SYMMETRY AND THE HYDROGEN ATOM

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Contents

1. The Electron Orbitals of the Hydrogen Atom

Electron orbitals are distinguished by three quantum numbers: the energy quantum number (n), the azimuthal quantum number (l), and the magnetic quantum number (m_l). n can take any integer value, $l = 1, ..., n-1$, and $m_l = -l, ..., l$. The energy quantum number gives the energy of the electron, the azimuthal quantum number roughly gives its shape, and the magnetic quantum number gives its orientation. For a long time I was mystified by the appearance of these numbers. This paper is the end of a long journey to understand them.

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Sections 2 through 5 are one leg of this journey - understanding how groups and their representations can tell us something about the eigenstates of a physical system. This is good conceptual background for what follows, although much of sections 4 and 5 are irrelevant to the sequel. Up to this point, the exposition is meant to be self-contained. Sections 6 and 7 are the second leg of the journey, and they require more sophistication from the reader, namely some knowledge of or familiarity with smooth manifolds. In this section, we discuss Lie groups, and how one particular Lie group can tell us things about the hydrogen atom.

2. Hamiltonians and Commuting Operators

2.1. **A Hamiltonian Formalism.** Quite often, when searching for the equilibrium or normal modes of a physical system, we must solve an eigenvalue equation. For example, if we are talking about a finite, constant-coefficient system of linear ordinary differential equations, the law of evolution is contained in a Hamiltonian matrix H. Given a state vector $x(t)$, H tells us in what direction the state evolves in an infinitesimal period of time,

$$\dot{x}(t) = Hx(t).$$

The normal modes of this system are of the form

$$x_i(t) = e^{-\lambda_i t} x_i,$$

where λ_i is an eigenvalue of H and x_i is its associated eigenvector.

In general, the Hamiltonian operator H need not be linear or constant in time, and our state space need not be either linear or finite dimensional. In quantum mechanics, we lose finite-dimensionality but retain linearity of both the Hamiltonian and the state space. The time evolution of a state $\alpha(x,t)$ is governed by a Hamiltonian operator, H, via the equation

$$\frac{\partial}{\partial t}\alpha(x,t) = -\frac{i}{\hbar} H\alpha(x,t).$$

To find the normal modes of this system, we assume that α is an energy eigenfunction α_E of H, so that it satisfies

$$\frac{\partial}{\partial t}\alpha_E(x,t) = -\frac{i}{\hbar} E\alpha_E(x,t).$$

Then, we can write it in the form

$$\alpha_E(x,t) = \exp\left(-\frac{i}{\hbar}Et\right) u_E(x),$$

and $u_E(x)$ satisfies the eigenfunction equation

$$Hu_E(x) - Eu_E(x) = 0.$$

2.2. **The Schrodinger Equation.** The Schrodinger equation

$$i\hbar\frac{\partial}{\partial t}\psi(x,t) = -\frac{\hbar^2}{2m}\nabla^2\psi(x,t) + V(x)\psi(x,t)$$

describes the time evolution of a wave function ψ governed by the Hamiltonian

$$H = \frac{p_{op}^2}{2m} + V(x).$$

Here $V(x)$ is a time-independent spatial potential, and p_{op} is the momentum operator. The energy eigenfunctions of H satisfy the eigenfunction equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(x)\right] u_E(x) - Eu_E(x) = 0.$$

Example. Let's look at the case of a particle in a 1-dimensional potential well. The particle's wave function satisfies the Schrodinger equation with V taking the form

$$V(x) = \begin{cases} V(x) = 0, & |x| \leq \frac{L}{2} \\ V(x) = \infty, & |x| > \frac{L}{2} \end{cases} .$$

This particle has momentum only in one (the x) direction, and inside the potential well it satisfies

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_E(x) = E\psi_E(x).$$

At the boundaries (since the walls are infinitely high there is no tunneling), the wave function must be zero. The solutions are

$$\psi_n(x) = \begin{cases} \sin\left(\frac{n\pi x}{L}\right), \text{ n even,} \\ \cos\left(\frac{n\pi x}{L}\right), \text{ n odd,} \end{cases}$$

with energies given by

$$E = \frac{n^2\pi^2\hbar^2}{2ma^2}.$$

□

2.3. **Degeneracy.** Hamiltonian operators frequently exhibit degeneracy. That is, the eigenfunctions with a given energy may not be unique. It is a fact that commuting operators, degenerate or not, are simultaneously diagonalizable.

Theorem 2.1. *If A, B are diagonalizable operators on some Hilbert space H with*

$$[A, B] = AB - BA = 0,$$

then there is a basis for H made up of simultaneous eigenvectors for A and B.

Nondegenerate Case. This is easy to see if A and B are nondegenerate. Let $Av = \lambda v$. Then,

$$ABv = BAv = \lambda Bv,$$

so Bv is an eigenvector of A with eigenvalue λ. Since A is nondegenerate, this means Bv is a multiple of v, so that v is also an eigenvector of B. □

In general, this means that if our Hamiltonian H is degenerate, and we have another operator A which commutes with it and is not degenerate on the same subspaces, we can distinguish its degenerate eigenstates by their eigenvalues under A.

3. Symmetry and Groups

Degeneracy in Hamiltonians and in physical systems in general is often due to some kind of symmetry. In other words, the Hamiltonian H commutes with a set of symmetry transformations. Symmetries are best described by algebraic objects called *groups*, and the symmetry transformations are called *representations* of those groups.

Definition 3.1. A **group** is a set of elements G and a binary operation

$$\begin{aligned} * : G \times G &\longrightarrow G \\ (g, h) &\longmapsto g * h \end{aligned}$$

with the following properties:

- **i.** For all $g, h, k \in G$, $g * (h * k) = (g * h) * k$;
- **ii.** There is a unique element $e \in G$ so that for any other $g \in G$, $g * e = e * g = g$;
- **iii.** For any $g \in G$, there is a unique element $g^{-1} \in G$ so that $gg^{-1} = g^{-1}g = e$.

A group can be specified by its multiplication table. Here are some examples.

3.1. **The Cyclic Group $\mathbb{Z}_n$.** The group $\mathbb{Z}_n$ is the group containing the powers of a single element, a, with $a^n = e$. This group can be thought of as the integers $\mod n$, with a^k equivalent to k; this is where the notation $\mathbb{Z}_n$ comes from. The multiplication tables for $\mathbb{Z}_2$ and $\mathbb{Z}_3$, the simplest cyclic groups, follow.

