Quantum Mechanics Course Thesis

The $\mathcal{SO}(4)$ Symmetry of the Hydrogen Atom

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Abstract: We introduce some basic concepts in algebraic group theory and review the "hidden" $\mathcal{SO}(4)$ symmetry of the bound hydrogen atom in non-relativistic quantum mechanics, using an analogue of classical Runge-Lenz vector and basic Lie group theory. This algebraic approach leads to a mathematical description of a higher dimension rotational symmetry for hydrogen atom. We examine also the entire energy spectrum of the hydrogen atom.

Contents

Prelude and acknowledgments

This note grows out of an assignment on solving hydrogen model from Prof Zwiebach's lectures [1]. I expand the material with more Lie group details and deform the method more group theoretical guided.

Though the detailed mathematics is first performed explicitly in the note, the methods in the note are far from original. They borrow heavily both from the books and the online resources listed below.

- Zwiebach, Barton. *Lecture notes.*
- Townsend, John S. *A modern approach to quantum mechanics.* University Science Books, 2000.
- Schiff, Leonard I. *Quantum mechanics.* McGraw-Hill, 1968.
- Weinberg, Steven. *Lectures on quantum mechanics.* Cambridge University Press, 2012.

Also, please note that for the derivation, there is a known explicit computing in the book

- Greiner, Walter, and Berndt Müller. *Quantum mechanics: symmetries.* Springer Science & Business Media, 2012,

starting from p.460. But in the note, we take a different approach mentioned in Prof Zwiebach's lecture notes, motivated by more insight into the degeneracy of energy levels.

[1] See http://ocw.mit.edu/courses/physics/8-05-quantum-physics-ii-fall-2013/index.htm.

1 Introduction

Symmetric objects are so singular in the natural world that physicists must have noticed them very early. Infinite models are constructed with the help of symmetry. In modern physics, for instance, we rely heavily on the Lagrangian/Hamiltonian, which is "the most general one that is invariant under some symmetries" [2]. This comment can be most easily in band theory, where we literally write down effective Hamiltonians from only the constraint of representations the bands follow. As another example, the celebrated eight-fold way in particle physics is conceived with $\mathcal{SU}(3)$ group in mind.

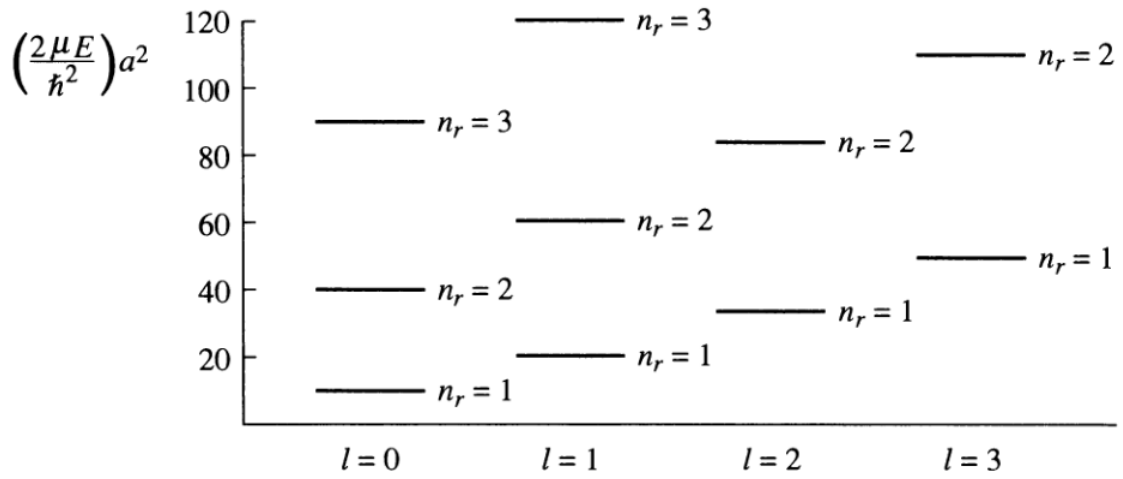

Figure 1: Numerically calculated energy levels of the hydrogen atom (from *Townsend*). Each line segment stands for a degeneracy of $2\ell + 1$. Note that no manifest degeneracy for different ℓ.

