Group Theory of the Periodic Table

John Tamanas

Periodic Table

A periodic system that classifies the chemical elements

Proposed by Dmitrii Mendeleev on Feb 17, 1869

Bill Gates's Periodic Table

QM of Periodic System

1. Principal and orbital quantum numbers (n,l) characterize orbitals
2. Pauli Exclusion Principle
3. Aufbau Principle - Electrons fill up energy levels in order of increasing energy.

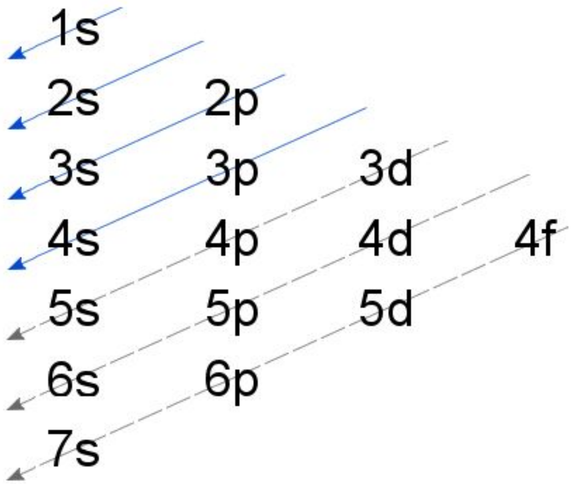
These are the properties we'll want to include in our description of the periodic table.

Derivation of Group Structure

We'll want to be able to exhibit/explain

1. Period doubling
2. Madelung rule

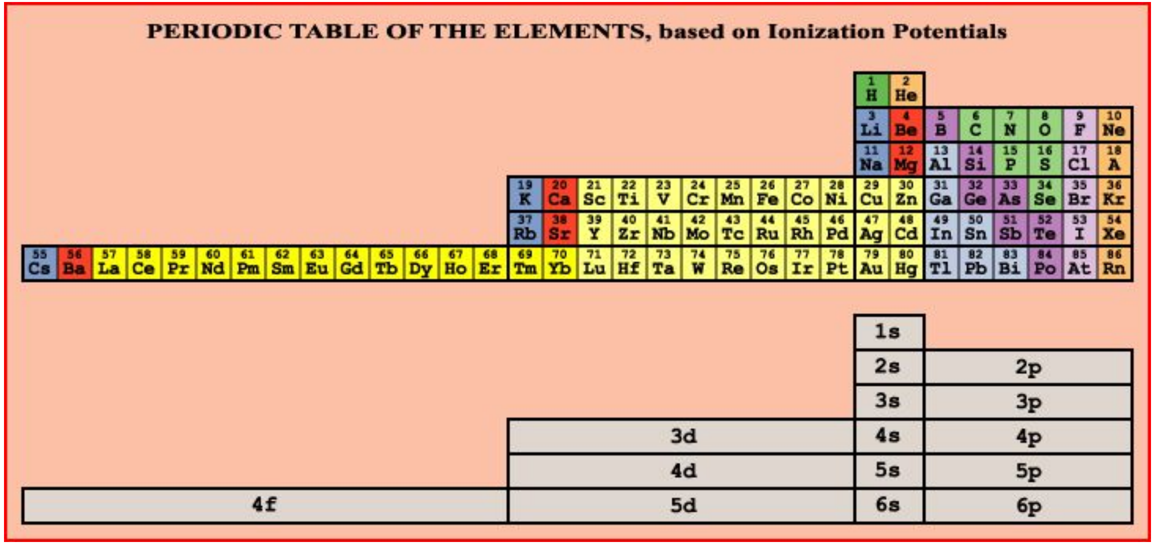
We'll do this by using the non-invariance group SO(4,2) of the hydrogenic orbitals



Period Doubling

The periods of the periodic table are of length 2 - 8 - 8 - 18 - 18 - 32 - 32 …

This is not trivial. For example, if electrons filled up atoms in terms of increasing n, the periods would be 2 - 8 - 18 - 32...



