Asymmetry of the Natural Line Profile for the Hydrogen Atom

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(Received 11 April 2001; published 14 September 2001)

The asymmetry of the natural line profile for transitions in hydrogenlike atoms is evaluated within a QED framework. For the Lyman-α $1s$-$2p$ absorption transition in neutral hydrogen this asymmetry results in an additional energy shift of 2.929 856 Hz. For the $2s_{1/2}$-$2p_{3/2}$ transition it amounts to $-1.512\,674$ Hz. As a new feature this correction turns out to be process dependent. The quoted numbers refer to the Compton-scattering process.

DOI: 10.1103/PhysRevLett.87.143003 PACS numbers: 31.30.Jv, 12.20.Ds, 31.15.–p

The problem of the natural line profile in atomic physics was considered first in terms of quantum mechanics by Weisskopf and Wigner [1]. Within the framework of modern QED it was first formulated for one-electron atoms by Low [2]. In [2] the occurrence of the Lorentz profile in the resonance approximation was described and the nonresonant corrections were estimated. Later the line profile QED theory has been modified also for many-electron atoms [3] (see also [4]) and has been applied to the theory of overlapping resonances in two-electron highly charged ions [5]. Within this formalism corrections to the energy levels, e.g., reference state QED corrections, have been evaluated [6].

One of the important consequences of the line profile theory is the occurrence of nonresonant (NR) corrections [2]. These corrections indicate the limit up to which the concept of the energy of an excited atomic state has a physical meaning—that is the resonance approximation. The exact theoretical value for the energy of an excited state defined, e.g., by the Green function pole, can be compared directly with measurable quantities only within the resonance approximation, for which the line profile is described by the two parameters: energy E and width Γ. Beyond this approximation the evaluation of E and Γ should be replaced by the evaluation of the line profile for the particular process. If the distortion of the Lorentz profile is still small one can formally consider the nonresonant correction as a correction to the energy shift. Unlike all other energy corrections, this correction depends on the particular process under consideration which has been employed for the measurement of the energy difference. The NR corrections were considered for H-like ions of phosphorus ($Z = 15$) and uranium ($Z = 92$) in [7,8]. While for uranium the NR correction was found to be negligible, its value was comparable with the experimental inaccuracy in the case of phosphorus.

In this paper we demonstrate that the concept of a transition energy depends on the measurement process. For this reason we evaluate the NR corrections for the neutral hydrogen atom. We consider the process of the resonance Compton scattering as a standard procedure for the determination of the energy levels. For this process the parametric estimate of the NR correction can be expressed as [2] (in relativistic units).

$$\delta = Cm\alpha^2(\alpha Z)^6, \tag{1}$$

where C is some numerical factor, α is the fine structure constant, and Z is the nuclear charge number.

The recent QED calculations for low-Z H-like atoms incorporate corrections of the order $m\alpha^2(\alpha Z)^5$ [9–12]; corrections of the order $m\alpha^2(\alpha Z)^6 \ln^3(\alpha Z)$ are also included [13,14]. For low-Z accurate Lamb-shift calculations to all orders in $Z\alpha$ have been performed recently [15,16].

Thus in principle the next order corrections to the energy levels should include NR corrections and will depend on the process of measurement under consideration. However the numerical factor C in Eq. (1) appears to be quite small: 10^{-3} for the Lyman-α transition (see below). There are no direct measurements of the Lyman-α transition frequency with an accuracy required in order to observe the correction (1). Modern experimental techniques employed in Lamb-shift measurements are based on two-photon resonances, e.g., for the transition $2s$-$1s$ [17–19]. Although the theoretical evaluation of the NR corrections to the two-photon resonances is more involved, we can state that the corresponding NR corrections will be of the same order of magnitude as the one considered here.

