Optical Quenching of Metastable Hydrogen

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This paper discusses the theory of the quenching of a metastable atomic state by means of a high-frequency electromagnetic wave. The particular problem for which numerical results are presented is that of the quenching of the metastable $2S$ state of atomic hydrogen by means of the light from a ruby laser. The general theory is worked out both by means of the quantum electrodynamical perturbation theory and by means of a strong signal theory. The relation between these two techniques is discussed.

1. INTRODUCTION

THE current status of laser development[1] makes it possible to generate monochromatic, coherent beams of light associated with electric field strengths up to a least 10^8 V/cm. Under these circumstances one may envisage a variety of situations in which the interaction of laser beams with matter is expected to lead to effects not observable at normal intensities.

The theoretical methods required for the understanding of such "high-intensity" effects are generally somewhat more sophisticated than those normally used in calculating optical transitions. Moreover, the reaction rate often varies in a markedly nonlinear way with the intensity of the incident light.[2]

The present investigation is the first part of what, it is hoped, will become an extensive program for the theoretical and experimental investigation of the interaction of high-intensity optical radiation with matter. In view of the many applications of lasers that are forseen, the importance of a better understanding of the processes involved is clear.

The effect discussed in this paper should be experimentally observable, and since the dipole matrix elements in hydrogen are known, an unambiguous comparison of theory and experiment should be possible.

The relevant energy levels in atomic hydrogen are indicated in Fig. 1. An isolated atom in a $2S_{1/2}$ state is metastable (with a mean lifetime of about $\frac{1}{8}$ sec) since it can decay only by 2-photon emission.[3–5] It is well known that a transition to the ground state can be easily induced by a dc electric field.[6]

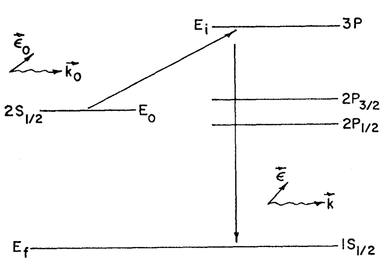

FIG. 1. Energy levels in atomic hydrogen.

The quenching of the $2S$ state by a weak dc field is generally understood in the following way. In the presence of the field there are two stationary states, the wave functions for each being a linear superposition of the wave functions for the $2S$ and $2P_{1/2}$ states. The decay probability essentially comes from the admixture of the $2P_{1/2}$ state. The field strength for which the Stark shift is equal to the Lamb shift is about 475 V/cm. For fields much weaker than this, the two states are almost pure $2S$ and $2P_{1/2}$. As the field strength is increased above 475 V/cm, a saturation condition is approached where the mixing is complete and both states decay at a rate given by the average of the decay rates of the pure states.

It is perhaps not immediately clear how this interpretation of dc quenching is related to that which one would naturally use in calculating the quenching rate in ac fields where one thinks more naturally in terms of transition probabilities rather than mixing of states. It will be shown, however, that the application of the usual techniques of nonrelativistic quantum electrodynamics leads to the correct dc result, provided that one is careful in taking account of all possible processes.

Light from a ruby laser contains photons of energy 0.0657 $(me^4/\hbar^2)$ which is just slightly less than the energy difference between the $3P$ and $2S$ states, 0.0695 $(me^4/\hbar^2)$. Accordingly, the most likely process by which optical quenching of the $2S$ state occurs consists of a virtual transition via the $3P$ state. If elementary perturbation theory is valid, this process is a linear one. The energy of the emitted photon is determined by conservation of energy and corresponds to a wavelength of about 1035 Å.

