On the recent measurement of 2s-4p transition frequency in hydrogen atom: evidence for importance of nonresonant corrections for description of atomic spectra

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We demonstrate that the present superaccurate measurements of transition processes between atomic states in hydrogen atom [1] reached the limit of accuracy when transition frequency can not be defined any more in a unique way. This was predicted earlier and is due to the necessity to include in the description of resonant processes the nonresonant corrections. The experimental spectral line profile becomes asymmetric and it becomes not possible to extract the value of transition frequency from this profile in a unique way. Nonresonant corrections depend on the type of experiment, on the experimental arrangement etc. However the line profile itself for any resonant process can be defined of cause with any desired level of accuracy. A popular modern search for the atomic frequency standards and atomic clocks is the search for transitions where the nonresonant corrections are negligible. Still one has to keep in mind that the limit of accuracy due to the nonresonant corrections always does exist. In this paper we present closed expressions for the resonant photon scattering cross sections on an atomic level with dependence on all atomic quantum numbers including fine and hyperfine structure. These expressions are given for different types of experiments with fixation of the initial (final) photon propagation directions and initial (final) photon polarization. Using these expressions we demonstrate that the transition frequencies in particular cases cannot be derived uniquely if the accuracy of measurement reaches the value quoted in [1].

I. INTRODUCTION

During the last decades the accuracy of spectroscopic measurements for hydrogen atom has grown up considerably and now reaches 15 digits for 1s − 2s transition frequency [2]. A question arises whether the improvement of accuracy of resonant transition frequency measurement can be endless or it is limited by some reasons? Here we ignore such problems as Doppler, collisional, blackbody broadening. One can imagine an experiment with a single cold atom in a trap, when the spectral line profile will be purely natural. This question was answered in [3–5] on the basis of Quantum Electrodynamics (QED). A QED theory of atomic spectral line profile was first developed by F. Low [6] wherefrom the existence of the nonresonant (NR) corrections also followed. Unlike the resonant value of transitions frequency, the NR corrections depend on the process of excitation of atomic level, on the type of experiment and on the method of extracting of transition frequency value from the experimental data. Therefore the refinement of the transition frequency value may have sence until the NR corrections are smaller than the accuracy of experiment. For all cases investigated in [3–5] and later works on the subject the NR corrections appeared to be negligible. In particular, according to [7] this was the case also for the two-photon transition frequency measurement for 1s − 2s transition in hydrogen in [2]. The situation changed when the results of the highly accurate measurement of the transition frequencies $2s_{1/2} \rightarrow 4p_{3/2}^{F=1}$ and $2s_{1/2} \rightarrow 4p_{3/2}^{F=2}$ were reported in [1]. The accuracy of these measurement was quoted to be considerably smaller than the observed interference effects. According to the line profile theory these interference effects manifest the existence of NR corrections. In the present paper we investigate the problem from this point of view. We derive expressions for the cross section of resonant photon scattering on hydrogen atom with the fine and hyperfine structure taken into account. These expressions contain dependence on the directions and polarizations of the incident (absorbed) and final (emitted) photons. This allows one to describe different types of experiments with different correlations between directions and polarizations of both photons. All these results are applied then to derivation of NR corrections to the photon scattering cross sections and transition frequencies. We focus on NR corrections originating from the neighbour fine structure level components as in [1] where mutual influence of transitions $2s_{1/2}^{F=0} \rightarrow 4p_{1/2}^{F=1}$ and $2s_{1/2}^{F=0} \rightarrow 4p_{3/2}^{F=1}$ was observed. First we consider NR corrections to $2s_{1/2}^{F=0} \rightarrow 4p_{1/2}^{F=1}$ transitions due to the quantum interference with $2s_{1/2}^{F=0} \rightarrow 4p_{3/2}^{F=1}$ transitions. Corresponding corrections to another transition $2s_{1/2}^{F=0} \rightarrow 4p_{3/2}^{F=1}$ are quite similar though have an opposite sign. 1We demonstrate that the NR corrections to these transitions do not depend on the type of experiment and on the experimental geometry. However they depend on the choice of fixation of the decay: they are different then when the detection process ends up in the state with $F = 0, 1, 2$. When the frequency of the final photon is not fixed at all, the result of the measurement begins to depend both on the type of the experiment and on the experimental arrangement (geometry).

II. QED THEORY OF RESONANT PHOTON SCATTERING ON ATOMIC ELECTRON WITH ACCOUNT FOR THE FINE AND HYPERFINE LEVEL STRUCTURE

For the accurate description of NR corrections to the atomic transition frequencies it is natural to employ the QED theory of atomic processes developed in particular in [8,9]. The resonant scattering corresponds to the case when the incident photon frequency is chosen to be equal to the difference of atomic level energies $\omega = E_n - E_i$ for the particular $n$ value. We de-
note by \(i, n, f\) the initial, intermediate and final atomic states. Then in the sum over intermediate states in the scattering amplitude only one term for the chosen \(n\) value should be retained. Accounting to the QED theory of spectral line profile \(^{6,8,9}\) in case of resonance an infinite set of Feynman graphs containing electron self-energy insertions in the electron line \(n\) should be taken into account. This leads to the arrival of the level width \(\Gamma_n\) in the energy denominator corresponding to the resonant state \(n\) of scattering amplitude. Taking into account the fine and hyperfine structure of atomic levels further we will understand the indices \(i, n, f\) as a standard set of quantum numbers: principal quantum number \(n\), electron orbital angular momentum \(l\), electron total electron momentum \(j\), atomic angular momentum \(F\) and its projection \(M_F\). With these notations the photon scattering amplitude for the scattering process in the nonrelativistic limit and in the resonant approximation is \(^{10}\)

\[
U = (E_{nljF} - E_{n,i,l,j,F_i})^{3/2}(E_{nljF} - E_{n,l;j,j,F_j})^{3/2}
\times \sum_{M_F,M_{F_j}} \langle n,l,i,j,F_i | \hat{\epsilon}_i \hat{d} | nljF M_F \rangle
\times \langle nljF | \hat{\epsilon}_f \hat{d} | n,l,f,j,F_j M_{F_j} \rangle,
\]

where \(\Gamma = \Gamma_{nljF}\). In Eq. (1) \(\hat{\epsilon}_i, \hat{\epsilon}_f\) are the polarizations of the incident and emitted photons, \(\hat{d} = \hat{e} \hat{r}\) is the operator of the electric dipole moment of the electron, \(e\) is the electron charge. Relativistic units are employed \(\hbar = c = 1\). Apart from scattering amplitude Eq. (1) there is another term with interchanged absorption and emission photons. This term does not contribute to the resonant scattering. Below we will take into account the NR corrections. However this term will not contribute also to the largest NR corrections and therefore will be neglected. Finally, the cross section of the resonant photon scattering reads

\[
\sigma_{if} = \frac{(E_{nljF} - E_{n,i,l,j,F_i})^3(E_{nljF} - E_{n,l;j,j,F_j})^3}{2F_i + 1}
\times \sum_{M_F,M_{F_j}} \frac{\langle n,l,i,j,F_i | \hat{\epsilon}_i \hat{d} | nljF M_F \rangle}{\sum_{M_F} \langle n,l,i,j,F_i | \hat{\epsilon}_i \hat{d} | nljF M_F \rangle}
\times \frac{\langle nljF | \hat{\epsilon}_f \hat{d} | n,l,f,j,F_j M_{F_j} \rangle}{\langle nljF | \hat{\epsilon}_f \hat{d} | n,l,f,j,F_j M_{F_j} \rangle^2}.
\]

Here we have summed over atomic angular momentum projections in the final state and averaged over the atomic angular momentum projections of initial state.