Consider the process of photon scattering on a one-electron atom. Resonance scattering implies that the frequency of the initial photon ω is close to the energy difference $\omega = E_{A'} - E_B$ where A' is some excited atomic state and B is the initial state. Within the resonance approximation we retain only the term $n = A'$ in the sum over intermediate states in the amplitude. Separating out the resonant term we express the corresponding amplitude in the form

$$U^{(2)}_{AB}(\omega jm\lambda;\omega' j' m' \lambda') = e^2\biggl(\frac{(\boldsymbol{\gamma}\boldsymbol{A}^*_{\omega' j' m' \lambda'})_{AA'}(\boldsymbol{\gamma}\boldsymbol{A}_{\omega jm\lambda})_{A'B}}{E_{A'} - E_B - \omega} + \sum_{n\neq A'}\frac{(\boldsymbol{\gamma}\boldsymbol{A}^*_{\omega' j' m' \lambda'})_{An}(\boldsymbol{\gamma}\boldsymbol{A}_{\omega jm\lambda})_{nB}}{E_n - E_B - \omega} + \sum_n \frac{(\boldsymbol{\gamma}\boldsymbol{A}^*_{\omega jm\lambda})_{An}(\boldsymbol{\gamma}\boldsymbol{A}^*_{\omega' j' m' \lambda'})_{nB}}{E_n - E_A + \omega}\biggr), \tag{2}$$

where $\boldsymbol{\gamma}$ are Dirac matrices, $\boldsymbol{A}_{\omega jm\lambda}$ is the vector potential of the electromagnetic field (photon wave function), and E_n are the one-electron energies. Initial, intermediate, and final states of an electron are denoted as B, n, A', and A, respectively. The initial and final photon states are $\omega jm\lambda$ and $\omega' j' m' \lambda'$, where ω is the frequency, jm denote the photon angular momentum and its projection, and the quantum number λ determines the parity of the photon state. The second and third terms in Eq. (2) represent the nonresonant corrections to the scattering amplitude.

The Lorentz line profile arises when we sum up all the electron self-energy insertions in the internal electron line within the resonance approximation [2]. After summation of the arising geometric progression one finds

$$U^{(2)}_{AB(A')} = e^2\,\frac{(\boldsymbol{\gamma}\boldsymbol{A}^*_{\omega' j' m' \lambda'})_{AA'}(\boldsymbol{\gamma}\boldsymbol{A}_{\omega jm\lambda})_{A'B}}{E_{A'} - E_B + [\hat{\Sigma}_R(\omega + E_A)]_{A'A'} - \omega}, \tag{3}$$

where $\hat{\Sigma}_R(\omega + E_A)$ is the renormalized electron self-energy operator.

In the resonance approximation we can substitute $\omega + E_A = E_{A'}$ in the denominator of Eq. (3). The real part of the matrix element $[\hat{\Sigma}_R(\omega + E_A)]_{A'A'}$ yields the lowest-order contribution to the Lamb shift while the imaginary part which is finite and not subject to renormalization indicates the total radiative (single-quantum) width of the level A': $[\hat{\Sigma}_R(\omega + E_A)]_{A'A'} = L^{\mathrm{SE}}_{A'} - i\Gamma_{A'}/2$. An additional contribution to the lowest-order Lamb shift $L^{\mathrm{VP}}_{A'}$ originates from the vacuum polarization graph. However, this graph gives no contribution to the width [4].

Taking the square modulus of the amplitude (2), integrating over the directions of the absorbed and emitted photons, and summing over polarizations we obtain the Lorentz profile for the absorption probability:

$$dW(\omega) = \frac{1}{2\pi}\,\frac{\Gamma_{A'A}\,d\omega}{(\omega^0_{A'A} + L^{\mathrm{SE}}_{A'} - \omega)^2 + \Gamma^2_{A'}/4}. \tag{4}$$

Here $dW(\omega)$ is the probability for photon absorption in the frequency interval $[\omega, \omega + d\omega]$, $\omega^0_{A'A} = E_{A'} - E_A$, and $\Gamma_{A'A}$ is the partial width of the level A', connected with the transition $A' \to A$. The inclusion of the Lamb shift L_A corresponding to the initial state A into the Lorentz profile (4) can be accomplished, if necessary, by the methods developed in [3,4]. The line profile for the emission process $A' \to A$ is described again by Eq. (4).

