HIDDEN SYMMETRY OF THE HYDROGEN ATOM

As we have seen, the spherical symmetry of the two-body central force problem made the orbital angular momentum a constant of the motion and thereby imposed a $2\ell + 1$ degeneracy of the energy levels for given $n$ and $\ell$ values. However, for the hydrogen atom there is a further degeneracy between levels with the same $n$ but different $\ell$ values. Here we wish to show that this degeneracy is due to a "hidden symmetry" which introduces another constant of the motion. Classically, this constant appears because the bound orbits for an attractive $1/r$ potential close on themselves (whereas in general the orbits are open and precess). Thus, for the Bohr model of the hydrogen atom the electron orbit is an ellipse in a plane perpendicular to $L$ and a vector $R$ along the semimajor axis is another constant of motion. We first examine the classical problem and evaluate $R$, which is called the Lenz vector. Then we reconsider the quantum treatment and show how this extra constant of the motion accounts for the special degeneracy.

**Classical hydrogen atom**

For the general two-body central force problem we have

$$E = \frac{1}{2}\mu \dot{r}^2 + \frac{L^2}{2\mu r^2} + V(r)$$

$$L = \mu r^2 \dot{\phi}$$

To obtain the orbit equation, we solve for $\dot{r}$ and $\dot{\phi}$ and take their ratio to eliminate time. Hence find

$$\phi = \phi_0 + \int_{r_0}^{r} \frac{(L/\mu r^2) dr}{\sqrt{2[E - \frac{L^2}{2\mu r^2} - V(r)]^{1/2}}}$$

where $r_0, \phi_0$ denotes some point on the orbit.
Hidden Symmetry – 2

Now take \( V(r) = -\frac{e^2}{r} \) and substitute \( u = \frac{1}{r} \), find

\[
\phi = \phi' - \int \frac{du}{\left[ L^2 E + \frac{2ue^2}{L^2} u - u^2 \right]^{1/2}}
\]

where the integral has been left indefinite by introducing the integration constant \( \phi' \)

The integral now has a standard form,

\[
\int \frac{dx}{\left[ a + bx + cx^2 \right]^{1/2}} = \frac{1}{\sqrt{-c}} \arccos \left[ \frac{-(b + 2cx)}{\sqrt{q}} \right], \text{ with } q = b^2 - 4ac.
\]

Here \( a = \frac{2ue^2}{L^2} \), \( b = \frac{2ue^2}{L^2} \), \( c = -1 \) and \( q = \left( \frac{2ue^2}{L^2} \right)^2 \left[ 1 + \frac{2EL^2}{ue^4} \right] \)

Thus find

\[
\phi = \phi' - \arccos \left( \frac{\left( \frac{1}{ue^2} - 1 \right)}{(1 + \frac{2EL^2}{ue^4})^{1/2}} \right)
\]

The orbit equation therefore is

\[
\frac{1}{r} = \frac{ue^2}{L^2} \left[ 1 + \left( 1 + \frac{2EL^2}{ue^4} \right)^{1/2} \cos(\phi - \phi') \right]
\]

This has the form of a conic section with one focus at the origin,

\[
\frac{1}{r} = C[1 + \epsilon \cos(\phi - \phi')]
\]

where \( C = \frac{ue^2}{L^2} \)

For \( \epsilon > 1 \) or \( E > 0 \) have hyperbola \( \epsilon = \left( 1 + \frac{2EL^2}{ue^4} \right)^{1/2} \)

\( \epsilon = 1 \) or \( E = 0 \) " parabola

\( \epsilon < 1 \) or \( E < 0 \) " ellipse = eccentricity

and for

\( \epsilon = 0 \) or \( E = -\frac{ue^2}{2L^2} \) have circle

In order to locate the semimajor axis of the ellipse along \( \phi = 0 \) and \( \phi = \pi \), must take \( \phi' = 0 \).

We now consider another derivation of the orbit equation which will prove useful in evaluating the Lenz vector. From Newton's Second Law,

\[
\mu \ddot{x} = F_x = -\frac{e^2}{x^2} \cos \phi = -\frac{ue^2}{L} \dot{\psi} \cos \phi
\]

\[
\mu \ddot{y} = F_y = -\frac{e^2}{y^2} \sin \phi = -\frac{ue^2}{L} \dot{\psi} \sin \phi
\]
Thus
\[ p_x = \mu \dot{x} = -\frac{ue^2}{L} \sin \phi + A \]
\[ p_y = \mu \dot{y} = \frac{ue^2}{L} \cos \phi + B \]
where A & B are integration constants

Since
\[ x = r \cos \phi \pm \dot{x} = r \dot{\cos \phi} - r \dot{\sin \phi} \]
\[ y = r \sin \phi \quad \dot{y} = r \dot{\sin \phi} + r \dot{\cos \phi} \]