III. APPLICATION TO THE DESCRIPTION OF DIFFERENT TYPES OF EXPERIMENTS ON THE MEASUREMENT OF ATOMIC TRANSITION FREQUENCIES

Expression Eq. (2) for the cross section of the resonant photon scattering on an atomic electron is quite general and can be used for the description of any experiment involving this process. We will concentrate on the experiment for observation of the spectral line shape of transition \(n_i,l,j,F_i \rightarrow n_f F\) and extracting the transition frequency from the experimental data. This corresponds to the experiment \(^{[1]}\). We will distinguish two types of experiments of that sort. In an experiment of the first type the directions of photon propagation are fixed: initial photon direction \(\hat{\nu}_i\) coincides with the direction of laser beam and the final photon direction \(\hat{\nu}_f\) is defined by position of detector. In the second type of experiment the initial photon polarization \(\hat{\epsilon}_i\) and the final photon direction \(\hat{\nu}_f\) are fixed; this is exactly the situation in experiment \(^{[1]}\). In the nonrelativistic limit the matrix elements in Eq. (2) do not depend explicitly on the photon directions \(\hat{\nu}_i\) and \(\hat{\nu}_f\). Implicitly this dependence enters via the transversality condition. Dependence on \(\hat{\nu}_i, \hat{\nu}_f\) becomes explicit after summation over photon polarizations. Then for the experiment of the type 1 we have to evaluate \(\sum_{\hat{\epsilon}_i, \hat{\epsilon}_f}\) for the experiment of the type 2 it is necessary to evaluate \(\sum_{\hat{\epsilon}_i, \hat{\epsilon}_f}\). To introduce the NR correction to the cross section Eq. (2) we have to take into account the next term of the scattering amplitude, closest by energy to the resonant term. The set of a quantum numbers for this additional state should allow to connect this state with initial state by absorption of an electric dipole photon. Therefore the neighbour fine structure components of the resonant level may give a noticeable NR correction as it was recently observed in \(^{[1]}\). In what follows we will consider the NR corrections originating from the states which have the same \(nl\) quantum numbers as the resonant state, but different values \(jF\). We will neglect the contribution quadratic in NR correction and will neglect the level width in the energy denominator corresponding to the NR state. The cross section we present in the form \(\sigma_{if} = \sigma_{if}^{\text{res}} + \sigma_{if}^{\text{nr}}\), where by \(\sigma_{if}^{\text{res}}\) we denote now the resonant contribution and \(\sigma_{if}^{\text{nr}}\) represents the NR correction. In the NR amplitude we take only the interference term between resonant and nonresonant amplitudes. For evaluating the cross section with Eq. (2) we employ the techniques of irreducible tensor operators (we follow notations given in \(^{[1]}\)). After lengthy but standard evaluations and after summation over all angular momenta projections we arrive at the following expressions (see supplementary materials for the derivation). For the experiment of the type 1 this results

\[
\sum_{\hat{\epsilon}_i, \hat{\epsilon}_f} \sigma_{if}^{\text{nr}} = 2 \sum_{n,l,j,F_i} \text{Re}(E_{nljF} - E_{n,i,l,j,F_i})^{3/2}
\times \langle E_{n',l',j',F'} - E_{n,l,j,F} \rangle^{3/2}(E_{nljF} - E_{n,l;j,j,F_j})^{3/2}
\times \langle E_{n',l',j',F'} - E_{n,l;j,j,F_j} \rangle^{3/2}
\times \sum_{xy} A_{xy}^{(1)}
\times \left\{ \nu^{1,i} \otimes \nu^{1,f} \right\}_y \otimes \left\{ \nu^{1,i} \otimes \nu^{1,f} \right\}_y^{(0)}
\times \{ \nu^{1,i} \otimes \nu^{1,f} \}_y \otimes \{ \nu^{1,i} \otimes \nu^{1,f} \}_y^{(0)}
\times \langle E_{nljF} - E_{n,l,j,F_i} - \omega - \frac{1}{2}(E_{nljF} - E_{n,l,j,F_i} - \omega) \rangle.
\]

Here \(\nu^{1,i}, \nu^{1,f}\) denote the irreducible tensors of the rank 1 corresponding to the vectors \(\hat{\nu}_i, \hat{\nu}_f\) respectively in the laboratory.
frame, symbol $\otimes$ denotes a tensor product and

$$A_{xy}^{(1)} = \frac{36(-1)^{F' - F + x - y}}{2F_i + 1} \Pi_x^2 \Pi_y \left\{ \begin{array}{c|cc} 1 & 1 & y \\ 1 & 1 & x \\ \end{array} \right\} \left\{ \begin{array}{c|cc} 1 & 1 & x \\ 1 & 1 & 1 \\ \end{array} \right\}^2$$

(4)

$$\times \left\{ \begin{array}{cc} 1 & x \\ F_i & F_i \\ \end{array} \right\} \left\{ \begin{array}{cc} 1 & x \\ F_i' & F_i' \\ \end{array} \right\} \times \langle n_i l_i j_i | F_i | d_1 \rangle | nljF \rangle \langle n' l' j' F' | d_1 \rangle | nljF \rangle$$

$$\times \langle n_f l_f j_f | F_f | d_1 \rangle | nl' j' F' \rangle \langle n_f l_f j_f | d_1 \rangle | nljF \rangle$$

(5)

where $\Pi_0 = \sqrt{2a + 1}$. The reduced matrix element of the dipole operator in Eq. (3) is given by [11]

$$\langle n' l' j' F' | d_1 | nljF \rangle = (-1)^{j' + j + I + t' + 1/2 + F}$$

$$\times \Pi'_F \Pi'_{l'j'} \left\{ \begin{array}{c|cc} j' & F' & l' \\ j & l & 1 \\ \end{array} \right\} \langle n' l' j' F' | d_1 \rangle | nl \rangle,$$

where $I$ is the nuclear spin ($I = 1/2$ for hydrogen atom) and

$$\langle n'l'|d_1|nl\rangle = e(-1)^{l} l' \Pi_{l'l'} \left( \begin{array}{c|cc} l & l' \\ 0 & 0 & 0 \\ \end{array} \right) \times \int_0^\infty r^3 R_{n'l'} R_{n'l} dr.$$  

Here $R_{nl}$ is the radial part of hydrogen wave function. Similar evaluations for an expression of the type 2 results

$$\sum_{\epsilon_f} \sigma_{1f}^{(2)} = \frac{1}{2} \sum_{nljF} \Re\langle E_{nljF} - E_{n_lj,F_1} \rangle^{3/2}$$

(7)

$$\times \langle n'l'j'F' - E_{n_fj,F_1} \rangle^{3/2}$$

$$\times \langle n'l'j'F' - E_{n_fj,F_1} \rangle^{3/2}$$

$$\times \langle (E_{n_fj,F} - E_{n_fj,F_1} - \omega - \frac{1}{2} \Gamma) (E_{n_fj,F'} - E_{n_fj,F_1} - \omega)$$

(8)

where

$$A_{xy}^{(2)} = \frac{6(-1)^{F' - F + x - y}}{2F_i + 1} \Pi_x^2 \Pi_y \left\{ \begin{array}{c|cc} 1 & 1 & y \\ 1 & 1 & x \\ \end{array} \right\} \left\{ \begin{array}{c|cc} 1 & 1 & x \\ 1 & 1 & 1 \\ \end{array} \right\}$$

$$\times \left\{ \begin{array}{cc} 1 & x \\ F_i & F_i \\ \end{array} \right\} \left\{ \begin{array}{cc} 1 & x \\ F_i' & F_i' \\ \end{array} \right\} \times \langle n_i l_i j_i | F_i | d_1 \rangle | nljF \rangle \langle n'l' j' F' | d_1 \rangle | nljF \rangle$$

$$\times \langle n_f l_f j_f | F_f | d_1 \rangle | nl' j' F' \rangle \langle n_f l_f j_f | d_1 \rangle | nljF \rangle$$

Tensor product in Eq. (3) can be expressed through trigonometric functions of the angles between the vectors $\vec{v}_i$, $\vec{v}_f$ (see supplementary materials). In Eq. (7) $e^{1+i}$ is the irreducible tensor of the rank 1 corresponding to the vector $\vec{e}_f$. The summation over $x$ in Eq. (3) and the summation over $y$ in Eq. (7) run over the values $x = 0, 1, 2$ and $y = 0, 1, 2$, respectively. The resonant contributions $\sum_{\epsilon_f} \sigma_{1f}^{res}$ and $\sum_{\epsilon_f} \sigma_{1f}^{res}$ to the total cross section are derived from Eqs. (3), (4), (5), (8) by setting $n'l'j'F' = nljF$. In the supplement we use the notations $A_{xy}^{(1,2) res}$ and $A_{xy}^{(1,2) nr}$ for the resonant and nonresonant contributions to the photon scattering cross section.

