Approximate Selection Rule for Orbital Angular Momentum in Atomic Radiative Transitions

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Abstract

We demonstrate that radiative transitions with $\Delta l = -1$ are strongly dominating for all values of $n$ and $l$, except small region where $l \ll n$.

It is well-known that the selection rule for the orbital angular momentum $l$ in electromagnetic dipole transitions, dominating in atoms, is $\Delta l = \pm 1$, i.e. in these transitions the angular momentum can both increase and decrease by unity. Meanwhile, the classical radiation of a charge in the Coulomb field is always accompanied by the loss of angular momentum. Thus, at least in the semiclassical limit, the probability of dipole transitions with $\Delta l = -1$ is higher. Here we discuss the question how strongly and under what exactly conditions the transitions with $\Delta l = -1$ dominate in atoms. (To simplify the presentation, we mean always, here and below, the radiation of a photon, i.e. transitions with $\Delta n < 0$. Obviously, in the case of photon absorption, i.e. for $\Delta n > 0$, the angular momentum predominantly increases.)

The analysis of numerical values for the transition probabilities in hydrogen presented in [1] has demonstrated that even for $n$ and $l$, comparable with unity, i.e. in a nonclassical situation, radiation with $\Delta l = -1$ can be much more probable than that with $\Delta l = 1$.

Later, the relation between the probabilities of transitions with $\Delta l = -1$ and $\Delta l = 1$ was investigated in [2] by analyzing the corresponding matrix elements in the semiclassical approximation. The conclusion made therein is also that the transitions with $\Delta l = -1$ dominate, and the dominance is especially strong when $l > n^{2/3}$.

Here we present a simple solution of the problem using the classical electrodynamics and, of course, the correspondence principle. Our results describe the situation not only in the semiclassical situation. Remarkably enough, they agree, at least qualitatively, with the results of [1], although the latter refer to transitions with $|\Delta n| \sim n \sim 1$ and $l \sim 1$, which are not classical at all.

We start our analysis with a purely classical problem. Let a particle with a mass $m$ and charge $-e$ moves in an attractive Coulomb field, created by a charge $e$, along an ellipse with large semi-axis $a$ and eccentricity $\varepsilon$. It is known [3] that the radiation intensity at a given harmonic $\nu$ is here

$$ I_{\nu} = \frac{4e^2\omega_0^3\nu^4a^2}{3c^3} \left( \xi_{\nu}^2 + \eta_{\nu}^2 \right); \quad (1) $$

$$ \xi_{\nu} = \frac{1}{\nu} J_\nu'(\nu\varepsilon), \quad \eta_{\nu} = \frac{\sqrt{1-\varepsilon^2}}{\nu\varepsilon} J_\nu(\nu\varepsilon). \quad (2) $$

In expressions (2), $J_\nu(\nu\varepsilon)$ is the Bessel function, and $J_\nu'(\nu\varepsilon)$ is its derivative. We use the Fourier transformation in the following form:

$$ x(t) = a \sum_{\nu=-\infty}^{\infty} \xi_\nu e^{i\nu\omega_0t} = 2a \sum_{\nu=0}^{\infty} \xi_\nu \cos \nu\omega_0t. $$


\[ y(t) = a \sum_{\nu=-\infty}^{\infty} \eta_{\nu} e^{i\nu \omega_0 t} = 2a \sum_{\nu=0}^{\infty} \eta_{\nu} \sin \nu \omega_0 t, \]

where all dimensionless Fourier components \( \xi_{\nu} \) and \( \eta_{\nu} \) are real, and \( \xi_{-\nu} = \xi_{\nu}, \eta_{-\nu} = -\eta_{\nu}. \)

We note that the Cartesian coordinates \( x \) and \( y \) are related here to the polar coordinates \( r \) and \( \phi \) as follows: \( x = r \cos \phi, y = r \sin \phi, \) where \( \phi \) increases with time. Thus, the angular momentum is directed along the \( z \) axis (but not in the opposite direction).

We note also that, since \( 0 \leq \varepsilon \leq 1, \) both \( J_{\nu}(\nu \varepsilon) \) and \( J'_{\nu}(\nu \varepsilon) \) are reasonably well approximated by the first term of their series expansion in the argument. Therefore, all the Fourier components \( \xi_{\nu} \) and \( \eta_{\nu} \) are positive.

In the quantum problem (where \( \nu = |\Delta n| \)), the probability of transition in the unit time is

\[ W_{\nu} = \frac{I_{\nu}}{\hbar \omega_0 \nu} = \frac{4 e^2 \omega_0^3 \nu^3 a^2}{3c^3 \hbar} \left( \xi_{\nu}^2 + \eta_{\nu}^2 \right), \quad \omega_0 = \frac{me^4}{\hbar^2 n^3}. \]  

Now, the loss of angular momentum with radiation is

\[ \dot{M} = \frac{2e^2}{3c^3} r \times \vec{r}. \]

Going over here to the Fourier components, we obtain

\[ \dot{M}_{\nu} = -\frac{4 e^2 \omega_0^3 \nu^2 a^2}{3c^3 \hbar} \vec{r}_{\nu} \times \dot{r}_{\nu}, \]

or (with our choice of the direction of coordinate axes, and with the angular momentum measured in the units of \( \hbar \))

\[ \dot{M}_{\nu} = -\frac{4 e^2 \omega_0^3 \nu^3 a^2}{3c^3 \hbar} 2\xi_{\nu} \eta_{\nu}. \]  

Obviously, the last expression is nothing but the difference between the probabilities of transitions with \( \Delta l = 1 \) and \( \Delta l = -1 \) in the unit time:

\[ \dot{M}_{\nu} = W_{\nu}^+ - W_{\nu}^-. \]  

