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Revisiting the quantum group symmetry of diatomic molecules

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Abstract. We propose a q-deformed model of anharmonic vibrations in diatomic molecules. We study the applicability of the model to the phenomenological Dunham expansion by comparison with experimental data. In contrast with other applications where it is difficult to find a physical interpretation for the deformation parameter, q, in our analysis it is directly related to the third-order coefficient in the Dunham expansion. We study the consistency of the parameters that determine the q-deformed system by comparing them with the vibrational terms fitted to 161 electronic states of diatomic molecules. We show how to include both positive and negative anharmonicities in a simple and systematic way.

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1 Introduction

Q-algebras were originally conceived as a means of solving the quantum Yang–Baxter equation [1], but in the last decade a great number of applications have been found in diverse areas of physics, ranging from the deformation of conformal-field theories [2] to optics [3] and nuclear and molecular spectroscopy [4–6]. On the other hand, algebraic models have been proposed and applied systematically in many fields, including in a relevant way the study of nuclei and molecules [7,8]. This kind of approach has simplified the n-body problem dramatically and has given rise to numerous new insights including, for example, a supersymmetric description of quartets of nuclei and the formulation of tractable models of polyatomic molecules [9]. In the latter case these methods combine the use of Lie-algebraic and discrete-symmetry techniques, which respectively describe the interactions and the global symmetry of these systems. In particular, the $su(2)$ algebra has been proposed as a basic algebraic structure, given its connection to the Morse potential [8]. This permits an algebraic treatment of anharmonicities, much in the same fashion as the harmonic-oscillator algebra is used in connection with harmonic motion. This phenomenon becomes increasingly important as vibrations are excited to states which are not necessarily higher in energy but correspond to overtone and combination modes. While the Morse potential leads to a fairly good approximation to the spectroscopic properties of most diatomic molecules, it has some limitations. For example, its energy eigenvalues contain only quadratic corrections to the equally-spaced harmonic behaviour, while terms of higher-order are often required in the phenomenological Dunham expansion [10] to produce an accurate fit to the observed vibrational energies.

While very useful, the Dunham expansion constitutes a rather complex theoretical framework. The potential is assumed to be expressible as a series expansion in powers of the relative displacement coordinate. The coefficients appearing in this expansion of the potential can then be related to the Dunham coefficients for the rotation-vibration energies. Wave functions can then be calculated by means of a recursive procedure [10,11]. This methodology, however, usually involves a very large number of independent parameters and other methods are often simpler to apply and involve less parameters. See, for example, the recent paper [12], where it is shown that a modified Lennard-Jones potential, involving 16 fitted parameters, gives results comparable to an unconstrained 62-parameter Dunham expansion. It is thus an interesting problem to see whether an algebraic framework can be constructed in such a way as to include higher order corrections, with as few parameters as possible, while maintaining its simplicity and providing a simpler way to determine the Hamiltonian and corresponding wave functions.

In this paper we investigate an extension of the $su(2)$ framework, by considering the q-deformation of the Morse Hamiltonian. We then test our ideas by comparing a series expansion of the q-Morse energy expression with

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experimental Dunham expansions for a large number of molecules. As a first step we restrict our analysis to test the consistency of this q-extension with respect to the Dunham expansion. A subsequent and more delicate test should include the evaluation of the q-deformed Morse vibrational eigenfunctions and the calculation of dipole intensities in the same fashion as for the $su(2)$ model. We wish to emphasize that, while other studies have considered the deformation of both vibrational and rotational degrees of freedom in molecules [4–6], our approach is simpler and more basic as we aim to generalise an already established model for vibrational spectroscopy that is not restricted to diatomic molecules but can be extended to polyatomic systems, by q-deforming the fundamental bond interaction. In addition, we test the q-deformation extensively by comparing with the Dunham parameters of 161 electronic states of diatomic molecules.

We now discuss the traditional treatment of anharmonic vibrations using the Dunham expansion.

2 Molecular anharmonic vibrations

The phenomenological description of the vibrational energy of diatomic molecules in a given electronic state is given by Dunham's expansion [10], traditionally written as:

$$E_v = hc\omega_e\left(v+\tfrac{1}{2}\right) - hc\omega_e x_e\left(v+\tfrac{1}{2}\right)^2 + hc\omega_e y_e\left(v+\tfrac{1}{2}\right)^3 + \ldots \qquad (1)$$

where c is the speed of light in vacuum and v is the vibrational quantum number. The vibrational molecular constants ω_e, x_e and y_e are obtained by fitting the potential curve to the experimental spectral data, $x_e \ll 1$, $y_e \ll x_e$. While the constant x_e is nearly always positive, the constant y_e can be positive or negative and is often very small [13]. The terms of quadratic and higher order with respect to $(v + 1/2)$ in expansion (1) account for the anharmonic character of molecular vibrations and the constant x_e is called the anharmonicity constant.

The expansion (1) is part of the more general Dunham description of the rotational-vibrational energy of molecules [10,14]

$$E_{v,J} = \sum_{l,m} y_{lm}\left(v+\tfrac{1}{2}\right)^l \{J(J+1)\}^m \qquad (2)$$

where J is the angular momentum and the coefficients y_{lm} are often called Dunham coefficients. Here, $y_{10} = hc\omega_e$, $y_{20} = -hc\omega_e x_e$, $y_{30} = hc\omega_e y_e$, and the vibrational part is obtained by taking the terms with $m = 0$, i.e. by ignoring the rotational bands built on each vibrational bandhead. These parameters are essential since structural information is contained fundamentally in the vibrational spectra. Rotation-vibration interaction can usually be treated in a perturbative fashion.

Dunham expansion provides a convenient, empirical and model-free way of organising a large quantity of spectral data. It also provides a procedure for comparing data with the calculations arising from model potentials such as the Morse potential. As explained in the Introduction, however, this expansion, has the disadvantage that it is quite complex and usually involves a large number of parameters. The determination of wavefunctions is also nontrivial [11].

If the expansion (1) is truncated to the quadratic term, one obtains essentially the discrete spectrum of the Morse potential

$$E_v^M = hc\omega_e\left\{v+\frac{1}{2} - x_e\left(v+\frac{1}{2}\right)^2\right\}. \qquad (3)$$

The Morse potential [15],

$$V^M(r-r_e) = D_e\left(1-e^{-\beta(r-r_e)}\right)^2 \qquad (4)$$

describes reasonably well the potential energy of diatomic molecules near the equilibrium bondlength r_e and accounts for the anharmonicity of the molecular vibrations. It is characterised by two parameters D_e (the depth of the minimum of the curve) and β (known as the restitution constant in the harmonic approximation) where $\beta > 0$. Using the Hamiltonian,

$$H^M = -\frac{\hbar}{2\mu}\nabla^2 + V_M \qquad (5)$$

where μ is the reduced mass of the molecule, Morse [15] solved the Schrödinger equation exactly, and found the quantised energy-levels

$$E_v^M = hc\left\{\beta\sqrt{\frac{D_e\hbar}{\pi c\mu}}\left(v+\tfrac{1}{2}\right) - \frac{\hbar\beta^2}{4\pi c\mu}\left(v+\tfrac{1}{2}\right)^2\right\}. \qquad (6)$$

Comparing the coefficients in the expressions (3) and (6), the well-known relations between the Morse parameters D_e and β and the Dunham coefficients are obtained as

$$D_e = \frac{\omega_e}{4x_e} \quad \text{and} \quad \beta = \sqrt{\frac{4\pi c}{\hbar}\mu\omega_e x_e}. \qquad (7)$$

These relations are also known as consistency conditions [13,16].