IV. DETERMINATION OF TRANSITION FREQUENCY

The dependence of the photon scattering cross section $\sum_{\epsilon_f} \sigma_{1f}^{res}$ on the incident photon frequency represents the natural line profile for the transition $n_l j_f F_i \rightarrow nljF$. In this paper we neglect the various types of the line broadening (Doppler, collisional etc.). Qualitatively our conclusions will remain valid for any type of realistic line profile (Voigt and Gauss) though the numerical values for transition frequencies may slightly change. The resonant transition frequency $\omega_{res}$ can be defined from $\sigma_{1f}^{res}$ by different ways. One evident way is to define $\omega_{res}$ as $\omega_{res} = \omega_{max}$, where $\omega_{max}$ corresponds to the maximum value of $\sigma_{1f}^{res}$. Then $\omega_{res}$ can be obtained from the condition

$$\frac{d}{d\omega} \sigma_{1f}^{res} (\omega) = 0.$$  

(9)

In the resonant approximation we immediately find

$$\omega_{res} = \omega_{max} = \omega_0 = E_{nljF} - E_{n_lj,F_1}.$$  

(10)

Until the line profile remains symmetric with respect to $\omega = \omega_{max}$ the definition (10) remains the same for any other way of extracting $\omega_{res}$ from the line profile.

For both types of experiments discussed above the expression for the photon scattering cross section can be parametrized in the form

$$\sigma_{1f}^{(1,2)} = C \left[ f_{res}^{(1,2)} \right]^2 + 2Re \left[ f_{nr}^{(1,2)} \right]^2,$$  

(11)

$$\left[ \omega_0 - \omega \right]^2 + \frac{\Gamma^2}{4} \Delta$$

$$f_{res}^{(1,2)} = \left[ E_{nljF} - E_{n_lj,F_1} \right] \left( E_{nljF'} - E_{n_lj,F_1} \right)^{3/2}$$

$$\times \sum_{xy} A_{xy}^{(1,2)} \left\{ a_{1,2}^{(1,2)} \otimes b_{1,2}^{(1,2)} \right\} \times \left\{ a_{1,2}^{(1,2)} \otimes b_{1,2}^{(1,2)} \right\} \otimes \left\{ a_{1,2}^{(1,2)} \otimes b_{1,2}^{(1,2)} \right\},$$  

(12)

where

$$A_{xy}^{(1,2)} = \frac{6(-1)^{F' - F + x - y}}{2F_i + 1} \Pi_x^2 \Pi_y \left\{ \begin{array}{c|cc} 1 & 1 & y \\ 1 & 1 & x \\ \end{array} \right\} \left\{ \begin{array}{c|cc} 1 & 1 & x \\ 1 & 1 & 1 \\ \end{array} \right\}$$

$$\times \left\{ \begin{array}{cc} 1 & x \\ F_i & F_i \\ \end{array} \right\} \left\{ \begin{array}{cc} 1 & x \\ F_i' & F_i' \\ \end{array} \right\} \times \langle n_i l_i j_i | F_i | d_1 \rangle | nljF \rangle \langle n'l' j' F' | d_1 \rangle | nljF \rangle$$

$$\times \langle n_f l_f j_f | F_f | d_1 \rangle | nl' j' F' \rangle \langle n_f l_f j_f | d_1 \rangle | nljF \rangle$$

$$\langle n_f l_f j_f | F_f | d_1 \rangle | nl' j' F' \rangle \langle n_f l_f j_f | d_1 \rangle | nljF \rangle$$

(13)

where

$$\omega_{res}^{(1,2)} = \omega_0 - \delta \omega^{(1,2)}$$

$$\delta \omega^{(1,2)} = \frac{f_{res}^{(1,2)} \Gamma^2}{4 \Delta}.$$  

(14)

With our definition of $\Delta$ this value corresponds to the lower component of the fine structure of the level $nl$. For the upper sublevel of two neighboring components we would receive the
TABLE I: The NR corrections to the transitions frequency \( 2s_{1/2} \rightarrow 4p_{1/2} \) with the account for the neighbouring \( 4p_{1/2} \) state and with different choice of the detected final photon (in kHz).

| Type of experiment | \( \tilde{v}_i \tilde{v}_j \) | \( \tilde{v}_i \tilde{v}_j \) |
|--------------------|-----------------|-----------------|
| Final state       |                 |                 |
| \( F = 0 \)       | 60.7130         | 60.7130         |
| \( s_{1/2} \rightarrow \) | -30.3565        | -30.3565        |
| \( F = 0 \)       | 60.7132         | 60.7132         |
| \( s_{1/2} \rightarrow \) | -30.3566        | -30.3566        |
| \( F = 0 \)       | 60.7137         | 60.7137         |
| \( s_{1/2} \rightarrow \) | -30.3569        | -30.3569        |
| \( F = 1 \)       | -30.3562        | -30.3562        |
| \( s_{3/2} \rightarrow \) | 6.0714          | 6.0714          |

The same expression as Eq. \((13)\) with opposite sign of \( \Delta \) and with \( \Gamma = \Gamma_{nlj'F'} \). NR correction in Eq. \((13)\) in some cases which we consider below could depend on the arrangement of the experiment i.e. on the angles between the vectors \( \vec{v}_i \) and \( \vec{v}_j \) in the experiment of the type 1 or on the angles between the vectors \( \tilde{v}_i \) and \( \tilde{v}_j \) in the experiment of the type 2.

V. APPLICATION TO \( 2s_{1/2} \rightarrow 4p_{1/2} \) AND \( 2s_{1/2} \rightarrow 4p_{1/2} \) TRANSITIONS

We are now in position to evaluate the transition frequency for \( 2s_{1/2} \rightarrow 4p_{1/2} \) transition with account for NR corrections originating from the neighboring \( 4p_{1/2} \) level. For this purpose we set in all equations \( n_i l_i = 2s, j_i = 1/2, F_i = 0 \), \( n_l = 4p, j = 1/2, F = 1, j' = 3/2, F' = 1 \). As the final states we have chosen states listed in Table I. Note that hyperfine structure of \( 1s \) and \( 2s \) electron shells was resolvable in experiments [1]. The results of evaluations are presented in Table I for evaluation of NR corrections we use Eqs. \((11), (12), (13)\) where in the energy differences in numerators we use theoretical values given in \((12)\) which incorporate relativistic, QED, nuclear size, the hyperfine structure etc. corrections. The same concerns the value of the widths \( \Gamma = \Gamma_{4p_{1/2}} = 1.289 \times 10^7 \) Hz and the fine structure interval \( \Delta = E_{4p_{1/2}} - E_{4p_{3/2}} = 1367433.3 \) kHz. These values give accurate enough result for \( \delta \omega \) valid with 4 digits.

As it can be seen from the Table II the NR corrections to the transition frequency \( 2s_{1/2} \rightarrow 4p_{1/2} \) do not depend on the type of experiment and consequently on the geometry of this experiment. However these NR corrections appear to depend strongly on the method of the frequency detection, i.e. on the choice of the state to which the excited \( 4p_{1/2} \) level finally decays. Moreover this dependence concerns only the quantum numbers of this final state and the result is nearly independent on the frequency of the final photon. The latter circumstance is understandable since the NR corrections according to Eq. \((14)\) are proportional to the ratio \( f_{\text{res}}/f_{\text{nr}} \) where the corresponding energy differences nearly cancel. When the hyperfine structure of the final levels is resolved the NR corrections differ only by the values of the total angular momentum of an atom \( F_f \) of the final hyperfine sublevel. This can be seen from the closed expressions \((3), (8), (11), (12)\) for NR corrections via \( j-j' \) symbols. Therefore for the transition frequency \( 2s_{1/2} \rightarrow 4p_{1/2} \) three different values corresponding to \( F_f = 0, 1, 2 \) with \( \omega_0 \) from \((12)\) and NR corrections from Table II can be given

\[
F_f = 0 \quad \omega_{\text{res}}^{\text{max}}(1,2) = 61520152497.8 \text{ kHz} \quad (15)
\]

\[
F_f = 1 \quad \omega_{\text{res}}^{\text{max}}(1,2) = 61520152588.9 \text{ kHz} \quad (15)
\]

\[
F_f = 2 \quad \omega_{\text{res}}^{\text{max}}(1,2) = 61520152552.4 \text{ kHz} \quad (15)
\]