Eliminate \( \dot{r} \) by
\[ -x \sin \phi + y \cos \phi = r \dot{\phi} = \frac{1}{\mu r} \]

So find
\[ \frac{1}{r} = \frac{ue^2}{L^2} - \frac{A}{L} \sin \phi + \frac{B}{L} \cos \phi \]

Again the conic section formula. In order to make \( r \) attain its minimum \((r_-)\) and maximum \((r_+)\) values at \( \phi = \pi \) and \( \phi = 0 \), respectively, need \( A = 0 \).
Thus
\[ \frac{1}{r} = \frac{ue^2}{L^2} [1 + \frac{BL}{\mu} \cos \phi] \]

Comparison with previous result gives \( \frac{BL}{\mu e^2} = \varepsilon \).

The **Lenz vector** is defined by
\[ \mathbf{R} = \frac{1}{\mu} (p_x \mathbf{L} - V(r) \mathbf{L}) \]

with \( V(r) = -\frac{e^2}{r} \)

Let us verify that this points along the semimajor axis of the elliptical orbit, i.e., along the x-axis. Note \( L_x = L_y = 0 \) and \( p_z = 0 \)
\[ (p_x \mathbf{L}) = p_y \mathbf{L} \hat{x} - p_x \mathbf{L} \hat{z} + 0 \]

Thus
\[ \mathbf{R} = \left( \frac{p_y \mathbf{L}}{\mu} - \frac{e^2}{r} \hat{x} \right) \hat{x} + \left( \frac{p_x \mathbf{L}}{\mu} - \frac{e^2}{r} \hat{y} \right) \hat{y} \]
\[ \mathbf{R} = \frac{L}{\mu} (p_y - \frac{ue^2}{L} \cos \phi) \hat{x} - \frac{L}{\mu} (p_x + \frac{ue^2}{L} \sin \phi) \hat{y} \]

Use now the results derived above, \( p_x = -\frac{ue^2}{L} \sin \phi \)
\[ p_y = \frac{ue^2}{L} \cos \phi + B \]

Find
\[ \mathbf{R} = \frac{L}{\mu} B \hat{x} + 0 \]

The Lenz vector points along the x axis and has magnitude
\[ \frac{L}{\mu} B = e^2 \varepsilon = \left[ e^4 + \left( \frac{2E L^2}{\mu} \right) \right]^{1/2}, \]

proportional to the coefficient of \(1/r\) in the potential and the eccentricity of the orbit.

\[ \varepsilon = \frac{\sqrt{a^2-b^2}}{a} = \left( 1 + \frac{2EL^2}{\mu e^2} \right)^{1/2} \]

\[ r_+ = a(1+\varepsilon) \]
\[ r_- = a(1-\varepsilon) \]
\[ a = -\frac{e^2}{2E} = \frac{e^2}{2|E|} \]
\[ b = a(1-e^2)^{1/2} \]

or
\[ b = \frac{L^2}{\mu e^2}. \]

Note \( R \cdot L = 0 \)

**Quantum hydrogen atom**

The Hamiltonian operator corresponding to the classical Lenz vector is

\[ R = \frac{1}{2\mu} (p \times L - L \times p) - \frac{e^2}{r} \]

Note: In symmetrizing the classical expression, use \( p \times L = -L \times p \)

It is readily shown that this is a constant of the motion, i.e. that \([R, H] = 0\). Also, the following properties of \( R \) can be proved:

\[ R^2 = e^4 + \frac{2H(L^2 + \eta^2)}{\mu} \]

\[ R \cdot L = L \cdot R = 0 \]

\[ [R_i, R_j] = i\hbar \varepsilon_{ijk} L_k \]

\[ [R_i, L_j] = \hbar \varepsilon_{ijk} R_k \]

Note that the quantum result for the square of the Lenz vector differs from the classical result \( R^2 = e^4 + \frac{2EL^2}{\mu} \), only by replacing \( L^2 \) by \( L^2 + \eta^2 \) and \( E \) by \( H \). The problem has the unusual feature that the Hamiltonian can be written in terms of other constants of the motion, \( R^2 \) and \( L^2 \).

It is convenient to absorb the factor \(-2H/\mu\) by redefining the Lenz vector as

\[ \kappa = \left( \frac{-\mu}{2H} \right)^{1/2} R. \]
Hidden Symmetry - 5

This is Hermitian when acting on eigenstates of \( H \) with negative eigenvalues (the states of interest here). It is also a constant of motion, as the operator \((-\mu/2H)^{1/2}\) commutes with \( \vec{R} \) and \( \vec{L} \). Now the formula for the square of the Lenz vector can be recast to obtain

\[
H = -\frac{\mu e^4}{2(K^2+L^2+\bar{R}^2)}
\]

Already we recognize the resemblance to the formula for energy eigenvalues.