Indeed, all symmetries simplifies problem if properly observed, but in physics mostly the need for a group theoretic approach is in the case of dynamical symmetry instead of geometrical symmetry. This is due to that the geometry meets the eye is more or less simple and not very physical, while the dynamical symmetry or "hidden symmetry", normally hinted by unusual properties, gives more insight to the problem. For example, in quantum mechanics, there is an utmost geometrical symmetric object, the infinite spherical well. The potential is of a nice form

$$V(r) = \begin{cases} 0 & \text{r<a,} \\ \infty & \text{r>a.} \end{cases} \tag{1.1}$$

The solution to the problem is boring. We plot the energy levels of the infinite spherical well. Note that no interesting degeneracy arise.

[2] By Yuval Grossman (Cornell) in Theoretical Concepts in Particle Physics, CERN Summer Student Lectures 2015.

The dynamical symmetry we introduce in this note, on the other hand, contains more surprising degeneracies. In classical mechanics, the the Kepler orbits are closed, which suggests there are more constants of motion other than the orbital angular momentum. The new conserved quantity together with angular momentum generates the $\mathcal{SO}(4)$ Lie groups. They are not geometrical but the symmetries in the phase space, hence the name. These symmetries lead to an algebraic approach to determine the energy levels.

1.1 Some definitions

Since we should be using jargon from group theory, we give a minimum set of concepts for readers not familiar with the topic to proceed.

Definition 1.1. *A **group** is a non-empty set $\mathcal{G}$ with a binary operation $\oplus : \mathcal{G} \times \mathcal{G} \to \mathcal{G}$ satisfying the following three properties:*

1. *(associativity) for all $g, h, f \in \mathcal{G}$, $(g \oplus h) \oplus f = g \oplus (h \oplus f)$,*
2. *(identity) there exists $e \in \mathcal{G}$ such that for all $g \in \mathcal{G}$, $g \oplus e = e \oplus g = g$,*
3. *(inverses) for all $g \in \mathcal{G}$, there exists $h \in \mathcal{G}$ such that $g \oplus h = h \oplus g = e$.*

The **rank** of a finitely generated group $\mathcal{G}$ can be understood as the maximum number of mutually commuting generators.

Definition 1.2. *A **Casimir operator** in a Lie group is a invariant bilinear form that commutes with every generators of the group.*

A prototypical example is the squared angular momentum operator $\mathbf{J}^2$, which is a Casimir element of the three-dimensional rotation group.

We also introduce the Lie groups we 'll use in a moment. All $n \times n$ unitary matrix forms the group $\mathcal{U}(n)$. Evidently the group has n^2 independent parameters. If we require the determinant of the matrices to be equal to $+1$, the new group is called $\mathcal{SU}(n)$, characterized by $n^2 - 1$ parameters. If we further require all matrices are real and orthonormal to each other, with determinant equal to unity, we obtain $\mathcal{SO}(n)$. The generators of any Lie group are defined in terms of the group elements that are infinitesimally close to the unit element. Thus, if the group has n parameters, the n generators specify an infinitesimal element of the group in terms of n infinitesimal real parameters.

2 Dynamical symmetries and degeneracy

The hydrogen atom is the very first model physicists can solve even before Schrödinger wrote down his equation. The method we introduce here was first proposed by Pauli (*Zs. f. Phys. 36, 336 (1926)*), and it utilizes more symmetry then a quantum mechanic textbook usually do. The method, in my opinion, reveals more physics than solving a partial differential equation, albeit it can't give more than the energy levels.