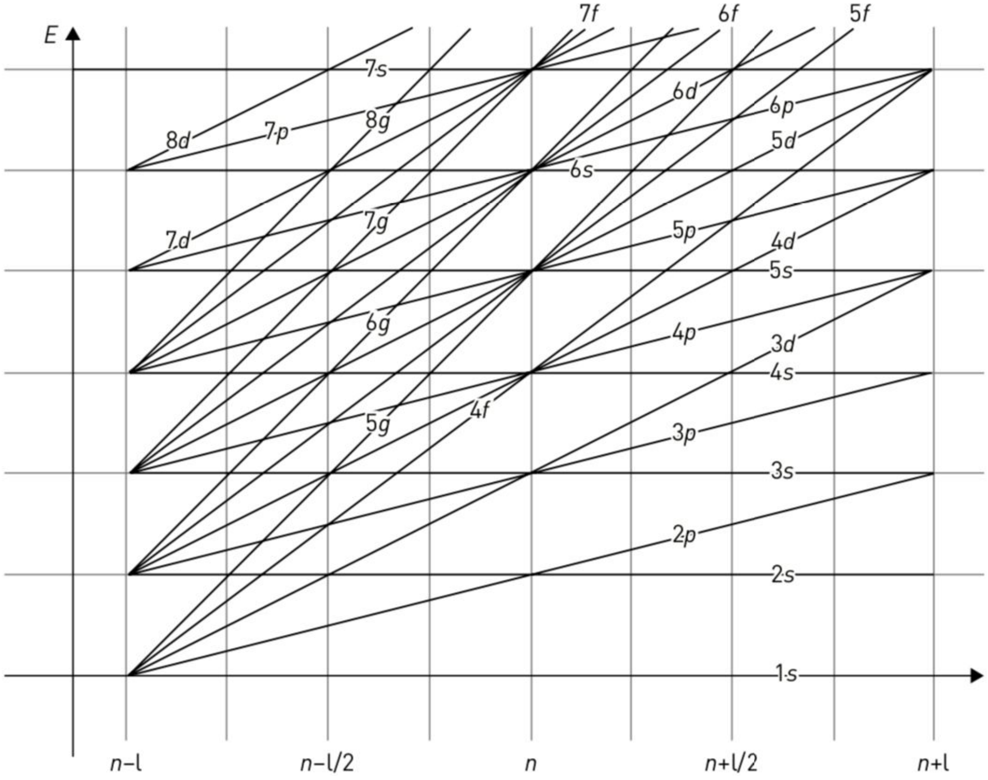
Madelung Rule

"With increasing nuclear charge Z, one-electron orbitals are filled according to increasing $N = n + l$. For fixed N, the orbitals are filled in order of increasing n."

This is why Potassium's electron configuration, for example, is [Ne]$3s^2 3p^6 4s^1$ rather than $3s^2 3p^6 3d^1$ that one would guess if orbitals were filled in terms of increasing n.

This naturally gives rise to the 2-8-8-18-18-... periodicity doubling.

Correlation diagram for different orbital filling rules



SO(4,2)⊗SU(2)

Chemistry is determined by electromagnetic interactions.

SO(4,2) is isomorphic to the conformal group in Minkowski space.

SO(4,2) is the maximal dynamical non-invariance group for a hydrogen-like atom.

SU(2) only handles spins, so we’ll mainly focus on SO(4,2).

Non-invariance group

Some of the generators of the Lie algebra will no longer commute with the Hamiltonian.

$$\left[\hat{\mathscr{H}}, \hat{X}_i\right] = f\left(\hat{X}_i\right) \in U(\mathfrak{g})$$

We will be generating spectra, which are infinite. Therefore, we will be considering a non-compact non-invariance group

Atomic Chess

King

Queen

Rook

Bishop

Knight

Atomic Chessboard

All elements belong to an (n,l) configuration on the chessboard.