These three values differ from each other by more than 90 kHz. This is 30 times larger than the accuracy of measurement quoted in \[(1)\] (3 kHz). Nevertheless all 3 numbers Eq. \((15)\) have equal rights to be called "transition frequency \( 2s_{1/2} - 4p_{1/2} \)." If in the process of the frequency measurement only the emission of the final photon is detected without fixation of its frequency, the averaging over all the final states should be done. In case of our interest this averaging looks like

\[
\delta \omega^{(1,2)} = \frac{\sum_{n_{lj}F'} f_{\text{res}} (1,2) \Gamma^2}{\sum_{n_{lj}F'} f_{\text{res}} (1,2) / 4\Delta}
\]

Now the NR correction begins to depend on the type of the experiment and on the angles between the vectors \( \vec{v}_i, \vec{v}_j \) in the experiment of the first type or between the vectors \( \vec{e}_i, \vec{e}_f \) in the experiment of the second type. The results for \( 2s_{1/2} \rightarrow 4p_{1/2} \) transition are presented in Fig. I

**FIG. 1:** The NR correction for the transition \( 2s_{1/2} \rightarrow 4p_{1/2} \) as the function of the angle between the vectors \( \vec{e}_i, \vec{e}_f \) for the experiment of the type 1 (solid line) and as the function of the angle between the vectors \( \vec{e}_i, \vec{e}_f \) in the experiment of the type 2 (dashed line) according to Eq. \((16)\).

The averaged NR correction according to Eq. \((16)\) and Fig. I vanishes for certain angles \( \theta_1 = 54.7^\circ \) and \( \theta_2 = 125.3^\circ \) which are the same for both types of experiment. The same "magic angles" arise in different areas of quantum physics where the interference of two electric dipole amplitudes is involved, for example in magnetic resonance spectroscopy \((15)\). The "magic angles" are connected with the roots of equation
\( P_2(x) = 0 \) where \( P_2 \) is the Legendre polynomial (see details in the supplement). Values in [13] coincide with quoted above for similar transitions. Evaluation of transition frequency \( 2s^F=0 \rightarrow 4p^F=1 \) with the use Eq. (16) for ”magic” angles with the theoretical \( \omega_0, \Gamma \) and \( \Delta \) gives

\[ \omega_{\text{res}}^{(1,2)} = 616520152558.5 \text{kHz} \]  

(17)

A similar evaluation of the transition frequency \( 2s^F=0 \rightarrow 4p^F=3/2 \) gives

\[ \omega_{\text{res}}^{(1,2)} = 616521519991.8 \text{kHz} \]  

(18)

However this way of obtaining transition frequencies from the experimental data is neither unique nor universal: the ”magic” angles will become different if any other but E1 transitions will be included in the decay.

VI. CONCLUSIONS

An analysis performed in this paper demonstrated that the frequencies of certain transitions (in particular \( 2s^F=0 \rightarrow 4p^F=1 \) transition) in hydrogen atom can not be defined uniquely with recent high accuracy of measurement. This happens due to the presence of NR corrections depending on the type of experiment, on the experimental arrangement and on the method of extracting the transition frequency values from the experimental data. Since the influence of the NR corrections is unavoidable the same situation will occur for any atomic transition as soon as the accuracy of measurement will become comparable with NR corrections.

The recent numerous works on the improvement of frequency standards and on the construction of new atomic clocks are based on the search for atomic transitions where NR corrections are negligible. However it is important to remember that the limit for the accuracy of transition frequency measurement does exist for any atomic transition.

The nonuniqueness of determination of transition frequency does not mean that it is impossible to extract the values for various constants (for example the proton radius and Rydberg constant in case of hydrogen atom) from atomic measurements. For accuracy of measurement of the line profile for a certain transition (or its characteristics like position of the maximum) there are no limits apart from the quantum mechanical uncertainty relations. These measurements should be compared with the theoretical calculations where the NR corrections are taken into account.

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Supplementary

In these supplementary materials we present a most general expression for the photon scattering cross section on the hydrogen atom. In this expression not only fine but also hyperfine structure of the atomic levels is taken explicitly into account. We also present the cross sections averaged over the initial photon projections and summed over the final photon projections. The "closed expression" means that the cross section is written in terms of $ij$-symbols and simple radial integrals. The angular evaluations are based on the book [1]. The earlier expressions for this cross section can be found in [2–4]. Using these expressions the nonresonant corrections to the various photon scattering expressions are derived. We start from the investigation of angular dependence of the photon scattering cross section on an atom in the experiment of the first type, i.e. when summation over nonresonant corrections to the various photon scattering expressions are derived. We proceed to the evaluation of expressions we give the basic relations that we will use below following the notations given in [1]. Components of vector product in cyclic basis $q = \pm 1, 0$ of two vectors $\vec{A}$ and $\vec{B}$

$$\left[ \vec{A} \times \vec{B} \right]_{1q} = -i\sqrt{2}\{A_1 \otimes B_1\}_{1q} = -i\sqrt{2}\sum_{\mu\nu} C^{1q}_{\mu1\nu} A_\mu B_\nu = -i\sqrt{6}(-1)^q \sum_{\mu\nu} \left( \begin{array}{ccc} 1 & 1 & 1 \\ \mu & \nu & -q \end{array} \right) A_\mu B_\nu \quad (S1)$$

Summation over polarization can be performed with the following relation

$$\sum_{\vec{e}} (\vec{e}^* \vec{a})(\vec{e} \vec{b}) = (\vec{\nu} \times \vec{a})(\vec{\nu} \times \vec{b}), \quad (S2)$$

Relations for the components $z$ of the irreducible tensors $A$ and $B$ of rank $y$

$$A^*_z = (A_{yz})^* = (-1)^z A_{y-z} = (-1)^z A_{y-z}, \quad (S3)$$

$$\sum_z A_{yz} B^*_z = (A_y \cdot B_y) = (-1)^{-y} \sqrt{2y + 1} \{A_y \otimes B_y\}_{00}. \quad (S4)$$

Components irreducible of tensor product of rank $y$ of two first rank tensors $A_1$ and $B_1$

$$\{A_1 \otimes B_1\}_{yz} = (-1)^z \sqrt{2y + 1} \sum_{\mu\nu} \left( \begin{array}{ccc} 1 & 1 & y \\ \mu & \nu & -z \end{array} \right) A_\mu B_\nu \quad (S5)$$

$$(\{A_1 \otimes B_1\}_{yz})^* = (-1)^{-z} \{A_1 \otimes B_1\}_{y-z} = \sqrt{2y + 1} \sum_{\mu\nu} \left( \begin{array}{ccc} 1 & 1 & y \\ \mu & \nu & z \end{array} \right) A_\mu B_\nu \quad (S6)$$

Now we perform angular algebra in matrix elements for the experiment of the 1st type, i.e. $\sum_{\vec{e}_i,\vec{e}_f} \sigma_{if}$. Taking the square modulus of matrix elements in the numerator of Eq. (1) of main text we find

$$\sum_{\vec{e}_i,\vec{e}_f} \sigma_{if} = \sum_{\vec{e}_i,\vec{e}_f} \sigma_{if}^{\text{res}} + \sum_{\vec{e}_i,\vec{e}_f} \sigma_{if}^{\text{nr}}, \quad (S7)$$

where $\sum_{\vec{e}_i,\vec{e}_f} \sigma_{if}^{\text{res}}$ is the resonant contribution to the differential cross section

$$\sum_{\vec{e}_i,\vec{e}_f} \sigma_{if}^{\text{res}} = \frac{1}{2F_i + 1} \left( E_{nljF} - E_{n,l,j,F_i} \right)^3 \left( E_{nljF} - E_{n,l,j,f} \right)^3 \quad (S8)$$

$$\times \sum_{\vec{e}_i,\vec{e}_f, nljFM_F} \sum_{M_F'} \sum_{M_F''} \left| \langle nljF | \vec{e}_f | nljFM_F' \rangle \langle nljFM_F' | \vec{e}_i | nljFM_F'' \rangle \langle nljFM_F'' | \vec{e}_i | nljFM_F \rangle \right|^2 \frac{E_{nljF} - E_{n,l,j,F_i} - \omega - \frac{\Gamma_{nljF}}{2}} {E_{nljF} - E_{n,l,j,F_i} - \omega - \frac{\Gamma_{nljF}}{2}} d\omega d\vec{\nu},$$