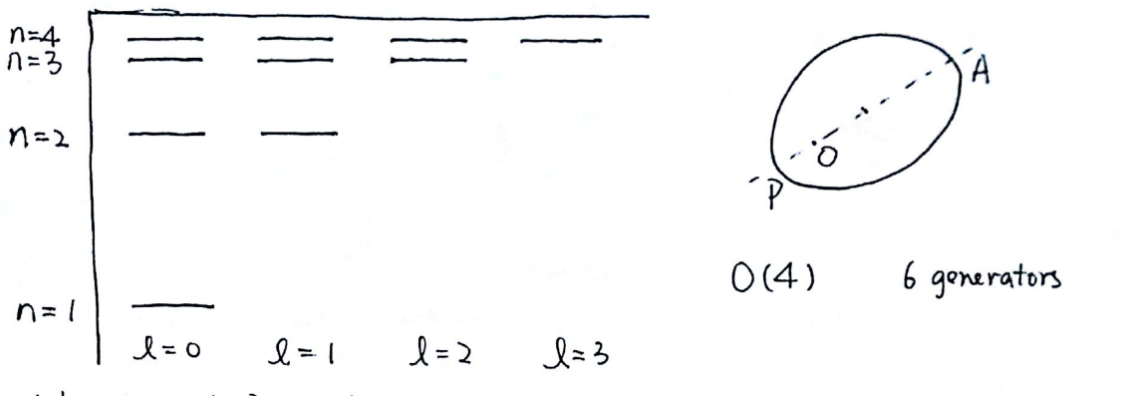

Figure 2: Left panel: the energy levels of the hydrogen atom. Each line segment stands for a degeneracy of $2\ell+1$. Right panel: a schematic trace of a particle under the force of an inverse-square central type. O is one of the focuses.

2.1 Background

The Hamiltonian for a hydrogen atom is

$$H = \frac{p^2}{2m} - \frac{e^2}{r}. \tag{2.1}$$

Following the standard procedure and solving the radial equation gives a quantized energy

$$E_n = -\frac{me^4}{2\hbar^2 n^2} = -\frac{me^4}{2\hbar^2(n_r+\ell+1)^2} = \frac{\alpha^2 mc^2}{2n^2}, \tag{2.2}$$

where $n = n_r+\ell+1$ is the principle quantum number, $\alpha = e^2/\hbar c \sim 1/137$ the fine-structure number. Note that $\alpha^2 \sim 5.33\times 10^{-5}$. Since the spin-orbit coupling has a characteristic energy of $\sim \alpha^4 mc^2$, the hyperfine spliting $\sim (m_e/m_p)\alpha^4 mc^2$, we can safely ignore these effects here. From eq. (2.2) we can infer the degeneracy of E_n to be

$$\sum_{\ell=0}^{n-1}(2\ell+1) = n^2. \tag{2.3}$$

To have a better understanding, we can plot this (indeed) fancy degeneracy in the left panel of fig. 2. However, the derivation in most textbooks won't disclose why physically this is true.

2.2 Classical Runge-Lenz vector

As others, our method also borrow quantities to understand these "incidents". From classical mechanics, we understand for Kepler type orbits, the conservation of H and $\vec{L}$ is not enough to keep the orbit closed. A small deviation of the potential, e.g. general relativity effect for the Mercury, induces a slow procession. To have a closed orbit like the

right panel of fig. 2, we need another constant of motion to characterize the orientation of the major axis in orbital plane. Such a vector is known as the Runge-Lenz vector, but first found by Laplace:

$$\vec{R} = \frac{\vec{p} \times \vec{L}}{m} - \frac{e^2}{r}\vec{r}. \tag{2.4}$$

It's easy to check the Runge-Lenz vector has the following properties.

$$\frac{d}{dt}\vec{R} = 0, \tag{2.5}$$

$$|\vec{R}|^2 = \frac{2H}{m}\vec{L}^2 + e^4, \tag{2.6}$$

$$\vec{L} \cdot \vec{R} = 0. \tag{2.7}$$

For the elliptical orbit of a classical particle, the Runge-Lenz vector $\vec{R}$ in fact points into the direction of the semi major axis of the ellipse, while the length of it is the eccentricity.

