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Metastability of 2s States of Hydrogenic Atoms*

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It has been found by Breit and Teller that double photon emission is the principal cause of decay of interstellar hydrogen atoms from their metastable 2s state and the mean life corresponding to this decay was bracketed by them between upper and lower limits. In the present note an account is given of a more accurate evaluation of the transition probability $A_\tau=(8.226\pm0.001)Z^6\ \mathrm{sec}^{-1}$, where Z is the atomic number. Relativistic effects on the atomic wave functions have been neglected in the calculations which are therefore accurate only for small Z.

I. INTRODUCTION

IT has been found by Breit and Teller[1] that double photon emission is the most probable mode of radiative decay of the metastable 2s state of hydrogen. They also found that the mean life τ corresponding to this mode of decay can be bracketed by the relation

$$6.5\ \mathrm{sec}^{-1}<1/\tau<8.7\ \mathrm{sec}^{-1}. \tag{1}$$

The hydrogen atom was treated by them as a Dirac electron in the field of a point charge and in the approximation of nonrelativistic radial wave functions. At the time, the mean life of the metastable state was of interest primarily in connection with interstellar hydrogen. Since then, the knowledge of the transition probability has become of additional value, the decay of the 2s state of ionized helium being of interest in atomic beam measurements.[2] It may also be of interest in connection with a possible test of the existence of an electric dipole moment of the electron.[3] In the present note an account is given of calculations of the probability of the double emission process which have been performed with a higher accuracy than those of BT.

The problem has changed aspect since the time of the first estimates through the discovery of the Lamb shift. The $2p_{\frac{1}{2}}$ state is now known to lie between the 2s and the 1s levels. Accordingly it is necessary to consider the way in which cascade emission $2s\rightarrow 2p_{\frac{1}{2}}\rightarrow 1s$ of two photons can affect the probability of double photon emission. It may be said at the outset that no appreciable effect of the cascade process is found. It nevertheless appears desirable to describe the considerations which lead to this conclusion.

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[1] G. Breit and E. Teller, Astrophys. J. **91**, 215 (1940); this paper will be referred to as BT in the text.

[2] R. Novick and E. Commins, Phys. Rev. **103**, 1897 (1956).

[3] The effect of the hypothetical electron dipole moment on the position of energy levels of hydrogen has been considered by G. Feinberg to whom the writers would like to express their thanks for a discussion and a prepublication copy of the manuscript. The possible effect of the admixture of the 2p state on the mean life mentioned by one of us (GB) in the discussion with Dr. Feinberg may constitute perhaps a test of the existence of the moment if accurate measurements of the mean life should be obtained.

II. DOUBLE AND CASCADE EMISSION

Double photon emission takes place through the virtual formation of atomic states n'' together with the formation of one of the final photons $h\nu'$ followed by the formation of the other final photon $h\nu''$ accompanied by the transition of the atom from the state n'' to the final state n'. The amplitude for this process has to be added to the amplitude for the transition from the initial state n to the state n'' together with the formation of the final photon $h\nu''$ followed by the formation of the final photon $h\nu'$ accompanied by the transition from n'' to n'. Amplitudes for different n'' are added and in the nonrelativistic problem are combined linearly with the amplitude arising from the terms in the interaction energy which are quadratic in the vector potential. If the level n'' has an energy intermediate between that of n and n' the usual calculation of double emission does not strictly apply because the probability amplitude for n'' with photon $h\nu'\cong E(nn'')$ grows until a state of equilibrium is reached between arrivals into n' and departures through emission of a second photon with energy $h\nu''\cong E(n''n')$. If the spontaneous emission coefficient $A(nn'')$ is much larger than $A(n''n')$, the atoms pile up rapidly in n'' and leave n'' at their leisure for n'. A typical case of cascade emission is obtained in this case. Similarly if there are no other ways of leaving the state n, cascade emission occurs even if $A(nn'')\ll A(n''n')$ but with a small number of atoms in the state n'' since they are quickly removed from n'' on account of the relatively large $A(n''n')$. In the limit of this very large $A(n''n')/A(nn'')$ there is no appreciable building up of the population in n'' and there is then no distinction between the cascade and double photon emissions.

