PHYSICAL REVIEW

Multiphoton Ionization of Atomic Hydrogen in the Ground State

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The general theory of multiphoton ionization of hydrogen atoms by simultaneous absorption of several photons is discussed. In the nonrelativistic dipole approximation, the calculations lead to a recursion relationship concerning angular functions and involve radial matrix elements containing many summations over intermediate states. A general method for exactly evaluating several sums is described in detail and applied to the photo-ionization of atomic hydrogen in the ground state. Numerical results are presented as dispersion curves of the transition rate σ_n/I^{N-1} for a range of wavelengths from 1000 up to 7200 Å.

I. INTRODUCTION

In recent years several experimental studies have been carried out to investigate the direct multiphoton ionization of neutral gas atoms by optical radiation.[1-5]

The theory of the simultaneous absorption of several photons by an atomic system has been treated by different authors.[6-12] Unfortunately, the accuracy of the numerical estimate is often limited by an approximate evaluation of the Nth-order transition matrix element. To eliminate this failure, the present paper reports a procedure for exactly computing, in a practical way, expressions involving many infinite summations over electronic eigenstates.

Section II contains an explicit formula for the N-photon ionization differential cross section.

The calculation of Nth-order transition matrix element breaks into two parts. The first concerns the angular functions and leads to a recursion relationship. The second requires the evaluation of radial matrix elements containing many infinite summations over intermediate states.

It is shown how a particular technique introduced by Dalgarno and Lewis[13] and reformulated by Schwartz and Tieman[14] can be handled in order to derive a general method for implicitly computing expressions including several sums. This sum rule, applied to the calculation of the considered absorption process, gives precise results.

Numerical values of the multiphoton ionization rate of atomic hydrogen, for $N = 2-8$ ($N = 8$ for the ruby laser), are presented in Sec. III.

II. TOTAL CROSS SECTION FOR MULTIPHOTON IONIZATION

Following perturbation theory and using the nonrelativistic dipole approximation, the differential cross section per atom for multiphoton ionization may be derived and written in the form

$$\frac{d\sigma_{nl}}{d\Omega} = \frac{\alpha}{2\pi} \left(\frac{I}{I_0}\right)^{N-1} |K_{fg}^{(N)}|^2 a_0^{\,2} E_p k, \quad (1)$$

where $d\sigma_{nl}/d\Omega$ is the differential cross section in cm²/sr, for each subshell described by quantum numbers (n, l). The quantity I is the light intensity in W/cm², $I_0 = 14.038 \times 10^{16}$ W/cm², α is the fine-structure constant, and a_0 is the Bohr radius. The

photon energy E_p, the wave number of the emitted electron, k, and the Nth-order matrix element, $K_{fg}^{(N)}$, are all dimensionless multiples of the atomic units.

The expression for $K_{fg}^{(N)}$ is

$$K_{fg}^{(N)} = \sum_{i_{N-1}} \sum_{i_{N-2}} \cdots \sum_{i_2} \sum_{i_1} \langle f|\vec{\epsilon} \cdot \vec{r}|i_{N-1}\rangle$$

$$\times \langle i_{N-1}|\vec{\epsilon} \cdot \vec{r}|i_{N-2}\rangle \cdots \langle i_2|\vec{\epsilon} \cdot \vec{r}|i_1\rangle\langle i_1|\vec{\epsilon} \cdot \vec{r}|g\rangle$$

$$\times \{[E_g - E_{N-1} + (N-1)E_p]\cdots[E_g - E_2 + 2E_p]$$

$$\times [E_g - E_1 + E_p]\}^{-1}, \quad (2)$$

where $\vec{\epsilon}$ is the unit polarization vector of the incident light. The quantities E_g and E_j represent the energies of the initial and intermediate states in atomic units, respectively. Hydrogenic bound-state wave functions[15] $|i_j\rangle$ and $|g\rangle = R_{nl}(r)Y_{lm}(\theta, \varphi)$ are written in the following form:

$$|i_j\rangle = R_{\nu\lambda}(r)Y_{\lambda\mu}(\theta, \varphi) = R(\nu\lambda|r)Y_{\lambda\mu}(\theta, \varphi). \quad (3)$$