2.3 Runge-Lenz operator

To translate the vector to quantum mechanics, we must first promote everything to operator and hermitianizing the Runge-Lenz operator, i.e.

$$\begin{aligned} \hat{R} &= \frac{1}{2}(\vec{R} + \vec{R}^\dagger) \\ &= \frac{1}{2m}(\vec{p} \times \vec{L} - \vec{L} \times \vec{p}) - \frac{e^2}{r}\vec{r} \\ &= \frac{1}{m}(\vec{p} \times \vec{L} - i\hbar\vec{p}) - \frac{e^2}{r}\vec{r}. \end{aligned} \tag{2.8}$$

Now we need to check if properties (2.5)- (2.7) remians true.

For eq. (2.5), we now need to prove $[\hat{R}, \hat{H}] = 0$. For simplicity, we denote $f = e^2/r$. Then $\hat{H} = \hat{p}^2/2m - f$, $\hat{R} = \frac{1}{m}(\vec{p} \times \vec{L} - i\hbar\vec{p}) - f\vec{r}$. With some careful calculations, we find

$$[\hat{p}^2, f\vec{r}] = \frac{\hbar}{i}[(\hat{p}\hat{r})\hat{r}\frac{f'}{r} + \frac{f'}{r}\hat{r}(\hat{r}\hat{p}) + \hat{p}f + f\hat{p}], \tag{2.9}$$

$$[\hat{p} \times \hat{L} - \hat{L} \times \hat{p}, f] = \frac{\hbar}{i}[(\hat{p}\hat{r})\hat{r}\frac{f'}{r} + \frac{f'}{r}\hat{r}(\hat{r}\hat{p}) - \hat{p}rf' - rf'\hat{p}], \tag{2.10}$$

where $f' := \frac{d}{dr} = -f/r$. It's now evident that

$$\begin{aligned} [\hat{H}, \hat{R}] &= -\frac{\hbar}{2mi}[\hat{p}(f + rf') + (f + rf')\hat{p}] \\ &= 0. \end{aligned} \tag{2.11}$$

Then we calculate the length-squared of the quantum Runge-Lenz vector. We first

note the following equations always hold true.

$$(\hat{L}\times\hat{p})\hat{r} = -\hat{L}^2, \tag{2.12}$$

$$i\hbar(\hat{p}\frac{\hat{r}}{r} - \frac{\hat{r}}{r}\hat{p}) = \frac{2\hbar^2}{r}, \tag{2.13}$$

$$(\hat{L}\times\hat{p})(\hat{p}\times\hat{L}) = -\hat{p}^2\hat{L}^2. \tag{2.14}$$

Now we can proceed further

$$\begin{aligned}
\hat{R}^2 &= [\frac{1}{m}(-\hat{L}\times\hat{p} + i\hbar\hat{p}) - \frac{e^2}{r}\hat{r}][\frac{1}{m}(\hat{p}\times\hat{L} - i\hbar\hat{p}) - \frac{e^2}{r}\hat{r}] \\
&= \frac{1}{m^2}[-(\hat{L}\times\hat{p})(\hat{p}\times\hat{L}) + i\hbar(\hat{L}\times\hat{p})\hat{p} + i\hbar\hat{p}(\hat{p}\times\hat{L}) + \hbar^2\hat{p}^2] - \frac{e^2}{m}[(-\hat{L}\times\hat{p} + i\hbar\hat{p})\frac{\hat{r}}{r} \\
&\quad + \frac{\hat{r}}{r}(\hat{p}\times\hat{L} - i\hbar\hat{p})] + e^4 \\
&= \frac{1}{m^2}(\hat{p}^2\hat{L}^2 + \hbar^2\hat{p}^2) - \frac{e^2}{m}(\frac{2\hat{L}^2}{r} + \frac{2\hbar^2}{r}) + e^4 \\
&= e^4 + \frac{2\hat{H}}{m}(\hat{L}^2 + \hbar^2).
\end{aligned} \tag{2.15}$$

Note the resemblance to the classical result!