$\mathbb{Z}_2$	e	a
e	e	a
a	a	e

$\mathbb{Z}_3$	e	a	a^2
e	e	a	a^2
a	a	a^2	e
a^2	a^2	e	a

3.2. **The Dihedral Group D_n.** D_n is the group of symmetries of an n-gon in the plane. Its elements include the identity, rotations through an angle of $2\pi\frac{k}{n}$, for $k = 1, ..., n-1$, and the n reflections across the lines containing the center of the polygon and each vertex. Note that the $n-1$ rotations along with the identity form a cyclic group, so $\mathbb{Z}_n$ is always contained in D_n. D_2, the group of symmetries of a "thickened" 2-gon, i.e. a rhombus or rectangle, is also known as the Klein four group. Its mulitptlication table appears below. T_h denotes reflection over the "horizontal midline", T_v is reflection over the "vertical midline", and R_π is rotation by π.

D_2	e	T_h	T_v	R_π
e	e	T_h	T_v	R_π
T_h	T_h	e	R_π	T_v
T_v	T_v	R_π	e	T_h
R_π	R_π	T_v	T_h	e

The multiplication table for D_3, the group of symmetries of an equilateral triangle, appears below. T_i denotes reflection over the line through vertex i and the center of the triangle, and R_θ is counterclockwise rotation through an angle θ.

D_3	e	T_a	T_b	T_c	$R_{\frac{2\pi}{3}}$	$R_{\frac{4\pi}{3}}$
e	e	T_a	T_b	T_c	$R_{\frac{2\pi}{3}}$	$R_{\frac{4\pi}{3}}$
T_a	T_a	e	$R_{\frac{4\pi}{3}}$	$R_{\frac{2\pi}{3}}$	T_b	T_c
T_b	T_b	$R_{\frac{2\pi}{3}}$	e	$R_{\frac{4\pi}{3}}$	T_c	T_a
T_c	T_c	$R_{\frac{4\pi}{3}}$	$R_{\frac{2\pi}{3}}$	e	T_a	T_b
$R_{\frac{2\pi}{3}}$	$R_{\frac{2\pi}{3}}$	T_c	T_a	T_b	$R_{\frac{4\pi}{3}}$	e
$R_{\frac{4\pi}{3}}$	$R_{\frac{4\pi}{3}}$	T_b	T_c	T_a	e	$R_{\frac{2\pi}{3}}$

3.3. **The Permutation Group S_n.** S_n is the group of permutations of n symbols. It contains $n!$ elements. Note that S_3 actually contains 6 elements, just like D_3. The two groups are actually the same - any symmetry of an equilateral triangle can be thought of as a permutation of the vertices. In fact, S_n always contains D_n.

4. Group Representations

Often, we are interested in the action of a group on a phase space, which is frequently a Hilbert space. (A finite-dimensional Hilbert space is just $\mathbb{R}^n$ for some n.) This action is usually by a linear transformation such as a rotation or a reflection. We call such an action a **representation** of the group, and if we restrict ourselves to rotations and reflections - called **unitary** transformations - then we have a unitary representation.

Definition 4.1. A unitary group representation of degree n is a map

$$\begin{aligned} D : G &\longrightarrow U(n) \\ g &\longmapsto D(g) \end{aligned}$$

so that

- **i.** $R(e) = I$.
- **ii.** For any $g, h \in G$, $R(gh) = R(g)R(h)$.

Examples. As we've already discussed, $\mathbb{Z}_n$ can be represented as a set of 2×2 rotation matrices:

$$D\left(a^k\right) = \left(\begin{array}{cc} \cos\left(2\pi\frac{k}{n}\right) & -\sin\left(2\pi\frac{k}{n}\right) \\ \sin\left(2\pi\frac{k}{n}\right) & \cos\left(2\pi\frac{k}{n}\right) \end{array} \right).$$

D_n can also be represented by a set of orthogonal matrices comprising rotations and reflections. For example, a two-dimensional representation of D_4 appears below.

$$D(e) = \begin{pmatrix} 1 & \\ & 1 \end{pmatrix}, \quad D(T_a) = \begin{pmatrix} -1 & \\ & 1 \end{pmatrix},$$

$$D(T_b) = \begin{pmatrix} 1 & \\ & -1 \end{pmatrix}, \quad D(T_c) = \begin{pmatrix} & 1 \\ 1 & \end{pmatrix}, \quad D(T_d) = \begin{pmatrix} & -1 \\ -1 & \end{pmatrix},$$

$$D\left(R_{\frac{\pi}{2}}\right) = \begin{pmatrix} & -1 \\ 1 & \end{pmatrix}, \quad D(R_\pi) = \begin{pmatrix} -1 & \\ & -1 \end{pmatrix}, \quad D\left(R_{\frac{3\pi}{2}}\right) = \begin{pmatrix} & 1 \\ -1 & \end{pmatrix}.$$

Any group can be represented "trivially" by a linear transformation on $\mathbb{R}$ - namely, the identity transformation. Thus, for any G, the trivial representation is

$$D(g) = 1.$$

□

4.1. **Irreducibility.** We can create a group representation of any dimension - for example, by sending all the group elements to the identity matrix of that dimension, or by appending extra dimensions to a known representation which stay fixed under the group representation. However, this is in some sense more information than we need.

On the other hand, in order to label states which transform under the representation of a group, we'd like to simultaneously diagonalize that representation as much as possible. (Each of the matrices in the representation can be diagonalized, but they cannot all be diagonalized simultaneously.) The concept of an irreducible representation will help us with both of these problems.

Definition 4.2. An irreducible representation of a group G is a representation such that the only subspaces left invariant by every element $D(g)$ are X and 0.

The trivial representation is always irreducible - indeed, every one-dimensional representation is.

Example. Aside from the traditional two-dimensional representation of D_3 as the symmetries of an equilateral triangle, we can think of it as S_3 and let it act on $\mathbb{R}^3$ by permuting the basis vectors $\{e_1(=a), \quad e_2(=b), \quad e_3(=c)\}$. Then, the six elements of D_3 are represented as

$$D(e) = \begin{pmatrix} 1 & & \\ & 1 & \\ & & 1 \end{pmatrix}, \quad D(T_a) = \begin{pmatrix} 1 & & \\ & & 1 \\ & 1 & \end{pmatrix},$$

$$D(T_b) = \begin{pmatrix} & & 1 \\ & 1 & \\ 1 & & \end{pmatrix}, \quad D(T_c) = \begin{pmatrix} & 1 & \\ 1 & & \\ & & 1 \end{pmatrix},$$

$$D\left(R_{\frac{2\pi}{3}}\right) = \begin{pmatrix} & & 1 \\ 1 & & \\ & 1 & \end{pmatrix}, \quad D\left(R_{\frac{4\pi}{3}}\right) = \begin{pmatrix} & 1 & \\ & & 1 \\ 1 & & \end{pmatrix}.$$

However, it is easy to see that this representation is not irreducible, because it leaves the subspace spanned by the vector $(1,1,1)$ invariant. The representation must also leave the subspace perpendicular to $(1,1,1)$ invariant. We can see how it acts on this plane by projecting the coordinate vectors - $e_1 = (1,0,0)$, $e_2 = (0,1,0)$, and $e_3 = (0,0,1)$ - onto this plane. The resulting vectors are

$$\hat{e}_1 = (\frac{2}{3}, -\frac{1}{3}, -\frac{1}{3}) \quad \hat{e}_2 = (-\frac{1}{3}, \frac{2}{3}, -\frac{1}{3}) \quad \hat{e}_3 = (-\frac{1}{3}, -\frac{1}{3}, \frac{2}{3})$$

which form an equilateral triangle in the plane whose normal is $(1,1,1)$. The representation acts on this plane just as we'd expect - via the rotations and reflections that leave the triangle with vertices $\hat{e}_1, \hat{e}_2, \hat{e}_3$ invariant. Thus, this three dimensional representation of D_3 is a "sum" of the trivial representation and the canonical two dimensional representation of D_3, acting on orthogonal subspaces. $\square$

In fact, the two dimensional representation of D_3 is irreducible, and it is true in general that any representation of a finite group can be "block diagonalized" as a sum of irreducible representations.

