{1}{4}\omega(\omega + 2)|N\omega\rangle \tag{6}$$

where the quantum number ω is given by

$$v = \tfrac{1}{2}(N - \omega). \tag{7}$$

N is related to the maximum number of vibrational states by

$$N = 2v_{max} \qquad \text{or} \qquad N = 2v_{max} + 1. \tag{8}$$

The vibrational spectrum is given by

$$E(N, \omega) = E_0 - A\langle C_2[SO(2, 1)]\rangle = E_0 - \frac{A}{4}\omega(\omega + 2) \tag{9}$$

where by $\langle \rangle$ we denote the eigenvalue of the enclosed operator. Using (7) this can be rewritten as

$$E(N, v) = E_0 - A\frac{N^2 - 1}{4} + AN(v + \tfrac{1}{2}) - A(v + \tfrac{1}{2})^2. \tag{10}$$

Rotational–vibrational molecular spectra are usually described in terms of the Dunham expansion [31, 32]

$$E(v, J) = \sum_{ik} Y_{ik}(v + \tfrac{1}{2})^i(J(J + 1))^k \tag{11}$$

where J is the angular momentum and Y_{ik} are the Dunham coefficients, which are fitted to experiment. (For empirical values of Dunham coefficients for several molecules see [33].) Ignoring rotation (i.e. ignoring the rotational bands built on the vibrational bandheads) one obtains the vibrational spectrum

$$E(v) = \sum_i Y_{i0}(v + \tfrac{1}{2})^i. \tag{12}$$

We remark that (10) corresponds to the first two non-vanishing powers of $(v + \tfrac{1}{2})$ contained in the Dunham expansion. The same result is obtained by solving [34] the Schrödinger equation for the Morse potential [20]. It is also obtained in the O(4) limit of the vibron model [35] for diatomic molecules, which has been extended to triatomic molecules [36, 37] and to higher-order terms [38]. The ratio Y_{20}/Y_{10} (the anharmonicity constant [22]) is in the present case proportional to $1/N$, a result similar to the one obtained in the vibron model [35].

In the quantum case, the generators of $SU_q(1, 1)$ satisfy the commutation relations [29, 30]

$$[K_0, K_\pm] = \pm K_\pm \qquad [K_+, K_-] = -[2K_0] \tag{13}$$

where q-numbers are defined by

$$[x] = \frac{q^x - q^{-x}}{q - q^{-1}}.$$ (14)

If q is real ($q = e^\tau$, where τ is real), q-numbers take the form

$$[x] = \frac{\sinh(\tau x)}{\sinh(\tau)}$$ (15)

while in the case that q is a phase ($q = e^{i\tau}$ with τ real), q-numbers are

$$[x] = \frac{\sin(\tau x)}{\sin(\tau)}.$$ (16)

In the limit $q \to 1$, relations (13) tends to the classical case (3).

The generators of $SU_q(1, 1)$ accept the following boson representation [29, 30]

$$K_+ = a_1^+ a_2^+ \qquad K_- = a_1 a_2 \qquad K_0 = \tfrac{1}{2}(N_1 + N_2 + 1)$$ (17)

where the bosons a_i^+, a_i ($i = 1, 2$) satisfy the relation

$$a_i a_i^+ - q a_i^+ a_i = q^{-N_i}$$ (18)

and

$$[N_i, a_i^+] = a_i^+ \qquad [N_i, a_i] = -a_i.$$ (19)

The second-order Casimir operator of $SU_q(1, 1)$ is [30]

$$C_2[SU_q(1, 1)] = [K_0][K_0 - 1] - K_+ K_- = [K_0][K_0 + 1] - K_- K_+.$$ (20)

Its eigenvalues are given in [30] as

$$C_2[SU_q(1, 1)]|\kappa\mu\rangle = [\kappa][\kappa - 1]|\kappa\mu\rangle$$ (21)

where

$$\kappa = \frac{1 + |n_1 - n_2|}{2} \qquad \mu = \frac{1 + n_1 + n_2}{2}$$ (22)

since the basis has the form $|\kappa\mu\rangle = |n_1\rangle|n_2\rangle$, with [30]

$$|n_i\rangle = \frac{1}{\sqrt{[n_i]!}} (a_i^+)^{n_i}|0\rangle$$ (23)

where the definition $[n]! = [1][2]\ldots[n]$ holds. The vibrational spectrum is given by

$$H = E_0 - A C_2[SU_q(1, 1)].$$ (24)