We then continue to property eq. (2.7). One can easily check that $\hat{L}\hat{R} = \hat{R}\hat{L} = 0$. But the full quantum analogy is the commutation relations between $\hat{L}$ and $\hat{R}$, i.e.

$$[L_i, L_j] = i\hbar\epsilon_{ijk}L_k \qquad [R_i, L_i] = 0 \tag{2.16}$$

$$[R_i, L_j] = i\hbar\epsilon_{ijk}R_k \qquad [R_i, R_j] = -\frac{2\hat{H}}{m}i\hbar\epsilon_{ijk}L_k. \tag{2.17}$$

The first three are easy to check by definition, while the fourth is rather tricky. We note that it's equivalent to

$$(\hat{R}\times\hat{R})_i = -\frac{2\hat{H}}{m}i\hbar\epsilon_{ijk}r_j p_k. \tag{2.18}$$

The calculation is actually so involved that *Weinberg* referred to as tedious. Here we simplify the progress by a trick given by Schwinger. First, we make the insight that for any to conserved operators S_1 and S_2, their commutation must also be conserved due to the Jacobi identity

$$[[S_1, S_2], H] + [[H, S_1], S_2] + [[S_2, H], S_1] = 0. \tag{2.19}$$

So $[R_i, R_j]$ is a conserved object. And our options are $\hat{L}$, $\hat{R}$ and $\hat{L}\times\hat{R}$. We narrow the options down by perform the parity operator: $\mathcal{P}\hat{r} = -\hat{r}$. Since

$$\mathcal{P}\hat{p} = -\hat{p} \qquad \mathcal{P}\hat{L} = \hat{L} \qquad \mathcal{P}\hat{R} = -\hat{R}, \tag{2.20}$$

the choice is $\hat{R} \times \hat{R} = \alpha \hat{L}$, where α is a constant we now determine.

$$\begin{aligned}
(\hat{R} \times \hat{R})_i &= \epsilon_{ijk} \left[\frac{1}{m} (\epsilon_{jmn} p_m \epsilon_{nab} r_a p_b - i\hbar p_j) - e^2 \frac{r_j}{r} \right] \left[\frac{1}{m} (\epsilon_{kmn} p_m \epsilon_{nab} r_a p_b - i\hbar p_k) - e^2 \frac{r_k}{r} \right] \\
&= \epsilon_{ijk} \left[\frac{1}{m} \left(\hat{p}^2 r_j - (\hat{p}\hat{r} + i\hbar) p_j \right) - e^2 \frac{r_j}{r} \right] \left[\frac{1}{m} \left(\hat{p}^2 r_k - (\hat{p}\hat{r} + i\hbar) p_k \right) - e^2 \frac{r_k}{r} \right] \\
&= \epsilon_{ijk} \left[\frac{1}{m^2} \left(- \hat{p}^2 r_j (\hat{p}\hat{r} + i\hbar) p_k - (\hat{p}\hat{r} + i\hbar) p_j \hat{p}^2 r_k \right) + \frac{e^2}{m} \left(\frac{r_j}{r} (\hat{p}\hat{r} + i\hbar) p_k + (\hat{p}\hat{r} + i\hbar) p_j \frac{r_k}{r} \right) \right] \\
&= -\frac{2\hat{H}}{m} i\hbar \epsilon_{ijk} r_j p_k.
\end{aligned} \tag{2.21}$$