The commutation relations obeyed by \( \vec{K} \) and \( \vec{L} \) are

\[
\begin{align*}
[K_i, K_j] &= i\hbar \epsilon_{ijk} L_k \\
[K_i, L_j] &= i\hbar \epsilon_{ijk} K_k \\
[L_i, L_j] &= i\hbar \epsilon_{ijk} L_k
\end{align*}
\]

These can be further simplified by defining the quantities

\[
M = \frac{1}{2}(L+K) \quad \text{and} \quad N = \frac{1}{2}(L-K)
\]

for which we find

\[
\begin{align*}
[M_i, M_j] &= i\hbar \epsilon_{ijk} M_k \\
[N_i, N_j] &= i\hbar \epsilon_{ijk} N_k \\
[M_i, N_j] &= 0
\end{align*}
\]

Thus \( M \) and \( N \) each obey the commutation rules for an angular momentum operator and commute with each other as well as with \( H \). Also, since \( \vec{K} \cdot \vec{L} = 0 \) we have \( M^2 = N^2 = \frac{1}{2}(L^2+K^2) \) and the Hamiltonian is given by

\[
H = -\frac{\mu e^4}{2(M^2+2N^2+\bar{R}^2)}
\]

Since \( M \) and \( N \) obey angular momentum commutation rules, we already know how to construct their eigenstates and eigenvalues. We can obtain simultaneous eigenstates of \( M^2, M_Z, N^2, \) and \( N_Z \). These we denote by \( |mM_u\rangle \), where

\[
\begin{align*}
M^2 |mm_u\rangle &= \hbar^2 m(m+1) |mm_u\rangle \\
N^2 | " \rangle &= \hbar^2 \rho(\rho+1) | " \rangle \\
M_Z | " \rangle &= \hbar \mu | " \rangle \\
N_Z | " \rangle &= \hbar \nu | " \rangle
\end{align*}
\]
Both $\mathcal{M}$ and $\mathcal{N}$ can take on the values 0, $\frac{1}{2}$, 1, $\frac{3}{2}$, ... whereas for each $\mathcal{M}$-value $\mu$ has the values

$$-\mathcal{M}, -\mathcal{M}+1, ..., \mathcal{M} - 1, \mathcal{M}$$

(2$\mathcal{M}$ + 1 values)

and for each $\mathcal{N}$-value $\nu$ has

$$-\mathcal{N}, -\mathcal{N}+1, ..., \mathcal{N} - 1, \mathcal{N}$$

(2$\mathcal{N}$ + 1 values)

However, as noted above the condition $R \cdot L = 0$ or $K \cdot L = 0$ requires that $M^2 = N^2$, so the only eigenstates relevant to the bound states of the hydrogen atom have $\mathcal{M} = \mathcal{N}$. These states $|\mathcal{M}\mathcal{N}\mu\nu\rangle$ are eigenstates of $\hat{H}$ since

$$\hat{H} |\mathcal{M}\mathcal{N}\mu\nu\rangle = -\frac{\mu e^4}{2\hbar^2 [4\mathcal{M}(\mathcal{M}+1)+1]} |\mathcal{M}\mathcal{N}\mu\nu\rangle$$

and hence the energy eigenvalues are given by

$$E = -\frac{\mu e^4}{2\hbar^2 (2\mathcal{M}+1)^2}$$

where $2\mathcal{M}+1$ is the principle quantum number $n$, with values 1, 2, 3...

For a fixed value of $\mathcal{M} = \mathcal{N}$, there are $2\mathcal{M}+1$ different $\mu$ values and $2\mathcal{M}+1$ different $\nu$ values. Thus there are $(2\mathcal{M}+1)(2\mathcal{N}+1) = n^2$ different states with the same energy, $E_n$.

Note that the $|\mathcal{M}\mathcal{N}\mu\nu\rangle$ are eigenstates of $L_z$ and $K_z$ but not eigenstates of $L^2$ or $K^2$. These states are linear combinations of the $|n\ell m\rangle$ hydrogen atom states with fixed $n$ and $m$ but different $\ell$ values. The $|\mathcal{M}\mathcal{N}\mu\nu\rangle$ states provide the appropriate representation for treating the Stark effect, in which the electric field perturbation mixes the degenerate $|n\ell m\rangle$ states.

The special degeneracies found for the isotropic oscillator can be analyzed in the same fashion. Again, the classical orbits are closed and elliptical so the Lenz vector is a constant of the motion.

The degeneracy of the hydrogen atom levels may also be treated by elegant group theory methods. The appropriate symmetry group proves to be the four-dimensional rotation group. This occurs because the six generators of infinitesimal rotations in four-space involve two angular momentum vectors with the same commutation relations as $L$ and $L$.

References:


Baym, Lectures on Quantum Mechanics.