One significant feature of the Morse potential is that the number of bound energy-levels is finite, i.e. $v = 0, 1, 2, \ldots [v_M]$, where the symbol $[\varkappa]$ denotes the largest integer smaller than or equal to $\varkappa$, and v_M indicates the position of the maximum of the Morse energy (3) with respect to vibrational quantum number v,

$$v_M = \frac{1}{2}\left(\frac{1}{x_e} - 1\right). \qquad (8)$$

The number of levels in the well is thus given by $[v_M] + 1$.

In what follows we will use Dunham expansion truncated to the cubic term. It is convenient to write the energies in the form:

$$E'_v = E_v/hc\omega_e = \left(v+\frac{1}{2}\right) - x_e\left(v+\frac{1}{2}\right)^2 + y_e\left(v+\frac{1}{2}\right)^3. \qquad (9)$$

The truncation is natural as the experimental data show that each of the coefficients in the expansion is much smaller than the preceding one, and furthermore the contribution of terms beyond the cubic term is negligibly small for all known diatomic molecules and seldom used in practice [13,14].

The model we propose in the next section aims to define a Hamiltonian which leads to Dunham-like formulae for the molecular vibrations using natural symmetry principles starting from an appropriate deformation of the Morse Hamiltonian.

3 The model and its approximations

3.1 The Hamiltonian

We shall use a Hamiltonian that can accommodate in different approximations both the Morse energy (3) and the Dunham expansion (9). This Hamiltonian is given by

$$H = \alpha\,(\hat{J}_+\hat{J}_- + \hat{J}_-\hat{J}_+) \tag{10}$$

where α is a constant which we shall choose below, $\hat{J}_+$ and $\hat{J}_-$ are the raising and lowering generators of the quantum group $U_q(su(2))$ [1] which is a deformation of the algebra $su(2)$, q is a complex number, called deformation parameter. Such deformations are called q-deformations and matters are arranged so that for $q = 1$ one recovers the classical situation (e.g., $su(2)$ in this case). To be close to the usual formalism we shall realise these generators in terms of anharmonic q-bosons. Their algebra, known as the quantum-oscillator algebra HW_q or the q-boson algebra, was introduced in [17–19], and is a generalisation of the Heisenberg–Weyl algebra obtained by introducing a deformation parameter q. The algebra is defined by:

$$aa^\dagger - q^{-1}a^\dagger a = q^{\hat{n}}\ , \quad [\hat{n}, a] = -a\ , \quad [\hat{n}, a^\dagger] = a^\dagger \tag{11}$$

where $a^\dagger$ is q-boson creation operator, a is q-boson annihilation operator, $\hat{n}$ is the boson number operator, and the boson commutation relations of the harmonic oscillator may be recovered for the value $q = 1$. The realization of $U_q(su(2))$ is taken from [20]:

$$\hat{J}_+ = a^+[2j - \hat{n}]_q\,, \quad \hat{J}_- = a, \quad \hat{J}_0 = \hat{n} - j \tag{12}$$

where the q-number $[z]_q$ is defined as:

$$[z]_q \;\equiv\; \frac{q^z - q^{-z}}{q - q^{-1}}.$$

In general j may be any complex number but in our context we shall take it to be real. These formulae indeed produce the standard relations of $U_q(su(2))$ [1]:

$$[\hat{J}_0, \hat{J}_\pm] = \pm\hat{J}_\pm\ , \qquad [\hat{J}_+, \hat{J}_-] = [2\hat{J}_0]_q. \tag{13}$$

Note that for q approaching unity these algebraic relations reduce to those of $su(2)$.

In general the basis of our system is determined by the application of the creation operator $a^\dagger$ on the vacuum. The latter is denoted by $|0\rangle$ and is characterised by the standard properties — the action of the annihilation operator a on $|0\rangle$ gives zero, and it is an eigenvector of the boson number operator:

$$a\,|0\rangle\, = 0\ , \qquad \hat{n}\,|0\rangle\, = \,\nu\,|0\rangle\,, \tag{14}$$

where ν may be an arbitrary complex number. The explicit basis is:

$$|n\rangle \;\equiv\; (a^\dagger)^n\,|0\rangle\,. \tag{15}$$

The action of the quantum group generators on this basis is:

$$\begin{aligned} \hat{J}_0\,|n\rangle &= (n + \nu - j)\,|n\rangle \\ \hat{J}_-\,|n\rangle &= q^\nu\,[n]_q\,|n-1\rangle \\ \hat{J}_+\,|n\rangle &= [2j - \nu - n]_q\,|n+1\rangle. \end{aligned} \tag{16}$$

For j a non-negative (half-)integer and $\nu = 0$ formulae (12) realise a unitary irreducible representation of $U_q(su(2))$ of dimension $2j + 1$ (for real q). To be close to this case below we shall suppose $\nu = 0$.

Substituting (12) in (10) we obtain:

$$H \;=\; \alpha\,\Big([2j]_q\,([2]_q\,[\hat{n}]_q\,q^{\epsilon\hat{n}} + 1) - [2]_q\,[\hat{n}]_q^2\,q^{\epsilon 2j}\,\Big) \tag{17}$$

where $\epsilon = \pm 1$ and we have used

$$aa^+ = [\hat{n} + 1]_q\,, \qquad a^+a = [\hat{n}]_q \tag{18}$$

and the q-summation formula:

$$[A + B]_q\, = [A]_q\,q^{\epsilon B} + [B]_q\,q^{-\epsilon A}\ . \tag{19}$$

Using (19) again we can recast (17) as:

$$H \;=\; \alpha\,\Big([\hat{n}]_q\,[2j - \hat{n}]_q\,[2]_q + [2j]_q\Big). \tag{20}$$

The action of this Hamiltonian on our basis is:

$$H\,|n\rangle \;=\; \mathcal{E}(n)\,|n\rangle \;=\; \alpha\,\Big([n]_q\,[2j - n]_q\,[2]_q + [2j]_q\Big)\,|n\rangle\ . \tag{21}$$

One motivation for (10) is that for $q = 1$ and choosing $\alpha = hc\omega_e/4j$ we obtain from (21) (essentially) the Morse case:

$$\mathcal{E}(n)_{q=1} = hc\omega_e\left(n + \frac{1}{2} - n^2/2j\right) \tag{22}$$

This expression has a local maximum at $n = j$ which is:

$$(\mathcal{E}_{q=1})_{\max} \;=\; \mathcal{E}(j)_{q=1} \;=\; \frac{1}{2}hc\omega_e(j + 1) \tag{23}$$

and the bound levels are below this value of j, i.e., we have the restriction:

$$n = 0, 1, \ldots, [j] \tag{24}$$

Comparing this with the Morse case we identify j with v_M in (8) which leads to the relation:

$$\frac{1}{x_e} = 2j+1. \tag{25}$$

This limiting case prompts us to choose in the general case: $\alpha = hc\omega_e/[2]_q\,[2j]_q$ and then we have:

$$H' = H/(hc\omega_e) = \frac{[\hat{n}]_q\,[2j-\hat{n}]_q}{[2j]_q} + \frac{1}{[2]_q}. \tag{26}$$

The eigenvalues are now:

$$\begin{aligned}\mathcal{E}'(n) = \mathcal{E}(n)/(\hbar\omega) &= \frac{[n]_q\,[2j-n]_q}{[2j]_q} + \frac{1}{[2]_q}\\ &= \frac{\sinh(n/p)\sinh\big((2j-n)/p\big)}{\sinh(1/p)\sinh(2j/p)} + \frac{1}{2\cosh(1/p)}\end{aligned} \tag{27}$$

where we have introduced a parameter p such that $q = e^{-1/p}$.