Theorem 4.3. *Any representation of a finite group with finite degree can be decomposed as a direct sum of irreducible representations.*

4.2. **Character Theory.** Of course, now we have the problem of decomposing an arbitrary group representation into a direct sum of irreducible representations, not to mention the problem of determining which representations are irreducible. All this is solved with character theory.

Definition 4.4. The **character** of a group representation D is the function

$$\begin{aligned} \chi : G &\longrightarrow \mathbb{C} \\ g &\longmapsto Tr\,(D(g)) \end{aligned}$$

Note that the character sends each group element to the sum of the eigenvalues of the operator representing it. Later it will be useful to think of characters as elements of $\mathbb{R}^{\#(G)}$, where $\#(G)$, the **order** of G, is the number of elements in G.

4.2.1. *Conjugacy Classes.* To understand how characters help us solve the problems above, we have to learn about another group-theoretic concept called a conjugacy class.

Definition 4.5. A **conjugacy class** of a group G is a subset H of elements of G with the property that

$$g^{-1}hg \in H$$

for any $g \in G$ and any $h \in H$. That is, H is invariant under conjugation by G.

A finite group G has a finite number of conjugacy classes, and can be decomposed into a disjoint union of its conjugacy classes:

$$G = \coprod_{i=1}^{m} C_i.$$

The conjugacy classes of $\mathbb{Z}_2$ are just the elements - $\{e\}$ is one conjugacy class, and $\{a\}$ is another. In fact this is true for any group in which the binary operation is commutative, called an abelian group, since

$$ghg^{-1} = gg^{-1}h = h$$

for any $g, h \in G$. The conjugacy classes of S_n correspond to the cycle types of the permutations.

Note that characters are constant on conjugacy classes:

$$\begin{aligned}\chi\left(g^{-1}hg\right) &= Tr\left(D\left(g^{-1}hg\right)\right)\\ &= Tr\left(D\left(g^{-1}\right)D(h)D(g)\right)\\ &= Tr\left(D(g)^{-1}D(g)D(h)\right)\\ &= Tr(D(h)) = \chi(h).\end{aligned}$$

In fact, conjugacy classes tell us a great deal about the irreducible representations of a group.

Theorem 4.6. *The number of irreducible representations of a group is the same as the number of conjugacy classes.*

Thus, for each group, we can make up a square table, called the **character table**, which gives the character on each conjugacy class, for each irreducible representation. The character table for $\mathbb{Z}_2$, with the trivial representation, *id*, already filled in, is

$\mathbb{Z}_2$	$\{e\}$	$\{a\}$
χ_{id}	1	1
χ_2		

For S_3, we have filled out the character table thus far:

S_3	$\{e\}$	$\{T_a, T_b, T_c\}$	$\{R_{\frac{2\pi}{3}}, R_{\frac{4\pi}{3}}\}$
χ_{id}	1	1	1
χ_{2d}	2	0	-1
χ_3			

4.2.2. *Orthogonality Relations.* How can we finish filling out these character tables? Using two remarkable facts.

Theorem 4.7. *Let G be a finite group, and let $i = 1, ..., m$ index its irreducible representations. If d_i is the degree of the ith irreducible representation, then*

$$\sum_i d_i^2 = \#(G).$$

Thus, for $\mathbb{Z}_2$, we have

$$\begin{aligned}&d_{id}^2 + d_2^2 = 1^2 + d_2^2 = 2\\ &\implies d_2 = 1\end{aligned}$$

so the other irreducible representation of $\mathbb{Z}_2$ is also one dimensional. For S_3, we have

$$\begin{aligned} d_{id}^2 + d_{2d}^2 + d_3^2 &= 1 + 4 + d_3^2 = 6 \\ &\implies d_3 = 1 \end{aligned}$$

so the remaining irreducible representation of S_3 is also one dimensional. The second remarkable fact is the following.

Theorem 4.8. *The rows of the character table are orthonormal, with the weighted inner product on* $\mathbb{R}^m$ *given by*

$$x^T \begin{pmatrix} \frac{\#(C_1)}{\#(G)} & & & \\ & \frac{\#(C_2)}{\#(G)} & & \\ & & \ddots & \\ & & & \frac{\#(C_3)}{\#(G)} \end{pmatrix} x.$$

By inspection, we can complete the character table of $\mathbb{Z}_2$ as follows:

$\mathbb{Z}_2$	$\{e\}$	$\{a\}$
χ_{id}	1	1
χ_2	1	-1

With a little algebra, we can complete the character table of S_3 as well:

S_3	$\{e\}$	$\{T_a, T_b, T_c\}$	$\{R_{\frac{2\pi}{3}}, R_{\frac{4\pi}{3}}\}$
χ_{id}	1	1	1
χ_{2d}	2	0	-1
χ_3	1	-1	1

Note that the third representation of S_3, when it is viewed as D_3, merely indicates whether the transformation is a reflection or a rotation.

To decompose a given group representation into irreducible representations, we use a third and final remarkable fact.

Theorem 4.9. *If a representation* D *can be written as a direct sum of irreducibles* D_i*, each appearing with multiplicity* k_i*, then*

$$\begin{aligned} k_i &= \frac{1}{\#(G)} \sum_{g \in G} \chi(g)^* \chi_i(g) \\ &= \sum_m \frac{\#(C_m)}{\#(G)} \chi(C_m)^* \chi_i(C_m). \end{aligned}$$

4.3. **Representations and Function Spaces.** If our state space is not linear, then the group of symmetries of the space cannot be represented as linear operators on the space. If our state space is not finite dimensional, then its group of symmetries may not be clear, and any group representation will be in the form of linear operators on the space.

