Two-Photon Ionization of Atomic Hydrogen*

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This paper discusses the general theory of two-photon ionization of a hydrogenic state in the nonrelativistic dipole approximation. An application is made to the photoionization of the metastable $2S$ state of atomic hydrogen by optical radiation, for example, by the light from a ruby laser. The sum over intermediate states is carried out exactly by means of an implicit technique. The results are given for a range of wavelengths from the threshold at 7290 down to 4556 Å. At 6943 Å, the total cross section per unit intensity is found to be 5.35×10^{-29} cm^4 W^{-1}. The lowest order damping corrections to the perturbation-theory results are worked out.

1. INTRODUCTION

THE theory of the photoeffect in hydrogen is an old problem in physics, which was successfully treated in the early days of quantum mechanics.[1–4] Those calculations were based on first-order perturbation theory and therefore described the process of a bound electron absorbing one photon and thereby being emitted from the atom. The possibility of a two-photon process, which proceeds via intermediate states has also been recognized for a long time,[5] but such a process did not appear to be of practical importance until the advent of lasers.

A straightforward application of quantum electrodynamics (see Sec. 2) shows that the cross section for a two-photon process contains the factor I/I_0 where I is the intensity of the radiation in W/cm^2 and I_0 is 7.019×10^{16} W/cm^2, which is the intensity corresponding to a root-mean-square field strength of 1 atomic unit or 5.142×10^9 V/cm. Because the matrix elements which enter for a second-order process contain energy denominators which may be small, two-photon effects may become significant for intensities considerably less than I_0, but in any case one may reasonably anticipate appreciable effects at practically attainable laser intensities.

Such considerations have led in recent years to a great upsurge of interest in multiphoton processes in general. Estimates for some of the nonlinear effects to be expected, particularly in solids, have been given by Kleinman[6] and Braunstein[7]; more detailed calculations have been carried out by Franken and Ward,[8] Armstrong, Bloembergen, Ducuing, and Pershan,[9] and by Bloembergen and Pershan.[10] The theory of the two-photon photoelectric effect in metals has been discussed by Smith.[11] Hammerling[12] has made approximate calculations of two-photon ionization rates for some negative ions, and Stabler[13] has made an estimate of the cross section to be expected for two-photon ionization of metastable hydrogen atoms by ruby laser light. It is clear that the theory of two-photon processes presents no difficulty in principle; however, detailed and exact calculations of the type reported in this paper do not appear to have been published previously.

Several observations of two-photon absorption have been reported. The effect has been observed in inorganic crystals[14] (CaF_2; Eu^{2+} and CdS), in cesium vapor,[15] in organic crystals,[16] and in several organic liquids.[17] In all these cases only a semiquantitative comparison with theory was possible.

There are basically two reasons why the calculations reported in the present paper are thought to be of interest.

Firstly, it seems reasonable to believe that a clean experimental observation of the effect, using a ruby laser and a beam of metastables, is feasible and could make possible a really quantitative comparison of theory and experiment for two-photon absorption in the optical range. The competing processes which would be present in such an experiment are (in order of importance), quenching accompanied by emission of an ultraviolet photon, coherent scattering, and quenching accompanied by the induced emission of a red photon as well as an ultraviolet photon. These processes have been analyzed in some detail by the

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[17] J. A. Giordmaine and J. H. Howe, Phys. Rev. Letters **11**, 207 (1963).

present author[18,19]; their rates are linear in the intensity (at least up to intensities of about 10^{11} W/cm^2). For intensities above about 10^6 W/cm^2 two-photon ionization is the dominant process.

Secondly, it is thought to be of interest to exhibit how the technique introduced by Schwartz and Tieman[20,21] for implicitly evaluating the sum over intermediate states for a hydrogenic atom can be applied to a two-photon absorption process. This technique has been applied also to the calculation of the quenching and scattering process mentioned in the last paragraph.[19]

The present calculations indicate that for light intensities of 6×10^{11} W/cm^2 at 6943 Å, the two-photon absorption rate due to a hydrogen atom in the $2S$ state is roughly equal to the one-photon absorption rate due to a hydrogen atom in the $3P$ state.[22] It should be noted, however, that the method used in this paper is no longer strictly valid at intensities of this order (see Sec. 4).

In Sec. 2, some general results applicable to the two-photon ionization of any hydrogenic state are presented. The special case of the $2S$ state is dealt with in Sec. 3. In Sec. 4 the lowest order damping corrections to the theory are worked out.

