A q-deformed Aufbau Prinzip

Tidjani Negadi, Maurice R. Kibler

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T Négadi* and M Kibler

Institut de Physique Nucléaire de Lyon, IN2P3-CNRS et Université Claude Bernard, F-69622 Villeurbanne Cedex, France

Abstract. A building principle working for both atoms and monoatomic ions is proposed in this Letter. This principle relies on the q-deformed "chain" $SO(4) > SO(3)_q$.

* Permanent address: Laboratoire de Physique Théorique, Institut de Physique, Université d'Oran, Es-Sénia, Oran, Algérie

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The theory of quantum algebras (ie, quasi-triangular Hopf algebras or deformations of quantum universal enveloping algebras) and quantum groups (ie, compact matrix pseudo-groups), which originated with the works of Kulish and Reshetikhin [1], Drinfel'd [2], Jimbo [3] and Woronowicz [4] (among others), continues to attract the attention of both mathematicians and physicists. Up to now, most of the physical applications of quantum groups have been devoted to statistical mechanics, in connection with the solutions of the quantum Yang-Baxter equation, to solvable models, in connection with the theory of quantum inverse scattering, and to rational conformal field theory. Recently, there have been several applications in the domain of molecular and nuclear spectroscopy (mainly vibrational-rotational spectroscopy) [5-10]. Furthermore, attempts to apply quantum groups to atomic spectroscopy (viz, fine structure of the Hydrogen atom) [11] and to solid-state physics (viz, formation of coherent structures) [12] have been suggested very recently.

It is the aim of this Letter to show that quantum groups can be also of interest in the field of chemical physics. More precisely, we want to show how the quantum algebra $su(2)_q$, one of the simplest quantum algebras, can be used to derive an *Aufbau Prinzip* for atoms and monoatomic ions.

It is well-known [13-21] that the atomic building principle for neutral atoms corresponds to the series

$$1s \ll 2s < 2p \ll 3s < 3p \ll 4s < 3d < 4p \ll 5s <$$
$$4d < 5p \ll 6s < 4f < 5d < 6p \ll 7s < 5f < 6d \cdots \tag{1}$$

while the one for N-positive ions (N = degree of ionization) corresponds to

the series

$$1s < 2s < 2p < 3s < 3p < 3d < 4s < 4p < 4d <$$
$$5s < 5p < 4f < 5d < 6s < 6p < 5f < 6d < 7s \cdots.$$

(2)

(The sign $\ll$ in (1) serves to indicate rare gas.) It is to be noted that among 99 neutral atoms, there are 20 exceptions to the series (1) [19]. The series (1), often referred to as the Madelung-Klechkovskii series (cf. Refs. [13] and [14]), thus presents an approximate character. In contradistinction, the series (2) exhibits a more universal character since it has only 5 exceptions for $N = 2$ and none for $3 \leq N \leq 6$ [19]. There is no model for describing in an unified way the series (1) and (2).

The model we present here for the simultaneous description of (1) and (2) starts from the $O(4)$ symmetry of the Hydrogen atom. From the work of Fock [22], we know that the discrete spectral problem for the Hydrogen atom in $\mathbf{R}^3$ is equivalent to that of a symmetrical rotor (or spherical top) in $\mathbf{R}^4$. In the case of a many-electron neutral atom, the $O(4)$ symmetry is broken by inter-electronic repulsions and relativistic effects. In this respect, the chain of groups $SO(4) \supset SO(3)$ furnishes relatively good quantum numbers, viz, n and ℓ (the principal and the orbital angular momentum quantum numbers). The model of Novaro [18] for neutral atoms relies on the chain $SO(4) \supset SO(3)$. In the latter model, the Hamiltonian H spanning the $n\ell$ shells reads

$$H \simeq \frac{1}{h+1} \qquad h = \frac{1}{2I}(\mathbf{\Lambda}^2 + \alpha\,\mathbf{L}^2)$$

(3)

where h is the Hamiltonian for an asymmetric rotor in $\mathbf{R}^4$. In equation (3), $\mathbf{\Lambda}$ and $\mathbf{L}$ stand for the angular momenta in $\mathbf{R}^4$ and $\mathbf{R}^3$, respectively, and α is the asymmetry parameter given by $\alpha = I/I' - 1$ in terms of the moments

of inertia I and I'. At this stage, it should be emphasized that the model based on (3) reproduces the series (1) in a reasonable way for $\alpha = 4/3$ [18] but that no admissible value of α reproduces the series (2).