In the nonresonant terms in Eq. (2) we can substitute $\omega = E_{A'} - E_B$. Then we arrive at the expression (we omitted the Lamb shift $L_{A'}$, which is not essential for our purposes)

$$U_{AB}(\omega jm\lambda;\omega' j' m' \lambda') = e^2\biggl(\frac{(\boldsymbol{\gamma}\boldsymbol{A}^*_{\omega' j' m' \lambda'})_{AA'}(\boldsymbol{\gamma}\boldsymbol{A}_{\omega jm\lambda})_{A'B}}{E_{A'} - E_B - \omega - i\Gamma_{A'}/2} + \sum_{n\neq A'}\frac{(\boldsymbol{\gamma}\boldsymbol{A}^*_{\omega' j' m' \lambda'})_{An}(\boldsymbol{\gamma}\boldsymbol{A}_{\omega jm\lambda})_{nB}}{E_n - E_{A'}} + \sum_n \frac{(\boldsymbol{\gamma}\boldsymbol{A}_{\omega jm\lambda})_{An}(\boldsymbol{\gamma}\boldsymbol{A}^*_{\omega' j' m' \lambda'})_{nB}}{E_n + E_{A'} - E_A - E_B}\biggr). \tag{5}$$

The differential cross section of the process is

$$d\sigma_{AB}(\omega jm\lambda;\omega' j' m' \lambda') = 2\pi|U^{(2)}_{AB}(\omega jm\lambda;\omega' j' m' \lambda')|^2\delta(E_A - E_B + \omega' - \omega)\,d\omega\,d\omega'. \tag{6}$$

The one-electron states A, A', B depend on the usual set of quantum numbers $A \equiv n_A l_A j_A m_A$, where n_A is the principal quantum number, l_A is the orbital angular momentum quantum number which determines the parity, and j_A, m_A are the total angular momentum and its projection. Integration over ω', summation over $j' m' \lambda', m_A$, and averaging over m, m_B yield

$$\sigma_{AB}(\omega jm\lambda) = \frac{2\pi}{(2j_B + 1)(2j + 1)}\sum_{j'\lambda'}\sum_{mm'}\sum_{m_A m_B}|U^{(2)}_{AB}[\omega jm\lambda;(\omega + E_B - E_A)j' m' \lambda']|^2 d\omega. \tag{7}$$

Substituting Eq. (5) into Eq. (7) and omitting the terms, quadratically dependent on the nonresonant contributions, we obtain $\sigma_{AB} = \sigma^{(0)}_{AB} + \sigma^{(1)}_{AB}$. The first term leads to the usual Lorentz line profile for the process under consideration

$$\sigma^{(0)}_{AB}(\omega jm\lambda) = \frac{1}{2\pi}\,\frac{2j_{A'} + 1}{2j + 1}\,\frac{\Gamma_{AA'}W_{BA'}(j\lambda)}{(E_{A'} - E_B - \omega)^2 + \Gamma^2_{A'}/4}, \tag{8}$$

where $W_{BA'}$ is the transition probability $B \to A'$,

$$W_{BA'} = \frac{2\pi}{2j_B + 1}\sum_{mm_B m_{A'}}|(\boldsymbol{\gamma}\boldsymbol{A}^*_{\omega jm\lambda})_{BA'}|^2, \tag{9}$$

and $\Gamma_{AA'} = \sum_{j'\lambda'} W_{AA'}(j'\lambda')$ is the partial width of the level A', connected with the transition $A' \to A$. It is assumed that the level B is stable ($\Gamma_B = 0$) or metastable ($\Gamma_B \ll \Gamma_{A'}$). The term $\sigma^{(1)}_{AB}$ that represents the interference between the resonant and nonresonant contributions to the amplitude is determined by

$$\sigma_{AB}^{(1)}(\omega j\lambda) = \frac{1}{2\pi}\frac{2j_{A'}+1}{2j+1}\mathrm{Re}\Bigg[\sum_{n\neq A'}\frac{\Gamma_{AA;A'n}W_{BB;nA'}(j\lambda)}{(E_{A'}-E_B-\omega-i\Gamma_{A'}/2)^*(E_n-E_{A'})} + \sum_{n}\frac{\Gamma_{An;A'B}W_{nB;AA'}(j\lambda)}{(E_{A'}-E_B-\omega-i\Gamma_{A'}/2)^*(E_n+E_{A'}-E_A-E_B)}\Bigg]d\omega\,, \tag{10}$$

where $W_{BB;nA'}(j\lambda)$ and $W_{nB;AA'}(j\lambda)$ are the "mixed" transition probabilities

$$W_{BB;nA'}(j\lambda) = \frac{2\pi}{2j_{A'}+1} \times \sum_{mm_Bm_{A'}m_n}(\boldsymbol{\gamma A}_{\omega jm\lambda})_{nB}(\boldsymbol{\gamma A}^*_{\omega jm\lambda})_{BA'}\,, \tag{11}$$

$$W_{nB;AA'}(j\lambda) = \frac{2\pi}{2j_{A'}+1} \times \sum_{mm_Am_Bm_{A'}m_n}(\boldsymbol{\gamma A}_{\omega jm\lambda})_{An}(\boldsymbol{\gamma A}^*_{\omega jm\lambda})_{BA'}\,, \tag{12}$$

and $\Gamma_{AB;CD} = \sum_{j'\lambda'}W_{AB;CD}(j'\lambda')$ is the "mixed" partial width.