In the case of the metastable state of hydrogen cascade emission $2s\rightarrow 2p_{\frac{1}{2}}\rightarrow 1s$ has a negligible influence, the probability of the transition to $2p_{\frac{1}{2}}$ being very small on account of the smallness of the transition frequency. The transition probability corresponding to this process is

$$A(2s\rightarrow 2p_{\frac{1}{2}})=\frac{1}{3}\left[\frac{12e^2\omega^3}{hc^3}a^2\right]\cong\frac{1}{5\times10^9\ \mathrm{sec}}. \tag{2}$$

Here the transition frequency of the Lamb shift levels is denoted by $\omega/(2\pi)$, a is the radius of the first Bohr orbit and the other symbols have their usual meaning. The quantity in square brackets is the transition probability in the imaginary case of a $2s \rightarrow 2p$ transition in a nonrelativistic problem with spinless particles and an energy difference equal to that between $2s$ and $2p_{\frac{1}{2}}$. The factor in front allows for the statistical weight of $2p_{\frac{1}{2}}$ being $\frac{1}{3}$ of that of $2p_{\frac{1}{2}}$ and $2p_{\frac{3}{2}}$ together. Comparison of (2) with (1) shows that cascade emission occurs with a negligible probability of the order of 10^{-8}.

The formula for the probability of double emission with one photon in frequency range $d\nu'$ at ν' is[4]

$$A(\nu')d\nu' = \frac{2^{10}\pi^6 e^4 \nu'^3 \nu''^3}{h^2 c^6} \times \left\langle \left| \sum_{n''} \left\{ \frac{\langle n'|(\mathbf{r}\cdot\mathbf{1}')|n''\rangle\langle n''|(\mathbf{r}\cdot\mathbf{1}'')|n\rangle}{\nu(n''n)+\nu''} + \frac{\langle n'|(\mathbf{r}\cdot\mathbf{1}'')|n''\rangle\langle n''|(\mathbf{r}\cdot\mathbf{1}')|n\rangle}{\nu(n''n)+\nu'} \right\} \right|^2 \right\rangle_{\mathrm{Av}} d\nu'. \quad (3)$$

Here ν'' is the frequency of the second photon related to ν' by

$$\nu'+\nu'' = [E(n)-E(n')]/h, \quad (3.1)$$

$\mathbf{r}$ is the displacement vector of the electron with respect to the proton, $\mathbf{1}'$, $\mathbf{1}''$ are respectively unit vectors in the direction of the electric intensities of the photons $h\nu'$, $h\nu''$ and the summation is carried out over all intermediate atomic states n''. For future reference it may be noted that Eq. (3) gives the emission probability into a frequency range of one of the photons for a preassigned photon pair and that if ν' is varied through the whole range available to it energetically the same pair will occur twice.

The quantities in the denominators contain transition frequencies designated in the convention

$$\nu(n''n) = [E(n'')-E(n)]/h. \quad (3.2)$$

The average is taken over directions of polarization vectors $\mathbf{1}'$, $\mathbf{1}''$ and directions of photon emission. If cascade emission is possible, one of the denominators in (3) nearly vanishes when

$$\nu' \cong \nu(nn''). \quad (4)$$

Equation (3) as it stands gives an infinite value of the integral of the transition probability over ν'. This infinity occurs because the radiation damping broadening of the intermediate state n'' is neglected in the derivation of (3). If the broadening is taken into account, then the resonance peak corresponding to (4) contributes to the probability the amount corresponding to cascade emission after equilibrium for the cascade process has been established.

In the general case one would thus have to calculate by means of a modified formula with imaginary parts in the denominators of (3). In the present problem, however, the extreme smallness of the transition probability $n \rightarrow n''$ shown by the comparison of (1) with (2) makes it unnecessary to evaluate the contribution of this region. Since for small values of either ν' or ν'' the factors ν'^3, ν''^3 depress the value of $A(\nu')$, the contributions to the total transition probability through the frequency region of order of magnitude $\nu(nn'')$ is negligible. The change in the value of the transition probability produced by neglecting the Lamb shift is therefore negligible also. The total transition probability may thus be calculated as though the $2p_{\frac{1}{2}}$ and $2s$ levels were exactly coincident. The ratio of the Lamb shift frequency to the $2p \rightarrow 1s$ transition frequency is of the order 10^6 and the weighting factor $\nu'^3\nu''^3$ is of the order 10^{-17} of its maximum value in the frequency region within which this alteration is important. The error committed is therefore of no practical interest.