where $\Gamma_{nljF}$ is the width of the initial level $nljF$ and $\omega$ is the energy of the final state.
and \[ \sum_{\vec{e}_i, \vec{e}_f} \sigma_{ij}^n = \frac{1}{2E_i + 1} (E_{njF} - E_{n_{ij}F_i}) \] is the nonresonant contribution to the cross section

\[
\sum_{\vec{e}_i, \vec{e}_f} \sigma_{ij}^n = \frac{1}{2E_i + 1} (E_{njF} - E_{n_{ij}F_i})^{3/2} (E_{n'j'F'} - E_{n_{ij}F_i})^{3/2}
\]

\[
\times 2 \text{Re} \sum_{\vec{e}_f} \sum_{nlFM} \sum_{n'l'F'M'} \frac{\langle n_{ij}F_iF_j | \vec{e}_f^* d | n_{lj}FM \rangle \langle n_{lj}FM | \vec{e}_i^* d | n_{lj}F_jF_f \rangle}{(E_{njF} - E_{n_{ij}F_i} - \omega - \frac{1}{2} \Gamma_{nlF})} \times \frac{\langle n'l'j'F'M' | \vec{e}_i^* d | n_{ij}F_iF_j \rangle \langle n_{lj}F_jF_f | \vec{e}_j^* d | n'l'j'F'M' \rangle}{(E_{n'j'F'} - E_{nlF})} \] \[ d\omega d\vec{e}_i. \]

Performing summation over polarizations in Eq. (S10) with the use of Eq. (S2) yields

\[
\sum_{\vec{e}_i, \vec{e}_f} \sigma_{ij}^n = \sum_{\vec{e}_i, \vec{e}_f} \sum_{nlFM} \sum_{n'l'F'M'} \frac{\langle n_{ij}F_iF_j | \vec{e}_f^* d | n_{lj}FM \rangle \langle n_{lj}FM | \vec{e}_i^* d | n_{lj}F_jF_f \rangle}{(E_{njF} - E_{n_{ij}F_i} - \omega - \frac{1}{2} \Gamma_{nlF})} \times \frac{\langle n'l'j'F'M' | \vec{e}_i^* d | n_{ij}F_iF_j \rangle \langle n_{lj}F_jF_f | \vec{e}_j^* d | n'l'j'F'M' \rangle}{(E_{n'j'F'} - E_{nlF})} \]

\[ = \sum_{nlFM} \sum_{n'l'F'M'} \frac{\langle n_{lj}F_jF_f | \vec{v}_f \times \vec{d} | n_{lj}FM \rangle \langle n'l'j'F'M' | \vec{v}_i \times \vec{d} | n_{ij}F_iF_j \rangle}{(E_{njF} - E_{n_{ij}F_i} - \omega - \frac{1}{2} \Gamma_{nlF})} \times \frac{\langle n_{lj}F_jF_f | \vec{v}_f \times \vec{d} | n{l}'j'F'M' \rangle \langle n_{lj}FM | \vec{v}_i \times \vec{d} | n_{ij}F_iF_j \rangle}{(E_{n'j'F'} - E_{nlF})}. \]

The scalar product of two vectors in Eq. (S10) can be written in terms of cyclic coordinates

\[
\sum_{\vec{e}_i, \vec{e}_f} \sigma_{ij}^n = \sum_{nlFM} \sum_{n'l'F'M'} \sum_{qq' \ldots} (-1)^{q'q} \frac{\langle n_{lj}F_jF_f | \vec{v}_i \times \vec{d} | n_{lj}FM \rangle \langle n'l'j'F'M' | \vec{v}_f \times \vec{d} | n{l}'j'F'M' \rangle \langle n_{lj}F_jF_f | \vec{v}_f \times \vec{d} | n_{lj}FM \rangle \langle n'l'j'F'M' | \vec{v}_i \times \vec{d} | n{l}'j'F'M' \rangle}{(E_{njF} - E_{n_{ij}F_i} - \omega - \frac{1}{2} \Gamma_{nlF})} \]

Using Eq. (S1) and applying Eckart-Wigner theorem for the dipole matrix elements Eq. (S11) is reduced to

\[
\sum_{\vec{e}_i, \vec{e}_f} \sigma_{ij}^n = \frac{36}{2+1} \sum_{\nu \nu' \mu \mu'} \sum_{q-q' \ldots} (-1)^{q'q} \left( \begin{array}{ccc} 1 & 1 & 1 \\ \mu & \nu & -q \\ \nu & \nu' & \mu' \end{array} \right) \left( \begin{array}{ccc} 1 & 1 & 1 \\ \mu' & \nu' & -q' \\ \mu & \nu & \mu' \end{array} \right) \left( \begin{array}{ccc} 1 & 1 & 1 \\ \mu' & \nu' & -q' \\ \mu & \nu & \mu' \end{array} \right) \] \[ \times \left( \begin{array}{ccc} F_i & 1 & F_f \\ -M_{F_i} & \nu & M_{F_f} \end{array} \right) \left( \begin{array}{ccc} F' & 1 & F_i \\ -M_{F_i} & \nu' & M_{F_f} \end{array} \right) \left( \begin{array}{ccc} F' & 1 & F_i \\ -M_{F_i} & \nu' & M_{F_f} \end{array} \right) \left( \begin{array}{ccc} F & 1 & F_i \\ -M_{F_i} & \nu' & M_{F_f} \end{array} \right) \]

\[ \times \frac{\langle n_{lj}F_f | d_i | n_{lj}FM \rangle \langle n{l}'j'F'M' | d_i | n_{l'j'F'} \rangle \langle n_{lj}F_f | d_i | n_{lj}FM \rangle \langle n{l}'j'F'M' | d_i | n_{l'j'F'} \rangle}{(E_{njF} - E_{n_{ij}F_i} - \omega - \frac{1}{2} \Gamma_{nlF})} \].

The reduced matrix elements in Eq. (S12) do not depend on projections of any angular momentum and are given by [1]

\[
\langle n'l'j'F'M' | d_i | nljF \rangle = (-1)^{l'+j'+l+l'+q+q+q+q} \Pi_{F'} \Pi_{F} \Pi_{l'} \Pi_{l} \left( \begin{array}{ccc} j' & F' & I' \\ j & F & I \end{array} \right) \left( \begin{array}{ccc} l' & j' & 1/2 \\ l & j & 1 \end{array} \right) \langle n'l' | d_i | nl \rangle, \]

where \( I \) is the nuclear spin (\( I = 1/2 \) for hydrogen atom) and

\[
\langle n'l' | d_i | nl \rangle = \epsilon (1)^{l'} \Pi_l \Pi_F \left( \begin{array}{ccc} l & 1 & l' \\ 0 & 0 & 0 \end{array} \right) \int_{0}^{\infty} r^3 R_{n'l'} R_{nl} dr. \]

(S14)
Here $R_{nl}$ is the radial part of hydrogen wave function and $\Pi_{\nu} = \sqrt{2a + 1}$. Then summations over projections of final and intermediate states and averaging over projections of initial state is performed independently with the use of Eq. (10) in section 12.1 of [1].

$$\sum_{M_F, M_{M_F}, M_{F_j}} (-1)^{F_i - M_{F_i} + F' - M_{F'} + F_j - M_{F_j} + F - M}$$

$$\times \left( \begin{array}{ccc} F_i & 1 & F \\ -M_{F_i} & \nu & M \end{array} \right) \left( \begin{array}{ccc} F' & 1 & F_i \\ -M_{F'} & \nu' & M_{F_i} \end{array} \right) \left( \begin{array}{ccc} F_j & 1 & F' \\ -M_{F_j} & \nu'' & M_{F'} \end{array} \right) \left( \begin{array}{ccc} F & 1 & F_j \\ -M_F & \nu'' & M_{F_j} \end{array} \right)$$

$$= (-1)^{F' - F} 2F_i + 1 \sum_{\nu \xi} (1)^{x - \xi} \Pi_{\nu}^2 \left( \begin{array}{ccc} 1 & x & 1 \\ -\nu & \xi & -\nu' \end{array} \right) \left( \begin{array}{ccc} 1 & x & 1 \\ -\nu'' & \xi & -\nu'' \end{array} \right) \left( \begin{array}{ccc} 1 & x & 1 \\ -\nu'' & \xi & -\nu'' \end{array} \right).$$