The occurrence of saturation effects at high intensities may be predicted by the following nonrigorous reasoning. As the intensity of the light is increased, the $2S$ and $3P$ states become more and more strongly coupled. At sufficiently high intensities, therefore, one would expect both states to decay to the ground state at the same rate, and this rate to be given by the average of their spontaneous decay rates. This in turn implies that at

[1] See, for example, The Proceedings of the Symposium on Optical Masers, Polytechnic Institute of Brooklyn, 1963 (to be published by the Polytechnic Press).
[2] P. A. Franken and J. F. Ward, Rev. Mod. Phys. **35**, 23 (1963).
[3] M. Goeppert Mayer, Ann. Physik **9**, 273 (1931).
[4] G. Breit and E. Teller, Astrophys. J. **91**, 215 (1940).
[5] J. Shapiro and G. Breit, Phys. Rev. **113**, 179 (1959).
[6] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic Press, Inc., New York, 1957), Sec. 67.

sufficiently high intensities the cross section will start to decrease and will, in fact, tend to vary inversely with the incident intensity so as to maintain a constant rate. Of course, the saturation discussed here is modified by the fact that quenching via other states (such as $4P$) is also possible.

2. PERTURBATION THEORY

The notation that will be used is that indicated in Fig. 1, $\mathbf{k}$ is the wave-vector in energy units ($|\mathbf{k}|=\hbar\omega$) and $\boldsymbol{\varepsilon}$ is a unit vector in the direction of polarization. Dipole matrix elements between states a, b will be denoted by $\mathbf{r}_{ab}$. The energy of an atomic state i is denoted by E_i^a.

From a formal standpoint, the process under consideration is simply that of the Raman effect, so that the application of perturbation theory to this problem may be found in the standard references.[7]

For a second-order transition from an initial state 0 through an intermediate state i to a final state f, there are two kinds of intermediate states leading to the emission of a photon with energy $k_1=E_0^a-E_f^a+k_0$: (a) $\mathbf{k}_0$ is absorbed first, then $\mathbf{k}_1$ is emitted. (b) $\mathbf{k}_1$ is emitted first, then $\mathbf{k}_0$ is absorbed.

The differential cross section is

$$\frac{d\sigma}{d\Omega}=r_0^2\left(\frac{m}{\hbar^2}\right)^2\frac{k_1}{k_0}\left\{\sum_i (E_i^a-E_0^a)(E_f^a-E_i^a)\times\left|\frac{(\boldsymbol{\varepsilon}_0\cdot\mathbf{r}_{i0})(\boldsymbol{\varepsilon}_1\cdot\mathbf{r}_{fi})}{E_0^a-E_i^a+k_0}+\frac{(\boldsymbol{\varepsilon}_1\cdot\mathbf{r}_{i0})(\boldsymbol{\varepsilon}_0\cdot\mathbf{r}_{fi})}{E_0^a-E_i^a-k_1}\right|\right\}^2, \quad (1)$$

where $r_0=e^2/mc^2$.

In computations, it is generally convenient to use atomic units so that energies are expressed in units of $(me^4/\hbar^2)$ and dipole matrix elements in units of $(\hbar^2/me^2)$. If this is done, Eq. (1) applies *without* the factor $(m/\hbar^2)^2$.

For the particular case of incident radiation from a ruby laser one may consider only the $3P$ intermediate state and the second term in Eq. (1) may be dropped because of the near-resonance condition associated with the first term.

Using $\lambda_0=6934$ Å, one obtains

$$d\sigma/d\Omega\cong 3.53\times10^{-23}|(\boldsymbol{\varepsilon}_0\cdot\mathbf{r}_{i0})(\boldsymbol{\varepsilon}_1\cdot\mathbf{r}_{fi})|^2\ \text{cm}^2/\text{sr}. \quad (2)$$

In Eq. (2), the dipole matrix elements are expressed in units of Bohr radii.

The perturbation theory result given by Eq. (1) apparently diverges as k_0 goes to zero. This is a typical infrared "catastrophe" and may be readily eliminated, as usual, provided that one sums properly over all possible transitions. It is, in fact, elementary[8] to demonstrate that