Each square represents $2(2l+1)$ substates

$n = 1,\dots,\infty$

$l = 0,\dots,n-1$

$n\backslash l$	0	1	2	3	4	5	6
7	$7s$	$7p$	$7d$	$7f$	$7g$	$7h$	$7i$
6	$6s$	$6p$	$6d$	$6f$	$6g$	$6h$	
5	$5s$	$5p$	$5d$	$5f$	$5g$		
4	$4s$	$4p$	$4d$	$4f$			
3	$3s$	$3p$	$3d$				
2	$2s$	$2p$					
1	$1s$						

King ♚ and Queen ♛

These can travel in all directions along the chessboard

Their moves are therefore allowed by SO(4,2)

$n\backslash l$	0	1	2	3	4	5	6
7	$7s$	$7p$	$7d$	$7f$	$7g$	$7h$	$7i$
6	$6s$	$6p$	$6d$	$6f$	$6g$	$6h$	
5	$5s$	$5p$	$5d$	$5f$	$5g$		
4	$4s$	$4p$	$4d$	$4f$			
3	$3s$	$3p$	$3d$				
2	$2s$	$2p$					
1	$1s$						

The Rook ♖ (Horizontal moves)

Moving horizontally on the chessboard means moving over states of different l, but same n.

Thinking of the correlation diagram, this is like the n-rule for orbital filling.

Explains “accidental symmetry” of n=2 Hydrogen.

Corresponds to dynamical SO(4).

$n\backslash l$	0	1	2	3	4	5	6
7	$7s$	$7p$	$7d$	$7f$	$7g$	$7h$	$7i$
6	$6s$	$6p$	$6d$	$6f$	$6g$	$6h$	
5	$5s$	$5p$	$5d$	$5f$	$5g$		
4	$4s$	$4p$	$4d$	$4f$			
3	$3s$	$3p$	$3d$				
2	$2s$	$2p$					
1	$1s$						

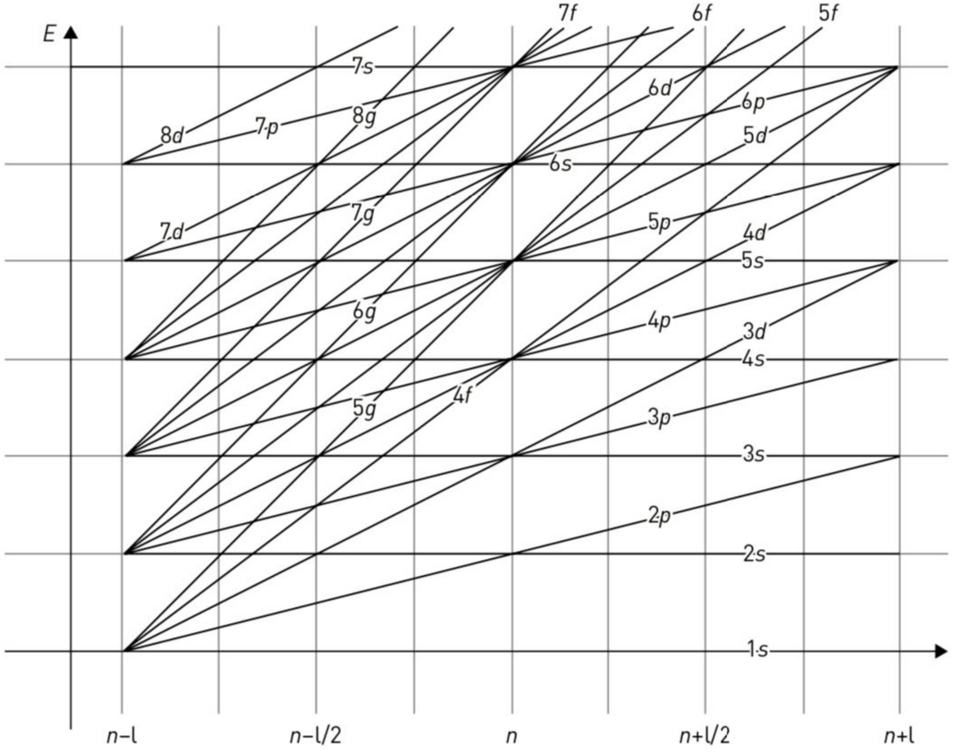
The Rook ♖ (Horizontal moves)

Moving horizontally on the chessboard means moving over states of different l, but same n.