2. SOME GENERAL RESULTS

The differential cross section per unit intensity may be derived by a straightforward application of second-order perturbation theory. The result is

$$\frac{1}{I}\frac{d\sigma}{d\Omega}=\frac{\alpha}{4\pi I_0}\left|\sum_i\frac{(\boldsymbol{\varepsilon}\cdot\mathbf{r})_{fi}(\boldsymbol{\varepsilon}\cdot\mathbf{r})_{i0}}{E_0-E_i+E_p}\right|^2 E_p k_e a^2. \tag{1}$$

In this equation, I is the light intensity in W/cm^2, $d\sigma/d\Omega$ is the differential cross section in cm^2/sr, I_0 is 7.019×10^{16} W/cm^2, α is the fine-structure constant and a is the Bohr radius. The remaining terms on the right-hand side of (1) are all dimensionless multiples of the atomic units defined on p. 3 of Ref. 4. E_0 and E_i are the energies of the initial and intermediate atomic states, respectively, in units of $(me^4/\hbar^2)$, E_p is the photon energy, k_e is the wave number of the emitted electron in units of $(me^2/\hbar^2)$, $\boldsymbol{\varepsilon}$ is the unit polarization vector of the incident radiation, and the $\mathbf{r}_{fi}$, $\mathbf{r}_{i0}$ represent dipole matrix elements in units of $(\hbar^2/me^2)^{5/2}$ and $(\hbar^2/me^2)$, respectively. The summation over intermediate states includes an integration over the positive energy states. The initial and intermediate states are normalized so that the probability of finding the electron within a large quantizing volume is unity. The final state is normalized so that at large distances from the atom it represents a Coulomb-modified plane wave of unit amplitude plus an *ingoing* Coulomb-modified spherical wave.[23] Equation (1) may be obtained either from semiclassical radiation theory or by using the quantized electromagnetic field. Also, one may use as a perturbation either the form containing the electric field or the form containing the vector potential.[24]

The energy of the emitted electron is determined by

$$\tfrac{1}{2}k_e^2=2E_p+E_0. \tag{2}$$

The above formulas are sufficient to determine how the cross section for two-photon ionization of a hydrogenic atom depends on the charge Z of the nucleus. The atomic energies are proportional to Z^2, the $\mathbf{r}_{i0}$ are proportional to Z^{-1} and the $\mathbf{r}_{fi}$ are proportional to $Z^{-5/2}$. Accordingly, one finds

$$\sigma(E_p,Z)=Z^{-8}\sigma(E_p/Z^2,1). \tag{3}$$

The angular distribution of the electrons may be determined with the help of the coordinate system shown in Fig. 1. The light travels along the positive z axis and the unit polarization vector $\boldsymbol{\varepsilon}$ defines the x axis. A primed coordinate system is defined with respect to the unprimed system by means of the Euler angles[25] $(\alpha,\beta,0)$. The outgoing electron travels along the *negative* z' axis.

In the notation of Ref. 4, one may write the initial-state wave function as

$$\varphi_0=R_{nl}(r)Y_{lm}(\theta,\varphi), \tag{4}$$

where (θ,φ) represent colatitude and azimuth coordinates, respectively, in the unprimed system. Similarly, if the intermediate state is one of the bound states, its wave function may be written as

$$\varphi_i=R_{\nu\lambda}(r)Y_{\lambda\mu}(\theta,\varphi). \tag{5}$$

If the intermediate state belongs to the continuum, the square of its wave function must contain a factor V^{-1}, where V is the quantizing volume, which is cancelled by a factor V appearing in the density of continuum states. However, it is not necessary to be concerned with the actual expression for the radial functions in this case since the sum over intermediate states is carried out implicitly as explained in the next section. The complex conjugate of the final-state wave

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[21] C. Schwartz, and T. J. Tieman, Ann. Phys. (N. Y.) **6**, 178 (1959).
[22] See, for example, Ref. 28.
[23] G. Breit and H. A. Bethe, Phys. Rev. **93**, 888 (1954). See also footnote 3 on p. 296 of Ref. 4.
[24] The identity of the results obtained using either of the last alternatives can be verified by means of Eq. (3) of Ref. 18. It follows also from the fact that these forms of the dipole perturbation arise from Hamiltonians that are equivalent to within a canonical transformation, see Ref. 5, for example. For a very complete treatment of the relation between the two forms of the electromagnetic perturbation see E. A. Power and S. Zienau, Phil. Trans. Roy. Soc. (London) **A251**, 427 (1959).
[25] See, for example, M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, New York, 1957), Chap. 4.

