Equal Radiation Frequencies
from Different Transitions in Hydrogen Atoms

Trung V. Phan
Department of Physics, Princeton University, Princeton, NJ 08544, USA
tvphan@princeton.edu

Kim Tuan Do
Department of Mathematics, Princeton University, Princeton, NJ 08544, USA
kdo@princeton.edu

(August 28, 2020)

1 Problem

Disregarding degeneracies and considering only different atomic levels, is it possible that two different transitions in hydrogen atom give the same frequency of radiation? That is, can different energy-level transitions in a hydrogen atom have photons of the same energy/frequency?¹

Figure 1: Energy-level transitions in a hydrogen atom. An electron jumps from an outer ring \( n_1 \) to an inner ring \( n_2 < n_1 \), with emission of a photon of energy \( \Delta E \propto n_2^{-2} - n_1^{-2} \).

2 Solution

The answer is definitely yes, and infinitely many transitions have been found [2], but to our knowledge a generalization is still lacking. In this note we will show a general solution, i.e., how all equifrequency-transition pairs can be obtained. This puzzle is a simple yet concrete example of how number theory can help understanding quantum systems, a curious theme

¹This question was asked during a PhD oral exam in 1997 at University of Colorado Boulder [1].
that emerges in theoretical physics [3], but which is usually inaccessible to high school and college students.

In quantum mechanics, the energy of the $n^{th}$ level of a hydrogen atom is given by $E(n) = -E_0/n^2$, where $n \in \mathbb{Z}^+$ is a positive integer and $E_0 = 13.6$ eV is the Rydberg energy (see, for example, [4]). For simplicity we will not consider any relativistic effects and other corrections (such as the effect of the proton magnetic moment) to the energy levels. The challenge is to find all transition pairs $(n_1 \to n_2 < n_1, n_3 \to n_4 < n_3)$ with equal radiation energies, which means,

$$\frac{1}{n_2^2} - \frac{1}{n_1^2} = \frac{1}{n_4^2} - \frac{1}{n_3^2} > 0.$$  \hspace{1cm} (1)

Here we will find a general solution of this equation, including trivial solutions where $n_1 = n_3$ and $n_2 = n_4$.

Consider the Diophantine equation [5] with a parameter $s \in \mathbb{Z}^+$ and unknowns $x, y, z \in \mathbb{Z}^+$,

$$x^2 - y^2 = sz^2.$$ \hspace{1cm} (2)

With any two solutions $(x_1, y_1, z_1)$ and $(x_2, y_2, z_2)$ to this equation, any positive integer pair $(t_1, t_2)$ satisfies,

$$x_1y_1t_1z_2 = x_2y_2t_2z_1,$$ \hspace{1cm} (3)

will give a solution to eq. (1),

$$(n_1, n_2, n_3, n_4) = (x_1t_1, y_1t_1, x_2t_2, y_2t_2),$$ \hspace{1cm} (4)

which can be checked by direct substitution. To generate all solutions $(t_1, t_2)$ to eq. (3), we use any $k \in \mathbb{Z}^+$ and $G = \gcd(x_1y_1z_2, x_2y_2z_1),$

$$t_1 = \frac{kx_2y_2z_1}{G}, \hspace{0.5cm} t_2 = \frac{kx_1y_1z_2}{G},$$ \hspace{1cm} (5)

where the operation $\gcd(\alpha, \beta)$ determines the greatest common divisor of $\alpha, \beta \in \mathbb{Z}^+$.

We can prove that the above procedure comprises all solutions of eq. (1). Start from this equation, denote $t'_1 = \gcd(n_1, n_2)$ and $t'_2 = \gcd(n_3, n_4)$. Write $n_1 = x'_1t'_1, n_2 = y'_1t'_1, n_3 = x'_2t'_2, n_4 = y'_2t'_2$. Note that $n_1 > n_2$ and $n_3 > n_4$ i.e., $x'_1 > y'_1$ and $x'_2 > y'_2$. Then, we rewrite eq. (1) as,

$$\frac{x'^2_1 - y'^2_1}{x'^2_2 - y'^2_2} = \left(\frac{x'_1y'_1t'_1}{x'_2y'_2t'_2}\right)^2,$$ \hspace{1cm} (6)

and put the fraction $x'_1y'_1t'_1/x'_2y'_2t'_2$ into irreducible form $z'_1/z'_2$ where $\gcd(z'_1, z'_2) = 1$ and both $z'_1$ and $z'_2$ are nonzero,

$$\frac{x'_1y'_1t'_1}{x'_2y'_2t'_2} = \frac{z'_1}{z'_2}. $$ \hspace{1cm} (7)

Thus,

$$\frac{x'^2_1 - y'^2_1}{x'^2_2 - y'^2_2} = \frac{z'^2_1}{z'^2_2},$$ \hspace{1cm} (8)

and hence there exists $s' \in \mathbb{Z}^+$ such that,

$$x'^2_1 - y'^2_1 = s'z'^2_1, \hspace{1.5cm} x'^2_2 - y'^2_2 = s'z'^2_2.$$ \hspace{1cm} (9)
Notice here that condition (7) is exactly eq. (3), and condition (9) provides us two solutions of eq. (2). Combined with the above paragraph, we see these two conditions, (7) and (9), are both necessary and sufficient. This completes the proof.