4.3.1. *Representations on Function Spaces.* Classically, our state space is finite-dimensional, and there is a group of symmetries acting directly on the space itself. However, in quantum mechanics our state space is usually infinite dimensional - it is the Hilbert space $L^2(X)$ of square-integrable functions on a finite-dimensional space X. If a group G acts on a space X via a representation D, then it also acts on the functions on X by the representation $\hat{D}$, defined so that

$$\hat{D}(g)f(x) = f\left(D(g)^{-1}x\right).$$

The inverse is what makes it a representation:

$$\begin{aligned}\hat{D}(gh)f(x) &= f\left(D(gh)^{-1}x\right) = f\left(D(h)^{-1}D(g)^{-1}x\right)\\ &= \hat{D}(h)f\left(D(g)^{-1}x\right) = \hat{D}(g)\hat{D}(h)f(x).\end{aligned}$$

4.3.2. *Group Actions.* If our state space, X, is not a vector space, or we are interested in the Hilbert space $L^2(X)$ of functions on a nonlinear space, like the sphere, we must generalize the idea of a group representation. A **group action** is just the generalization we seek.

Definition 4.10. An action of a group G on a space X is a map

$$\begin{aligned}G \times X &\longrightarrow X\\ (g, x) &\longmapsto gx\end{aligned}$$

so that

- **i.** $ex = x$ for any $x \in X$.
- **ii.** For any $g, h \in G$, $(gh)x = g(hx)$.

We say G acts on X.

It is easy to check that any group representation is a group action, with

$$gx = D(g)x.$$

However, not every group action is a representation. If we restrict any group representation to a subset of the linear space X which is not itself a linear space, we obtain a group action. For example, D_3 acts on the vectors $\hat{e}_1$, $\hat{e}_2$, and $\hat{e}_3$, but its action is not a representation. Likewise the set $U(n)$ of all rotations and reflections of $\mathbb{R}^n$ acts on the unit sphere S^{n-1}, but since S^{n-1} is not a linear space, this cannot be a representation.

What is convenient about the above formalism is that, even when X is a nonlinear space, like a manifold, its group of symmetries G acts on it. Then, $L^2(X)$ is a linear space, and the action of G on X induces a representation of G on $L^2(X)$, defined by

$$\hat{D}(g)f(x) = f(g^{-1}x).$$

5. Symmetry and Physical Systems

Now, we saw in the previous section that we can decompose any representation into a direct sum of irreducible representations. Thus, if we have a system whose Hamiltonian commutes with a group representation, we can label the eigenstates of that Hamiltonian not only by their energy, but also by how they transform under the group representation. To be more precise, we can label them by which irreducible representation of the group they transform under.

Theorem 5.1. *If a hermitian operator H commutes with all the elements $D(g)$ of a representation of the group G, then we can shoose the eigenstates of H to transform according to irreducible representations of G. In other words, we can choose the eigenstates of H to live in a subspace on which an irreducible factor of D acts.*

5.1. Labeling Eigenstates With Projection Operators.

How do we go about labeling the eigenstates of our Hamiltonian? We can create an operator P_i which projects an eigenstate onto the subspace transforming according to irreducible representation D_i. This operator is defined to be

$$P_i = \sum_{g \in G} \chi_i(g) D_i(g).$$

When we apply P_i to a degenerate eigenstate of our Hamiltonian, we obtain an eigenstate which also lives in the subspace of X transforming according to irreducibe representation D_i.

Example. Let's see how all this works in the case of a particle trapped in a potential well. The Hamiltonian is invariant under the parity operator

$$px = -x.$$

Since $p^2 x = x$, the parity operator and the identity operator together form a representation of $\mathbb{Z}_2$. This representation acts on the coordinate of the well, but it also acts on the functions inside the well via

$$pf(x) = f(-x).$$

Looking at the character table for $\mathbb{Z}_2$, we can form the projection operators for both irreducible representations of $\mathbb{Z}_2$:

$$\begin{aligned} P_{id} &= (1)I + (1)p = I + p \\ P_2 &= (1)I + (-1)p = I - p. \end{aligned}$$

If we act on functions with these operators, we recover the spaces

$$\begin{aligned} P_{id} f(x) &= f(x) + f(-x) \\ P_2 f(x) &= f(x) - f(-x) \end{aligned}$$

which, we can see, are the spaces of even and odd functions, respectively. Thus, we can always choose the energy eigenstates of our Hamiltonian to be either even or odd, as sin and cos are. □

This is all fine and good, but why do we want to label our eigenstates by some irreducible representation? The real usefulness of this approach becomes apparent when we don't even know what our Hamiltonian is, and we only know the symmetries of our system. In this case, we may be able to find eigenstates of our system using only the projection operators.

Example. Consider three blocks of equal mass, connecting by springs of equal stiffness and length, which are free to slide on a frictionless surface. This system can be described by a vector with six components,

$$(r_{11}, \quad r_{12}, \quad r_{21}, \quad r_{22}, \quad r_{31}, \quad r_{32}),$$

where r_{j1} is the x-component of the jth block, and r_{j2} is the y-component of the jth block. We can regard this as a tensor product of the two dimensional space in which the x and y coordinates live with a three dimensional space of the configuration of the blocks.

Now, this system has two different kinds of symmetries. Firstly, we can permute the indices of the blocks. This symmetry can be represented by the three dimensional representation of D_3 written above. Secondly, the coordinates of the blocks in the plane can be reflected and rotated according to the symmetries of an equilateral triangle. This symmetry can be represented by the canonical, irreducible two dimensional representation of D_3. Altogether, the symmetry group of the system can be represented by the tensor product of these two representations, in which we multiply each element in a 3×3 representation of one element of D_3 with a 2×2 representation of another element of D_3, and then replace the elements in the blocks to form a 6×6 matrix. So, for example,

$$D\left(R_{\frac{2\pi}{3}}\right) = \begin{pmatrix} & & & & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ & & & & \frac{\sqrt{3}}{2} & -\frac{1}{2} \\ -\frac{1}{2} & -\frac{\sqrt{3}}{2} & & & & \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & & & & \\ & & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & & \\ & & \frac{\sqrt{3}}{2} & -\frac{1}{2} & & \end{pmatrix}$$