function may be written as

$$\varphi_f^*=\sum_L (i)^L\pi[2(2L+1)]^{1/2} \times k_e^{-1/2}e^{i\eta_L}R_L^c(k_e,r)Y_{L0}(\theta'), \quad (6)$$

where θ' represents the colatitude referred to the primed coordinate system,

$$\eta_L=\arg\Gamma(L+1-i/k_e), \quad (7)$$

and $R_L^c(k_e,r)$ is the regular solution of the differential equation for the radial function for a positive-energy electron in the field of a proton, normalized on the energy scale[4]; its asymptotic value is given by

$$R_L^c(k_e,r)\sim(1/r)(2/\pi k_e)^{1/2} \times\sin(k_e r-\tfrac{1}{2}L\pi+\eta_L+k_e^{-1}\ln 2k_e r). \quad (8)$$

According to the well-known theorem of Gordon,[26] the asymptotic form of φ_f represents a Coulomb-modified plane wave traveling along the negative z' axis together with an incoming Coulomb-modified spherical wave.

In order to calculate the matrix elements, one may[27] express $Y_{L0}(\theta')$ in terms of the angles (θ,φ). It is in fact easily shown[25] that

$$Y_{LO}(\theta')=\sum_M\left(\frac{4\pi}{2L+1}\right)^{1/2}Y_{LM}(\theta,\varphi)Y_{LM}^*(\beta,\alpha). \quad (9)$$

The selection rules require that for the intermediate states,

$$\lambda=l+1 \quad \text{or} \quad l-1,$$

and for the final states,

$$L=l+2,\ l, \quad \text{or} \quad l-2.$$

If one uses Eqs. (4)–(9) and performs some standard manipulations[25] involving Clebsch-Gordan coefficients one finds finally

$$(1/I)(d\sigma/d\Omega) = (\pi^2\alpha/8I_0)|M_{l+2}+M_l+M_{l-2}|^2E_p a^2, \quad (10)$$

where

$$M_{l+2}=P_{l+1,l+2}(E_p)e^{i\eta_{l+2}}\left[\frac{1}{(2l+3)(2l+5)^{1/2}(2l+1)^{1/2}}\right] \times\{[(l-m+1)(l-m+2)(l-m+3)(l-m+4)]^{1/2}Y_{l+2,m-2}(\beta,\alpha) +[(l+m+1)(l+m+2)(l+m+3)(l+m+4)]^{1/2}Y_{l+2,m+2}(\beta,\alpha) -2[(l+1-m)(l+1+m)(l+2-m)(l+2+m)]^{1/2}Y_{l+2,m}(\beta,\alpha)\}, \quad (11)$$

$$M_{l-2}=P_{l-1,l-2}(E_p)e^{i\eta_{l-2}}\left[\frac{1}{(2l-1)(2l+1)^{1/2}(2l-3)^{1/2}}\right] \times\{[(l+m)(l+m-1)(l+m-2)(l+m-3)]^{1/2}Y_{l-2,m-2}(\beta,\alpha) +[(l-m)(l-m-1)(l-m-2)(l-m-3)]^{1/2}Y_{l-2,m+2}(\beta,\alpha) -2[(l+m)(l-m)(l+m-1)(l-m-1)]^{1/2}Y_{l-2,m}(\beta,\alpha)\}, \quad (12)$$

$$M_l=-P_{l+1,l}(E_p)e^{i\eta_l}\left[\frac{1}{(2l+1)(2l+3)}\right] \times\{[(l+m)(l+m-1)(l-m+1)(l-m+2)]^{1/2}Y_{l,m-2}(\beta,\alpha) +[(l-m)(l-m-1)(l+m+1)(l+m+2)]^{1/2}Y_{l,m+2}(\beta,\alpha) -[(l-m+1)(l-m+2)+(l+m+1)(l+m+2)]Y_{l,m}(\beta,\alpha)\} -P_{l-1,l}(E_p)e^{i\eta_l}\left[\frac{1}{(2l-1)(2l+1)}\right] \times\{[(l+m)(l+m-1)(l-m+1)(l-m+2)]^{1/2}Y_{l,m-2}(\beta,\alpha) +[(l-m)(l-m-1)(l+m+1)(l+m+2)]^{1/2}Y_{l,m+2}(\beta,\alpha) -[(l+m)(l+m-1)+(l-m)(l-m-1)]Y_{l,m}(\beta,\alpha)\}. \quad (13)$$

[26] W. Gordon, Z. Physik **48**, 180 (1928). See also N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford University Press, New York, 1952), Chap. 3.

[27] For an alternative procedure, see M. L. Rustgi, W. Zernik, G. Breit, and D. J. Andrews, Phys. Rev. **120**, 1881 (1960).