2.4 From 3D to 4D

Since $\hat{H}$ is independent of time and commutes with both $\hat{L}$ and $\hat{R}$, we replace $\hat{H}$ with E and define

$$\hat{R}' := \sqrt{-\frac{m}{2E}} \hat{R}, \tag{2.22}$$

which gives cleaner relations with $\hat{L}$ as

$$[R'_i, R'_j] = i\hbar \epsilon_{ijk} L_k. \tag{2.23}$$

We know $\hat{L}$ formed a closed algebra and corresponds to the group $\mathcal{SO}(3)$. With the help of the commutations, we can show there is another closed algebra formed by $\hat{L}$ and $\hat{R}$. First we relabel $\hat{r}$, $\hat{p}$, $\hat{L}$ as

$$\hat{r} = (r_1, r_2, r_3) \qquad \hat{p} = (p_1, p_2, p_3) \qquad \hat{L} = (L_{23}, L_{31}, L_{12}), \tag{2.24}$$

and $\hat{R}'$ as

$$\hat{R}' = (L_{14}, L_{24}, L_{34}). \tag{2.25}$$

Note that if we write $L_{ij} := r_i p_j - r_j p_i$ and let $[r_i, p_j] := i\hbar\delta_{ij}$, we readily establish the full commutation relations between $\hat{L}$ and $\hat{R}'$. Thus even only formally, we generalized $\hat{L}$ from 3D to 4D. And the 6 generators effectively generate the group $\mathcal{SO}(4)$.

2.5 The group $\mathcal{SO}(4)$

To better the understanding of the mass we performed, we interpret the result from another angle. It can be proved that there is a homomorphism from the group $\mathcal{SO}(4)$ to $\mathcal{SO}(3) \otimes \mathcal{SO}(3)$, that is, two independent angular momentum can be constructed.

Define

$$\hat{I} = \frac{1}{2}(\hat{L} + \hat{R}') \qquad \hat{K} = \frac{1}{2}(\hat{L} - \hat{R}'). \tag{2.26}$$

Their properties are as follows

$$[I_i, I_j] = i\hbar\epsilon_{ijk} I_k, \qquad [K_i, K_j] = i\hbar\epsilon_{ijk} K_k, \tag{2.27}$$

$$[\hat{I}, \hat{K}] = 0, \qquad [\hat{I}, \hat{H}] = [\hat{K}, \hat{H}] = 0. \tag{2.28}$$

Note that $\mathcal{SO}(4)$ is of rank 2, which gives two Casimir operators[3], i.e.

$$\hat{I}^2 = \frac{1}{4}(\hat{L} + \hat{R}')^2, \qquad \hat{K}^2 = \frac{1}{4}(\hat{L} - \hat{R}')^2. \tag{2.29}$$

The eigenvalues are

$$I^2 = i(i+1)\hbar^2, \qquad K^2 = k(k+1)\hbar^2, \qquad i, k = 0, \frac{1}{2}, 1, \ldots. \tag{2.30}$$

Due to he cross term that vanishes as we have checked, $\hat{I}^2 = \hat{K}^2$ and $i = k$. A third operator is needed for the energy levels, that is, $\hat{C} := (\hat{L}^2 + \hat{R}'^2)/2 = \hat{I}^2 + \hat{K}^2 = 2k(k+1)\hbar^2$, $k = 0, \frac{1}{2}, 1, \ldots$. On the other hand,

$$\begin{aligned} \hat{C} &= \frac{1}{2}(\hat{L}^2 + \hat{R}'^2) \\ &= \frac{1}{2}(\hat{L}^2 - \frac{m}{2E}\hat{R}^2) \\ &= \frac{me^4}{4E} - \frac{1}{2}\hbar^2. \end{aligned} \tag{2.31}$$

Thus

$$E = -\frac{me^4}{2\hbar^2(2k+1)^2}. \tag{2.32}$$

We identify $n = 2k + 1$, hacing values $1, 2, 3, \ldots$.

The reason we use half-integer values for i, k is $\hat{L} = \hat{I} + \hat{K}$ and $i = k$. By the rules of addition of angular momentum, ℓ can take any value ranging from $i + k = 2k = n - 1$ to $|i - k| = 0$, by integer steps. Or in representation language,

$$\frac{1}{2}\mathbf{(n\text{-}1)} \otimes \frac{1}{2}\mathbf{(n\text{-}1)} = \mathbf{n\text{-}1} \oplus \mathbf{n\text{-}2} \oplus \ldots \oplus \mathbf{1} \oplus \mathbf{0}, \tag{2.33}$$

which more naturally describe fig. 2. Thus the range of ℓ for a given n is actually constrained by the physical restriction that it can only take integer values up to $n - 1$.