Now, the projection onto the trivial representation of D_3 is

$$P_{id} = \begin{pmatrix} \frac{1}{4} & \frac{\sqrt{3}}{12} & -\frac{1}{4} & \frac{\sqrt{3}}{12} & 0 & -\frac{\sqrt{3}}{6} \\ \frac{\sqrt{3}}{12} & \frac{1}{12} & -\frac{\sqrt{3}}{12} & \frac{1}{12} & 0 & -\frac{\sqrt{3}}{6} \\ -\frac{1}{4} & -\frac{\sqrt{3}}{12} & \frac{1}{4} & -\frac{\sqrt{3}}{12} & 0 & \frac{\sqrt{3}}{6} \\ \frac{\sqrt{3}}{12} & \frac{1}{12} & -\frac{\sqrt{3}}{12} & \frac{1}{12} & 0 & -\frac{\sqrt{3}}{6} \\ 0 & 0 & 0 & 0 & 0 & 0 \\ -\frac{\sqrt{3}}{6} & -\frac{1}{6} & \frac{\sqrt{3}}{6} & -\frac{1}{6} & 0 & \frac{1}{3} \end{pmatrix}$$

$$= \begin{pmatrix} \frac{1}{2} \\ \frac{\sqrt{3}}{6} \\ -\frac{1}{2} \\ \frac{\sqrt{3}}{6} \\ 0 \\ -\frac{1}{\sqrt{3}} \end{pmatrix} \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{6} & -\frac{1}{2} & \frac{\sqrt{3}}{6} & 0 & -\frac{1}{\sqrt{3}} \end{pmatrix}$$

which is just the projection onto the state

$$\left(\frac{1}{2}, \frac{\sqrt{3}}{6}, -\frac{1}{2}, \frac{\sqrt{3}}{6}, 0, -\frac{1}{\sqrt{3}}\right),$$

seen to be a "breathing mode" for the system, where the triangle grows and shrinks while retaining its shape. P_2 is the projection onto the state

$$\left(-\frac{\sqrt{3}}{6}, \frac{1}{2}, -\frac{\sqrt{3}}{6}, -\frac{1}{2}, -\frac{1}{\sqrt{3}}, 0\right),$$

which is a rotation around the center of mass. ☐

6. Lie Groups and Lie Algebras

A Lie group is a group with infinitely many elements, which has a kind of continuous structure. Intuitively, we know how close the elements of G are to one another. Technically, we equip G with much more than a topological structure - in fact, we give it the smooth structure of a manifold. This definition brings with it all kinds of structures - for example tangent and cotangent spaces - which I will not go into here.

6.1. **Lie Algebras.**

Lie groups have infinitely many elements, and so we cannot write down a multiplication table for a Lie group. However, we can still get a handle on Lie groups through their correspondence with a canonical vector space called the Lie algebra corresponding to the group.

Definition 6.1. The Lie algebra $\mathfrak{g}$ of a Lie group G is

$$\mathfrak{g} = T_eG,$$

the tangent space to G at the identity.

There are two other useful interpretations of $\mathfrak{g}$. To see the first of these, we introduce a map from G to itself.

Definition 6.2. Left translation by $g \in G$ is the map L_g given by

$$\begin{aligned} L_g :& G \longrightarrow G \\ & h \longmapsto L_g(h) = gh. \end{aligned}$$

The derivative of left translation is a map on TG, which acts by translating the basepoint of a tangent vector:

$$\begin{aligned} L_{g*} :& T_hG \longrightarrow T_{gh}G \\ & X_h \longmapsto X_{gh}. \end{aligned}$$

Given $X \in \mathfrak{g}$, we can use L_{g*} to translate X over G, creating a **left-invariant vector field**. In fact, all the left-invariant vector fields can be obtained in this way, and we can say more.

Proposition 6.3. *There is a one to one correspondence between the elements of $\mathfrak{g}$ and the left-invariant vector fields on G, where a left-invariant vector field satisfies the equation*

$$L_{g*}X_h = X_{gh}.$$

Thus, we can also think of the Lie algebra as the set of left-invariant vector fields on G, and we see that this set has the same dimension as G. Finally, on any manifold M, we can define an "exponential map" from TM to M by

$$\begin{aligned} \exp :& TM \longrightarrow M \\ & tX_p \longmapsto \exp_p(tX) = \phi_X^t(p), \end{aligned}$$

where X is a smooth vector field, ϕ_X^t is the flow associated to X, and t is any real number so that the map exists.

When we restrict this map on TG to $\mathfrak{g}$, we obtain the canonical exponential map of a Lie algebra onto its Lie group, which we will denote simply exp. The integral curves for left-invariant vector fields exist for all times. This is easy to see because the flow associated to any vector field exists for short time, but for left-invariant vector fields this solution can be left-translated to obtain a solution for all times. It is a fact that if G is compact, exp is onto. Also, since X is left-invariant, we have $\phi^t_X(g) = \phi^t_X(ge) = g\phi^t_X(e)$, and thus we also have the equation

$$\exp((s+t)X) = \phi^{s+t}_X(e) = \phi^t_X(\phi^s_X(e)) = \phi^s_X(e)\phi^t_X(e) = \exp(sX)\exp(tX),$$

which justifies the name "exponential map". (Another justification is that for matrix groups, this map is simply the matrix exponential.) Thus we have obtained the following result.

Proposition 6.4. *The curve* $\exp(tX)$*, for* $t \in \mathbb{R}$*, is the unique one-parameter subgroup of* G *having tangent vector* X *at* e*.*

This gives us a third interpretation of g, as the set of all one-parameter subgroups of G passing through e.

6.2. **The Lie Bracket.**

All vector spaces of a given dimension are isomorphic, but all Lie groups having the same dimension are not isomorphic. The Lie algebras of different Lie groups are distinguished by a structure called a **Lie bracket**, which encodes information about the group product. To define the Lie bracket we first introduce the **commutator map**,

$$\begin{aligned} C :& G \times G \longrightarrow G \\ & (g,h) \longmapsto ghh^{-1}g^{-1}. \end{aligned}$$

Now, we can define the Lie bracket as the derivative of the commutator map restricted to $\mathfrak{g}$.

Definition 6.5. The Lie bracket is the map

$$\begin{aligned} C_* := [,] :& \mathfrak{g} \times \mathfrak{g} \longrightarrow \mathfrak{g} \\ & (X,Y) \longmapsto [X,Y] = X \circ Y - Y \circ X. \end{aligned}$$

In composing X and Y we are thinking of them as differential operators on $C^\infty G$. The Lie bracket for matrix groups is just the matrix commutator

$$[A,B] = AB - BA.$$

Regardless of how the Lie bracket operation is defined on a given Lie algebra, we can always write the bracket of two basis elements X_i, X_j for $\mathfrak{g}$ as a particular linear combination of the other basis elements:

$$[X_i, X_j] = \sum_k f_{ijk} X_k.$$

In fact, we can skip the step of defining the Lie bracket operation at all, and merely give the f_{ijk} for all values of i, j, k. These numbers are called the **structure constants** of the Lie algebra. A Lie algebra can be described completely by giving these n^3 numbers - much easier than writing down an infinitely large multiplication table.

6.3. **Representations of Lie Algebras.** Just as it is often easier to describe the Lie algebra of a Lie group, it is often more convenient to write down a representation of a Lie algebra, and extend it to a representation of the Lie group using the exponential map.

Definition 6.6. A unitary representation of a Lie algebra $\mathfrak{g}$ with structure constants f_{ijk} is a map

$$\begin{aligned} D : \mathfrak{g} &\longrightarrow U(n) \\ X &\longmapsto D(X) \end{aligned}$$

so that

$$[D(X_i), D(X_j)] = \sum_k f_{ijk} D(X_k),$$

where $[,]$ is the matrix commutator.