It is important to emphasize that in the sum over n in Eq. (10) only the states n with the same symmetry (i.e., with the same $j_{A'}\lambda_{A'}$) survive. Thus we keep the same averaging factor $(2j_{A'}+1)^{-1}$ in Eqs. (11) and (12). Note also that for the fixed transition $B \to A'$ the type of the absorbed photon $(j\lambda)$ will be also fixed.

We assume that the standard way of measuring the resonance frequency is employed which is connected with the determination of the maximum in the probability distribution for the given process. In the pure resonance case the maximum condition $\frac{d}{d\omega}\sigma_{AB}^{(0)}(\omega) = 0$ corresponds to the resonance frequency value $\omega_{\max} = E_{A'} - E_B$. If we take into account the correction $\sigma_{AB}^{(1)}(\omega)$, the result will be different, i.e., $\frac{d}{d\omega}[\sigma_{AB}^{(0)}(\omega) + \sigma_{AB}^{(1)}(\omega)] = 0$ with $\omega_{\max} = E_{A'} - E_B + \delta$ and

$$\delta = \frac{1}{4}\frac{\Gamma_{A'}^2}{\Gamma_{AA'}W_{BA'}}\mathrm{Re}\Bigg[\sum_{n\neq A'}\frac{\Gamma_{AA;A'n}W_{BB;nA'}(j\lambda)}{E_n-E_{A'}} + \sum_{n}\frac{\Gamma_{An;A'B}W_{nB;AA'}(j\lambda)}{E_n+E_{A'}-E_A-E_B}\Bigg]. \tag{13}$$

Thus the value of $\omega_{\max}$ for the probability distribution in the photon scattering process cannot be compared directly with the energy difference between the two levels. The process-dependent nonresonant correction δ should be taken into account. This result holds also if we include any QED corrections in $E_{A'}, E_B$. The order of magnitude of the correction δ follows from the standard estimates for the allowed transition probabilities (also the mixed ones) $m\alpha(\alpha Z)^4$ and the transition energies $m(\alpha Z)^2$, i.e., $\delta \approx [m\alpha(\alpha Z)^4]^2/[m(\alpha Z)^2] = m\alpha^2(\alpha Z)^6$. These orders of magnitude are the same whether or not the level $E_{A'}$ is removed from E_B by a fine (hyperfine) structure splitting [2].

Consider now the neutral hydrogen atom in the nonrelativistic approximation. We put $B = A = 1s$, $A' = 2p$. Then the line profile will correspond to the Lyman-α transition. In this case $\Gamma_{A'} = \Gamma_{AA'} = W_{BA'}$ and the matrix elements of the electron-photon interaction are $(\boldsymbol{\gamma A}^*_{\omega jm\lambda})_{BA'} = (\boldsymbol{\gamma A}_{\omega jm\lambda})_{A'B} \to (U_{1m})_{1s2p}$, where

$$U_{1m} = \frac{4}{3}\alpha^{3/2}\pi^{1/2}\omega_0^{3/2}rY_{1m} \tag{14}$$

and $\omega_0 = E_{2p} - E_{1s}$. In Eq. (14) and below we use atomic units. Employing a partial-wave expansion for the Coulomb Green function the first term of the correction δ can be written as

$$\delta_1 = \frac{1}{2}\frac{\alpha^6}{3^7}\int_0^\infty\int_0^\infty dr_1\,dr_2\,r_1^3r_2^3\psi_{1s}^*(r_1) \times \tilde{G}^1_{E_{A'}}(r_1;r_2)\psi_{1s}(r_2)\,, \tag{15}$$

where $\tilde{G}^1_{E_{A'}}$ denotes the radial part of the nonrelativistic "modified" Coulomb Green function and ψ_{1s} is the radial Schrödinger wave function.