Remark 2.1. We need to clarify that our considerations are only limited to bound states. For scattering states, $E > 0$, $\hat{R}'$ need to be modified to stay Hermitian. Then commutations are messed up. The parts from $\hat{I}$, $\hat{K}$ would be invalid.

Remark 2.2. There is yet another way to understand the degeneracy, from directly the group $\mathcal{SO}(4)$. More geometrical than physical. We do not discuss the method here. But for the intrigued, see Weinberg p.145.

[3]It's defined that a Casimir operator of a group commutes with all generators of the group.

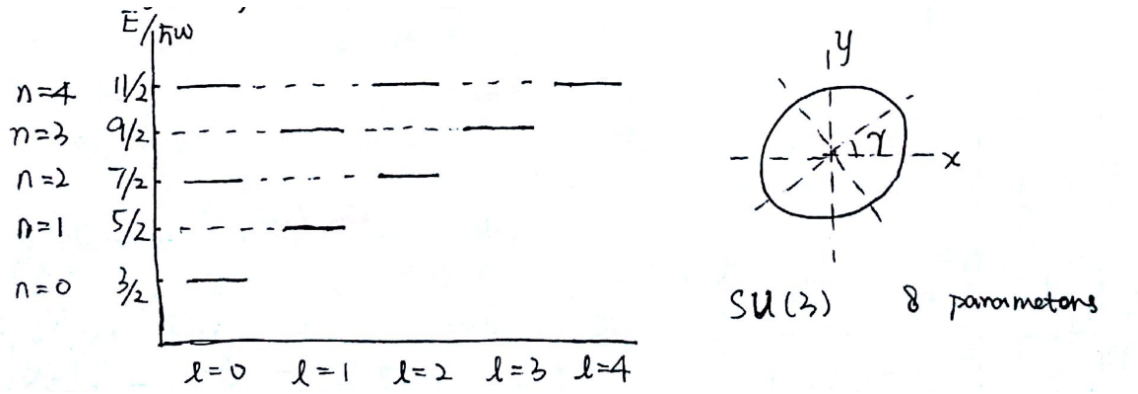

Figure 3: Left panel: the energy levels of the 3D isotropic harmonic oscillator. Each line segment stands for a degeneracy of $2\ell+1$. Right panel: a particular solution of the classical orbit problem is an ellipse with semimajor axis a and semiminor axis b, which has its major axis oriented so as to make an angle γ with the x axis. Point of attraction is O.

2.6 3D isotropic harmonic oscillator

Another interesting object we will not discuss in detail is the 3D isotropic harmonic oscillator, with the symmetry of $\mathcal{SU}(3)$ type. Still we show the energy levels in fig. 3 for another feature of hydrogen atom. One note that there is a very distinct property for the degeneracy from fig. 2.

That is, states of even and odd l are degenerate in fig. 2, albeit $\hat{L}$ has a well-defined parity as seen in eq. 2.20. The two generators case is the reason. Since $\hat{L}$ is axial and $\hat{R}$ polar, and the states are generated by both, they lost the well defined parity. In the harmonic oscillator case, there is only one generator presence, and states has a well-defined parity.

3 Concluding remarks

In conclusion, we can say that the bound states of the hydrogen atom can be determined by the principal quantum number n, which takes the values $n = 1, 2, \ldots$. For given n, we have n^2 states with angular momenta $\ell = 0, 1, \ldots, n-1$, and energy E_n given by eq. (2.2), or eq. (2.32).

We finally remark that this symmetry is not limited to the problem discussed here, despite its antiquity. It can be more general, i.e. the n-dimensional hydrogen atom has the $\mathcal{SO}(n+1)$ and the isotropic oscillator has the $\mathcal{SU}(n)$ symmetry. And objects that shares the same symmetry can be analysed much the same way.