Accidental Symmetry of Hydrogen Atom

IDC412 Seminar Delivery

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Contents

Degeneracy of Hydrogen and Symmetry of the Hamiltonian

In quantum mechanics, the bound-state solution of the hydrogen atom is known to have a n^2 degeneracy in the energy levels. The Hamiltonian is given as:

$$\hat{H} = \frac{\vec{p}^2}{2m} - \frac{k\vec{r}}{r} \tag{1}$$

We also know that in quantum mechanics, "degeneracy implies symmetry". Observe that the Hamiltonian is invariant under rotations in 3D.

$SO(3)$ and Rotational Invariance

For example; invariance under rotation in 3D (associated group $SO(3)$) leads to conservation of angular momentum, which translates into $2l+1$ degeneracy of angular momentum eigenstates. We notice $\sum_{l=00}^{n-1}(2l+1) = n$. And the hydrogen atom appears to have degeneracy

$$n^2 = \sum_{l_1=0}^{n-1}\sum_{l_2=0}^{n-1}(2l_1+1)(2l_2+1)$$

the occurrence of extra $(2l+1)$ hints at a larger symmetry group.

BUT HOW DO WE FIND THIS SYMMETRY GROUP?

Classical Kepler Problem and LRL Vector

Let us take some help from the old man (the classical mechanics). In classical Kepler's problem (remember, it has the same Hamiltonian!), we come across a conserved vector quantity termed the "Laplace- Runge-Lenz" (LRL) vector which is defined as

$$\vec{A} = \frac{\vec{p} \times \vec{L}}{m} - \frac{k\vec{r}}{r} \tag{2}$$

and it is easy to show that $\frac{d\vec{A}}{dt} = \{\vec{A}, H\} = 0$. Hence, it is a conserved vector quantity.

Quantum Mechanics LRL Vector

In quantum mechanics, we define a Hermitian version of the LRL vector, and we define it as:

$$\vec{A} = \frac{1}{2m_2}\left[\vec{p}\times\vec{L} - \vec{L}\times\vec{p}\right] - \frac{k\vec{r}}{r} \tag{3}$$

It can be shown that the algebra it follows is given as

$$[L_i, H] = 0 \quad [A_i, H] = 0$$

$$\begin{aligned} [L_i, A_j] &= i\hbar\epsilon_{ijk}A_k \\ [L_i, L_j] &= i\hbar\epsilon_{ijk}L_k \\ [A_i, A_j] &= -i\hbar\epsilon_{ijk}L_k\frac{2}{m_2}H \end{aligned} \tag{4}$$

Same algebra is followed by Lorentz Group generators, but with a $+$ve sign for last commutator.

Some more useful identities

- Some useful relations:

$$\begin{aligned} \vec{A}\cdot\vec{L} &= \vec{L}\cdot\vec{A} = 0 \\ A^2 = \vec{A}\cdot\vec{A} &= k^2 + \frac{2}{m_e}H(L^2+\hbar^2) \end{aligned} \tag{5}$$

We will need them soon to see some beautiful mathematics!!.

SO(4) hyperspherical symmetry of bound state solutions

Suppose that there exists a bound state with energy $E < 0$ for the Hamiltonian given in Eq.1. Let $\mathcal{H}(E)$ be the eigenspace in $\mathcal{H}$ with energy value E. We will restrict the action of all of our operators to this eigenspace, and we can multiply Eq. 3 with a dimensionful constant to make it the same dimensionally as the angular momentum. In this subspace, we define

$$\tilde{A}_i = \sqrt{\frac{-m}{2E}} A_i \tag{6}$$

we see that $[\tilde{A}_i] = [\hbar] = [L_i]$.

Using $\tilde{A}_i$ we define:

$$\begin{aligned} T_i &= \frac{1}{2}(L_i + \tilde{A}_i) \\ S_i &= \frac{1}{2}(L_i - \tilde{A}_i) \end{aligned} \tag{7}$$

and using the commutation relation form Eq. 4, we get

$$\begin{aligned} [E, T_i] = [E, S_i] &= 0 \\ T^2 &= S^2 \\ [T_i, S_j] &= 0 \\ [T_i, T_j] &= i\hbar\epsilon_{ijk} T_k \\ [S_i, S_j] &= i\hbar\epsilon_{ijk} S_k \end{aligned} \tag{8}$$

From the above commutation relations, it looks like we have two independent “angular momentum”-like operators (or algebra) in the eigenspace. And if that is the case, then the whole algebra must be:

$$SO(3) \oplus SO(3) \cong SO(4)$$

and this INDEED IS THE CASE!!
Hence, the ”accidental symmetry” or ”dynamical group” of the hydrogen atom problem is $SO(4)$. Or in other words, the solution set of hydrogen atoms is invariant under rotations in some fictitious 4D. $SO(4)$ is the four dimensional rotation group but does not represent a physical rotation for Hydrogen $\longrightarrow$ this is called a dynamical symmetry

Energy eigenvalues using the T^2 operator

Since the above problem has "angular momentum"-like operators, we can do our usual Schwinger approach of ladder operators for "angular momentum". Performing the same exercise as in the case of angular momentum or harmonic oscillator. We get for some $\psi \in \mathcal{H}(E)$, where ψ is the simultaneous eigenstate of T, S_z, T_z

$$T^2\psi = t(t+1)\hbar^2\psi, \text{ ,where } t \in \{0, \frac{1}{2}, 1, \ldots\} \tag{9}$$

Using Eq. 6 and Eq. 5 we can check that

$$\tilde{A}^2 + L^2 = 4T^2 = \hbar^2 - \frac{k^2 m_e}{2E} \tag{10}$$

i.e., the action of T^2 on $\mathcal{H}(E)$ is simply multiplication by the $\frac{\hbar^2}{4} - \frac{k^2 m_e}{8E}$ and by our claim from Eq. 9 we need

$$\begin{gathered} t(t+1)\hbar^2 = \frac{\hbar^2}{4} - \frac{k^2 m_e}{8E} \\ \boxed{E_{2t+1} = \frac{-m_e k^2}{2\hbar^2(2t+1)^2}} \end{gathered} \tag{11}$$

we identify the principal quantum number n as $2t+1$. Furthermore, for a given value of t, our previous claim tells us that there are exactly $(2t+1)^2 = n^2$ linearly independent states in $\mathcal{H}(E_n)$.

References

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