Thinking of the correlation diagram, this is like the n-rule for orbital filling.

Explains "accidental symmetry" of n=2 Hydrogen.

Corresponds to SO(4) dynamical symmetry.



The Rook ♖ (Vertical moves)

Moving vertically with fixed l is the same as moving radially

Therefore, vertical moves correspond to raising and lower operators of the radial group, SO(2,1).

$$\hat{Q}_{\pm} = \hat{Q}_1 \pm i\hat{Q}_2$$

$$SO(4,2) \supset SO(4) \otimes SO(2,1)$$

$n \backslash l$	0	1	2	3	4	5	6
7	7*s*	7*p*	7*d*	7*f*	7*g*	7*h*	7*i*
6	6*s*	6*p*	6*d*	6*f*	6*g*	6*h*	
5	5*s*	5*p*	5*d*	5*f*	5*g*		
4	4*s*	4*p*	4*d*	4*f*			
3	3*s*	3*p*	3*d*				
2	2*s*	2*p*					
1	1*s*						

The Knights ♞

(n-l/2) (main knight)

- Connects (n,l) with (n+1,l+2) and (n-1,l-2).
- Identified with SU(3).

(n+l/2) (second knight)

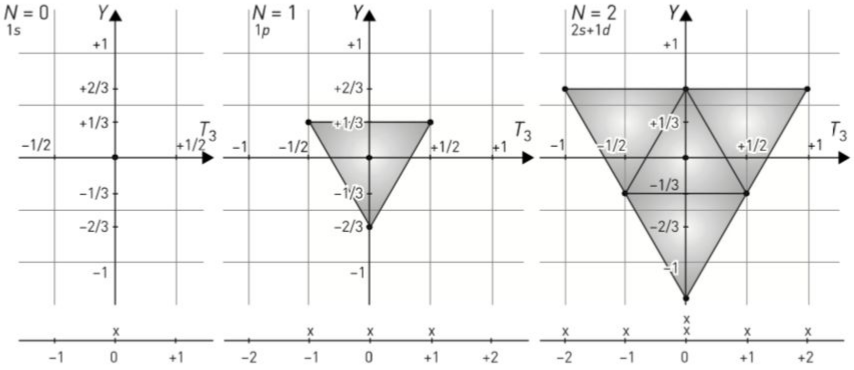
- Connects (n,l) with (n+1,l-2) and (n-1,l+2).

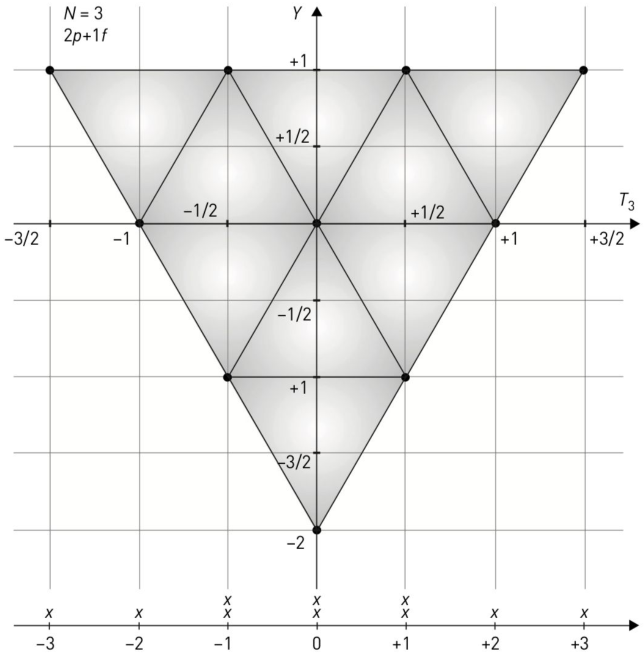
$n\backslash l$	0	1	2	3	4	5	6
7	7*s*	7*p*	7*d*	7*f*	7*g*	7*h*	7*i*
6	6*s*	6*p*	6*d*	6*f*	6*g*	6*h*	
5	5*s*	5*p*	5*d*	5*f*	5*g*		
4	4*s*	4*p*	4*d*	4*f*			
3	3*s*	3*p*	3*d*				
2	2*s*	2*p*					
1	1*s*						