The final-state wave function belongs to the continuum and behaves asymptotically like a modified Coulomb plane wave of unit amplitude plus an incoming modified Coulomb spherical wave.[15,16]

$$|f\rangle = (8\pi^3/k)^{\frac{1}{2}}\sum_L i^L e^{i\eta_L} R_{WL}(r)$$

$$\times \sum_M Y_{LM}(\theta, \varphi)Y_{LM}^*(\beta, \gamma), \quad (4)$$

where L and M are the angular momentum quantum numbers, β and γ represent colatitude and azimuth coordinates of the ejected electron, respectively. $R_{WL}(k,r)$ is the radial wave function normalized on the energy scale.

$$\eta_L = \arg\Gamma(L + 1 - i/k). \quad (5)$$

Although the differential cross section is written in terms of the light intensity I, Eq. (1) is an analogous form of the transition rate derived in detail by Bebb and Gold.[12]

In order to calculate the Nth-order matrix element, it is convenient to separate the variables. The angular contribution to $K_{fg}^{(N)}$ may be easily calculated, making use of a standard relationship

between spherical harmonics. After averaging on the magnetic quantum number one finds,

$$K_{fg}^{(N)}$$

$$= (8\pi^3/k)^{\frac{1}{2}} i^L e^{i\eta L} Y_{LM}(\beta, \gamma)[1/(2l+1)] \sum_{m=-l}^{+l}$$

$$\times \{A(l)\delta(l_1, l+1) + B(l)\delta(l_1, l-1)\}$$

$$\times \{A(l_1)\delta(l_2, l_1+1) + B(l_1)\delta(l_2, l_1-1)\} \cdots$$

$$\times \{A(l_{N-1})\delta(L, l_{N-1}+1)$$

$$+ B(l_{N-1})\delta(L, l_{N-1}-1)\}$$

$$\times \mathcal{P}(l_1, l_2, \cdots, l_{N-1}, L \mid E_p), \quad (6)$$

where $\delta(l, \lambda)$ is used for the Kronecker symbol $\delta_{l, \lambda}$.

$$A(l_i) = \left\{ \frac{(l_i - m + 1)(l_i + m + 1)}{(2l_i + 1)(2l_i + 3)} \right\}^{1/2},$$

$$B(l_i) = \left\{ \frac{(l_i - m)(l_i + m)}{(2l_i - 1)(2l_i + 1)} \right\}^{1/2}. \quad (7)$$

The symbols $\delta(l, \lambda)$ express the selection rules for orbital and magnetic quantum numbers, $\Delta l_i = \pm 1$, $\Delta m_i = 0$. $\mathcal{P}(l_1, l_2, \cdots, l_{N-1}, L \mid E_p)$ represents the radial contribution to $K_{fg}^{(N)}$. In this notation, the orbital quantum numbers of intermediate states are contained in the left-hand side of the bracket and parameters are placed in the right-hand side.

$$\mathcal{P}(l_1, l_2, \cdots, l_{N-1}, L \mid E_p)$$

$$= \int_0^\infty R(n, l \mid r) V(l_1, l_2, \cdots, l_{N-1}, L \mid r, E_p) r^2 dr. \quad (8)$$

In Eq. (8), the function $V(l_1, l_2, \cdots, l_{N-1}, L \mid r, E_p)$ is defined by

$$V(l_1, l_2, \cdots, l_{N-1}, L \mid r, E_p)$$

$$= \sum_{n_1} \sum_{n_2} \cdots \sum_{n_{N-1}}$$

$$\times \int_0^\infty \frac{R_{WL}(k, r_{N-1}) R(n_{N-1}, l_{N-1} \mid r_{N-1}) r_{N-1}^3 dr_{N-1}}{E_g - E_{N-1} + (N-1)E_p} \cdots$$

$$\times \int_0^\infty \frac{R(n_3, l_3 \mid r_2) R(n_2, l_2 \mid r_2) r_2^3 dr_2}{E_g - E_2 + 2E_p}$$

$$\times \int_0^\infty \frac{R(n_2, l_2 \mid r_1) R(n_1, l_1 \mid r_1) r_1^3 dr_1}{E_g - E_1 + E_p} R(n_1, l_1 \mid r) r. \quad (9)$$

The $(N-1)$ summations over the n_j are extended over the complete set of all possible intermediate states of the Hamiltonian of the unperturbed atom, discrete plus continuum. Because of the sensitivity of the $V(l_1, l_2, \cdots, l_{N-1}, L \mid r, E_p)$ function to small contributions from each state, a careful computation of the sums is required, especially when the energy $(E_g + jE_p)$ lies in a region of the spectrum where the density of states becomes important.