Now we can consider the sum over indices $\nu'' \nu''' q'$. This summation is performed independently on indices $\nu'' q'$ with the use of Eq. (6) in section 12.1 of [1]. Terms in Eq. (S12) depending on variables $\nu'' \nu''' q'$ are

$$\sum_{\nu'' \nu''' q'} (1)^{x - \xi} \left( \begin{array}{ccc} 1 & 1 & 1 \\ \mu & \nu & q' \end{array} \right) \left( \begin{array}{ccc} 1 & 1 & 1 \\ \nu'' & \nu''' & q \end{array} \right) \left( \begin{array}{ccc} 1 & x & 1 \\ -\nu & \xi & -\nu' \end{array} \right)$$

$$= \sum_{\nu'' \nu''' q'} (1)^{x - \xi} \left( \begin{array}{ccc} 1 & 1 & 1 \\ \mu & \nu & q' \end{array} \right) \left( \begin{array}{ccc} 1 & x & 1 \\ -\nu'' & \xi & -\nu'' \end{array} \right) \left( \begin{array}{ccc} 1 & 1 & 1 \\ \nu & \nu'' & q' \end{array} \right)$$

$$= (-1)^{x - \xi} \left( \begin{array}{ccc} 1 & x & 1 \\ -\nu & \xi & -\mu \end{array} \right) \left( \begin{array}{ccc} 1 & x & 1 \\ 1 & 1 & 1 \end{array} \right) \left( \begin{array}{ccc} 1 & x & 1 \\ 1 & 1 & 1 \end{array} \right).$$

Another sum over indices $\nu'' q'$ is reduced in a similar way as follows

$$\sum_{\nu'' q'} (1)^{x - \xi} \left( \begin{array}{ccc} 1 & 1 & 1 \\ \mu & \nu'' & q' \end{array} \right) \left( \begin{array}{ccc} 1 & 1 & 1 \\ q & \mu & \nu'' \end{array} \right) \left( \begin{array}{ccc} 1 & x & 1 \\ -\nu & \xi & -\nu' \end{array} \right)$$

$$= (-1)^{x - \xi} \sum_{\nu'' q'} (1)^{x - \xi} \left( \begin{array}{ccc} 1 & 1 & 1 \\ \mu & \nu'' & q' \end{array} \right) \left( \begin{array}{ccc} 1 & 1 & 1 \\ q & \mu & \nu'' \end{array} \right) \left( \begin{array}{ccc} 1 & x & 1 \\ -\nu & \xi & -\nu'' \end{array} \right)$$

$$= (-1)^{x - \xi} \left( \begin{array}{ccc} 1 & x & 1 \\ -\mu' & \xi & -\mu \end{array} \right) \left( \begin{array}{ccc} 1 & x & 1 \\ 1 & 1 & 1 \end{array} \right).$$

Collecting together results of Eqs. (S13), (S16), (S17) yields

$$\sum_{\tilde{c}_i, \tilde{c}_j} \sigma_{ij} = \frac{(-1)^{F' - F}}{2F_i + 1} \sum_{x} \sum_{\xi} \sum_{\mu \nu \nu''} (1)^{2x - \xi} \Pi_{\nu}^2 \left( \begin{array}{ccc} 1 & x & 1 \\ -\mu & \xi & -\mu \end{array} \right) \left( \begin{array}{ccc} 1 & x & 1 \\ -\mu'' & \xi & -\mu'' \end{array} \right)$$

$$\times \nu^1_{\mu}, \nu^1_{\nu}, \nu^1_{\nu''}, f^1_{\mu}, f^1_{\nu}, f^1_{\nu''} \left( \begin{array}{ccc} 1 & x & 1 \\ F_i & F & F \end{array} \right) \left( \begin{array}{ccc} 1 & x & 1 \\ F' & F & F \end{array} \right) \sum_{n_{lj}l'j}' \sum_{n_{lj}l'j}' \sum_{n_{lj}l'j}' \sum_{n_{lj}l'j}' \sum_{n_{lj}l'j}' \sum_{n_{lj}l'j}' \sum_{n_{lj}l'j}' \sum_{n_{lj}l'j}' \sum_{n_{lj}l'j}' \sum_{n_{lj}l'j}' \sum_{n_{lj}l'j}' \sum_{n_{lj}l'j}' \sum_{n_{lj}l'j}' \sum_{n_{lj}l'j}'$$

$$\times 2 \Re \left[ \frac{\langle n_{lj}l'j|d_{l}|n_{lj}l'j \rangle \langle n_{lj}l'j|d_{l}|n_{lj}l'j \rangle \langle n_{lj}l'j|d_{l}|n_{lj}l'j \rangle \langle n_{lj}l'j|d_{l}|n_{lj}l'j \rangle \langle n_{lj}l'j|d_{l}|n_{lj}l'j \rangle \langle n_{lj}l'j|d_{l}|n_{lj}l'j \rangle \langle n_{lj}l'j|d_{l}|n_{lj}l'j \rangle \langle n_{lj}l'j|d_{l}|n_{lj}l'j \rangle \langle n_{lj}l'j|d_{l}|n_{lj}l'j \rangle \langle n_{lj}l'j|d_{l}|n_{lj}l'j \rangle \langle n_{lj}l'j|d_{l}|n_{lj}l'j \rangle \langle n_{lj}l'j|d_{l}|n_{lj}l'j \rangle}{(E_{nljF} - E_{n_{lj}l'jF_i} - \omega - \frac{1}{2} \Gamma_{nljF})(E_{n_{lj}l'jF_i} - E_{nljF})} \right] d\omega d\tilde{\nu}.$$

Two two remaining $3jm$ symbols in Eq. (S13) can be considered separately. Using Eq. (5) in section 12.1 of [1] and Eqs. (S3)–(S6), the following sequence of equalities can be written for the sum over $\xi$ in Eq. (S18)

$$\sum_{\xi} (-1)^{x - \xi} \left( \begin{array}{ccc} 1 & x & 1 \\ -\mu' & \xi & -\mu \end{array} \right) \left( \begin{array}{ccc} 1 & x & 1 \\ -\mu'' & \xi & -\mu'' \end{array} \right)$$

$$= \sum_{y \xi} (1)^{x - y} \sqrt{2y + 1} \left( \begin{array}{ccc} 1 & x & 1 \\ 1 & 1 & y \end{array} \right) \left( \begin{array}{ccc} 1 & x & 1 \\ 1 & 1 & y \end{array} \right) \left( \begin{array}{ccc} 1 & x & 1 \\ 1 & 1 & y \end{array} \right).$$

Substitution of Eq. (S19) into Eq. (S18) yields

$$\sum_{\tilde{c}_i, \tilde{c}_j} \sigma_{ij} = \frac{(-1)^{F' - F}}{2F_i + 1} \sum_{x} \sum_{\xi} \sum_{\mu \nu \nu''} (1)^{2x - \xi} \Pi_{\nu}^2 \left( \begin{array}{ccc} 1 & x & 1 \\ -\mu & \xi & -\mu \end{array} \right) \left( \begin{array}{ccc} 1 & x & 1 \\ -\mu'' & \xi & -\mu'' \end{array} \right)$$

$$= \frac{(-1)^{F' - F}}{2F_i + 1} \sum_{x} \sum_{\xi} \sum_{\mu \nu \nu''} (1)^{2x - \xi} \Pi_{\nu}^2 \left( \begin{array}{ccc} 1 & x & 1 \\ -\mu & \xi & -\mu \end{array} \right) \left( \begin{array}{ccc} 1 & x & 1 \\ -\mu'' & \xi & -\mu'' \end{array} \right).$$
\[
\sum_{\tilde{e}_i, \tilde{e}_f} \sigma^{nf}_{ij} = 2 \text{Re} \left[ \frac{f^{(1)}_{nr}}{(E_{nljF} - E_{n_{l}l_{j}F_{i}} - \omega - \frac{1}{2} \Gamma_{nljF}) \left( E'_{n'_{l'}l'_{j'}F'_{i'}} - E_{nljF} \right)} \right] d\omega d\tilde{\nu},
\] (S21)