III. CALCULATIONS FOR THE MODIFIED PROBLEM

According to the parity selection rule the only intermediate states to be considered are p states.[5] Relativistic effects in the positions of the levels are of relative order α^2 and may be neglected. Relativistic effects on the values of dipole matrix elements are of the same relative importance. The mean life τ and the total transition probability A_τ are obtained from (3) by means of

$$\frac{1}{\tau} = A_\tau = \tfrac{1}{2}\int_0^{\nu(nn')} A(\nu')d\nu', \quad (5)$$

which is Eq. (6.1) of BT, the factor $\frac{1}{2}$ arising from the significance of (3) mentioned between Eqs. (3.1) and (3.2). Averaging over directions of polarization vectors and photon directions needed for (3) has been performed by BT and gave their Eq. (6.2). Direct substitution in terms of the quantity C of BT, an explicit expression for which is written out as an unnumbered equation on p. 233 of BT, gives

$$A(\nu')d\nu' = \frac{3^2\alpha^7 c}{2^{12}\pi a} y^3(1-y)^3 \left\{ \sum_{m=2}^{\infty} R_{mp}{}^{1s} R_{mp}{}^{2s} \times \left[\frac{1}{\frac{1}{3}-\frac{4}{3}m^{-2}+y} + \frac{1}{\frac{4}{3}-\frac{4}{3}m^{-2}-y} \right] + \int_0^\infty C_{1s}C_{2s} \left[\frac{1}{\frac{1}{3}+\frac{4}{3}x^2+y} + \frac{1}{\frac{4}{3}+\frac{4}{3}x^2-y} \right] dx \right\}^2 dy. \quad (6)$$

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[4] Maria Göppert, Naturwissenschaften **17**, 932 (1929); Maria Göppert Mayer, Ann. Physik **9**, 401 (1931).

[5] If the electron should have a small electric dipole moment, the above statement will have to be modified and the double-photon emission probability will be slightly affected.

Here

$$y=\nu'/\nu_{nn'}=(8ah/3e^2)\nu', \tag{6.1}$$

$$R_{mp}{}^{is}=\int_0^\infty R_{is}(r)R_{mp}(r)r^3dr, \quad (i=1,2), \tag{6.2}$$

where $R_{is}(r)$, $R_{mp}(r)$ are radial functions for states is and mp, respectively the normalization convention being

$$\int_0^\infty R_{is}{}^2(r)r^2dr=\int_0^\infty R_{mp}{}^2(r)r^2dr, \tag{6.3}$$

and the m standing for the principal quantum number. The quantities C_{1s}, C_{2s} are radial integrals for the continuum and are written out explicitly as Eqs. (6.8), (6.9) of BT where references to the literature of the subject may be found. The quantity i/x is analogous to the principal quantum number m of the virtual state in the discrete part of the spectrum and is related to the energy E of the state by

$$E=x^2(e^2/2a), \tag{6.4}$$

so that $-1/m^2$ corresponds to x^2. In Eqs. (6), (6.2), (6.3) the unit of length for r is the Bohr radius a. The quantity y is the frequency of one of the photons expressed in terms of the maximum value of this frequency as a unit. In the present work the emitted frequencies were expressed in terms of the Rydberg frequency through the introduction of

$$\eta=\nu'(2ah/e^2). \tag{6.5}$$

Substitution in (6), making use of the equations of BT already referred to, gives

$$A(\nu')=(2^{25}/3^3)\alpha^6\eta^3(\tfrac{3}{4}-\eta)^3|M(\eta)+M(\tfrac{3}{4}-\eta)|^2, \tag{7}$$