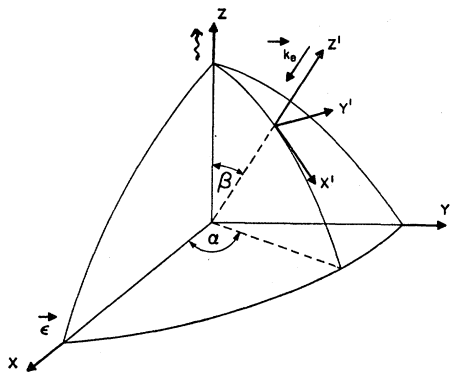

FIG. 1. Coordinate system used. The plane polarized light is incident along the positive z axis. The photoelectron travels along the negative z' axis.

In Eqs. (11)–(13), the quantities $P_{\lambda L}(E_p)$ are defined by

$$P_{\lambda L}(E_p) = \sum_\nu \frac{\langle R_L{}^c(k_e,r)\,|\,r\,|\,R_{\nu\lambda}(r)\rangle\langle R_{\nu\lambda}(r)\,|\,r\,|\,R_{nl}(r)\rangle}{E_n - E_\nu + E_p}. \quad (14)$$

The bound-bound and bound-free radial matrix elements occurring in (14) have, of course, been widely discussed in the literature.[28]

In connection with the evaluation of bound-free radial matrix elements, the following very useful relation which does not appear to have been previously published may be derived:

$$\int_0^\infty r^{L+1} R_L{}^c(k,r) e^{-pr} dr = \frac{2^{L+1}}{(1-e^{-2\pi/k})^{1/2}} [(1+k^2)(1+4k^2)\cdots(1+L^2k^2)]^{1/2} \times \frac{\exp[-2k^{-1}\,\mathrm{arc\,cot}(p/k)]}{(p^2+k^2)^{L+1}}, \quad (15)$$

where $p>0$ and $0 \leqslant \mathrm{arc\,cot}(p/k) \leqslant \pi/2$. This result may be obtained by noting that the quantity $r^{L+1}R_L{}^c(k, r)$ may be expressed in terms of a confluent hypergeometric function which has a well-known contour integral representation[29]; after some simple changes of variable this quantity may be transformed into the standard form for an inverse Laplace transform, from which (15) follows immediately. Any desired bound-free matrix element may be obtained from (15) by differentiating the required number of times with respect to p. The relation (15) is also required in the implicit summation over intermediate states described in the next section.

3. CALCULATIONS FOR THE H 2S STATE

If one simply substitutes $l=0$, $m=0$ in Eqs. (13) and (11), one obtains

$$M_0 = (\tfrac{2}{3})\pi^{-1/2} e^{i\eta_0} P_0(E_p), \quad (16)$$

$$M_2 = (\tfrac{2}{3})\pi^{-1/2}[1 - 3\sin^2\beta\cos^2\alpha] e^{i\eta_2} P_2(E_p), \quad (17)$$

where the subscript λ on $P_{\lambda L}$, Eq. (14), has been dropped. One notes that the angular distribution arises from an s wave, a d wave, and an interference term. The interference term does not, of course, contribute to the total cross section. The exponential terms in (16) and (17) may be simplified by using the cosine rule applied to the vectors $\Gamma(1-i/k_e)$, $\Gamma(3-i/k_e)$ in the complex plane, and the factorial property of the gamma function. One finds that

$$e^{i(\eta_2-\eta_0)} = \frac{2k_e{}^2-1}{(4k_e{}^4+5k_e{}^2+1)^{1/2}} + i\frac{3k_e}{(4k_e{}^4+5k_e{}^2+1)^{1/2}}. \quad (18)$$

Energy conservation for this case requires that

$$\tfrac{1}{2}k_e{}^2 = 2E_p - \tfrac{1}{8}. \quad (19)$$

If one now substitutes the results (16)–(18) in Eq. (10), one obtains

$$(1/I)(d\sigma/d\Omega) = (\alpha/18I_0)(\pi a^2)E_p\,|\,M\,|^2, \quad (20)$$

where

$$|\,M\,|^2 = a + b\sin^2\beta\cos^2\alpha + c\sin^4\beta\cos^4\alpha. \quad (21)$$