$$\sum_i (E_i^a-E_0^a)(E_f^a-E_i^a)\times\left\{\frac{(\boldsymbol{\varepsilon}_0\cdot\mathbf{r}_{i0})(\boldsymbol{\varepsilon}_1\cdot\mathbf{r}_{fi})}{E_0^a-E_i^a+k_0}+\frac{(\boldsymbol{\varepsilon}_1\cdot\mathbf{r}_{i0})(\boldsymbol{\varepsilon}_0\cdot\mathbf{r}_{fi})}{E_0^a-E_i^a-k_1}\right\}$$
$$=-k_1k_0\sum_i\left\{\frac{(\boldsymbol{\varepsilon}_0\cdot\mathbf{r}_{i0})(\boldsymbol{\varepsilon}_1\cdot\mathbf{r}_{fi})}{E_0^a-E_i^a+k_0}+\frac{(\boldsymbol{\varepsilon}_1\cdot\mathbf{r}_{i0})(\boldsymbol{\varepsilon}_0\cdot\mathbf{r}_{fi})}{E_0^a-E_i^a-k_1}\right\}. \quad (3)$$

If one uses the right-hand side of Eq. (3), the quenching rate remains finite as $k_0\to 0$. Approximating the result, as before, by taking only the first term and only the $3P$ intermediate state, one obtains

$$d\sigma/d\Omega\cong 3.10\times10^{-23}|(\boldsymbol{\varepsilon}_0\cdot\mathbf{r}_{i0})(\boldsymbol{\varepsilon}_1\cdot\mathbf{r}_{fi})|^2\ \text{cm}^2/\text{sr}. \quad (4)$$

All the results so far have been for the process where the energy of the emitted light is given by $[(E_0^a-E_f^a)+k_0]$. There is, of course, also the possibility of a process, where the energy of the emitted light is given by $[(E_0^a-E_f^a)-k_0]$ and two photons $\mathbf{k}_0$ are present in the final state. For this process, there are again two possible sequences of events: (a) $\mathbf{k}_0$ is emitted first, then $\mathbf{k}_2$ is emitted. (b) $\mathbf{k}_2$ is emitted first, then $\mathbf{k}_0$ is emitted. If the emission of $\mathbf{k}_0$ is *induced* the theory is analogous to that for the previous case, and the cross section becomes

$$\frac{d\sigma}{d\Omega}=r_0^2\left(\frac{m}{\hbar^2}\right)^2k_0k_2^3\left|\sum_i\left\{\frac{(\boldsymbol{\varepsilon}_0\cdot\mathbf{r}_{i0})(\boldsymbol{\varepsilon}_2\cdot\mathbf{r}_{fi})}{E_0^a-E_i^a-k_0}+\frac{(\boldsymbol{\varepsilon}_2\cdot\mathbf{r}_{i0})(\boldsymbol{\varepsilon}_0\cdot\mathbf{r}_{fi})}{E_0^a-E_i^a-k_2}\right\}\right|^2. \quad (5)$$

Since this process and the previous one lead to orthogonal final states, the cross sections are simply additive.

The second process is clearly relatively unimportant for quenching at optical frequencies, at least in the small field case.

For quenching by dc fields the two processes contribute practically equal amounts to the cross section. Moreover, in this case, both processes lead to the same final state so that the amplitudes must be added rather than the cross sections, and the only important matrix element is that between the $2S$ and $2P_{1/2}$ states. One may regard the quenching of a metastable state by a dc electric field as simply a Raman effect induced by photons of zero energy, where all possible processes must be taken into account.

If, in the second process, both photons are emitted *spontaneously*, one of course obtains the natural 2-photon decay rate.[3–5]

The radial matrix elements occurring in Eq. (4) are well known[9]; they are given by

$$|r|^2_{2S\to3P}=9.18,$$
$$|r|^2_{3P\to1S}=0.267.$$

[7] W. Heitler, *The Quantum Theory of Radiation* (Clarendon Press, Oxford, 1954), 3rd ed., Sec. 19.

[8] P. A. M. Dirac, *The Principles of Quantum Mechanics* (Oxford University Press, New York, 1947), 3rd ed., pp. 247 and 248.

[9] See, for example, Ref. 6, Sec. 63.