In fact, it is possible to find all the irreducible representations of a Lie group $\mathfrak{g}$ using only the structure constants f_{ijk}. In general, this is a complicated process, which I will not go into here. In the simplest case, which is the one relevant to the hydrogen atom, it is much easier.

If a Lie group acts on a space X, then its Lie algebra is always represented on the space of functions on X as a collection of differential operators. This is true only because of the continuous nature of Lie groups. Namely, if $\{X_i\}_{i=1}^n$ is a basis for $\mathfrak{g}$, we can define differential operators $\{D_i\}_{i=1}^n$ by

$$D_i f(x) = \frac{\partial}{\partial t}\Big|_{t=0} f\left(\exp(tX_i)^{-1} x\right).$$

This is just the derivative of f along the curve $\gamma(t) = \exp(tX_i)x \subset X$, obtained by allowing the one-parameter group $\exp(tX_i)$ to act on x. In physics terminology, this is expressed by saying that D_i is the infinitesimal generator of the action $\exp(tX_i)$. Note that

$$\begin{aligned} \left(D_i D_j - D_j D_i\right) f(x) = \lim_{s\to 0, t\to 0} \frac{1}{st} \Big[& f\left(\exp(tX_i)^{-1} \exp(tX_j)^{-1} x\right) \\ & - f\left(\exp(tX_j)^{-1} \exp(tX_i)^{-1} x\right) \Big]. \end{aligned}$$

It takes some more work to show that this is a representation of $\mathfrak{g}$; I leave this as an exercise for the reader.

7. SU(2) and the Hydrogen Atom

To find the electron orbitals of the hydrogen atom, the full Schrodinger equation in three dimensions is solved, with the boundary condition being that the magnitude of the solutions decays to zero at infinity. In other words, the potential is

$$V(x) = 0,$$

so the wavefunctions solve

$$-\frac{\hbar^2}{2m} \nabla^2 \phi_E(x) = E \phi_E(x).$$

Now, the Hamiltonian here is just

$$-\frac{\hbar^2}{2m} \nabla^2,$$

where

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2},$$

or, in spherical coordinates,

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right].$$

It is clear from the Cartesian representation of ∇^2 that this Hamiltonian is invariant under rotations about the origin; that is, the Hamiltonian commutes with the action on $\mathbb{R}^3$ of $SO(3)$, the group of rotations in three dimensions.

7.1. **SO(3) and SU(2).**

$SO(3)$ is one example of a Lie group. An element $U \in SO(3)$ is orthogonal, so it satisfies

$$U^T U = I.$$

$U^T U$ is symmetric, and so has only six independent elements. Thus, the above relation contains six equations the elements of U must satisfy. Since U has nine elements to begin with, $SO(3)$ is a three dimensional manifold.

$SO(3)$ is closely related to another Lie group called $SU(2)$. $SU(2)$ is the set of all 2×2 unitary complex matrices with determinant one. It turns out that $SU(2)$ is a double cover of $SO(3)$, that is, it's in two-to-one correspondence with $SO(3)$, since both U and $-U$ induce the same transformation of $\mathbb{R}^3$.

7.2. **The Irreducible Representations of $SU(2)$.**

$\mathfrak{su}(2)$, the Lie algebra of $SU(2)$, is known to satisfy the structure equations

$$[\sigma_i, \sigma_j] = \sum_k i\epsilon_{ijk}\sigma_k,$$

where the ϵ_{ijk} are the entries in the Levi-Civita tensor, or the sign of the permutation (ijk).

$SU(2)$ is the simplest compact nonabelian Lie group, and finding its representations using the structure constants of $\mathfrak{su}(2)$ is not too hard. First, define

$$A^- = \frac{1}{\sqrt{2}}(\sigma_1 + i\sigma_2) \qquad A^+ = \frac{1}{\sqrt{2}}(\sigma_1 - i\sigma_2)$$

and note that

$$[\sigma_3, A^-] = -A^-, \qquad [\sigma_3, A^+] = A^+, \qquad [A^+, A^-] = \sigma_3.$$

Now, let D be a representation of $\mathfrak{su}(2)$ of degree n, and pick a basis of $\mathbb{R}^n$ which diagonalizes $D(\sigma_3)$. (Note that since the elements of the Lie algebra do not commute, only one of them can be diagonalized at a time.) Now let v be an eigenvector of $D(\sigma_3)$, with eigenvalue α. Then,

$$\begin{aligned} D(\sigma_3)D(A^-)v &= \left(\left[D(\sigma_3), D(A^-)\right] + D(A^-)D(\sigma_3)\right)v \\ &=(\alpha - 1)D(A^-)v, \\ D(\sigma_3)D(A^+)v &= \left(\left[D(\sigma_3), D(A^+)\right] + D(A^+)D(\sigma_3)\right)v \\ &=(\alpha + 1)v. \end{aligned}$$

Thus $D(A^-)v$ is an eigenvector of $D(\sigma_3)$ with eigenvalue $\alpha - 1$, and $D(A^+)v$ is an eigenvector of $D(\sigma_3)$ with eigenvalue $\alpha - 1$. This explains our notation; we call A^+ the **raising element**, and A^- is the **lowering element**. It is also a fact that $D(A^+)$ is the adjoint of $D(A^-)$.

Let λ be the largest eigenvalue of $D(\sigma_3)$, and let v_λ be a unit eigenvector for it. Then, we have

$$D(A^+)v_\lambda = 0, \qquad D(A^-)v_\lambda = c_\lambda v_{\lambda-1},$$

where c_λ is some constant and $v_{\lambda-1}$ is a unit eigenvector for $\lambda - 1$. To find c_λ, we compute

$$\begin{aligned}\|D(A^-)v_\lambda\|^2 =&\langle D(A^-)v_\lambda, D(A^-)v_\lambda\rangle\\ =&\langle v_\lambda, D(A^+)D(A^-)v_\lambda\rangle\\ =&\langle v_\lambda, \left[D(A^+), D(A^-)\right] v_\lambda\rangle\\ =&\langle v_\lambda, D(\sigma_3)v_\lambda\rangle\\ =&\lambda\|v_\lambda\|^2 = \lambda.\end{aligned}$$

Thus, $c_\lambda = \sqrt{\lambda}$. Likewise, we have

$$\begin{aligned}D(A^+)v_{\lambda-1} =&\frac{1}{\sqrt{\lambda}}D(A^+)D(A^-)v_\lambda\\ =&\frac{1}{\sqrt{\lambda}}\left[D(A^+), D(A^-)\right] v_\lambda\\ =&\frac{1}{\sqrt{\lambda}}D(\sigma_3)v_\lambda\\ =&\sqrt{\lambda}v_\lambda.\end{aligned}$$