The coefficients a, b, and c are given by

$$a = P_0{}^2 + P_2{}^2 - \frac{(2-4k_e{}^2)}{(4k_e{}^4+5k_e{}^2+1)^{1/2}} P_0P_2, \quad (22)$$

$$b = 3\frac{(2-4k_e{}^2)}{(4k_e{}^4+5k_e{}^2+1)^{1/2}} P_0P_2 - 6P_2{}^2, \quad (23)$$

$$c = 9P_2{}^2. \quad (24)$$

For ruby laser light, the energy denominator in Eq. (14) becomes quite small for the $3P$ intermediate state, so this state is clearly the most important. One might also expect the $2P$ intermediate state to have some effect as the $2S$ to $2P$ radial matrix elements are relatively large.[28] By explicit calculation, including only those two intermediate states, one finds the following approximate values of $P_0(E_p)$ and $P_2(E_p)$ at $\lambda = 6943$ Å:

$$P_0 \cong 155 - 4350 \cong -4200, \quad (25)$$

$$P_2 \cong -610 - 12\,800 \cong -13\,400. \quad (26)$$

In (25) and (26), the first numbers on the left come from the $2P$ intermediate state and the second (much

[28] See for instance Ref. 4, especially Secs. 61–63. For additional values of bound-bound radial matrix elements, see R. Herdan and T. P. Hughes, Astrophys. J. **133**, 294 (1961). For additional results for bound-free transitions see J. Harriman, Phys. Rev. **101**, 594 (1956); A. Burgess, Monthly Notices of the Roy. Astron. Soc. **118**, 477 (1958); B. H. Armstrong and H. P. Kelly, J. Opt. Soc. Am. **49**, 949 (1959).

[29] See, for example, N. F. Mott and H. S. W. Massey, Ref. 26.

larger) numbers from the $3P$ state. The most important final state is the d state.

An exact implicit evaluation of $P_0(E_p)$ and $P_2(E_p)$, which takes into account all possible intermediate states including those in the continuum, may be carried out by means of the method of Schwartz and Tieman.[30]

One defines a quantity $U_L(r,E_p)$ by

$$U_L(r,E_p)=\sum_{n=2}^{\infty}\frac{rR_{n1}(r)\int_0^{\infty}R_{n1}(r')R_L^c(k_e,r')r'^3dr'}{E_2-E_n+E_p}, \quad (27)$$

where the summation includes both the negative and the positive energy states. Hence, one has

$$P_L(E_p)=\int_0^{\infty}R_{20}(r)U_L(r,E_p)r^2dr. \quad (28)$$

The Laplace transform of $U_L(r,E_p)$,

$$S_L(p,E_p)=\int_0^{\infty}U_L(r,E_p)e^{-pr}dr, \quad (29)$$

may be shown[19] by means of the Schrödinger equation and the closure condition to obey the first-order differential equation

$$(-\tfrac{1}{8}+E_p+p^2/2)(d^2S_L/dp^2)+(2p-1)(dS_L/dp)=\int_0^{\infty}R_L^c(k_e,r)r^4e^{-pr}dr. \quad (30)$$

By means of Eq. (15) one may now derive the differential equations satisfied by S_0 and S_2.

$$(-\tfrac{1}{8}+E_p+p^2/2)(d^2S_0/dp^2)+(2p-1)(dS_0/dp)=\frac{16}{(1-e^{-2\pi/k_e})^{1/2}}\left[\frac{(2-3_p)(p^2+k_e^2)+6p^3-11p^2+6p-1}{(p^2+k_e^2)^4}\right]\times\exp[-2k_e^{-1}\operatorname{arc\,cot}(p/k_e)], \quad (31)$$

and

$$(-\tfrac{1}{8}+E_p+p^2/2)(d^2S_2/dp^2)+(2p-1)(dS_2/dp)=\frac{16[(1+k^2)(1+4k^2)]^{1/2}}{(1-e^{-2\pi/k_e})^{1/2}}\left[\frac{3p-1}{(p^2+k_e^2)^4}\right]\times\exp[-2k_e^{-1}\operatorname{arc\,cot}(p/k_e)]. \quad (32)$$

From Eqs. (28) and (29) one sees that

$$P_L(E_p)=\frac{1}{\sqrt{2}}\left(\frac{d^2S_L}{dp^2}\right)_{p=1/2}+\frac{1}{2\sqrt{2}}\left(\frac{d^3S_L}{dp^3}\right)_{p=1/2}. \quad (33)$$

The boundary condition for Eqs. (31) and (32) follows from the definitions (27) and (29) and is that S_L and all its derivatives are finite for all positive values of p. Thus, provided that E_p is less than the *one-photon* ionization energy one can determine a boundary value of dS_L/dp at the value of p for which the coefficient of d^2S_L/dp^2 vanishes. Then Eqs. (31) and (32) may be solved numerically and the $P_L(E_p)$ determined from Eq. (33).[31]

The method breaks down for photon energies greater than the one-photon ionization threshold; this simply corresponds to the fact that the energy denominator in Eq. (14) can become zero in this case. Also, one can show that the solutions of Eqs. (31) and (32) are singular at values of E_p corresponding to the Balmer lines, as one would expect. This last problem should, however, be dealt with by means of the "strong signal" approach[32] described in Sec. 4.