This eigenvalue function is similar to that given in formula (25) of Bonatsos et al. [6], though their approach is not the same as the present one, (a pair of q-bosons is used and the Hamiltonian is different). Furthermore, we note that in [6] their formula (25) does not follow (for $q \neq 1$) from the Hamiltonian given in their formula (24).

Note that in this form it is transparent that the eigenvalue function has only one extremum as the extremal condition is:

$$\frac{\sinh\big((2j-2n)/p\big)}{p\sinh(1/p)\sinh(2j/p)} = 0 \tag{28}$$

and this is a local maximum at $n = j$ (as in the undeformed Morse case (22)), the maximum value being:

$$\mathcal{E}_{\max} = \mathcal{E}'(j) = ([j]_q + 1)\,\frac{1}{2\cosh(1/p)} \tag{29}$$

which is, of course, a deformation of (23).

3.2 The case of positive molecular constant y_e

One way to use this Hamiltonian is to suppose that q is real and close to 1. We then expand to second order in $1/p$: $q = e^{-1/p} = 1 - 1/p + 1/2p^2 + \cdots$ and:

$$\begin{aligned} q^m &= 1 - m/p + m^2/2p^2 + \dots\ ,\\ [m]_q &= \frac{\sinh(m/p)}{\sinh(1/p)} = m\{1 + (m^2-1)/6p^2\} + \cdots \end{aligned} \tag{30}$$

Further, one would consider the eigenvalues of $\hat{n}$ which are significantly smaller than p and apply (30) for $m \to \hat{n}$. However, using this directly would not give exactly the Dunham expansion. In order to be closer to the Dunham expansion we expand the eigenvalue function (27) as a function of n around $-1/2$ (as in [6]) and obtain:

$$\begin{aligned}\mathcal{E}'(n) = &\left\{1 - \frac{\sinh\big((2j+\frac{1}{2})/p\big)}{\sinh(2j/p)}\right\}\frac{1}{2\cosh(1/2p)}\\ &+ \left\{\frac{n+\frac{1}{2}}{p}\,\sinh\big((2j+1)/p\big)\right.\\ &- \frac{(n+\frac{1}{2})^2}{p^2}\,\cosh\big((2j+1)/p\big)\\ &\left. + \frac{2}{3}\frac{(n+\frac{1}{2})^3}{p^3}\,\sinh\big((2j+1)/p\big) - \cdots\right\}\\ &\times\frac{1}{\sinh(1/p)\sinh(2j/p)}.\end{aligned} \tag{31}$$

This expansion is also appropriate in the region when $n+1/2$ is much smaller than p. Note that we make no restriction on the values of j, an assumption which turns out to be justified. We also see that the coefficient of $(n+1/2)^3$ is positive which means that this expression corresponds to the case when the molecular constant (Dunham coefficient) y_e is positive. The cases of negative molecular constant y_e will be considered below.

We consider the expression in (31) truncated to a cubic polynomial in $(n+1/2)$. The quadratic equation for its extrema has the following solutions:

$$n_\pm = \tfrac{1}{2}p\left\{\coth\left(\frac{2j+1}{p}\right) \pm \sqrt{\coth^2\left(\frac{2j+1}{p}\right) - 2}\right\} - \frac{1}{2} \tag{32}$$

One is inclined to require that the discriminant be strictly positive:

$$\tanh^2\left(\frac{2j+1}{p}\right) < \frac{1}{2}$$

or

$$\frac{2j+1}{p} \ < \ \frac{1}{2}\log_e(3+2\sqrt{2}) \ \approx \ 0.88 \tag{33}$$

In this case there are two extrema. The extremum at n_- is a local maximum. The value n_- is a deformation of the Morse value j, and if $j \ll p$ one can expand n_- as

$$n_- = j + \frac{(2j+1)^3}{12p^2} + \cdots \tag{34}$$

The extremum at n_+ is a local minimum. The value n_+ grows rapidly with p:

$$n_+ = \frac{p^2}{2j+1} - \frac{1}{2} + \mathcal{O}(p^{-2}).$$

Thus, the eigenvalues n cannot be near n_+, and one cannot use the potential well around it.

Thus, when the restriction (33) holds, and similar to the Morse case, we shall be interested in the region:

$$n = 0, 1, \dots, [n_-]. \tag{35}$$

However, j and p will be determined by the experimental data and we shall see that there are cases when (33) does not hold. In those cases, the potential does not have a local maximum, i.e., there are cases when the Dunham expansion has a different behaviour from the Morse expansion. Yet we are interested in small values of n when the two potentials do not differ significantly. Thus, in these cases we shall be interested in the Morse region (24): $n = 0, 1, \ldots, [j]$, though j shall be determined from the Dunham expansion.

We would like now to check how the expansion (31) corresponds to the Dunham expansion, which can be done independently of whether (33) holds or not.

First, we take the ratio of the coefficients of the linear to the cubic term in $(n + 1/2)$ both in the Dunham expansion (9) and in our expression (31), and we find:

$$\frac{1}{y_e} = \frac{3}{2}p^2. \tag{36}$$

This means that p can be determined from the value of y_e as

$$p = \sqrt{\frac{2}{3y_e}}. \tag{37}$$

By taking the ratio of the coefficients of the linear to the quadratic terms in $(n + 1/2)$ both in the Dunham expansion (9) and in our (31), we obtain:

$$\frac{1}{x_e} = p \tanh \frac{2j+1}{p} \ . \tag{38}$$

This is a deformation of the usual relation of the Morse model (25), and if $j \ll p$ one can expand:

$$\frac{1}{x_e} = 2j + 1 - \frac{(2j+1)^3}{3p^2} + \ldots$$

when $p \to \infty$, and correspondingly, $y_e \to 0$, the Morse case applies.

More important is that (38) gives a test for the applicability of our model. By noting that the function $\tanh z < 1$ for any real z, it follows that we have:

$$1 > \tanh \frac{2j+1}{p} = \frac{1}{p\, x_e} = \sqrt{\frac{3y_e}{2x_e^2}}.$$

Thus, we have the following restriction on our model for the experimental values x_e and y_e:

$$\frac{y_e}{x_e^2} < \frac{2}{3}. \tag{39}$$

As $y_e/x_e^2 \to 2/3$ (with values below 2/3), $j \to \infty$.