We can continue this process, obtaining a decreasing sequence of eigenvalues $\lambda - k$ with unit eigenvectors $v_{\lambda-k}$ satisfying the relationships

$$\begin{aligned}D(A^-)v_{\lambda-k} &= c_{\lambda-k}v_{\lambda-k-1}\\ D(A^+)v_{\lambda-k-1} &= c_{\lambda-k}v_{\lambda-k}.\end{aligned}$$

By using the fact that $D(A^-)$ and $D(A^+)$ are adjoint, we obtain

$$\begin{aligned}c_{\lambda-k}^2 =&\|c_{\lambda-k}v_{\lambda-k}\|^2\\ =&\|D(A^+)v_{\lambda-k-1}\|^2\\ =&\langle v_{\lambda-k-1}, D(A^-)D(A^+)v_{\lambda-k-1}\rangle\\ =&\langle v_{\lambda-k-1}, \left(D(A^+)D(A^-) - D(\sigma_3)\right) v_{\lambda-k-1}\rangle\\ =&c_{\lambda-k-1}^2 - \lambda + k + 1.\end{aligned}$$

We can solve this recursion relation to find that

$$c_{\lambda-k} = \sqrt{\frac{1}{2}(k+1)(2\lambda - k)}.$$

Fortunately, we cannot go on applying the lowering element forever. At some point, we reach an integer m for which there is an associated eigenvector $v_{\lambda-n}$ for which we have

$$D(A^-)v_{\lambda-n} = 0.$$

But this implies that

$$c_{\lambda-n} = \sqrt{\frac{1}{2}(n+1)(2\lambda - n)} = 0,$$

so that we must have $2\lambda - n = 0$, and so we finally uncover λ's identity - it is $\frac{n}{2}$ for some integer n. We also see that the smallest eigenvalue of $D(\sigma_3)$ is $\frac{n}{2} - n = -\frac{n}{2}$. Since the eigenvalues of $D(\sigma_3)$ are spaced one apart, this means that there are $2\lambda + 1 = n + 1$ eigenvalues of $D(\sigma_3)$.

So we see that $\mathfrak{su}(2)$ has an irreducible representation for every integer m, called the **spin $\frac{n}{2}$ representation**. The spin $\frac{n}{2}$ representation has dimension $2n + 1$. Each such representation corresponds to an irreducible representation of the group $SU(2)$. The spin zero representation is the trivial representation, with dimension one. The spin $\frac{1}{2}$ representation is given by

$$\sigma_1 = \begin{pmatrix} & 1 \\ 1 & \end{pmatrix} \qquad \sigma_2 = \begin{pmatrix} & \text{-i} \\ \text{i} & \end{pmatrix} \qquad \sigma_3 = \begin{pmatrix} 1 & \\ & \text{-1} \end{pmatrix}.$$

The spin one representation is given by

$$\sigma_1 = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \qquad \sigma_2 = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & \text{-i} & 0 \\ \text{i} & 0 & \text{-i} \\ 0 & \text{i} & 0 \end{pmatrix},$$

$$\sigma_3 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \text{-1} \end{pmatrix}.$$

Finally, note that for any eigenvector v of $D(\sigma_3)$, where D is the spin $\frac{n}{2}$ representation of $SU(2)$, we have

$$\left[D(\sigma_3)^2 + D(A^+)D(A^-) + D(A^-)D(A^+)\right] v = \frac{n}{2}\left(\frac{n}{2} + 1\right) v.$$

The transformation on the left can be rewritten

$$D(\sigma_1)^2 + D(\sigma_2)^2 + D(\sigma_3)^2$$

and it is a constant multiple of the identity transformation. That multiple tells us the dimension of the irreducible representation under which v transforms. In general, such a transformation or operator is called a **Casimir invariant**.

The representation theory of $\mathfrak{su}(2)$ is crucial to understanding the representation theory of more general Lie algebras. It turns out that every (compact) Lie algebra has a maximal abelian subalgebra called the **Cartan subalgebra**. The representations of elements of the Cartan subalgebra are all simultaneously diagonalizable, and the simultaneous eigenvectors can then be associated with a vector of eigenvalues (one for each basis element of the Cartan subalgebra) called a weight. These weights can be ordered, and each irreducible representation of the Lie group can be identified by its highest weight, just as each irreducible representation of $\mathfrak{su}(2)$ was identified by the highest eigenvalue of $D(\sigma_3)$. What's more, for each basis element of the Cartan subalgebra, there is a three-dimesional subspace of the Lie algebra that looks like $\mathfrak{su}(2)$, so in a sense every Lie group contains many copies of $SU(2)$.

Since $\mathfrak{su}(2)$ is represented on the space of functions on S^2, we can decompose this (infinite-dimensional) space of functions as a sum of (finite-dimensional) spaces which carry irreducible representations of $\mathfrak{su}(2)$. Thus, if $H^{n/2}_{\mathfrak{su}(2)}$ is an n-dimensional vector space on which $\mathfrak{su}(2)$ acts irreducibly according to the spin-$n/2$ representation, we can write

$$L^2(S^2) \subset H^0_{\mathfrak{su}(2)} \oplus H^{1/2}_{\mathfrak{su}(2)} \oplus H^1_{\mathfrak{su}(2)} \oplus H^{3/2}_{\mathfrak{su}(2)} \oplus \dots$$

Furthermore, since the Hamiltonian governing the electron orbitals of hydrogen commutes with the action of $SU(2)$ on $\mathbb{R}^3$ (via projection onto $SO(3)$), we can choose the solutions of the time-independent Schrödinger equation to lie in one of these subspaces, and, even better, to transform according to one of the spin representations of $SU(2)$.

7.3. **Angular Momentum.** However, this still doesn't tell us what the solutions to the time-independent Schrödinger equation living in $H^{n/2}_{\mathfrak{su}(2)}$ look like. To answer this question, we need to know how $\mathfrak{su}(2)$ is represented on the space of functions on S^2. We know this representation will take the form of a collection of differential operators. These differential operators will correspond to differentiation in the direction of the group action, and they are what is referred to in the physics literature as the infinitesimal generators of rotations. For example, the infinitesimal generator of rotation around the z-axis is just the derivative as we change θ, $\frac{\partial}{\partial\theta}$. Quantum physicists multiply their operators by $-\frac{i}{\hbar}$, and they express the relationship between a rotation and its infinitesimal generator by writing

$$R_\theta = \exp\left(-\frac{i}{\hbar}\frac{\partial}{\partial\theta}\right) \sim I - \frac{i}{\hbar}\frac{\partial}{\partial\theta}.$$