Finally, the differential cross section per unit intensity is expressed in the form

$$(1/I)(d\sigma/d\Omega)=A+B\sin^2\beta\cos^2\alpha+C\sin^4\beta\cos^4\alpha, \quad (34)$$

and the total cross section per unit intensity is

$$\sigma/I=4\pi A+\tfrac{4}{3}\pi B+\tfrac{4}{5}\pi C. \quad (35)$$

The results of the numerical calculations are presented in Table I. A graph of the total cross section per unit intensity versus wavelength is given in Fig. 2.

One notes that the cross section is finite at threshold just as in the one-photon case. This is, of course, just a consequence of the fact that the particles that con-

[30] See Refs. 19–21. A similar application has been made by M. H. Mittleman and F. A. Wolfe, Phys. Rev. **128**, 2686 (1962), to the coherent scattering of light by hydrogen atoms in the ground state. Similar calculations have been carried out for the ground state by M. N. Adamov, Dokl. Akad. Nauk SSSR 133, 315 (1961) [English transl.: Soviet Phys.—Doklady **5**, 768 (1961)] and for the $n=2$ states by M. N. Adamov, V. K. Kogan, and B. I. Orlov, Opt. i Spektroskopiya **14**, 737 (1963) [English transl.: Opt. Spectry. (USSR) **14**, 391 (1963)]. Adamov *et al.* define the polarizability as being one-half of the more conventional value defined on p. 357 of Ref. 4. The results of their calculations for the $2S$ state are in reasonable agreement with those obtained by the present author as an intermediate step in the work reported in Ref. 19.

[31] A slight difficulty that arises is that although the boundary conditions determine a starting value for the first derivative, the value of the second derivative at the same point is indeterminate. One can get around this problem, however, by developing a series for the solution which converges in the neighborhood of the starting value of p. Details of this work will be given in a future paper by the present author and R. W. Klopfenstein.

[32] In this connection, the following points might perhaps be noted: The usual perturbation theory of quantum electrodynamics is essentially a method whereby *all* possible states of the system are taken into account but an expansion is made in terms of a finite number of photons. First-order perturbation theory describes one-photon processes, second-order theory describes two-photon processes, and so on. If any of the energy denominators involved becomes very small, this type of expansion clearly becomes useless. In such cases, however, it is sometimes reasonable to confine ones attention solely to a *finite* number of states, in which case the Schrödinger equation including the perturbation can be solved exactly. This is what is meant by a "strong signal" treatment; it is essentially what is done, for example, in the theory of resonance fluorescence described by W. Heitler, *The Quantum Theory of Radiation* (Oxford University Press, New York, 1954), Sec. 20. See also M. Mizushima, Phys. Rev. **132**, 951 (1963). However, if the field strength in the incident beam becomes comparable to one atomic unit, then it is clearly not legitimate to calculate results either for a finite number of photons or for a finite number of states.

TABLE I. Values of second-order radial matrix elements, defined following Eq. (17); angular distribution coefficients, defined by Eq. (34); and total cross section per intensity, given by Eq. (35). The numbers in parentheses indicate powers of 10.