together with notations
\[
f^{(1)}_{\text{res}} = \left( E_{nljF} - E_{n_{l}l_{j}F_{i}} \right)^{3/2} \left( E_{nljF} - E_{n_{l}l_{j}F_{i}} \right)^{3/2} \sum_{xy} A^{(1), \text{res}}_{xy} \left\{ \left\{ \nu^{l_{i}} \otimes \nu^{l'_{i}} \right\}_{y} \otimes \left\{ \nu^{l_{j}} \otimes \nu^{l'_{j}} \right\}_{y} \right\}_{00}
\] (S22)
\[
f^{(1)}_{nr} = \left( E_{nljF} - E_{n_{l}l_{j}F_{i}} \right)^{3/2} \left( E_{n'l'j'F'i'} - E_{n_{l}l_{j}F_{i}} \right)^{3/2} \sum_{xy} A^{(1), \text{nr}}_{xy} \left\{ \left\{ \nu^{l_{i}} \otimes \nu^{l'_{i}} \right\}_{y} \otimes \left\{ \nu^{l_{j}} \otimes \nu^{l'_{j}} \right\}_{y} \right\}_{00}
\] (S23)
\[
A^{(1), \text{res}}_{xy} = \frac{36(-1)^{x-y}}{2F_{i} + 1} \Pi_{M}^{2} \Pi_{\nu} \left\{ \begin{array}{ccc} 1 & 1 & y \\ 1 & 1 & x \\ 1 & 1 & 1 \\ 1 & 1 & 1 \\ \end{array} \right\} \left\{ \begin{array}{ccc} 1 & x & 1 \\ F & F & F \\ F & F & F \\ \end{array} \right\}
\times |\langle n_{l}l_{j}F_{i} || d_{1} || n_{l}l_{j}F_{i} \rangle | \langle n_{l}l_{j}F_{i} || d_{1} || n_{l}l_{j}F_{i} \rangle |^{2}
\] (S24)
\[
A^{(1), \text{nr}}_{xy} = \frac{36(-1)^{F'_{i} - F + x-y}}{2F_{i} + 1} \Pi_{M}^{2} \Pi_{\nu} \left\{ \begin{array}{ccc} 1 & 1 & y \\ 1 & 1 & x \\ 1 & 1 & 1 \\ 1 & 1 & 1 \\ \end{array} \right\} \left\{ \begin{array}{ccc} 1 & x & 1 \\ F' & F' & F' \\ F' & F' & F' \\ \end{array} \right\}
\times |\langle n_{l}l_{j}F_{i} || d_{1} || n_{l}l_{j}F_{i} \rangle | \langle n_{l}l_{j}F_{i} || d_{1} || n_{l}l_{j}F_{i} \rangle |^{2}
\] (S25)

Now we can consider the second type of experiment, i.e. differential cross section \( \sigma^{nf}_{ij} \). Taking square of modulus in Eq. (S20), performing summation over photon polarization vector \( \tilde{e}_{f} \), summation over projections in final states and averaging over projections in initial states we find
\[
\sum_{\tilde{e}_{i}} \sigma^{nf}_{ij} = \frac{1}{2F_{i} + 1} \sum_{M_{F_{i}}} \sum_{M_{F_{i}}} \sum_{nljFM} \sum_{n'l'j'FM'} \frac{|\langle n_{l}l_{j}F_{i} || M_{F_{i}} \rangle \langle n_{l}l_{j}F_{i} || M_{F_{i}} \rangle | |\langle n_{l}l_{j}F_{i} || M_{F_{i}} \rangle | |\langle n_{l}l_{j}F_{i} || M_{F_{i}} \rangle |}{(E_{nljF} - E_{n_{l}l_{j}F_{i}} - \omega - \frac{1}{2} \Gamma_{nljF})}
\] (S26)

The scalar product of two vectors in Eq. (S26) can be written in cyclic coordinate space
\[
\sum_{\tilde{e}_{i}} \sigma^{nf}_{ij} = \frac{6}{2F_{i} + 1} \sum_{M_{F_{i}}} \sum_{M_{F_{i}}} \sum_{nljFM} \sum_{n'l'j'FM'} \sum_{q'q''} (-1)^{q + q' + q''}
\times |\langle n_{l}l_{j}F_{i} || M_{F_{i}} \rangle | |\langle n_{l}l_{j}F_{i} || M_{F_{i}} \rangle | |\langle n_{l}l_{j}F_{i} || M_{F_{i}} \rangle |}{(E_{nljF} - E_{n_{l}l_{j}F_{i}} - \omega - \frac{1}{2} \Gamma_{nljF})}
\] (S27)

Using Eq. (S1) for cyclic components of vector product and applying Eckart-Wigner theorem for the dipole matrix elements in Eq. (S27) we find
\[
\sum_{\tilde{e}_{i}} \sigma^{nf}_{ij} = - \frac{6}{2F_{i} + 1} \sum_{M_{F_{i}}} \sum_{M_{F_{i}}} \sum_{q'q''} (-1)^{q + q' + q''} \left( -1 \right)^{F_{i} - M_{F_{i}} + F'_{i} - M_{F_{i}} - F_{i} - M_{F_{i}} + F_{i} - M_{F_{i}}}
\times |\langle n_{l}l_{j}F_{i} || d_{1} || n_{l}l_{j}F_{i} \rangle | |\langle n_{l}l_{j}F_{i} || d_{1} || n_{l}l_{j}F_{i} \rangle | |\langle n_{l}l_{j}F_{i} || d_{1} || n_{l}l_{j}F_{i} \rangle |}{(E_{nljF} - E_{n_{l}l_{j}F_{i}} - \omega - \frac{1}{2} \Gamma_{nljF})}
\] (S28)
Then summation over projections of angular momentum in final, intermediate and initial states in Eq. (S28) is performed independently on the reduced matrix elements and vector components

\[
\sum_{M_{F}, M_{F'}, M_{F''}} (-1)^{F_i - M_{F'} + F' - M_{F'} + F_j - M_{F''} + F - M} (S29)
\]

\[
\times \left( \begin{array}{ccc}
F_i & 1 & F_j \\
-M_{F'}, -q' & M_{F'} & \\
F' & 1 & F_j
\end{array} \right) \left( \begin{array}{ccc}
F_j & 1 & F_j \\
-M_{F'} & \nu' & M_{F''} \\
F_j & 1 & F_j
\end{array} \right) = (-1)^{F''}(-1)^{q'+q''} \sum_{x \xi}(1-x^\xi \Pi_x^2) \left( \begin{array}{ccc}
1 & x & 1 \\
q & -x & q'
\end{array} \right) \left( \begin{array}{ccc}
1 & x & 1 \\
-\nu' & \xi & -\nu
\end{array} \right) \left( \begin{array}{ccc}
1 & x & 1 \\
F' & F' & F
\end{array} \right) = \left( \begin{array}{ccc}
1 & x & 1 \\
F' & F' & F
\end{array} \right)
\]

Substitution of Eq. (S29) into equation (S28) yields

\[
\sum_{\xi} \sigma_{ij}^{nr} = \frac{6(-1)^{F''}}{2F_i + 1} \sum_{\nu} \sum_{\nu'} \sum_{q} (-1)^{q'+q''} (S30)
\]

\[
\times \left( \begin{array}{ccc}
1 & x & 1 \\
q & -x & q'
\end{array} \right) \left( \begin{array}{ccc}
1 & x & 1 \\
-\nu' & \xi & -\nu
\end{array} \right) \left( \begin{array}{ccc}
1 & x & 1 \\
\mu' & \nu' & q''
\end{array} \right) = (-1)^{x} \left( \begin{array}{ccc}
1 & 1 & 1 \\
1 & 1 & 1
\end{array} \right) \sum_{\xi} (-1)^{x-\xi} \left( \begin{array}{ccc}
1 & x & 1 \\
q' & -x & q'
\end{array} \right) \left( \begin{array}{ccc}
1 & 1 & 1 \\
\xi & \mu' & \mu
\end{array} \right)
\]

Then using Eq. (5) in section 12.1 of [1] for the sum over \( \xi \), Eq. (S31) reduces to

\[
= (-1)^{x} \left( \begin{array}{ccc}
1 & 1 & 1 \\
1 & 1 & 1
\end{array} \right) \sum_{y} (-1)^{y-z} \sqrt{2y+1} \left( \begin{array}{ccc}
1 & 1 & 1 \\
q' & \mu' & -z
\end{array} \right) e^{1 y \nu_{1}^{1}} \mu' \sqrt{2y+1} \left( \begin{array}{ccc}
1 & 1 & 1 \\
\mu & q & z
\end{array} \right) e^{1 y \nu_{1}^{1}} \mu' \left( \begin{array}{ccc}
1 & 1 & 1 \\
1 & 1 & 1
\end{array} \right)
\]