Using the relation $|n_1 - n_2| = \omega + 1$ one obtains

$$E(N, \omega) = E_0 - A\left[\frac{\omega}{2}\right]\left[\frac{\omega + 2}{2}\right]$$ (25)

which in the limit $q \to 1$ tends to (9). Using, further, (7) one has

$$E(N, v) = E_0 - A\left[v - \frac{N}{2}\right]\left[v + 1 - \frac{N}{2}\right]$$ (26)

which is the q-generalization of (10).

It is interesting to check how (26) is related to (10) and to the Dunham expansion (12). This can be done by replacing the q-numbers in (26) by their equals from (15) (or (16)), subsequently taking the Taylor expansions of the hyperbolic (or trigonometric) functions, collecting together terms containing the same power of $(v+\frac{1}{2})$, and finally summing up the coefficients of each power of $(v+\frac{1}{2})$. In the case of real q the final result is

$$
\begin{aligned}
E(N,v) = E_0 + \frac{A}{\sinh(\tau)^2}[& -\tfrac{1}{2}(\cosh(\tau)-\cosh(\tau N)) + \tau\sinh(\tau N)(v+\tfrac{1}{2}) \\
& -\tau^2\cosh(\tau N)(v+\tfrac{1}{2})^2 + \tfrac{2}{3}\tau^3\sinh(\tau N)(v+\tfrac{1}{2})^3 - \tfrac{1}{3}\tau^4\cosh(\tau N)(v+\tfrac{1}{2})^4 \\
& + \tfrac{2}{15}\tau^2\sinh(\tau N)(v+\tfrac{1}{2})^5 - \tfrac{2}{45}\tau^6\cosh(\tau N)(v+\tfrac{1}{2})^6 + \ldots]
\end{aligned} \tag{27}
$$

while in the case of q being a phase the final result is

$$
\begin{aligned}
E(N,v) = E_0 + \frac{A}{\sin(\tau)^2}[& -\tfrac{1}{2}(\cos(\tau)-\cos(\tau N)) + \tau\sin(\tau N)(v+\tfrac{1}{2}) \\
& -\tau^2\cos(\tau N)(v+\tfrac{1}{2})^2 + (-\tfrac{2}{3})\tau^3\sin(\tau N)(v+\tfrac{1}{2})^3 - (-\tfrac{1}{3})\tau^4\cos(\tau N)(v+\tfrac{1}{2})^4 \\
& + \tfrac{2}{15}\tau^5\sin(\tau N)(v+\tfrac{1}{2})^5 - \tfrac{2}{45}\tau^6\cos(\tau N)(v+\tfrac{1}{2})^6 + \ldots].
\end{aligned} \tag{28}
$$

The following remarks can now be made:

(i) Both (27) and (28) reduce to (10) in the limit $q \to 1$ ($\tau \to 0$).

(ii) While (10) contains only the first two non-vanishing powers of $(v+\frac{1}{2})$, (27) and (28) contain all possible powers. Thus (27) and (28) correspond to the full Dunham expansion (12). However, while the Y_{ik} coefficients in (12) are not related to each other, their counterparts in (27) (or (28)) are interrelated, since they all depend on τ and N.

(iii) The anharmonicity constant (i.e. the ratio Y_{20}/Y_{10}), which in the classical case (10) is fixed to $-1/N$, is here $-\tau/\sinh(\tau N)$ (in (27)) or $-\tau/\sin(\tau N)$ (in (28)). Therefore the anharmonicity constant is not fixed by N (or, equivalently through (8), by v_{max}). This extra freedom is useful when one attempts to fit experimental data, as will be demonstrated below.