Our model is not applicable (even if we consider complex j) for the case $y_e/x_e^2 > 2/3$.

In the cases when (39) holds from (38) we determine the value of j using the value of p from (37), i.e.,

$$j = \tfrac{1}{2}\left\{ \sqrt{\frac{2}{3y_e}}\ \text{arctanh}\left(\sqrt{\frac{3y_e}{2x_e^2}}\right) - 1 \right\}. \tag{40}$$

It is useful to write down the formula for n_- in terms of x_e and y_e using (37) and (38):

$$n_- = \frac{x_e}{3y_e}\left(1 - \sqrt{1 - \frac{3y_e}{x_e^2}}\right) - \frac{1}{2} \tag{41}$$

from which it is clear that the restriction (33) translates into:

$$\frac{y_e}{x_e^2} < \frac{1}{3} \tag{42}$$

which is indeed stronger than (39), but is not a restriction on the applicability of our model.

In the case when $y_e/x_e^2 \ll 1$ we can use the expansion:

$$\text{arctanh}\ z = z + z^3 + \cdots$$

and obtain from (40):

$$j = \frac{1}{2x_e} - \frac{1}{2} + \frac{3y_e}{4x_e^3} + \cdots \tag{43}$$

3.3 The case of negative molecular constant y_e

In order to accommodate the situation when the molecular constant y_e is negative we have to consider the deformation parameter q to be a phase (though not a root of unity), or equivalently to make the replacement: $p \mapsto \mathrm{i}p$, then $q \mapsto q = e^{\mathrm{i}/p}$. Almost everything may be obtained from what we have in the case of real q by this replacement. In particular, one needs:

$$\begin{aligned}
\sinh(z/p) &\mapsto -i\sin(z/p)\ , \\
[z]_q &\mapsto \frac{\sin(z/p)}{\sin(1/p)}\ , \\
\cosh(z/p) &\mapsto \cos(z/p)\ , \\
(1/p)\sinh(a/p) &\mapsto -(1/p)\sin(a/p), \\
(1/p^3)\sinh(a/p) &\mapsto +(1/p^3)\sin(a/p), \\
\sinh(1/p)\sinh(a/p) &\mapsto -\sin(1/p)\sin(a/p).
\end{aligned}$$

We start with the analogues of (20):

$$H'_- = \frac{[\hat{n}]_q\,[2j - \hat{n}]_q}{[2j]_q} + \frac{1}{[2]_q}\ , \tag{44}$$

and (27)

$$\mathcal{E}'_-(n)\ = = \frac{\sin(n/p)\sin\big((2j-n)/p\big)}{\sin(1/p)\sin(2j/p)} + \frac{1}{2\cos(1/p)}. \tag{45}$$

This function is very different from (27), in particular, it has an infinite number of extrema since the extremum condition is:

$$\frac{\sin\big((2j-2n)/p\big)}{p\sin(1/p)\sin(2j/p)} = 0 \tag{46}$$

i.e., the extrema are at: $n = j + kp\pi/2$, $k = 0, \pm 1, \pm 2, \ldots$ We would again be interested in the region restricted by the first positive local maximum:

$$n = 0, 1, \ldots, [j].$$

This is also consistent with our aim of fitting the Dunham expansion. The maximal value is:

$$\mathcal{E}'_{-,\max} = \left(\frac{\sin(j/p)}{\sin(1/p)} + 1 \right) \frac{1}{2\cos(1/p)} \tag{47}$$

which is a deformation of (23).

The expansion of n around $-1/2$ is:

$$\begin{aligned} \mathcal{E}'_{-}(n) = & \left\{ 1 + \frac{\sin\left((2j + \frac{1}{2})/p\right)}{\sin(2j/p)} \right\} \frac{1}{2\cos(1/2p)} \\ & + \left\{ \frac{n + \frac{1}{2}}{p} \sin\left((2j+1)/p\right) \right. \\ & - \frac{(n + \frac{1}{2})^2}{p^2} \cos\left((2j+1)/p\right) \\ & \left. - \frac{2}{3} \frac{(n + \frac{1}{2})^3}{p^3} \sin\left((2j+1)/p\right) - \cdots \right\} \\ & \times \frac{1}{\sin(1/p)\sin(2j/p)} \end{aligned} \tag{48}$$

i.e., this is suitable for the Dunham expansion with negative y_e. We consider the expansion in (48) truncated to a cubic polynomial in $(n + 1/2)$. As such it has two extrema at the points:

$$n_{\pm} = \frac{1}{2} p \left\{ \mp \sqrt{\cot^2\left(\frac{2j+1}{p}\right) + 2} - \cot\left(\frac{2j+1}{p}\right) \right\} - \frac{1}{2}. \tag{49}$$

The value n_+ is negative and thus inaccessible. The extremum at n_- is a local maximum.

Further, we take the ratio of the coefficients of the linear to the cubic terms in $(n+1/2)$ both in Dunham's (9) and in our (48) and we obtain:

$$\frac{1}{y_e} = -\frac{3}{2} p^2 < 0. \tag{50}$$

This means that p is determined from the value of y_e:

$$p = \sqrt{-\frac{2}{3y_e}}\ , \quad y_e < 0. \tag{51}$$

We next similarly take the ratio of the coefficients of the linear to the quadratic terms in $(n + 1/2)$ and obtain:

$$\frac{1}{x_e} = p \, \tan \frac{2j+1}{p}. \tag{52}$$

From this we could determine the value of j using the value of p from (51). However, further we have to distinguish whether $x_e > 0$ (which holds in most cases) or $x_e < 0$.

- $x_e > 0 \Rightarrow \tan \dfrac{2j+1}{p} > 0$

Then we have for the value n_-:

$$n_- = \frac{x_e}{3|y_e|} \left(\sqrt{1 + \frac{3|y_e|}{x_e^2}} - 1 \right) - \frac{1}{2}, \quad x_e > 0, \quad y_e < 0. \tag{53}$$

This is a deformation of the Morse value, and if $j \ll p$ we can expand:

$$n_- = j - \frac{(2j+1)^3}{12p^2} + \cdots \tag{54}$$

Thus, similarly to the Morse case we shall be interested in the region:

$$n = 0, 1, \ldots, [n_-]. \tag{55}$$

The value of j is obtained from (52):

$$j = \frac{1}{2} \left\{ \sqrt{-\frac{2}{3y_e}} \arctan\left(\sqrt{-\frac{3y_e}{2x_e^2}} \right) - 1 \right\}\ , \qquad x_e > 0\ , y_e < 0\ . \tag{56}$$