The Knights ♞

Main knight gives Cartan-Weyl diagrams

$$N = 2n - l - 2$$





The Bishops ♝

Madelung ($n+l$)

- Associated with ╲ diagonals

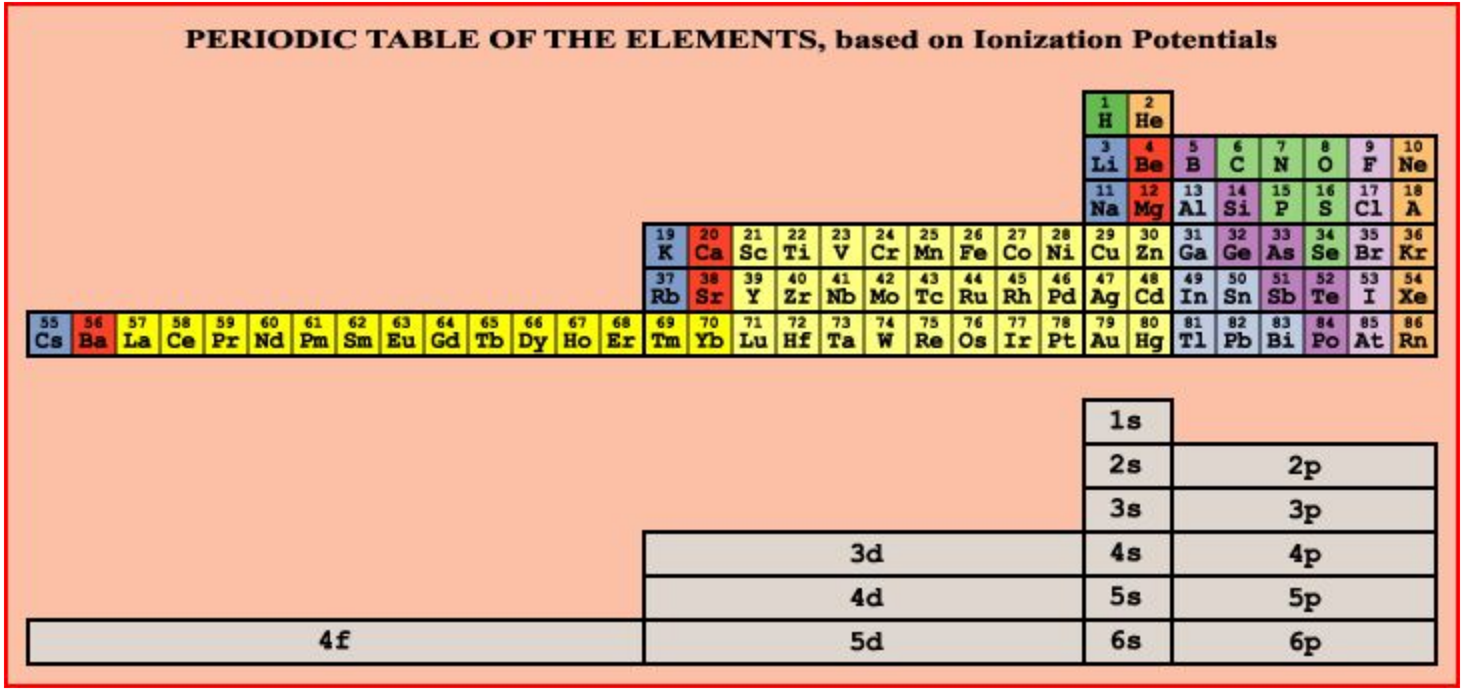
Regge (n-l)

- Associated with ╱ diagonals

Can be identified with SO(3,2), the anti-De Sitter group.