We now attempt the briefest possible comparison with experimental data. We consider the case of H_2 in its $X\,^1\Sigma_g^+$ state, which has been considered in the case of the vibron model [35] as well. Since in this state of H_2 it is experimentally known that $v_{max} = 14$, from (8) one finds that $N = 28$ or $N = 29$. As in the case of the vibron model [35], we consider $N = 29$. ($N = 28$ also gives very similar results.) As data we use the results for the vibrational levels obtained through the Rydberg–Klein–Rees (RKR) method [39] reported in [40]. We first fitted the data using the classical expression (10). When attempting to use (27) one is driven to failure, while (28) gives a result much better than (10), as can be seen in table 1, where the quality of the fits is indicated by the quantity

$$
\sigma = \sqrt{\frac{1}{M} \sum_{v_{min}}^{v_{max}} (E_v(\exp) - E_v(\mathrm{th}))^2} \tag{29}
$$

where M is the number of states used in the fit. Thus the data indicate that q should be a phase, and not a real number. This conclusion is the same as the one drawn from the comparison of the q-rotor (having the symmetry $SU_q(2)$) with the rotational spectra of deformed [15, 16] and superdeformed [17] nuclei, as well as to the rotational spectra of diatomic molecules [18]. It should also be pointed out that the parameter τ remains small in all cases.

Table 1. Vibrational spectra in the $X\,^1\Sigma_g^+$ state of H_2. v is the vibrational quantum number, E_v (RKR) are the empirical data [40] (in units of cm^{-1}), E_v (th-q) are the theoretical predictions in the quantum case (26), while E_v (th-c) are the predictions in the classical case (10). The parameters of the fits are shown in the lower part of the table. In both cases N has been fixed to 29, so that only E_0, A and τ have been used as free parameters. σ is the RMS deviation defined in (29).

v	E_v (RKR)	E_v (th-q)	E_v (th-c)
0	2 170	2 599	773
1	6 331	6 255	5 684
2	10 257	9 936	10 232
3	13 952	13 586	14 416
4	17 420	17 147	18 235
5	20 662	20 563	21 692
6	23 676	23 782	24 784
7	26 458	26 753	27 512
8	29 001	29 429	29 877
9	31 294	31 768	31 878
10	33 320	33 734	33 515
11	35 057	35 297	34 788
12	36 472	36 430	35 698
13	37 521	37 117	36 244
14	38 143	37 348	36 425
N		29	29
E_0		37 290	36 380
A		230.3	181.9
τ		0.0626	0
σ		369	933

In conclusion, we have shown that the quantum algebra $SU_q(1,1)$ can be used for the description of vibrational spectra of diatomic molecules, in the same way as the quantum algebra $SU_q(2)$ can be used for the description of rotational spectra of molecules [18] and nuclei [15–17]. The second-order Casimir operator of $SU_q(1,1)$ corresponds to a special form of the Dunham expansion containing all powers of $(v+\frac{1}{2})$, while in the classical case of $SU(1,1)$ only the first two non-vanishing powers of $(v+\frac{1}{2})$ are obtained [22–28].

In the classical case the relation between the second-order Casimir operator of $SO(2,1)$ and the eigenvalues of the Morse potential is known [28]. It is interesting to find the relation between the second-order Casimir operator of $SU_q(1,1)$ and the eigenvalues of the Morse potential in the quantum case. For the latter, the q-Schrödinger equation [41] for the Morse potential should be solved. In addition, it is worth evaluating dissociation rates for the Morse potential in the quantum case, by generalizing the procedure outlined in [42]. It is also of interest to study the q-generalization of the U(3) limit of the vibron model for diatomic molecules [35], since its O(4) limit is equivalent to the SO(2,1) approach of [28], which was generalized here. This opens the question of studying in addition the q-generalization of the vibrational, rotational and γ-unstable limits of the interacting Boson model (IBM) of nuclear structure ([43], for recent overviews see [44, 45]). Work in these directions is in progress.