Since the function arctan is multivalued, in the last formula we take the value which is closest to the Morse value from (25). Analogously, we use this for the following expansion which is valid when $-y_e \ll x_e^2$:

$$j = \frac{1}{2x_e} - \frac{1}{2} - \frac{3y_e}{4x_e^3} + \cdots \tag{57}$$

- $x_e < 0 \Rightarrow \tan \dfrac{2j+1}{p} < 0$

In this case the relevant parameter is j' which is complementary to j with respect to $p\pi/2$. Then,

$$\tan \frac{2j+1}{p} = \tan\left(\pi - \frac{2j'+1}{p} \right) = -\tan \frac{2j'+1}{p}$$

and instead of (52) we shall use:

$$\frac{1}{|x_e|} = p \, \tan \frac{2j'+1}{p}. \tag{58}$$

Further, for the value at which there is maximum we have:

$$\begin{aligned} n_- &= \frac{1}{2} p \left\{ \sqrt{\cot^2\left(\frac{2j'+1}{p}\right) + 2} + \cot\left(\frac{2j'+1}{p}\right) \right\} - \frac{1}{2} \\ &= \frac{|x_e|}{3|y_e|} \left(\sqrt{1 + \frac{3|y_e|}{x_e^2}} + 1 \right) - \frac{1}{2}. \end{aligned} \tag{59}$$

This is not a deformation of the Morse value, since it increases with p and will not be useful for our purpose. As with a case above we shall be interested in the region:

$$n = 0, 1, \ldots, [j']. \tag{60}$$

The value of j' is obtained from (58):

$$j' = \tfrac{1}{2}\left\{\sqrt{-\frac{2}{3y_e}}\,\arctan\left(\sqrt{-\frac{3y_e}{2x_e^2}}\,\right) - 1\right\}\ , \qquad x_e < 0\ , y_e < 0\ . \quad (61)$$

In the last formula we take the value closest to the Morse value with respect to j', i.e., $j' = 1/(2|x_e|) - 1/2$. Analogously, we use this for the following expansion which is valid when $-y_e \ll x_e^2$:

$$j' = \frac{1}{2|x_e|} - \frac{1}{2} - \frac{3y_e}{4x_e^3} + \cdots \qquad (62)$$

4 Analysis of experimental data

In this section we calculate the values of the independent parameters p and j of the model. These parameters are derived in terms of the well-known experimental molecular constants x_e and y_e. We can verify the applicability of the model and its restrictions by applying it to 161 electronic states of diatomic molecules for which values of the molecular constants are known. Furthermore, having the model parameters p and j one can calculate the vibrational energies of diatomic molecules using the eigenvalues of the q-deformed Hamiltonian as described in the previous section.

The parameter p is obtained by a re-parametrization of the quantum deformation parameter q ($q = e^{-1/p}$ or $q = e^{\mathrm{i}/p}$ respectively). This parameter is directly related to the coefficient y_e in the cubic term of the Dunham expansion. The other parameter j is related to the coefficients x_e and y_e in the Dunham expansion. From our model the number of bound vibrational states generated by the electronic states of the diatomic molecule can be easily estimated. When the potential curve has a maximum, the number of vibrational states is determined by the value of $[n_-]$. In the absence of the local maximum, the number of vibrational levels is restricted by $[j]$. To remind, the symbol $[\varkappa]$ denotes the largest integer smaller than or equal to $\varkappa$.

In the tables below we have calculated the independent parameters p and j of the model, using the values of the molecular constants compiled by Herzberg [13] for 161 electronic states of diatomic molecules. The molecules are listed in alphabetical order in the first column of the tables[1] and the corresponding electronic states are given in the second column. For convenience, in the third and fourth column we display the values of the anharmonic molecular constants x_e and y_e calculated from the data published in [13]. The values of the model parameters p and j are given in the fifth and sixth columns. In the seventh column, we give the value of $[n_-]$ where appropriate.

In Table 1 we display the cases when the molecular constants x_e and y_e are positive and the values of the parameters p and j are calculated from (37) and (40) respectively. In the cases when $y_e/\left(x_e\right)^2 < 1/3$, the potential curve for a given electronic state has a local maximum and the maximal number of vibrational levels is determined by the value of $[n_-]$, where $[n_-]$ is calculated from (41).

When $1/3 < y_e/\left(x_e\right)^2 < 2/3$, Dunham potential curve truncated to the cubic term does not have a local extremum, which is indicated by "–" in the column for $[n_-]$. In these cases the maximal number of vibrational levels in the model is determined by the value $[j]$.

As discussed in the previous section, when $y_e/\left(x_e\right)^2 > 2/3$, the model cannot be applied in its present form. The experimental data in [13] shows that this condition is satisfied for 30 electronic states of the following diatomic molecules: $^{75}\mathrm{As}_2$ state $\mathrm{X}\,^1\varSigma_g^+$, $^{11}\mathrm{B}^{79}\mathrm{Br}$ state $\mathrm{A}\,^1\Pi$, $^{209}\mathrm{Bi}^{19}\mathrm{F}$ state A, $^{12}\mathrm{C}_2$ state $\mathrm{B}\,^3\Pi_g$, $^{40}\mathrm{Ca}^{19}\mathrm{F}$ state $\mathrm{A}\,^2\Pi$, $^1\mathrm{H}_2$ state $\mathrm{B}\,^1\Sigma_u^+$, $^1\mathrm{H}^2\mathrm{H}$ states $\mathrm{C}\,^1\Pi_u$ and $\mathrm{B}\,^1\Sigma_u^+$, $^2\mathrm{H}_2$ states $\mathrm{C}\,^1\Pi_u$, $\mathrm{B}\,^1\Sigma_u^+$ and $\mathrm{X}\,^1\Sigma_g^+$, $^3\mathrm{H}_2$ state $\mathrm{a}\,^3\Sigma_g^+$, $\mathrm{Hg}^{35}\mathrm{Cl}$ state $\mathrm{X}\,^2\Sigma^+$, $\mathrm{Hg}^1\mathrm{H}^+$ state $\mathrm{X}\,^1\Sigma^+$, $\mathrm{Hg}^2\mathrm{H}^+$ state $\mathrm{X}\,^1\Sigma^+$, $^{113}\mathrm{In}^1\mathrm{H}$ state $\mathrm{X}\,^1\Sigma^+$, $^{39}\mathrm{K}_2$ state $\mathrm{B}\,^1\Pi_u$, $^7\mathrm{Li}^2\mathrm{H}$ state $\mathrm{X}\,^1\Sigma^+$, $^{24}\mathrm{Mg}^1\mathrm{H}$ state $\mathrm{A}\,^2\Pi_r$, $^{55}\mathrm{Mn}^{16}\mathrm{O}$ state A, $^{23}\mathrm{NaK}$ state $\mathrm{C}^1\Pi$, $^{14}\mathrm{N}^{16}\mathrm{O}$ state $\mathrm{B}\,^2\Pi$, $^{31}\mathrm{P}_2$ state $\mathrm{A}\,^1\Sigma_u^+$, Pb_2 state A, $^{80}\mathrm{Se}_2$ state $\mathrm{X}\,^1\Sigma^+$, $^{28}\mathrm{Si}^{16}\mathrm{O}$ state $\mathrm{A}\,^1\Pi$, $^{28}\mathrm{SiTe}$ state E, YbCl state $\mathrm{B}\,^2\Pi$ and $^{90}\mathrm{Zr}^{16}\mathrm{O}$ state $\mathrm{a}\,^1\Sigma$.