To generate the set of all nonzero integer solutions \((x, y, z)\) to eq. (2), we will need the set of all non-zero rational solutions \((a, b)\) to its dehomogenized version (by dividing both sides of eq. (2) by \(1/y^2\)),

\[
a^2 - 1 = sb^2. \tag{10}
\]

(which looks much like the Pell equation [6], but can be solved by simpler methods). By taking any \((a, b) = (a_1/a_2, b_1/b_2)\) that satisfies eq. (10) and any \(l \in \mathbb{Z}\), we obtain all triples,

\[
(x, y, z) = \left(\frac{la_1b_2}{G_2}, \frac{la_2b_2}{G_2}, \frac{la_2b_1}{G_2}\right), \tag{11}
\]

of eq. (2) where \(G_2 = \gcd(a_2, b_2)\).

Figure 2: Geometric representation of curve eq. (10) and line \(b = q(a - 1)\) in the \(a-b\) plane. The intersection in the first quadrant gives a solution to eq. (10).

A geometric way [5] to deal with eq. (10) is to draw in the \(a-b\) plane a line passing through \((1, 0)\) with a rational slope \(q \in \mathbb{Q}\), say the line \(b = q(a - 1)\), as in Fig. 2. For \(q^2 \neq 1/s\), this line will cut the curve (10) at another point,

\[
(a, b) = \left(\frac{sq_1^2 + 1}{sq_1^2 - 1}, \frac{q}{sq_1^2 - 1}\right), \tag{12}
\]

and more importantly, all solutions of eq. (10) can be attained this way by varying \(q\). Note that \(q = 0\) gives \(z = 0 \notin \mathbb{Z^+}\), and changing the sign of \(q\) changes the sign of \((a, b)\). Hence, if we let \(q = q_1/q_2\) where \(q_1 \in \mathbb{Z}\setminus\{0\}, q_2 \in \mathbb{Z^+}\) then \(a = a_1/a_2, b = b_1/b_2\) where,

\[
a_1 = sq_1^2 + q_2^2, \quad a_2 = sq_1^2 - q_2^2, \tag{13}
\]

\[
b_1 = 2q_1q_2, \quad b_2 = sq_1^2 - q_2^2. \tag{14}
\]

The positive triple \((x, y, z)\) can be obtained now from eq. (11) with the correct sign choice.
In summary, we can generate a solution \((x, y, z)\) to eq. (2) with parameter \(s \in \mathbb{Z}^+\) from any number \(q = q_1/q_2 \neq 0\). Given the pair, we go through eqs. (13)-(14), pick a value \(l \in \mathbb{Z}\) and use equation (11) to arrive at \((x, y, z)\). Then, with two such solutions, say \((x_1, y_1, z_1)\) and \((x_2, y_2, z_2)\), we pick a value \(k \in \mathbb{Z}^+\) and use eq. (5) to get \((t_1, t_2)\) before plugging in eq. (4) to get a pair \((n_1 \rightarrow n_2, n_3 \rightarrow n_4)\). See Fig. 3 for a demonstration.

Figure 3: A demonstration of the procedure to get an equifrequency transition pair. Here we start by selecting \(s = 6\), then from \((q_1, q_2) = (5, 7)\) and \(l = 5\) we get \((x_1, y_1, z_1) = (995, 505, 350)\), from \((q_1, q_2) = (1, 1)\) and \(l = 7\) we get \((x_2, y_2, z_2) = (49, 35, 14)\). Then, with \(k = 4\) we arrive at \((n_1 \rightarrow n_2, n_3 \rightarrow n_4) = (6825700 \rightarrow 3464300, 3939404 \rightarrow 2813860)\), which can be checked to satisfy eq. (1).

We thank Duy V. Nguyen and the xPhO journal club for their support to share this finding to a wider audience.

References

[1] Y. Kantor, Question 06/00: Hydrogen atom, https://www.tau.ac.il/~kantor/QUIZ/00/Q06.00.html

[2] Y. Kantor, Answer to the Question 06/00: Hydrogen atom, https://www.tau.ac.il/~kantor/QUIZ/00/A06.00.html