References

[1] Kulish P P and Reshetikhin N Yu 1981 *Zapiski Semenarov LOMI* **101** 101
[2] Sklyanin E K 1982 *Funct. Anal. Appl.* **16** 262
[3] Drinfeld V G 1986 *Quantum Groups, Proc. Int. Congr. of Mathematics* ed A M Gleason (Providence, RI: American Mathematical Society) p 798
[4] Jimbo M 1986 *Lett. Math. Phys.* **11** 247
[5] Witten E 1990 *Nucl. Phys.* B **330** 285
[6] Abe E 1980 *Hopf Algebras* (Cambridge: Cambridge University Press)
[7] Jimbo M 1989 *Braid Group, Knot Theory and Statistical Mechanics* ed C N Yang and M L Ge (Singapore: World Scientific) p 111
[8] Biedenharn L C 1989 *J. Phys. A: Math. Gen.* **22** L873
[9] Macfarlane A J 1989 *J. Phys. A: Math. Gen.* **22** 4581
[10] Jannussis A 1990 *Preprint* University of Patras
[11] Ng Y J 1990 *J. Phys. A: Math. Gen.* **23** 1023
[12] Song X C 1990 *J. Phys. A: Math. Gen.* **23** L821
[13] Yan H 1990 *J. Phys. A: Math. Gen.* **23** L1155
[14] Batchelor M T, Mezincescu L, Nepomechie R I and Rittenberg V 1990 *J. Phys. A: Math. Gen.* **23** L141
[15] Raychev P P, Roussev R P and Smirnov Yu F 1990 *J. Phys. G: Nucl. Phys.* **16** L137
[16] Bonatsos D, Argyres E N, Drenska S B, Raychev P P, Roussev R P and Smirnov Yu F 1990 *Phys. Lett.* **251B** 477
[17] Bonatsos D, Drenska S B, Raychev P P, Roussev R P and Smirnov Yu F 1990 *Preprint* NCSR Demokritos
[18] Bonatsos D, Raychev P P, Roussev R P and Smirnov Yu F 1990 *Chem. Phys. Lett.* **175** 300
[19] Mariscotti M A J, Scharff-Goldhaber G and Buck B 1969 *Phys. Rev.* **178** 1864
[20] Morse P M 1929 *Phys. Rev.* **34** 57
[21] Herzberg G 1950 *Molecular Spectra and Molecular Structure Spectra of Diatomic Molecules* vol 1 (Toronto: Van Nostrand)
[22] Levine R D 1983 *Chem. Phys. Lett.* **95** 87
[23] Wulfman C E and Levine R D 1983 *Chem. Phys. Lett.* **97** 361
[24] Alhassid Y, Iachello F and Gürsey F 1983 *Chem. Phys. Lett.* **99** 27
[25] Alhassid Y, Gürsey F and Iachello F 1983 *Ann. Phys.* **148** 346
[26] Wulfman C E and Levine R D 1984 *Chem. Phys. Lett.* **104** 9
[27] Brajamani S and Singh C A 1990 *J. Phys. A: Math. Gen.* **23** 3421
[28] Lee D J, Shin K J and Kim S K 1990 *Chem. Phys. Lett.* **175** 87
[29] Kulish P P and Damaskinsky E V 1990 *J. Phys. A: Math. Gen.* **23** L415
[30] Ui H and Aizawa N 1990 *Mod. Phys. Lett.* A **5** 237
[31] Dunham J L 1932 *Phys. Rev.* **41** 721
[32] Ogilvie J F and Tipping R H 1983 *Int. Rev. Phys. Chem.* **3** 3
[33] Miller C E, Finney A A and Inman F W 1973 *Atomic Data* **5** 1
[34] Flügge S 1974 *Practical Quantum Mechanics* (Berlin: Springer)
[35] Iachello F and Levine R D 1982 *J. Chem. Phys.* **77** 3046
[36] van Roosmalen O S, Iachello F, Levine R D and Dieperink A E L 1983 *J. Chem. Phys.* **79** 2515
[37] van Roosmalen O S, Benjamin I and Levine R D 1984 *J. Chem. Phys.* **81** 5986
[38] Kim S K, Cooper I L and Levine R D 1986 *Chem. Phys.* **106** 1
[39] Rydberg R 1931 *Z. Phys.* **73** 376
Klein O 1932 *Z. Phys.* **76** 226
Rees A L G 1947 *Proc. Phys. Soc.* **59** 998
[40] Weissman S, Vanderslice J T and Battino R 1963 *J. Chem. Phys.* **39** 2226
[41] Minahan J A 1990 *Mod. Phys. Lett.* A **5** 2625
[42] Alhassid Y, Engel J and Iachello F 1986 *Phys. Rev. Lett.* **57** 9
[43] Arima A and Iachello F 1976 *Ann. Phys.* **99** 253; 1978 *Ann. Phys.* **111** 201; 1979 *Ann. Phys.* **123** 468
[44] Iachello F and Arima A 1987 *The Interacting Boson Model* (Cambridge: Cambridge University Press)
[45] Bonatsos D 1988 *Interacting Boson Models of Nuclear Structure* (Oxford: Clarendon)