In fact, a basis for the infinitesimal generators of rotations is given by the quantum analogs of angular momentum, the angular momentum operators. In classical mechanics, angular momentum is defined as

$$L = x \times p,$$

where x is the position of a particle, and p is its momentum. In quantum mechanics, we make x and p into operators. In one dimension, the operators $\mathbf{x}$ and $\mathbf{p}$ act on functions of one variable in the following way:

$$\mathbf{x}f = f(x), \qquad\qquad \mathbf{p}f = \frac{\partial}{\partial x}f.$$

They satisfy the commutation relations

$$[\mathbf{x}, \mathbf{p}] = -i\hbar$$

(Note that momentum is actually the infinitesimal generator of translation.) Now, we define in three dimensions the vectors of operators

$$\vec{\mathbf{x}} = (\mathbf{x}, \mathbf{y}, \mathbf{z}), \qquad\qquad \vec{\mathbf{p}} = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right).$$

Finally, we define the vector of angular momentum operators as

$$L = -i\hbar\left(\vec{\mathbf{x}} \times \vec{\mathbf{p}}\right).$$

Using index (x_i) rather than x, y, z notation, we can write the i^{th} component of L as

$$L_i = -i\hbar \epsilon_{ijk} \mathbf{x}_j \mathbf{p}_k.$$

Note that these operators act not on $\mathbb{R}^3$ itself, but on functions on $\mathbb{R}^3$. Let us examine L_z and see how it generates rotations about the z-axis. We have

$$\begin{aligned} L_z &= -i\hbar \left(\epsilon_{312} \mathbf{x} \frac{\partial}{\partial y} + \epsilon_{321} \mathbf{y} \frac{\partial}{\partial x} \right) \\ &= -i\hbar \left(\mathbf{x} \frac{\partial}{\partial y} - \mathbf{y} \frac{\partial}{\partial x} \right) \\ &= -i\hbar \frac{\partial}{\partial \theta}, \end{aligned}$$

as can be checked by noting that

$$\theta = \arctan \frac{y}{x}$$

and

$$\frac{\partial}{\partial y} = \frac{\partial \theta}{\partial y} \frac{\partial}{\partial \theta}, \qquad \frac{\partial}{\partial x} = \frac{\partial \theta}{\partial x} \frac{\partial}{\partial \theta}.$$

The three components of the angular momentum operator are a representation of $\mathfrak{su}(2)$ on S^2, a fact we can check by verifying the commutation relations

$$[L_i, L_j] = \sum_k \epsilon_{ijk} L_k.$$

7.4. **Spherical Harmonics.** Now, we can use the components of the angular momentum operator to find the functions transforming according to each representation of $SU(2)$. We form the Casimir invariant

$$L^2 = L_x^2 + L_y^2 + L_z^2.$$

If l is a half-integer, and $\psi(\theta, \phi)$ transforms according to the spin l representation of $SU(2)$, then ψ solves the eigenvalue equation

$$L^2 \psi(\theta, \phi) = l(l+1) \psi(\theta, \phi).$$

This equation can be solved using the technique of separation of variables. If we let $\psi(\theta, \phi) = T(\theta) P(\phi)$, then we obtain the differential equations

$$\begin{aligned} &\frac{1}{P(\phi)} \frac{\partial^2}{\partial \phi^2} P(\phi) = -m^2 \\ &l(l+1) \sin^2(\theta) + \frac{\sin(\theta)}{T(\theta)} \frac{\partial}{\partial \theta} \left[\sin(\theta) \frac{\partial}{\partial \theta} T(\theta) \right] = m^2 \end{aligned}$$

We know from representation theory that there can only be $2l + 1$ independent solutions to these equations, and the periodic boundary conditions on the sphere confirm this, restricting m to lie between l and $-l$. These boundary conditions also restrict l to be a whole number greater than one, and so we lose the spin $n + \frac{1}{2}$ representations of $SU(2)$.

The solutions to these equations are called **spherical harmonics**, and written $Y_l^m(\theta, \phi)$. The spherical harmonic transforming according to the spin 0 representation is

$$Y_0^0(\theta, \phi) = \frac{1}{2}\sqrt{\frac{1}{\pi}}.$$

The spherical harmonics for $l = 1$ are

$$\begin{aligned} Y_1^1(\theta, \phi) &= -\frac{1}{2}\sqrt{\frac{3}{2\pi}} e^{i\phi} \sin\theta, \\ Y_1^0(\theta, \phi) &= \frac{1}{2}\sqrt{\frac{3}{\pi}} \cos\theta, \\ Y_1^{-1}(\theta, \phi) &= \frac{1}{2}\sqrt{\frac{3}{2\pi}} e^{-i\phi} \sin\theta. \end{aligned}$$

The spherical harmonics are eigenfunctions of $-i\hbar\frac{\partial}{\partial\phi}$. Thus, as expected, we have

$$-i\hbar\frac{\partial}{\partial\phi} Y_0^0 = 0,$$

$$-i\hbar\frac{\partial}{\partial\phi} Y_1^1 = \hbar Y_1^1, \qquad -i\hbar\frac{\partial}{\partial\phi} Y_1^0 = 0, \qquad -i\hbar\frac{\partial}{\partial\phi} Y_1^{-1} = -\hbar Y_1^{-1}.$$

In fact, the complete set of symmetries of S^2 are given by a group called $PSL(2, \mathbb{C})$, which is otherwise known as the **Lorentz group**. The analogs of the spherical harmonics for the Lorentz group are functions known as the **hypergeometric series**. In fact, any Lie group can be viewed as the group of symmetries of a suitable **symmetric space**, and so such functions can be developed for any Lie group; the generalizations are also called hypergeometric series.

Another result from Lie theory, the **Peter-Weyl Theorem**, says that any function in $L^2(S^2)$ can be decomposed uniquely as an infinite sum of spherical harmonics. This is the analog of the Fourier transform on S^1 in two dimensions. In fact, the functions on an arbitrary symmetric space can be decomposed as sums of the hypergeometric series corresponding to its group of symmetries; as far as I can tell, this is the subject of study in abstract harmonic analysis.

7.5. **The Electron Orbitals in the Flesh.** How are the spherical harmonics related to the electron orbitals of hydrogen? It turns out that we can write the Hamiltonian for the hydrogen atom in terms of L^2, because

$$\nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2} r - \frac{1}{\hbar^2 r^2} L^2.$$

Thus the eigenfunction equation

$$-\frac{\hbar^2}{2m}\nabla^2 \phi_E(r, \theta, \phi) = E\phi_E(r, \theta, \phi)$$

can be solved by the ansatz

$$\phi_E = R(r) Y_l^m(\theta, \phi).$$

The resulting equation for R is

$$\frac{1}{r}\frac{\partial^2}{\partial r^2} rR(r) = \frac{l(l+1)}{r^2} R(r),$$

so that the radial part of the hydrogen orbital depends on l. This is the link between the energy of the orbital and the possible irreducible representation of $SU(2)$ under which it may transform.

Symmetry and the hydrogen atom