The basic ingredient of our model is to replace the chain $SO(4) \supset SO(3)$ by the q-deformed "chain" $SO(4) > SO(3)_q$. More precisely, we replace the constant α by a q-dependent parameter and the operator $\mathbf{L}^2$ (whose eigenvalues are $\ell(\ell+1)$, with $\ell \in \mathbf{N}$) by the Casimir operator of the quantum algebra $so(3)_q$. Therefore, the Hamiltonian h is replaced by

$$h_q = \frac{1}{2I} \left(\mathbf{\Lambda}^2 + \alpha(q) \, [\ell]_q [\ell+1]_q \right) \tag{4}$$

where the $[\ ]_q$-integers are defined through

$$\begin{aligned}
[x]_q &= \frac{q^x - q^{-x}}{q - q^{-1}} \quad \text{for} \quad x \in \mathbf{N} \\
&= q^{x-1} + q^{x-3} + \ldots + q^{-x+1} \quad \text{for} \quad x \in \mathbf{N} - \{0\}.
\end{aligned} \tag{5}$$

Because $\mathbf{L}$ is the projection of $\mathbf{\Lambda}$ on a privileged axis, the q-deformation takes place along this axis. Thus, it seems natural to deform the inertial moment I' (the one with respect to the privileged axis) without modification of the inertial moment I (the one with respect to the three axes perpendicular to the privileged axis). Hence, we use the same I in (3) and (4). The description of our Hamiltonian model h_q is complete once the function $\alpha(q)$ is fixed. We shall adopt the linear law

$$\alpha(q) = 3 - \frac{5}{3} q. \tag{6}$$

Finally, we note that we can, of course, substitute for the operator $\mathbf{\Lambda}^2$ in (4), as well as in (3), its eigenvalues $\lambda(\lambda+2) \equiv (n-1)(n+1)$, with $\lambda \in \mathbf{N}$.

There are two interesting limiting cases for the model based on (4)-(6). The case $q = 1$ (ie, $\alpha = 4/3$) corresponds to the Novaro [18] model for

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neutral atoms and the case $q = 9/5 = 1.8$ (ie, $\alpha = 0$) to the Hydrogen atom.

Let us now examine the capabilities of our model. In this model, the negative energies of the various nl shells are given by the eigenvalues of the Hamiltonian

$$H_q = \frac{E_0}{h_q + 1} \tag{7}$$

where E_0 is some arbitrary (negative) energy which reduces to the energy of the ground state of the Hydrogen atom for $q = 9/5$. Following an usual practice in chemical physics and quantum chemistry, we note that the ordering afforded by (7) is the same as that obtained from

$$\sqrt{\varepsilon_q(n, \ell) + 1} = \sqrt{n^2 + \alpha(q) \, [\ell]_q \, [\ell + 1]_q}. \tag{8}$$

More precisely, we shall use

$$
\begin{aligned}
\varepsilon_q(n, s) + 1 &= n^2 \\
\varepsilon_q(n, p) + 1 &= n^2 + (3 - \tfrac{5}{3}q)(q + q^{-1}) \\
\varepsilon_q(n, d) + 1 &= n^2 + (3 - \tfrac{5}{3}q)(q + q^{-1})(q^2 + 1 + q^{-2}) \\
\varepsilon_q(n, f) + 1 &= n^2 + (3 - \tfrac{5}{3}q)(q^2 + 1 + q^{-2})(q^3 + q + q^{-1} + q^{-3})
\end{aligned}
\tag{9}
$$

for ordering the energies of the orbitals ns, np, nd and nf.

We now discuss the results arising from equations (7)-(9). First, let us consider the case of positive ions. From formulas (9), we can see that the series (2) is reproduced for $1.15 \leq q \leq 1.30$. Therefore, the range $q = 1.15\text{-}1.30$ is appropriate for $1 < N < 7$. Second, we note that for $1.6 \leq q \leq 1.8$, the order of the shells is hydrogenlike (in the sense of energy increasing with n). Such an order is convenient for highly-ionized atoms.

Third, the case of neutral atoms is obtained for $q = 0.85$. Indeed, the value $q = 0.85$ reproduces the series (1) with a reasonable agreement : for $n \leq 6$, the agreement is perfect and for $n > 6$, the ordering (1) is respected with a deviation of less than 8%. This result reflects the fact that the Madelung-Klechkovskii rule presents several exceptions.

In conclusion, we have derived a q-model (*Aufbau Prinzip*) which describes in an unified way (through equations (4)-(9)) neutral atoms, positive monoatomic ions, highly-ionized atoms and hydrogenlike ions. For neutral atoms, this model with $q = 0.85$ gives a refinement of the Novaro model (which corresponds to $q = 1$). The model for positively charged ions (corresponding to $q = 1.15$-1.30) is entirely new. The application described in this Letter, which concerns the periodic structure of chemical elements, parallels the recent applications to nuclear [5,10], atomic [11], molecular [5-9] and solid-state [12] physics. Along the same vein (ie, the q-deformation of level splitting problems), we may reconsider the problem of mass formulas for nuclei and elementary particle physics. This problem shall be tackled in a forthcoming paper. Despite the present increase of pessimism concerning the quantum group invasion (possibly the quantum group pest), all these applications should invite one to pursue the investigations of quantum groups.

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