$n\backslash l$	0	1	2	3	4	5	6
7	$7s$	$7p$	$7d$	$7f$	$7g$	$7h$	$7i$
6	$6s$	$6p$	$6d$	$6f$	$6g$	$6h$	
5	$5s$	$5p$	$5d$	$5f$	$5g$		
4	$4s$	$4p$	$4d$	$4f$			
3	$3s$	$3p$	$3d$				
2	$2s$	$2p$					
1	$1s$						

Left Step Periodic Table



So what about period doubling?

The bishops, which represent SO(3,2) symmetries, thus divide SO(4,2) into two sets: $n+l$ even and $n+l$ odd.

And so the period doubling we see (2-18-18-32-32-...) is due to SO(4,2) breaking into SO(3,2).

Under SO(3,2) the manifold splits into two subsets.

Raising Bishops to Operators

We introduce $\hat{S} Y_l^m = (l + 1/2)\, Y_l^m$ from O(4,2).

This operator does not commute with all SO(4,2) operators. Not a bad thing!

With $\hat{Q}_3 = \frac{1}{2}\left(R\hat{P}^2 + R\right)$ and $\boldsymbol{B}$, one can define

$$\hat{M}_3 = \frac{1}{\sqrt{2}}\left[\hat{B}_3, \hat{Q}_3 - \hat{S}\right] \qquad \hat{R}_3 = \frac{1}{\sqrt{2}}\left[\hat{B}_3, \hat{Q}_3 + \hat{S}\right]$$

$$\hat{M}_\pm = \frac{1}{\sqrt{2}}\left[\hat{B}_\pm, \hat{Q}_3 - \hat{S}\right] \qquad \hat{R}_\pm = \frac{1}{\sqrt{2}}\left[\hat{B}_\pm, \hat{Q}_3 + \hat{S}\right]$$

Regge Operators

$$\hat{R}_3\,|nlm\rangle = -\sqrt{2}\alpha_m^{l+1}u_{l+1}^{n+1}\,|(n+1)(l+1)m\rangle + \sqrt{2}\alpha_m^{l}u_l^{n}\,|(n-1)(l-1)m\rangle,$$

$$\hat{R}_\pm\,|nlm\rangle = \pm\sqrt{2}\gamma_{\pm m}^{l+1}u_{l+1}^{n+1}\,|(n+1)(l+1)(m\pm 1)\rangle \pm\sqrt{2}\beta_{\pm m}^{l-1}u_l^{n}\,|(n-1)(l-1)(m\pm 1)\rangle,$$

Madelung Operators

$$\hat{M}_3 \,|nlm\rangle = -\sqrt{2}\alpha^{l}_{m} v^{n}_{l} \,|(n+1)(l-1)\, m\rangle + \sqrt{2}\alpha^{l+1}_{m} v^{n-1}_{l+1} \,|(n-1)(l+1)\, m\rangle\,,$$

$$\hat{M}_\pm \,|nlm\rangle = \mp\sqrt{2}\beta^{l-1}_{\pm m} v^{n}_{l} \,|(n+1)(l-1)(m\pm 1)\rangle \mp \sqrt{2}\gamma^{l+1}_{\pm m} v^{n-1}_{l+1} \,|(n-1)(l+1)(m\pm 1)\rangle$$

Recap

We took SO(4,2) then broke it into SO(3,2).

We then realized we could break this further into two subsets, one for each Bishop.

So we introduced a new operator to create SO’(3,1) (tilted SO(3,1)).

Now have an algebra $\mathfrak{so}$(4,2)-like algebra with Madelung and Regge operators.

Let’s look at algebraic structure.

Algebraic Structure

Not very different from standard SO(4), SO(3,1) algebras.