Using these results, and some standard manipulations, one obtains from Eq. (4)

$$d\sigma/d\Omega = 0.845\times10^{-23}[|a_\perp|^2+|a_{\parallel}|^2]\ \text{cm}^2/\text{sr}, \quad (6)$$

where

$$a_\perp = \epsilon_{0\perp}, \quad (7)$$

$$a_{\parallel} = \epsilon_{0\parallel}\cos\theta. \quad (8)$$

Here $a_\perp$, $a_{\parallel}$ denote reaction amplitudes for the photons k_1 to be polarized perpendicular or parallel to the reaction plane; $\epsilon_{0\perp}$, $\epsilon_{0\parallel}$ denote the component of $\boldsymbol{\varepsilon}_0$, with

$$\epsilon_{0\perp}^2+\epsilon_{0\parallel}^2=1, \quad (9)$$

and θ is the angle between $\mathbf{k}_0$ and $\mathbf{k}_1$.

Certain general predictions regarding the relation between the polarization of the incident and scattered radiation can be made.

(a) If the incident radiation is polarized perpendicular to the scattering plane, the scattered radiation is polarized perpendicular to the scattering plane. (b) If the incident radiation is polarized in the scattering plane, the scattered radiation is polarized in the scattering plane. (c) If the incident radiation is unpolarized and $\theta=90°$, the scattered radiation is polarized perpendicular to the scattering plane. (d) If the incident radiation is unpolarized and $\theta=0$ or $180°$, the scattered radiation is unpolarized.

It should be noted that it is quite possible to obtain linearly polarized light from a solid-state laser by cutting the crystal at a suitable angle to the optic axis.[10]

If the incident light is unpolarized ($\epsilon_{0\perp}^2=\epsilon_{0\parallel}^2=\frac{1}{2}$) and the polarization of the scattered light is not measured, the differential cross section is given by

$$d\sigma/d\Omega \cong 4.2\times10^{-24}[1+\cos^2\theta]\ \text{cm}^2/\text{sr}, \quad (10)$$

and the total cross section is

$$\sigma\cong 7.1\times10^{-23}\ \text{cm}^2. \quad (11)$$

3. STRONG SIGNAL THEORY

The previous analysis may be interpreted by saying that the process of interest consists predominantly of photoexcitation from the $2S$ state to the $3P$ state and decay of the $3P$ state to the $1S$ ground state. From the fact that the laser beams to be used in the experiment are very intense it follows that the $2S$-$3P$ transitions may be treated by semiclassical radiation theory and the spontaneous decay from $3P$ to $2S$ may be neglected. Furthermore, in the time dependence of the applied field, $\cos\omega_0 t\sim\frac{1}{2}(e^{i\omega_0 t}+e^{-i\omega_0 t})$, that exponential term may be neglected[11] which corresponds to the unlikely process in which transitions from $2S$ to $3P$ are accompanied by emission of a photon or transition from $3P$ to $2S$ by the absorption of a photon. Bloch and Siegert[12] have analyzed the effect of including such antiresonant terms in the theory of magnetic resonance experiments.

Denoting the amplitudes of the $2S$ and $3P$ states by a and b, respectively, one may write[13]

$$i\hbar\dot{a}=\tfrac{1}{2}V^*e^{i(\omega_0-\omega_{ba})t}b-\tfrac{1}{2}i\hbar\gamma_a a, \quad (12)$$

$$i\hbar\dot{b}=\tfrac{1}{2}Ve^{-i(\omega_0-\omega_{ba})t}a-\tfrac{1}{2}i\hbar\gamma_b b. \quad (13)$$

In these equations the γ's are spontaneous-decay constants, defined so that the amplitudes of a state subject only to spontaneous decay to the ground state would be

$$a(t)=e^{-\frac{1}{2}\gamma_a t}. \quad (14)$$

It is well known that γ is just the width of the Lorentzian level profile. The quantity V is defined by

$$V=\langle b|e\mathbf{E}\cdot\mathbf{r}|a\rangle, \quad (15)$$

where $\mathbf{E}$ is the peak field strength.