In Table 2 we show the cases when the molecular constant x_e is positive while the molecular constant y_e is negative and the values of the parameters p and j are calculated from (51) and (56) respectively. Here, the model works without any restrictions. The number of vibrational levels is determined by $[n_-]$, where $[n_-]$ is calculated from (53). The experimental data shows that when $[n_-] \sim j$, the value of j is at least three times smaller than the value of p.

Our model in its present form is designed for molecules where the potential is such that, in fact, only terms up to third order are needed to describe molecular vibrations. This is in agreement with the experimental data suggesting that contributions of terms of higher order are seldom used. However, the model can be easily extended to include fourth order and higher order terms if necessary.

The model gives a better fit for those electronic molecular states the potential of which has a maximum. These are the fourteen molecular states in Table 1 of the molecules $^9\mathrm{Be}^{16}\mathrm{O}$, $^{209}\mathrm{Bi}^{35}\mathrm{Cl}$, $^{40}\mathrm{Ca}^{35}\mathrm{Cl}$, $^{12}\mathrm{C}^{16}\mathrm{O}^+$, $^1\mathrm{H}_2$, $^2\mathrm{H}_2$, $^1\mathrm{H}^{35}\mathrm{Cl}$, $^{39}\mathrm{K}_2$, $^7\mathrm{Li}_2$, $^{14}\mathrm{N}_2$, $^{23}\mathrm{Na}^{79}\mathrm{Br}$, $^{28}\mathrm{Si}^{16}\mathrm{O}$, $\mathrm{Sr}^{19}\mathrm{F}$ and $^{64}\mathrm{Zn}^1\mathrm{H}$ as well as all molecular states listed in Table 2.

There are six electronic states $\mathrm{A}^1\Sigma^+$ of the diatomic molecules $^{133}\mathrm{Cs}^1\mathrm{H}$, $^{39}\mathrm{K}^2\mathrm{H}$, $^7\mathrm{Li}^1\mathrm{H}$, $^7\mathrm{Li}^2\mathrm{H}$, $^{23}\mathrm{Na}^1\mathrm{H}$ and $\mathrm{Rb}^1\mathrm{H}$ in [13], for which the values of both molecular constants x_e and y_e are negative. The model can accommodate these cases and the values of the parameters p and j', calculated from (51) and (61), are given in Table 3. To remind the reader that j' replaces j as independent parameter in these cases. The number of vibrational levels is determined by $[j']$. As we have pointed out the case $x_e < 0$ is not a deformation of the Morse potential. Thus, it does

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[1] Some of the elements in the three tables have not been given an isotope number. This is a reflection of the information recorded in the source [13].

Table 1. Parameters of the model for positive molecular constants x_e and y_e.

molecule	state	molecular constants		model parameters		
		$10^3 x_e$	$10^4 y_e$	p	j	$[n_-]$
$^{27}Al^1H$	X $^1\Sigma^+$	17.3217	1.54526	65.68	44.53	–
$^{27}Al^2H$	X $^1\Sigma^+$	12.4906	0.808614	90.80	62.31	–
$^9Be^{16}O$	A$^1\Pi$	7.3538	0.296180	150.03	112.54	–
	X$^1\Sigma^+$	7.95369	0.150270	210.63	71.99	81
$^{209}Bi^{35}Cl$	B	9.33829	0.039653	410.03	54.31	55
$^{11}B^{16}O$	A $^2\Pi$	8.84985	0.388673	130.97	84.90	–
$^{40}Ca^{35}Cl$	A $^2\Pi$	3.17895	0.0328857	450.25	194.16	272
$^{12}C^{16}O$	X $^1\Sigma^+$	6.17701	0.141336	217.18	104.02	–
$^{12}C^{16}O^+$	A $^2\Pi$	8.65524	0.0838636	281.95	60.87	63
$^1H_2$	d $^3\Pi_u$	27.9434	3.71061	42.39	25.69	–
	a $^3\Sigma_g^+$	26.8873	3.45238	43.94	26.82	–
	X $^1\Sigma_g^+$	26.8452	0.659811	100.52	19.06	19
$^1H^2H$	d $^3\Pi_u$	24.2092	2.82295	48.60	30.02	–
	e $^3\Sigma_u^+$	27.1367	2.73991	49.33	23.33	–
	a $^3\Sigma_g^+$	23.2928	2.59916	50.64	31.10	–
	X $^1\Sigma_g^+$	24.8771	3.81678	41.79	40.66	–
$^2H_2$	d $^3\Pi_u$	19.6279	1.43009	68.28	32.42	–
	e $^3\Sigma_u^+$	22.1695	1.84371	60.13	28.76	–
	a $^3\Sigma_g^+$	19.0684	1.80291	60.81	39.11	–
	D $^1\Pi_u$	18.5536	0.360696	135.95	28.01	28
$^1H^3H$	d $^3\Pi_u$	22.4267	2.36973	53.04	31.95	–
	a $^3\Sigma_g^+$	21.9751	2.30591	53.77	32.92	–
$^3H_2$	d $^3\Pi_u$	16.1321	1.15880	75.85	43.06	–
$^1H^{35}Cl$	X $^1\Sigma^+$	17.4095	0.187307	188.66	29.16	29
$^1H^{35}Cl^+$	A $^2\Sigma^+$	24.6483	2.12979	55.95	25.19	–
$^1H^{19}F$	X $^1\Sigma^+$	21.764	2.368	53.06	34.43	–
Hg^2H	X $^2\Sigma$	50.1733	11.1842	24.41	13.49	–
$^{127}I_2$	A $^3\Pi_u$	22.7273	1.81818	60.55	27.40	–
$^{39}K_2$	D $^1\Pi_u$	14.6104	0.162338	202.65	30.26	35
KBr	X $^1\Sigma^+$	3.0303	0.047619	374.12	174.08	–
KCl	X $^1\Sigma^+$	3.21429	0.0392857	411.94	164.61	–
$^{39}K^{127}I$	X $^1\Sigma^+$	3.30189	0.0471698	375.94	208.96	–
$^7Li_2$	A $^1\Sigma_u^+$	6.16168	0.0704639	307.59	89.76	96
$^7Li^1H$	X $^1\Sigma^+$	16.5048	1.16174	75.75	41.09	–
$Li^{127}I$	X $^1\Sigma^+$	3.33333	0.0377778	420.08	187.61	–
$^{14}N_2$	X $^1\Sigma_g^+$	6.12644	0.0318273	457.67	84.86	87
$^{23}Na^{79}Br$	X $^1\Sigma^+$	3.65079	0.0253968	512.35	152.33	165
$^{23}Na^1H$	X $^1\Sigma^+$	16.8231	1.36495	69.89	43.46	–
$^{23}Na^{127}I$	X $^1\Sigma^+$	2.62238	0.034965	436.65	293.55	–
$^{16}O_2$	X $^3\Sigma_g^-$	7.63939	0.345491	138.91	121.64	–
Rb^1H	X $^1\Sigma^+$	15.1051	0.800623	91.25	41.44	–
$^{28}Si^{14}N$	B $^2\Sigma^+$	16.2386	1.13695	76.57	42.01	–
$^{28}Si^{16}O$	X $^1\Sigma^+$	4.86864	0.0264889	501.68	108.59	112
$Sr^{19}F$	A $^2\Pi$	4.4673	0.039534	410.65	125.03	136
$^{64}Zn^1H$	X $^2\Sigma^+$	34.3	2.4757	51.89	15.99	17