λ(Å)	P_0	P_2	A	B	C	$\frac{\sigma}{I}$(cm⁴/W)
7290.1	−1.719(3)	−8.506(3)	1.463(−30)	−1.100(−29)	2.068(−29)	2.427(−29)
7119.2	−2.197(3)	−9.708(3)	1.871(−30)	−1.434(−29)	2.758(−29)	3.278(−29)
7000.0	−2.731(3)	−1.114(4)	2.432(−30)	−1.887(−29)	3.696(−29)	4.437(−29)
6943.5	−3.094(3)	−1.215(4)	2.871(−30)	−2.242(−29)	4.430(−29)	5.346(−29)
6800.4	−4.753(3)	−1.689(4)	5.436(−30)	−4.314(−29)	8.740(−29)	1.073(−28)
6661.3	−1.083(4)	−3.472(4)	2.224(−28)	−1.808(−28)	3.770(−28)	4.719(−28)
6472.0	1.125(4)	3.083(4)	1.697(−29)	−1.394(−28)	3.061(−28)	3.987(−28)
6300.0	3.503(3)	8.102(3)	1.111(−30)	−9.215(−30)	2.171(−29)	2.991(−29)
6200.0	2.379(3)	4.881(3)	3.870(−31)	−3.196(−30)	8.006(−30)	1.160(−29)
6075.1	1.614(3)	2.748(3)	1.160(−31)	−9.137(−31)	2.591(−30)	4.140(−30)
6000.0	1.314(3)	1.935(3)	5.635(−32)	−4.028(−31)	1.301(−30)	2.288(−30)
5900.0	1.014(3)	1.148(3)	2.159(−32)	−9.888(−32)	4.653(−31)	1.026(−30)
5800.0	7.865(2)	5.736(2)	1.068(−32)	2.613(−33)	1.182(−31)	4.422(−31)
5695.4	5.978(2)	1.172(2)	1.090(−32)	9.208(−33)	5.025(−33)	1.882(−31)
5600.0	4.543(2)	−2.156(2)	1.626(−32)	−2.896(−32)	1.729(−32)	1.266(−31)
5500.0	3.223(2)	−5.100(2)	2.500(−32)	−9.473(−32)	9.855(−32)	1.650(−31)
5360.4	1.526(2)	−8.764(2)	4.196(−32)	−2.224(−31)	2.986(−31)	3.460(−31)
5300.0	7.841(1)	−1.035(3)	5.176(−32)	−2.949(−31)	4.212(−31)	4.734(−31)
5200.0	−5.796(1)	−1.331(3)	7.464(−32)	−4.602(−31)	7.102(−31)	7.948(−31)
5100.0	−2.422(2)	−1.750(3)	1.177(−31)	−7.622(−31)	1.251(−30)	1.432(−30)
5000.0	−5.956(2)	−2.605(3)	2.437(−31)	−1.624(−30)	2.827(−30)	3.364(−30)
4915.1	−1.738(3)	−5.505(3)	1.040(−30)	−6.974(−30)	1.285(−29)	1.613(−29)
4873.0	−7.613(3)	−2.064(4)	1.434(−29)	−9.549(−29)	1.822(−28)	2.380(−28)
4852.3	1.286(4)	3.221(4)	3.463(−29)	−2.287(−28)	4.455(−28)	5.970(−28)
4811.3	2.057(3)	4.351(3)	6.257(−31)	−4.000(−30)	8.200(−30)	1.171(−29)
4700.0	5.751(2)	5.905(2)	1.522(−32)	−4.832(−32)	1.546(−31)	3.774(−31)
4649.3	3.935(2)	1.514(2)	5.676(−33)	2.674(−33)	1.028(−32)	1.084(−31)
4600.0	2.681(2)	−1.436(2)	6.690(−33)	−1.233(−32)	9.338(−33)	5.590(−32)
4556.3	1.748(2)	−3.587(2)	1.138(−32)	−4.910(−32)	5.885(−32)	8.519(−32)

stitute the final state of the system are an electron and a proton.[33] By an extension of the conventional terminology one might refer to the absorption edge shown in Fig. 2 as the $L_I^{(2)}$ absorption edge.

An experimental verification of these calculations would be particularly interesting in view of the fact that there has, apparently, been no experimental check of even the one-photon ionization cross section for atomic hydrogen.[34]

4. DAMPING CORRECTIONS

It will be assumed in this section that the frequency of the incident photons is close to that of one of the Balmer lines, so that only one intermediate state need be considered. In particular, typical numbers will be given for the case of ruby laser light with only the intermediate $3P$ state taken into account.

The amplitudes of the $2S$ and $3P$ states will be denoted by a, b, respectively. The differential cross section for *one-photon* ionization of the $3P$ state can be derived by elementary perturbation theory, and may be written as

$$d\sigma_b/d\Omega = (\alpha/2\pi)|\boldsymbol{\varepsilon}\cdot\mathbf{r}_{if}|^2 E_p k_e a^2. \quad (36)$$

Equation (36) is to be compared with Eq. (1); the meaning of the symbols and the units used are identical. The numerical value of σ_b for ruby laser light is 3.2