Eliminating b from Eqs. (12) and (13), one obtains

$$\ddot{a}+\tfrac{1}{2}(\gamma_a+\gamma_b)\dot{a}+\tfrac{1}{4}\gamma_a\gamma_b a-i(\omega_0-\omega_{ba})(\dot{a}+\tfrac{1}{2}\gamma_a a)+(|V|^2/4\hbar^2)a=0. \quad (16)$$

Assuming a solution of the form

$$a(t)=A_1e^{\mu_1 t}+A_2e^{\mu_2 t}, \quad (17)$$

the boundary conditions

$$a(0)=1,\quad \dot{a}(0)=-\tfrac{1}{2}\gamma_a, \quad (18)$$

lead to

$$A_1=(\mu_2+\tfrac{1}{2}\gamma_a)/(\mu_2-\mu_1), \quad (19)$$

$$A_2=(-\mu_1-\tfrac{1}{2}\gamma_a)/(\mu_2-\mu_1). \quad (20)$$

Putting $\Omega=\omega_{ba}-\omega_0$ in Eq. (16) gives

$$\mu=-\tfrac{1}{2}[\tfrac{1}{2}(\gamma_b+\gamma_a)+i\Omega]\pm\tfrac{1}{2}\{[\tfrac{1}{2}(\gamma_b-\gamma_a)+i\Omega]^2-|V|^2/\hbar^2\}^{1/2}. \quad (21)$$

Case 1. $|V|^2\ll\hbar^2|\frac{1}{2}(\gamma_b-\gamma_a)+i\Omega|^2$

This is the small-perturbation limit. Expanding the square root in Eq. (21) gives

$$\mu_1\cong\frac{-\frac{1}{4}|V|^2/\hbar^2}{\frac{1}{2}(\gamma_b-\gamma_a)+i\Omega}-\tfrac{1}{2}\gamma_a, \quad (22)$$

$$\mu_2\cong-\tfrac{1}{2}\gamma_b+i\Omega. \quad (23)$$

Hence, one finds

$$|a(t)|^2=e^{-\Gamma t}, \quad (24)$$

where the decay rate Γ is given by

$$\Gamma=-(\mu_1+\mu_1^*)=(\gamma_b-\gamma_a)\frac{\frac{1}{4}V^2/\hbar^2}{\Omega^2+\frac{1}{4}(\gamma_b-\gamma_a)^2}+\gamma_a. \quad (25)$$

[10] D. F. Nelson and R. J. Collins, in *Advances in Quantum Electronics*, edited by J. R. Singer (Columbia University Press, New York, 1961).

[11] I. I. Rabi, Phys. Rev. **51**, 652 (1937).

[12] F. Bloch and A. Siegert, Phys. Rev. **57**, 522 (1940).

[13] Equations of the form (12) and (13) have been very widely used, particularly in radio-frequency resonance work. However, a rigorous deduction from quantum electrodynamics does not appear to have been published and the nature of the approximations involved is therefore not clear. One might expect that in very high fields the energies and radiative lifetimes of the atomic states should differ from their field-free values.

This result may be interpreted as the sum of an induced and a spontaneous decay rate.

The results obtained by Lamb and Retherford[14,15] are given by (25), with $\gamma_a=0$.

Case 2. $|V|^2 \gg \hbar^2|\frac{1}{2}(\gamma_b-\gamma_a)+i\Omega|^2$

This is the strong-field limit. Expanding the square root in Eq. (21) gives

$$\mu_1 \cong +\tfrac{1}{2}\frac{i|V|}{\hbar}-\tfrac{1}{4}(\gamma_b+\gamma_a)-\tfrac{1}{2}i\Omega, \qquad (26)$$

$$\mu_2 \cong -\tfrac{1}{2}\frac{i|V|}{\hbar}-\tfrac{1}{4}(\gamma_b+\gamma_a)-\tfrac{1}{2}i\Omega. \qquad (27)$$

Hence,

$$|a(t)|^2=\tfrac{1}{2}e^{-\frac{1}{2}(\gamma_b+\gamma_a)t}+\tfrac{1}{2}e^{-(\gamma_b+\gamma_a)t}\cos[|V|t/\hbar]. \qquad (28)$$

This solution gives $a(0)=1$ as it should. For $t>0$ the second term which is rapidly varying may be neglected so that one obtains

$$|a(t)|^2=\tfrac{1}{2}e^{-\frac{1}{2}(\gamma_b+\gamma_a)t}, \quad t>0. \qquad (29)$$

This result indicates saturation, i.e., the maximum quenching rate can never exceed $\frac{1}{2}(\gamma_b+\gamma_a)$.