Finally, taking into account and Eqs. (S3)–(S6) and substituting result Eq. (S32) into Eq. (S28) we find

\[
\sum_{\xi} \sigma_{ij}^{res} = \frac{f_{res}^{(2)}}{(E_{nljF} - E_{nl_{ij}F', \omega})^2 - \frac{\nu_{1}^{1} \mu_{1}^{1}}{4}} d\omega d\nu', (S33)
\]

\[
\sum_{\xi} \sigma_{ij}^{nr} = 2Re \left[ \frac{f_{nr}^{(2)}}{(E_{nljF} - E_{nl_{ij}F', \omega} - \frac{1}{2} \Gamma_{nljF}')(E_{nl'jF'} - E_{nljF})} \right] d\omega d\nu', (S34)
\]

where the following notations are introduced

\[
f_{res}^{(2)} = (E_{nljF} - E_{nl_{ij}F'})^3 (E_{nljF} - E_{nl_{ij}F'})^3 \sum_{xy} A_{xy}^{(2),res} \left\{ \{ e^{1,1 \mu \nu_{1}^{1}} \}_y \otimes \{ e^{1,1 \mu \nu_{1}^{1}} \}_y \right\}_{00}
\]

\[
f_{nr}^{(2)} = (E_{nljF} - E_{nl_{ij}F'})^{3/2} (E_{nljF} - E_{nl_{ij}F'})^{3/2} \sum_{xy} A_{xy}^{(2),nr} \left\{ \{ e^{1,1 \mu \nu_{1}^{1}} \}_y \otimes \{ e^{1,1 \mu \nu_{1}^{1}} \}_y \right\}_{00}
\]
$$A^{(2),\text{xy}}_{xy} = \frac{6(-1)^y}{2F_i + 1} \Pi_x \Pi_y \left\{ \begin{array}{ll} 1 & 1 \\ 1 & x \end{array} \right\} \left\{ \begin{array}{ll} 1 & 1 \\ 1 & 1 \end{array} \right\} \left\{ \begin{array}{ll} 1 & 1 \\ 1 & F_i \\ F \end{array} \right\} \left\{ \begin{array}{ll} 1 & 1 \\ F & F \end{array} \right\} \cdot$$

$$\times \langle n_l i_j F_i | d_1 | n_l j F \rangle \langle n_l j F | d_1 | n_f f_j F_f \rangle |^2, $$

$$A^{(2),\text{nr}}_{xy} = \frac{6(-1)^{F_i-F-y}}{2F_i + 1} \Pi_x \Pi_y \left\{ \begin{array}{ll} 1 & 1 \\ 1 & x \end{array} \right\} \left\{ \begin{array}{ll} 1 & 1 \\ 1 & 1 \end{array} \right\} \left\{ \begin{array}{ll} 1 & 1 \\ 1 & F' \end{array} \right\} \left\{ \begin{array}{ll} 1 & 1 \\ F' & F \end{array} \right\} \cdot$$

$$\times \langle n_l i_j F_i | d_1 | n_l j' F' \rangle \langle n_l j' F' | d_1 | n_f f_j F_f \rangle \langle n_l j F | d_1 | n_f f_j F_f \rangle.$$  

Tensor product in Eqs. (S22), (S23), (S35), (S36) can be expressed through trigonometric functions of the angle between the vectors $\vec{a}$ and $\vec{b}$.

The term with $y = 0$ in the last factor in Eqs. (S22), (S23), (S35), (S36) reduces to the square of scalar of two vectors $\vec{a}$ and $\vec{b}$.

$$\left\{ \begin{array}{ll} a_1^{(1,2)} \otimes b_1^{(1,2)} \end{array} \right\}_0 \otimes \left\{ \begin{array}{ll} a_1^{(1,2)} \otimes b_1^{(1,2)} \end{array} \right\}_0 = \frac{1}{3} \cos^2 \theta_{(1,2)}$$

where $a_1^{(1)} = \nu_1^{1,1}$, $a_1^{(2)} = e_1^{1,1}$, $b_1^{(1)} = b_1^{(2)} = \nu_1^{1,1}$ and $\theta_{(1,2)}$ is the angle between vectors $\vec{a}$ and $\vec{b}$. The term with $y = 1$ in Eqs. (S22), (S23), (S35), (S36) reduces to the square of the vector product of vectors $\vec{a}$ and $\vec{b}$.

$$\left\{ \begin{array}{ll} a_1^{(1,2,3)} \otimes b_1^{(1,2,3)} \end{array} \right\}_1 \otimes \left\{ \begin{array}{ll} a_1^{(1,2,3)} \otimes b_1^{(1,2,3)} \end{array} \right\}_1 = \frac{1}{2 \sqrt{3}} \sin^2 \theta_{(1,2)}.$$  

The term with $y = 2$ reduces to the scalar product of the two irreducible tensors of the rank 2.

$$\left\{ \begin{array}{ll} a_1^{(1,2)} \otimes b_1^{(1,2)} \end{array} \right\}_2 \otimes \left\{ \begin{array}{ll} a_1^{(1,2)} \otimes b_1^{(1,2)} \end{array} \right\}_2 = \frac{1}{6 \sqrt{5}} (3 + \cos^2 \theta_{(1,2)}).$$

The Eqs. (S20), (S21), (S33), (S34) together with Eqs. (S39)-(S41) conclude the derivation of Eqs. (5) and (9) in the main text.

Now we are in position to find out the dependence on the angle $\theta_{(1,2)}$ for the NR correction averaged over all the final states, i.e. for the Eq. (16) in the main text.

$$\delta \omega^{(1,2)} = \sum_{n_f f_j F_f} \frac{f^{(1,2)}_{nr}}{f^{(1,2)}_{res}} \frac{\Gamma^2}{4 \Delta}$$

For this purpose we set in all equations $n_l i_j = 2s$, $j_i = 1/2$, $F_i = 0$, $n_l = 4p$, $j = 1/2$, $F = 1$, $j' = 3/2$, $F' = 1$. Then performing summation in Eq. (S42) for the experiment of the 1st type we find.

$$\delta \omega^{(1)} = \frac{5 I_{4p1s}^2 + 5 I_{4p2s}^2 + 5 I_{4p3s}^2 + 5 I_{4p3d}^2}{40 (I_{4p1s}^2 + I_{4p2s}^2 + I_{4p3s}^2 + I_{4p3d}^2)} \frac{\Gamma^2}{4 \Delta} (1 + 3 \cos 2 \theta_{(1,2)})$$

where

$$I_{n'l'nl} = \int_0^{\infty} r^2 R_{n'l'}^2 R_{nl} dr,$$

and $R_{nl}$ is the radial part of hydrogen wave function. In Eq. (S43) we neglected the fine structure dependencies for the energies in Eqs. (S22) and (S23), then ratio of energies close to 1 for each term of the sum over final states in Eq. (S42). In the same way for the second type of the experiment we find

$$\delta \omega^{(2)} = \frac{5 I_{4p1s}^2 + 5 I_{4p2s}^2 + 5 I_{4p3s}^2 + 5 I_{4p3d}^2}{20 (I_{4p1s}^2 + I_{4p2s}^2 + I_{4p3s}^2 + I_{4p3d}^2)} \frac{\Gamma^2}{4 \Delta} (1 + 3 \cos 2 \theta_{(2,1)}).$$

The angular factor in Eqs. (S43) and (S45) can be also expressed in terms of Legendre polynomial of second order using the equality $P_2(\cos \theta_{(1,2)}) = \frac{1}{2}(1 + 3 \cos 2 \theta_{(1,2)})$. Solving equation $1 + 3 \cos 2 \theta_{(1,2)} = 0$ for the variable $\theta_{(1,2)}$ one can easily find that NR correction vanishes at the angles $\theta_{(1,2)} = \frac{1}{2}(\pm \arccos \frac{1}{2} + 2\pi n)$ (with $n \in \mathbb{Z}$). This result can be obtained for any set of initial and intermediate quantum numbers and corresponds to Fig. 1 of the main text.

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