Of course, the total probability (3) can be written as

\[ W_{\nu} = W_{\nu}^+ + W_{\nu}^- . \]

From explicit expressions (3) and (4) it is clear that inequality \( W_{\nu}^+ \ll W_{\nu}^- \) holds if \( 2\xi_{\nu} \eta_{\nu} \approx \xi_{\nu}^2 + \eta_{\nu}^2, \) or \( \eta_{\nu} \approx \xi_{\nu}. \) The last relation is valid for \( \varepsilon \ll 1, \) i.e. for orbits close to circular ones. (The simplest way to check it, is to use in formulae (2) the explicit expression for the Bessel function at small argument: \( J_{\nu}(\nu \varepsilon) = (\nu \varepsilon)^{\nu}/(2^\nu \nu !).\))

This conclusion looks quite natural from the quantum point of view. Indeed, it is the state with the orbital quantum number \( l \) equal to \( n - 1 \) (i.e. with the maximum possible value for given \( n \)) which corresponds to the circular orbit. In result of radiation \( n \) decreases, and therefore \( l \) should decrease as well.

The surprising fact is, however, that in fact the probabilities \( W_{\nu}^- \) of transitions with \( \Delta l = -1 \) dominate numerically everywhere, except small vicinity of the maximum possible
eccentricity $\varepsilon = 1$. For instance, if $\varepsilon \simeq 0.9$ (which is much more close to 1 than to 0!), then at $\nu = 1$ the discussed probability ratio is very large, it constitutes

$$\frac{W^-_{\nu}}{W^+_{\nu}} \simeq 12.$$  

The change with $\varepsilon$ of the ratio of $W^+_{\nu}$ to $W^-_{\nu}$ for two values of $\nu$ is illustrated in Fig. 1. The curves therein demonstrate in particular that with the increase of $\nu$, the region

where $W^-_{\nu}$ and $W^+_{\nu}$ are comparable, gets more and more narrow, i.e. when $\nu$ grows, the corresponding curves tend more and more to a right angle.

Let us go over now to the quantum problem. In the semiclassical limit, the classical expression for the eccentricity

$$\varepsilon = \sqrt{1 + \frac{2EM^2}{m^4}}$$  

is rewritten with usual relations $E = -\frac{me^4}{(2\hbar^2n^2)}$ and $M = \hbar l$ as

$$\varepsilon = \sqrt{1 - \frac{l^2}{n^2}}.$$  

In fact, the exact expression for $\varepsilon$, valid for arbitrary $l$ and $n$, is [3]:

$$\varepsilon = \sqrt{1 - \frac{l(l+1) + 1}{n^2}}.$$  

Clearly, in the semiclassical approximation the eccentricity is close to unity only under condition $l \ll n$. If this condition does not hold, one may expect that in the semiclassical limit the transitions with $\Delta l = -1$ dominate. In other words, as long as $l \ll n$, the probabilities of transitions with decrease and increase of the angular momentum are
comparable. But if the angular momentum is not small, it is being lost predominantly in radiation. This situation looks quite natural.

The next point is that with the increase of $|\Delta n| = \nu$, the region where $W^-_\nu$ and $W^+_\nu$ are comparable, gets more and more narrow in agreement with the observation made in [2].

However, we do not see any hint at some special role (advocated in [2]) of the condition $l > n^{2/3}$ for the dominance of transitions with $\Delta l = -1$.

As mentioned already, the analysis of the numerical values of transition probabilities [1] demonstrates that even for $n$ and $l$ comparable with unity and $|\Delta n| \simeq n$, i.e. in the absolutely nonclassical regime, the transitions with $\Delta l = -1$ are still much more probable than those with $\Delta l = 1$. The results of this analysis for the ratio $W^-/W^+$ in some transitions are presented in Table 3.1 (first line). Then we indicate in Table 3.1 (last line)

|                | $W_{4p\rightarrow 3s}$ | $W_{4p\rightarrow 3d}$ | $W_{5p\rightarrow 4s}$ | $W_{5p\rightarrow 4d}$ | $W_{5p\rightarrow 5f}$ | $W_{5p\rightarrow 5d}$ | $W_{6p\rightarrow 4s}$ | $W_{6p\rightarrow 4d}$ |
|----------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| exact value    | 10                     | 3.75                   | 28                     | 72                     | 10.67                  | 13.7                   |                        |                        |
| $\bar{\varepsilon}$ | 0.87                  | 0.92                   | 0.81                   | 0.75                   | 0.90                   | 0.92                   |                        |                        |
| $\nu = |\Delta n|$ | 1                      | 1                      | 1                      | 1                      | 2                      | 3                      |                        |                        |
| semiclassical value | 17.6                  | 8.7                    | 34                     | 58                     | 17.2                   | 15.7                   |                        |                        |

Table 3.1

the values of these ratios obtained in the naïve (semi)classical approximation. Here for the eccentricity $\bar{\varepsilon}$ we use the value of expression (9), calculated with $l$ corresponding to the initial state; as to $n$, we take its value average for the initial and final states.

The table starts with the smallest possible quantum numbers where the transitions, which differ by the sign of $\Delta l$, occur, i.e. with the ratio $W_{4p\rightarrow 3s}/W_{4p\rightarrow 3d}$. This table demonstrates that the ratio of the classical results to the exact quantum-mechanical ones remains everywhere within a factor of about two. In fact, if one uses as $\bar{\varepsilon}$ expression (8), calculated in the analogous way, the numbers in the last line change considerably. It is clear, however, that the classical approximation describes here, at least qualitatively, the real situation.
References

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[4] L.D. Landau and E.M. Lifshitz, Quantum Mechanics, Nauka, 1974; §36.