The time dependence of the state b is found to be

$$b=\frac{2i\hbar}{V^*}e^{i\Omega t}\left[\frac{(\mu_1+\frac{1}{2}\gamma_a)(\mu_2+\frac{1}{2}\gamma_a)}{\mu_2-\mu_1}\right](e^{\mu_1 t}-e^{\mu_2 t}). \qquad (30)$$

In the large-field limit, after initial transients have died out, this gives

$$|b(t)|^2=\tfrac{1}{2}e^{-\frac{1}{2}(\gamma_b+\gamma_a)t}, \quad t>0. \qquad (31)$$

In a very strong field, $|a(t)|^2$ and $|b(t)|^2$ are equal.

4. DISCUSSION OF STRONG-SIGNAL AND PERTURBATION THEORY

The small perturbation limit of the strong-signal theory should give a result consistent with that of perturbation theory. In order to verify this, one may take Eq. (25), set $\gamma_a=0$ and neglect the damping term in the denominator:

$$\Gamma=\gamma_b\frac{\frac{1}{4}|V|^2}{(E_0{}^a-E_i{}^a+k_0)^2}. \qquad (32)$$

This exponential decay rate may be identified with the transition probability per unit time, $w_{f|i}$, calculated by perturbation theory, since the latter quantity is derived for times short compared to the decay time of the initial state.

In Eq. (32) Γ is the total induced decay rate of the $2S$ state. It is clear from the physical interpretation of the process however, that one may interpret Γ as the induced decay rate into unit solid angle provided that γ_b is interpreted as the spontaneous decay rate into unit solid angle of the intermediate $3P$ state. In this way one can make the connection with the differential cross section calculated by perturbation theory. If one now substitutes the well-known expression for the spontaneous decay rate into unit solid angle

$$\gamma_b=\frac{e^2}{2\pi\hbar^4c^3}k_1{}^3|\boldsymbol{\varepsilon}_1\cdot\mathbf{r}_{fi}|^2, \qquad (33)$$

and uses (15) and the relation $E^2/8\pi=nk_0$, where n is the number of photons per unit volume, one obtains the dominant term of the perturbation theory result.

The strong-signal theory provides the damping corrections to perturbation theory. It is also clear from the correspondence between perturbation theory and the small perturbation limit of strong-signal theory that the criterion for the validity of perturbation theory is[16]

$$|V|^2 \ll \hbar^2|\tfrac{1}{2}(\gamma_b-\gamma_a)+i\Omega|^2. \qquad (34)$$

One should note that, in this experiment, $\hbar(\omega_{ba}-\omega_0)=0.0038(me^4/\hbar^2)\cong 0.1$ eV. Thus, the saturation effect will be observable when $|V|\gtrsim 0.1$ eV or when $E\cong 10^7$ V/cm. For field strengths smaller than this, perturbation theory is valid.

It is clear from Eqs. (32) and (33), that the angular distribution predicted by the strong signal theory is, in the small perturbation limit, precisely the same as that predicted by perturbation theory. However, in the strong-field limit, Eqs. (29) and (31) indicate an isotropic angular distribution.

Comparison with theory would probably be simplest for a comparatively low-power unfocused laser. Consider for instance a ruby laser emitting a 100-J pulse in 200 μsec. Assuming a laser-beam cross section of about 0.25 cm^2, the field strength would be about 5×10^4 V/cm. Considering the presence of spikes in the output power, one might expect field strengths in the range 10^4–10^6 V/cm. In this region, the quenching rate Γ, Eq. (25), is simply proportional to the mean-square field strength, and works out to be about 10^3 sec^{-1}, which seems high enough to be observable.

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[14] W. E. Lamb, Jr., and R. C. Retherford, Phys. Rev. **79**, 549 (1950).

[15] W. E. Lamb, Jr., Phys. Rev. **85**, 259 (1952).

[16] Equation (34) merely expresses the condition for higher order terms in the perturbation theory treatment of the $2S$ to $3P$ transition to be small.