Table 2. Parameters of the model for positive molecular constant x_e and negative molecular constant y_e.

molecule	state	molecular constants		model parameters		
		$10^3 x_e$	$-10^4 y_e$	p	j	$[n_-]$
$^{109}\mathrm{Ag}^{81}\mathrm{Br}$	B $^3\Pi_0^+$	24.613	3. 3186	44. 82	16. 00	14
$^{109}\mathrm{Ag}^{35}\mathrm{Cl}$	B $^3\Pi_0^+$	21.352	3. 380 8	44. 41	17. 53	16
$^{109}\mathrm{Ag}^{127}\mathrm{I}$	B $^3\Pi_0^+$	12.866	39.08 8	13. 06	8. 67	7
$^{27}\mathrm{Al}^{79}\mathrm{Br}$	A $^1\Pi$	21.534	17.73 2	19. 39	10. 90	9
$^{27}\mathrm{Al}^{35}\mathrm{Cl}$	A $^1\Pi$	9. 712	4. 800 4	37. 27	22. 30	19
$^{27}\mathrm{Al}^{19}\mathrm{F}$	A $^1\Pi$	10.329	2. 272 5	54. 16	28. 23	25
$^{197}\mathrm{Au}^{1}\mathrm{H}$	A $^1\Sigma^+$	32.979	23.53 93	16. 83	8. 45	7
	X $^1\Sigma^+$	18.707	0.1908 9	186.88	25. 53	25
$^{197}\mathrm{Au}^{2}\mathrm{H}$	X $^1\Sigma^+$	13.245	0.1761 5	194. 54	35. 51	34
$^{11}\mathrm{B}^{35}\mathrm{Cl}$	A $^1\Pi$	13.407	1. 179 2	75. 19	28. 88	26
$^{9}\mathrm{Be}^{1}\mathrm{H}$	A $^2\Pi$	1 9.064	2. 395	52. 76	20. 14	18
	X $^2\Sigma^+$	17.245	2. 428 8	52. 39	21. 40	19
$^{9}\mathrm{Be}^{1}\mathrm{H}^+$	A $^1\Sigma^+$	10.026	0.2 5744	160. 92	44. 14	42
	X $^2\Sigma^+$	17.91	0.09 452 2	265.58	27. 02	26
$^{9}\mathrm{Be}^{2}\mathrm{H}^+$	A $^1\Sigma^+$	7. 7435	1. 459 3	67. 59	36. 29	32
	X $^2\Sigma^+$	13.261	0.36416	135.30	33. 90	32
$^{9}\mathrm{Be}^{16}\mathrm{O}$	B $^1\Sigma^+$	5. 6503	0.0019696	1839.8	87. 72	87
$^{209}\mathrm{Bi}_2$	B	2. 2759	0.035852	431.22	170.86	159
	X $^1\Sigma_g^+$	1.8684	0.1 34329	222.78	130.53	117
$^{209}\mathrm{Bi}^{79}\mathrm{Br}$	*A*	3. 9291	7. 57854	29. 66	21. 07	18
$^{12}\mathrm{C}_2$	c $^1\Pi_g$	8. 7392	22.22 1	17.32	11.80	10
	A $^3\Pi_g$	9. 1935	2. 833 5	48. 51	27. 42	24
$^{35}\mathrm{Cl}_2^+$	A $^2\Pi$	9. 2958	0.22715	171. 32	47. 53	45
	X $^2\Pi$	7. 3123	0.6728	99. 54	46. 36	42
$^{35}\mathrm{Cl}^{19}\mathrm{F}$	A $^3\Pi_{0+}$	6.6882	12.06 7	23. 51	16.13	14
$^{12}\mathrm{C}^{16}\mathrm{O}$	d $^3\Pi_i$	6.7007	0.9887 6	82. 112	43. 34	39
$^{12}\mathrm{C}^{16}\mathrm{O}^+$	X $^2\Sigma^+$	6. 8484	0.003161 4	1452. 2	72. 26	72
$^{133}\mathrm{Cs}_2$	B $^1\Pi_u$	2. 2784	0.054952	348. 31	156. 24	143
	X $^1\Sigma_g^+$	1. 9064	0.03 912 8	412. 77	186. 09	171
$^{63}\mathrm{Cu}^{2}\mathrm{H}$	A $^1\Sigma^+$	17.022	3. 379 6	44. 41	20. 01	18
$^{1}\mathrm{H}_2$	e $^3\Sigma_u^+$	29.966	1. 971 9	58. 15	14. 65	14
$^{202}\mathrm{Hg}^{81}\mathrm{Br}$	X $^3\Sigma$	5. 2095	0.4833 5	117. 44	59.50	54
$\mathrm{Hg}^{1}\mathrm{H}$	A $^2\Pi_{3/2}$	20.248	2. 080 4	56. 61	19. 81	18
	X $^2\Sigma^+$	5 9.845	21.26 8	17. 70	6. 20	5
$\mathrm{Hg}^{1}\mathrm{H}^+$	A $^1\Sigma^+$	26.564	47.21 2	11. 88	7. 02	6
$\mathrm{Hg}^{2}\mathrm{H}^+$	A $^1\Sigma^+$	18.865	23.75 9	16. 75	10.09	8
$^{127}\mathrm{I}_2$	G $^1\Sigma_u^+$	3. 6039	0.2119 9	177. 34	88.36	80
	X $^1\Sigma_g^+$	2. 8555	0.04171 1	399. 79	143. 3	134
$^{127}\mathrm{I}^{35}\mathrm{Cl}$	A $^3\Pi_1$	9. 28469	1. 60515	64. 45	32.74	29
$^{115}\mathrm{In}^{1}\mathrm{H}$	A $^1\Sigma^+$	41.7581	46.96 93	11. 91	6. 107	5
$\mathrm{In}^{16}\mathrm{O}$	X $^2\Sigma$	5. 27671	4. 05354	40. 55	27. 08	24
$^{7}\mathrm{Li}_2$	B $^1\Pi_u$	10.1746	2. 361 97	53. 13	28. 06	25
	X $^1\Sigma_g^+$	7. 37558	0.165040	200.98	59.14	56