Because the structure constants are operators (and not constants), this is a nonlinear algebra.

$$\left[\hat{L}_i,\ \hat{L}_j\right] = i\varepsilon_{ijk}\hat{L}_k,$$

$$\left[\hat{L}_i, \hat{\mathcal{R}}_j\right] = i\varepsilon_{ijk}\hat{\mathcal{R}}_k,$$

$$\left[\hat{\mathcal{R}}_i, \hat{\mathcal{R}}_j\right] = -i\varepsilon_{ijk}\zeta_R\hat{L}_k;$$

$$\left[\hat{L}_i,\ \hat{L}_j\right] = i\varepsilon_{ijk}\hat{L}_k,$$

$$\left[\hat{L}_i, \hat{\mathcal{M}}_j\right] = i\varepsilon_{ijk}\hat{\mathcal{M}}_k,$$

$$\left[\hat{\mathcal{M}}_i, \hat{\mathcal{M}}_j\right] = +i\varepsilon_{ijk}\zeta_M\hat{L}_k;$$

$$\zeta_R = \frac{\hat{Q}_3 + \hat{S}}{\hat{S}}$$

$$\zeta_M = \frac{\hat{Q}_3 - \hat{S}}{\hat{S}}.$$

Casimir Operators

$\mathbf{so}(3,1)$ is an algebra of order r = 6 and rank l = 2. By Racah's theorem, there are two Casimir operators in each group.

$$\hat{C}_2 = \hat{\mathbf{L}} \cdot \hat{\mathcal{M}} = 0$$

$$\hat{C}_2 = \hat{\mathbf{L}} \cdot \hat{\mathcal{R}} = 0$$

Casimir Operators

Madelung Algebra

$$\hat{\mathcal{M}}^2 = \frac{3}{8} - \frac{1}{2}\frac{\hat{Q}_3 - \hat{S}}{\hat{S}} + \frac{1}{2}\left(\hat{Q}_3 - \hat{S}\right)^2$$

$$\hat{C}_1 = f\left(\hat{L}^2\right) + \hat{\mathcal{M}}^2 = \frac{7}{8} + \frac{1}{2}\left(\hat{Q}_3 + \hat{S}\right)^2$$

$$f\left(\hat{L}^2\right) = \left(\frac{\hat{Q}_3 + \hat{S}}{\hat{S}} - 1\right)\left(1 + 2\hat{L}^2\right)$$

$$\hat{C}_1 = \left(\frac{n^2 + n}{2} + 1\right)$$

$$\hat{C}_2 = \hat{\mathbf{L}} \cdot \hat{\mathcal{M}} = 0$$

Regge Algebra

$$\hat{\mathcal{R}}^2 = \frac{3}{8} + \frac{1}{2}\frac{\hat{Q}_3 + \hat{S}}{\hat{S}} + \frac{1}{2}\left(\hat{Q}_3 + \hat{S}\right)^2$$

$$\hat{C}_1 = f\left(\hat{L}^2\right) - \hat{\mathcal{R}}^2 = -\frac{7}{8} - \frac{1}{2}\left(\hat{Q}_3 - \hat{S}\right)^2$$

$$f\left(\hat{L}^2\right) = \left(\frac{\hat{Q}_3 + \hat{S}}{\hat{S}} - 1\right)\left(1 + 2\hat{L}^2\right)$$

$$\hat{C}_1 = -\left(\frac{n^2 - n}{2} + 1\right)$$

$$\hat{C}_2 = \hat{\mathbf{L}} \cdot \hat{\mathcal{R}} = 0$$

Conclusion

We played some atomic chess and realized some hidden group theoretic structure in the periodic table.

The group that best describes the elements is $SO(4,2) \otimes SU(2)$.

“Atoms are Christian because they listen to bishops.”

References

1. A. Ceulemans and P. Thyssen. “Shattered Symmetry: Group Theory from the Eightfold way to the Periodic Table”.

2. M. Kibler. “A Group-Theoretical Approach to the Periodic Table of Chemical Elements: Old and New Developments”. arxiv:quant-ph/0503039

Thank you