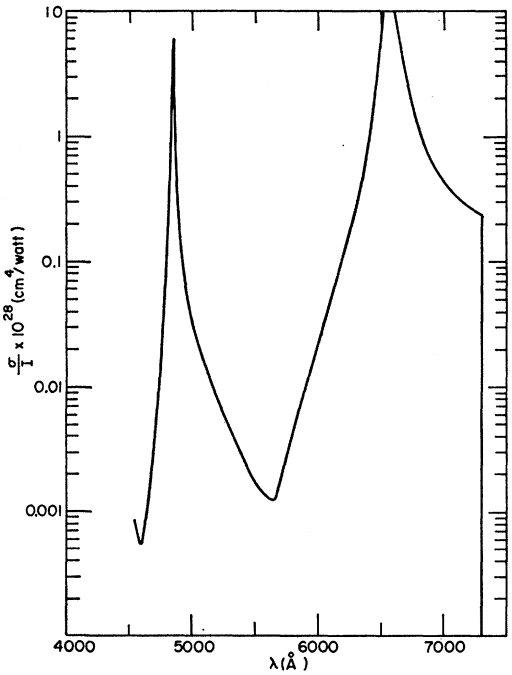

FIG. 2. Graph of σ/I, the total cross section per unit intensity versus the wavelength of the incident light.

[33] E. P. Wigner, Phys. Rev. 73, 1002 (1948).
[34] R. W. Ditchburn and U. Öpik, *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962), Chap. 3.

$\times 10^{-17}$ cm^2. Let F be the photon flux in cgs units. In the absence of both excitation from the $2S$ state and radiative decay, the amplitude of the $3P$ state would evidently be given by

$$b(t)=b(0)e^{(-1/2)\sigma_b F t}, \tag{37}$$

at least as long as the intensity of the beam is not so high that two-photon ionization of the $3P$ state or other higher order processes are significant.

The strong-signal equations may now be written down exactly as in Ref. 18, they are (in cgs units).

$$i\hbar\dot{a}=\tfrac{1}{2}V^* e^{i(\omega_0-\omega_{ba})t}b-\tfrac{1}{2}i\hbar\gamma_a a, \tag{38}$$

$$i\hbar\dot{b}=\tfrac{1}{2}Ve^{-i(\omega_0-\omega_{ba})t}a-\tfrac{1}{2}i\hbar(\gamma_b+\sigma_b F)b, \tag{39}$$

where γ_a, γ_b are spontaneous decay constants, $V=-\langle b|e\mathbf{E}\cdot\mathbf{r}|a\rangle$ with $\mathbf{E}$ the peak field strength in the incident beam, ω_0 the light frequency, and $\hbar\omega_{ba}=E_b-E_a$.

The "small perturbation" solution to these equations is applicable when

$$|V|^2\ll\hbar^2|\tfrac{1}{2}(\gamma_b+\sigma_b F-\gamma_a)+i\Omega|^2, \tag{40}$$

where $\Omega=\omega_{ba}-\omega_0$. This implies in the present case an intensity $I\ll 10^{11}$ W/cm^2. Under these conditions, the decay rate of the $2S$ state is given by the obvious generalization of Eq. (25) of Ref. 18.

$$\Gamma_a=\gamma_a+(\gamma_b-\gamma_a)\frac{\tfrac{1}{4}|V|^2|\hbar^2}{\Omega^2+\tfrac{1}{4}(\gamma_b+\sigma_b F-\gamma_a)^2}+\frac{\tfrac{1}{4}\sigma_b F|V|^2|\hbar^2}{\Omega^2+\tfrac{1}{4}(\gamma_b+\sigma_b F-\gamma_a)^2}. \tag{41}$$

These terms are immediately interpretable as the natural (two-photon) decay rate, the quenching rate with an additional width due to the (one-photon) photoionization of the $3P$ state, and the (two-photon) photoionization rate of the $2S$ state.

If one uses Eq. (36) in (41), one finds for the differential cross section per unit intensity for two-photon ionization of the $2S$ state.

$$\frac{1}{I}\frac{d\sigma}{d\Omega}=\frac{1}{I_0}\left(\frac{\alpha}{4\pi}\right)\left[\frac{|\boldsymbol{\varepsilon}\cdot\mathbf{r}_{0,3p}|^2|\boldsymbol{\varepsilon}\cdot\mathbf{r}_{3p,f}|^2}{(E_0-E_{3p}+E_p)^2+W^2}\right]E_p k_e a^2, \tag{42}$$

where the matrix elements and energies are dimensionless multiples of atomic units. As one might expect, this corresponds to the perturbation theory result, Eq. (1), with only the $3P$ intermediate state considered and with inclusion of a width W given by

$$W=\tfrac{1}{2}\hbar(\gamma_b+\sigma_b F-\gamma_a). \tag{43}$$

One notes finally that γ_a is negligible for the $2S$ state and $\sigma_b F\cong\gamma_b$ for intensities $I\cong 2\times 10^6$ W/cm^2.

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