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

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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]

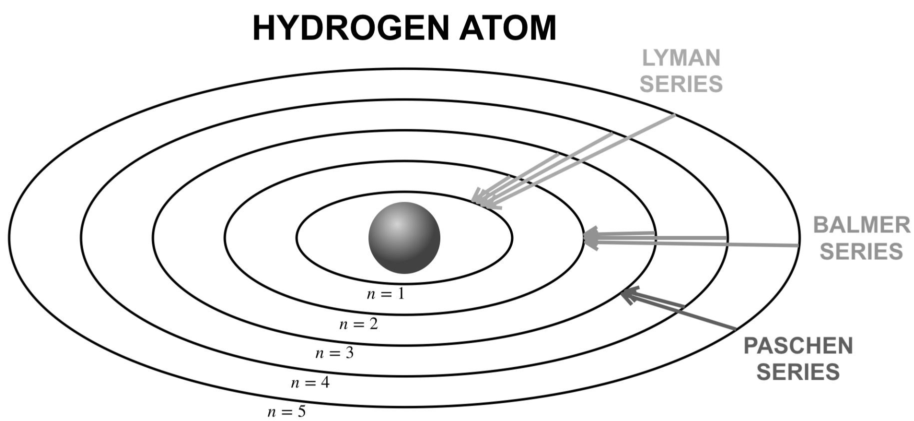

Figure 1: Energy-level transitions in a hydrogen atom. An electron jumps from an outer ring n_1 to an inner ring $n_2 < n_1$, with emission of a photon of energy $\Delta E \propto n_2^{-2} - n_1^{-2}$.

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

[1] This 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,

$$\frac{1}{n_2^2} - \frac{1}{n_1^2} = \frac{1}{n_4^2} - \frac{1}{n_3^2} > 0. \tag{1}$$

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 $x, y, z \in \mathbb{Z}^+$,

$$x^2 - y^2 = sz^2. \tag{2}$$

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,

$$x_1 y_1 t_1 z_2 = x_2 y_2 t_2 z_1, \tag{3}$$

will give a solution to eq. (1),

$$(n_1, n_2, n_3, n_4) = (x_1 t_1, y_1 t_1, x_2 t_2, y_2 t_2), \tag{4}$$

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 $G = \gcd(x_1 y_1 z_2, x_2 y_2 z_1)$,

$$t_1 = \frac{k x_2 y_2 z_1}{G}, \qquad t_2 = \frac{k x_1 y_1 z_2}{G}, \tag{5}$$

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 $n_1 = x'_1 t'_1,\ n_2 = y'_1 t'_1,\ n_3 = x'_2 t'_2,\ n_4 = y'_2 t'_2$. 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,

$$\frac{x_1'^2 - y_1'^2}{x_2'^2 - y_2'^2} = \left(\frac{x'_1 y'_1 t'_1}{x'_2 y'_2 t'_2}\right)^2, \tag{6}$$

and put the fraction $x'_1 y'_1 t'_1 / x'_2 y'_2 t'_2$ into irreducible form z'_1/z'_2 where $\gcd(z'_1, z'_2) = 1$ and both z'_1 and z'_2 are nonzero,

$$\frac{x'_1 y'_1 t'_1}{x'_2 y'_2 t'_2} = \frac{z'_1}{z'_2}. \tag{7}$$

Thus,

$$\frac{x_1'^2 - y_1'^2}{x_2'^2 - y_2'^2} = \frac{z_1'^2}{z_2'^2}, \tag{8}$$

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

$$x_1'^2 - y_1'^2 = s' z_1'^2, \qquad x_2'^2 - y_2'^2 = s' z_2'^2. \tag{9}$$

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 $G_2 = \gcd(a_2, b_2)$.

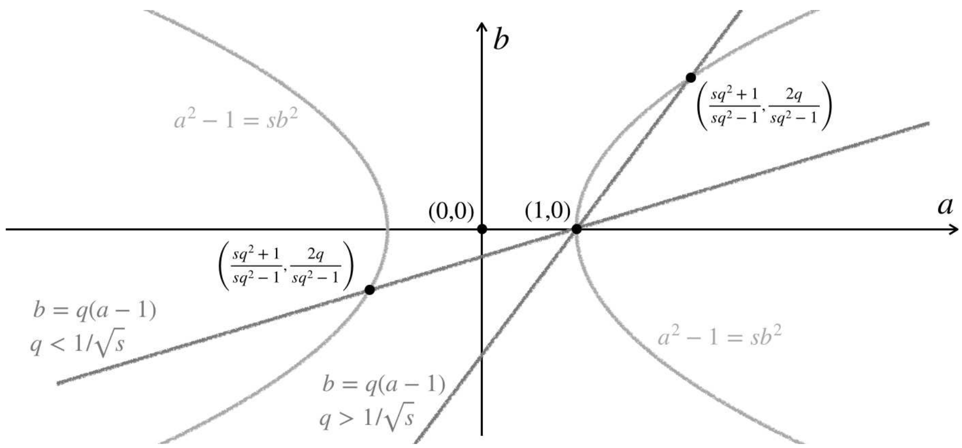

Figure 2: Geometric representation of curve eq. (10) and line $b = q(a-1)$ in the a-b plane. The intersection in the first quadrant gives a solution to eq. (10).

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,

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

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 $q_1 \in \mathbb{Z}\backslash\{0\}, q_2 \in \mathbb{Z}^+$ then $a = a_1/a_2$, $b = b_1/b_2$ where,

$$a_1 = sq_1^2 + q_2^2, \qquad a_2 = sq_1^2 - q_2^2, \tag{13}$$

$$b_1 = 2q_1q_2, \qquad b_2 = sq_1^2 - q_2^2. \tag{14}$$

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 $(n_1 \to n_2, n_3 \to n_4)$. See Fig. 3 for a demonstration.

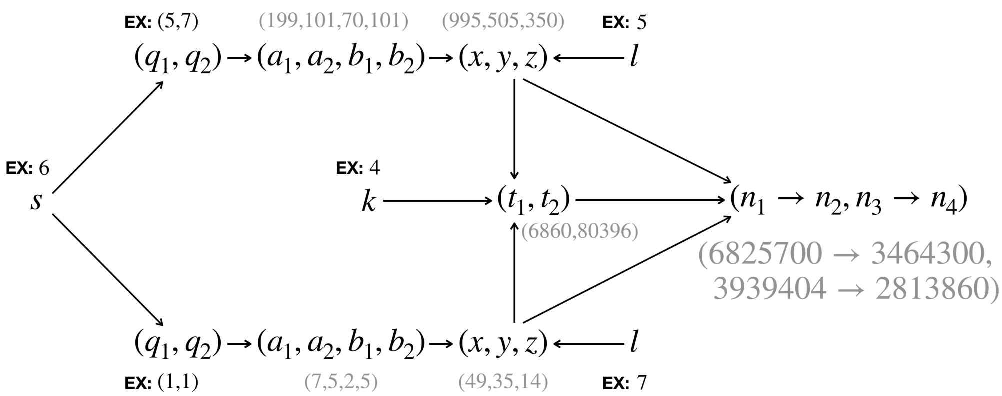

Figure 3: A demonstration of the procedure to get an equifrequency transition pair. Here we start by selecting $s = 6$, then from $(q_1, q_2) = (5, 7)$ and $l = 5$ we get $(x_1, y_1, z_1) = (995, 505, 350)$, from $(q_1, q_2) = (1, 1)$ and $l = 7$ we get $(x_2, y_2, z_2) = (49, 35, 14)$. Then, with $k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

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