We evaluate Eq. (15) with the Sturmian expansion for the radial Coulomb Green function $\tilde{G}^1_{E_{A'}}$ that we take from [20]

$$\tilde{G}^l_{E_{A'}}(r_1;r_2) = \frac{1}{2}\sum_{m=l+1,m\neq n}^{\infty}\frac{m^4}{m-n}R_{ml}(r_1)R_{ml}(r_2) + 4R_{nl}(r_2)\left\{5/4R_{nl}(r_1) + r_1\frac{d}{dr_1}R_{nl}(r_1)\right\} + 4R_{nl}(r_1)\left\{5/4R_{nl}(r_2) + r_2\frac{d}{dr_2}R_{nl}(r_2)\right\}, \tag{16}$$

where R_{nl} are the radial Coulomb wave functions. Insertion of Eq. (16) into Eq. (15) and integration over r_1, r_2 for $E_{A'} = 2p$ results in

$$\delta_1 = \frac{\alpha^6}{3}\left(\frac{2}{3}\right)^{16}\left(\sum_{m=3}^{\infty}\frac{(m+1)!}{(m-2)\,(m-2)!}\,{}_2F_1^2(2-m,5;4;2/3) + 7/2\right), \tag{17}$$

where ${}_2F_1$ denotes a hypergeometric function. The expansion in Eq. (17) converges very fast and for $m = 10$ it gives an error less than 10^{-6}. We obtain for the first term $\delta_1 = 2.127\,209 \times 10^{-3}\alpha^6 = 2.116\,899\,8$ Hz.

The second term of the correction δ can be cast into a form similar to Eq. (15) but with the "normal" Coulomb Green function. In this case it is convenient to use for the corresponding radial Green function $G_E^l(r_1;r_2)$ the representation [20]

$$G_E^l(r_1;r_2) = \frac{Z}{\nu} \sum_{m=2}^{\infty} \frac{m^4}{m-\nu} R_{ml}(2r_1/\nu) R_{ml}(2r_2/\nu)\,, \tag{18}$$

where $\nu = Z/\sqrt{-2E} = 2/\sqrt{7}$. Now we obtain

$$\delta_2 = 4\alpha^6 \frac{\nu^7}{(\nu+1)^{10}} \left(\frac{2}{3}\right)^7 \sum_{m=2}^{\infty} \frac{(m+1)m(m-1)}{m-\nu} \times {}_2F_1^2(2-m,5;4;2/(\nu+1))\,. \tag{19}$$

Retaining only six terms of the expansion (18) yields an accuracy of 10^{-6}. For the second term (19) results $\delta_2 = 0.821\,625 \times 10^{-3}\alpha^6 = 0.817\,643\,37$ Hz and finally

$$\delta_{1s,1s}^{(2p)} = \delta_1 + \delta_2 = 2.929\,856 \text{ Hz}. \tag{20}$$

It should be mentioned that the Lyman-α resonance consists of two peaks in the scattering experiment, corresponding to the two fine structure components. In the nonrelativistic approximation the distortion of these two peaks is equal and defined by Eq. (20).

We have also performed an analogous calculation for the transition $2s_{1/2} \to 2p_{3/2} \to 1s_{1/2}$. In this case $B = 2s_{1/2}$, $A = 1s_{1/2}$, and $A' = 2p_{3/2}$. The result is

$$\delta_{2s,1s}^{(2p_{1/2})} = -\left(\frac{2}{3}\right)^{16} \alpha^6 = -1.512\,674 \text{ Hz}. \tag{21}$$

Concluding, we can state that the NR corrections are comparable with some QED corrections to the Lamb shift recently included in the consideration [12]. The level of accuracy of modern experiments with neutral hydrogen for the two-photon transition $2s$-$1s$ is estimated in total to be 46 Hz [19] and is approaching the magnitude of these nonresonant corrections. The derivation of the two-photon NR corrections requires the consideration of the two-photon resonance scattering on a hydrogen atom. The corresponding expression for the amplitude will contain two energy denominators unlike Eq. (2). However, only one of them will become resonant while the other one appears as a nonresonant factor and will not change the order of magnitude of the total amplitude. Accordingly, the interference term (10) defining the resonance shift will lead to values of the same order of magnitude as the corrections (20).

The work of L. L. and D. S. was supported by the RFBR Grant No. 99-02-18526. G. P. and G. S. acknowledge financial support from BMBF and GSI.

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