Table 2. *Continued.*

molecule	state	molecular constants		model parameters		
		$10^3 x_e$	$-10^4 y_e$	p	j	$[n_-]$
$^{24}\mathrm{Mg}^{1}\mathrm{H}$	$\mathrm{X}\ ^2\Sigma^+$	21.0604	1.00287	81.53	21.00	20
$^{24}\mathrm{Mg}^{1}\mathrm{H}^+$	$\mathrm{A}\ ^1\Sigma^+$	6.00335	3.17825	45.80	29.33	26
	$\mathrm{X}\ ^2\Sigma^+$	17.8140	3.00832	47.08	20.05	18
$^{24}\mathrm{Mg}^{2}\mathrm{H}^+$	$\mathrm{A}\ ^1\Sigma^+$	4.24725	1.43207	68.23	43.46	38
	$\mathrm{X}\ ^2\Sigma^+$	13.2888	1.36149	69.98	28.25	26
$^{14}\mathrm{N}_2$	$\mathrm{C}\ ^3\Pi_u$	8.39271	10.5646	25.12	16.62	14
	$\mathrm{A}\ ^3\Sigma_u^+$	9.51197	0.171189	197.34	47.80	46
	$\mathrm{a}\ ^1\Pi_g$	7.55965	2.06204	56.86	32.62	29
$^{14}\mathrm{N}_2^+$	$\mathrm{B}\ ^2\Sigma_u^+$	9.58328	2.22122	54.79	29.28	26
	$\mathrm{X}\ ^2\Sigma_g^+$	7.31065	0.181226	191.80	58.91	56
$^{23}\mathrm{Na}_2$	$\mathrm{B}\ ^1\Pi_u$	5.09169	0.756119	93.90	52.31	47
	$\mathrm{X}\ ^1\Sigma_g^+$	4.55944	0.169566	198.28	82.36	76
$^{23}\mathrm{Na}^{1}\mathrm{H}$	$\mathrm{A}\ ^1\Sigma^+$	17.4179	6.34256	32.42	16.63	15
$\mathrm{Na}^{23}\mathrm{K}$	$\mathrm{D}\ ^1\Pi$	4.25894	0.990509	82.04	50.14	44
	$\mathrm{A}\ ^1\Sigma^+$	1.09205	0.487163	116.98	83.95	75
$^{14}\mathrm{N}^{16}\mathrm{O}$	$\mathrm{A}\ ^2\Sigma^+$	6.10636	1.18079	75.14	42.35	38
	$\mathrm{X}\ ^2\Pi_{3/2}$	7.33842	0.00630358	1028.40	67.24	67
	$\mathrm{X}\ ^2\Pi_{1/2}$	7.33707	0.00630242	1028.49	67.25	67
$^{16}\mathrm{O}_2$	$\mathrm{B}\ ^3\Sigma_u^-$	11.4256	5.35867	35.27	20.45	18
	$\mathrm{b}\ ^1\Sigma_g^+$	9.73695	0.0750338	298.08	48.95	48
$^{16}\mathrm{O}^{1}\mathrm{H}$	$\mathrm{A}\ ^2\Sigma^+$	29.8475	2.03427	57.25	14.66	14
$^{31}\mathrm{P}_2$	$\mathrm{X}\ ^1\Sigma_g^+$	3.59289	0.0682957	312.43	113.18	106
$\mathrm{Pb}^{79}\mathrm{Br}$	$\mathrm{A}\ ^2\Sigma$	2.62295	1.83607	60.26	42.11	37
PbSe	D	2.78361	0.210084	178.14	98.41	88
$^{85}\mathrm{Rb}_2$	C	1.84315	0.356259	136.80	90.04	80
	$\mathrm{X}\ ^1\Sigma_g^+$	16.7598	0.144902	214.50	28.60	28
$^{28}\mathrm{Si}^{32}\mathrm{S}$	E	3.46964	0.815366	90.43	56.77	50
	$\mathrm{D}\ ^1\Pi$	4.64844	0.878906	87.09	51.15	45
$^{28}\mathrm{SiSe}$	E	6.31477	1.03627	80.21	43.69	39
$^{120}\mathrm{Sn}^{16}\mathrm{O}$	$\mathrm{D}\ ^1\Sigma^+$	5.28665	2.31720	53.64	34.22	30
SnS	E	3.69429	0.406711	128.03	71.77	64
$^{120}\mathrm{Sn}^{32}\mathrm{Se}$	E	3.91658	0.00813835	286.21	103.74	97
SnTe	I	5.44188	0.130605	225.93	76.64	72
	B	6.64351	0.564481	108.68	50.87	46
$\mathrm{Sr}^{19}\mathrm{F}$	$\mathrm{B}\ ^2\Sigma$	3.80446	0.143179	215.78	94.81	87
$^{205}\mathrm{Tl}^{81}\mathrm{Br}$	$\mathrm{A}\ ^3\Pi_0^+$	47.5443	20.3102	18.12	7.29	6
$\mathrm{Zn}^{1}\mathrm{H}^+$	$\mathrm{X}\ ^1\Sigma^+$	20.3549	1.04384	79.92	21.53	20

Table 3. Parameters of the model for negative molecular constants x_e and y_e.

molecule	state	molecular constants		model parameters		
		$-10^3 x_e$	$-10^4 y_e$	p	j'	j
$^{133}\mathrm{Cs}^{1}\mathrm{H}$	$\mathrm{A}\ ^1\Sigma^+$	27.9412	17.1569	19.71	10.02	20.94
$^{39}\mathrm{K}^{2}\mathrm{H}$	$\mathrm{A}\ ^1\Sigma^+$	11.3322	2.74561	49.28	25.65	51.75
$^{7}\mathrm{Li}^{1}\mathrm{H}$	$\mathrm{A}\ ^1\Sigma^+$	123.487	178.527	6.111	2.324	7.275
$^{7}\mathrm{Li}^{2}\mathrm{H}$	$\mathrm{A}\ ^1\Sigma^+$	77.3998	65.2091	10.11	4.084	11.80
$^{23}\mathrm{Na}^{1}\mathrm{H}$	$\mathrm{A}\ ^1\Sigma^+$	17.4179	6.34256	32.42	16.63	34.30
$\mathrm{Rb}^{1}\mathrm{H}$	$\mathrm{A}\ ^1\Sigma^+$	16.7621	6.90924	31.06	16.441	32.35

not behave like (deformed) oscillator models do and yet our model can handle it.

5 Conclusions and outlook

In this paper we have considered a q-deformation of a general Hamiltonian constructed from the raising and lowering generators of the quantum group deformation of the algebra $su(2)$ and have obtained an expression for the eigenvalues of this Hamiltonian which can be interpreted as the phenomenological Dunham expansion of the vibrational energies of diatomic molecules. The expansion is truncated to the cubic term mainly for practical reasons as the experimental results suggest that the contribution of terms of higher order is often negligibly small and seldom used. We have formulated a model of the anharmonic vibrations of diatomic molecules which in different approximations leads to Morse or Dunham results. The parameters of the model are obtained in terms of the well-known experimental molecular constants and this gives a clear test for the applicability of the model and its restrictions. The model can accommodate both the positive and the negative values of the anharmonic constant y_e. Using all data available in [13], we have tested the model in a global fashion for a large set of diatomic molecules and conclude that it fits well with the experimental data for all states, except for about 30 electronic states for which the values of x_e are not much larger than the values of y_e, as required by the model. In these cases the model could be expanded by adding to the Hamiltonian terms corresponding to the rotational energies in order to obtain a q-deformed version corresponding to the general Dunham expansion (2). Next, in order to test these ideas further, intensity data should be studied. This would involve a procedure where a consistent q-deformed dipole operator is defined and the wave functions for each molecule evaluated within our approximation. Finally, a more ambitious project would be to extend these studies to polyatomic molecules, following, for example, the methodology of reference [9].

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