where

$$M(\eta)=\sum_{m=2}^{\infty}\frac{R(m)}{1-\eta-m^{-2}}+\int_0^\infty\frac{R_c(x)dx}{1-\eta+x^2}, \tag{7.1}$$

and

$$\begin{aligned} R(m)&=-1/(2^5 3^3), && (m=2)\\ &=\frac{m^7(m-1)^{m-2}(m-2)^{m-3}}{(m+1)^{m+2}(m+2)^{m+3}}, && (m>2) \end{aligned} \tag{7.2}$$

while

$$R_c(x)=x(1+x^2)^{-2}(1+4x^2)^{-3}\left[1-\exp\left(-\frac{2\pi}{x}\right)\right]^{-1} \times\exp\left\{-\frac{2}{x}[\tan^{-1}x+\tan^{-1}2x]\right\}. \tag{7.3}$$

The subscript c on $R_c(x)$ stands for "continuum", $R_c(x)$ playing the same role for the continuum as $R(m)$ does for the discrete spectrum. The quantity $A(\nu')$ as defined by (3) is dimensionless. The conversion to atomic units for the radial integrals took place in BT and yielded (6). In going from (6) to (7) dy was expressed in terms of $d\nu'$. Thus (7) gives the dimensionless $A(\nu')$ defined by (3). The transition probability A_τ owes its dimensions to the factor $d\nu'$ in the integral on the right hand side of (5). Numerical quadrature was used to evaluate the transition probability A_τ making use of (5), (7), (7.1), (7.2), and (7.3). The integrand was calculated for values of η at intervals of 0.0375 throughout the range $0\leq\eta\leq 0.75$. The contributions to $M(\eta)$ from $m=2$ through $m=7$ were obtained by direct substitution in (7.2). From $m=8$ to $m=\infty$ the approximation

$$R(m)=e^{-6}\left[\frac{1}{m^3}+\frac{8}{m^5}+O\left(\frac{1}{m^7}\right)\right]\cong e^{-6}\left(\frac{1}{m^3}+\frac{8}{m^5}\right) \tag{7.4}$$

was employed. The expansion used here is readily obtained from (7.2) by taking the natural logarithm of $m^3R(m)$ and expanding in reciprocal powers of m, which yields $-6-8/m^2+O(1/m^4)$ from which (7.4) follows on expanding the exponential of the natural logarithm. From (7.4) one obtains

$$\sum_{n=m}^{\infty}\frac{R(n)}{1-\eta-n^{-2}}\cong\frac{e^{-6}}{1-\eta}\left[\sum_{n=m}^{\infty}n^{-3}+\frac{9-8\eta}{1-\eta}\sum_{n=m}^{\infty}n^{-5}\right], \tag{7.5}$$

which was used in the evaluation of the contribution to $M(\eta)$ in the part of the discrete spectrum beyond $m=7$, use having been made of tables of Riemann's ζ function. Comparing values obtained from (7.5) with values calculated without approximation from (7.2), it has been estimated that the error caused by the approximate character of (7.5) is $\sim$1/23 000 of the leading $m=2$ term.

The contribution of the continuous spectrum to $M(\eta)$ was evaluated by numerical quadrature of the integrand in (7.1) employing (7.3). The integrand was tabulated for this purpose at intervals of 0.05 in the range $0\leq x\leq 1$ and at intervals of 0.10 in $1\leq x\leq 2$. These tabulations were carried out at intervals of 0.0375 in the range $0\leq\eta\leq 0.75$. The integral in Eq. (7.1) was then calculated by Simpson's rule in the limits $x=0$ to $x=2$. The integrand was sufficiently small for $x>2$ to justify the omission of the integral from $x=2$ to $x=\infty$. Finally the quadrature in Eq. (5) was performed numerically with the result (8.226 ± 0.001) sec^{-1}.

Equation (3) contains frequencies ν with total power 5 and lengths with total power 4. Since the ν depend on atomic number Z as Z^2 and lengths as $1/Z$, the factor representing the dependence on Z is $Z^{10-4}=Z^6$ and the transition probability is

$$1/\tau=A_\tau=(8.226\pm 0.001)Z^6\ \text{sec}^{-1}. \tag{8}$$