In extending the implicit technique introduced by Schwartz and Tieman[14] to the calculation of expressions such as $V(l_1, l_2, \cdots, l_{N-1}, L \mid r, E_p)$, it appears that summations may be carried out exactly. We introduce the most general functions

$$V(l_j, l_{j+1}, \cdots, l_{N-1}, L \mid r, E_p)$$

$$= \sum_{nj} r R(n_j, l_j \mid r) \int_0^\infty \frac{dr_j}{E_g - E_j + jE_p} r_j^2 R(n_j, l_j \mid r_j)$$

$$\times V(l_{j+1}, l_{j+2}, \cdots, l_{N-1}, L \mid r_j, E_p). \quad (10)$$

To perform the jth sum over n_j, one must consider the Schrödinger equation

$$D_j(r) r R(n_j, l_j \mid r)$$

$$= \left(\frac{1}{2} \frac{d^2}{dr^2} + \frac{1}{r} - \frac{l_j(l_j+1)}{2r^2} \right) r R(n_j, l_j \mid r)$$

$$= -E_j r R(n_j, l_j \mid r). \quad (11)$$

One can easily check that $V(l_j, l_{j+1}, \cdots, l_{N-1}, L \mid r, E_p)$ satisfies the inhomogeneous differential equation

$$(E_g + jE_p + D_j) V(l_j, l_{j+1}, \cdots, l_{N-1}, L \mid r, E_p)$$

$$= \sum_{nj} \int_0^\infty dr_j r R(n_j, l_j \mid r) r_j R(n_j, l_j \mid r_j) r_j$$

$$\times V(l_{j+1}, l_{j+2}, \cdots, l_{N-1}, L \mid r_j, E_p). \quad (12)$$

Using the closure condition, Eq. (12) becomes

$$(E_g + jE_p + D_j) V(l_j, l_{j+1}, \cdots, l_{N-1}, L \mid r, E_p)$$

$$= r V(l_{j+1}, l_{j+2}, \cdots, l_{N-1}, L \mid r, E_p). \quad (13)$$

By means of $(N-1)$ equations analogous to Eq. (13), the $(N-1)$ sums, included in the expression of $V(l_1, l_2, \cdots, l_{N-1}, L \mid r, E_p)$ may be evaluated.

Finally the $V(l_1, l_2, \cdots, l_{N-1}, L \mid r, E_p)$ function is the solution of the set of second-order differential equations.

$$\{E_g + (N-1)E_p + D_{N-1}(r)\} V(l_{N-1}, L \mid r, E_p)$$

$$= r^2 R_{WL}(k, r),$$

$$\{E_g + (N-2)E_p + D_{N-2}(r)\} V(l_{N-2}, l_{N-1}, L \mid r, E_p)$$

$$= r V(l_{N-1}, L \mid r, E_p), \quad (14)$$

$$\cdots$$

$$\{E_g + E_p + D_1(r)\} V(l_1, l_2, \cdots, l_{N-1}, L \mid r, E_p)$$

$$= r V(l_2, l_3, \cdots, l_{N-1}, L \mid r, E_p).$$

In order to obtain a simpler differential system, we note that the exponential included in the structure of the bound hydrogenic radial function allows us to express the quantity $\mathcal{P}(l_1, l_2, \cdots, l_{N-1}, L \mid r, E_p)$ as a sum of derivatives of the Laplace transform of $V(l_1, l_2, \cdots, l_{N-1}, L \mid r, E_p)$ computed at the point $p = 1/n$.

Let us define

$$S(l_j, l_{j+1}, \cdots, l_{N-1}, L \,|p, E_p)$$
$$= \int_0^\infty V(l_j, l_{j+1}, \cdots, l_{N-1}, L \,|r, E_p) e^{-pr} dr \quad (15)$$

and

$$y(l_j, l_{j+1}, \cdots, l_{N-1}, L \,|p)$$

$$= \left(\frac{d}{dp}\right)^{l_j} S(l_j, l_{j+1}, \cdots, l_{N-1}, L \,|p), \quad (16)$$

$$\alpha_j^2 = -2(E_g + jE_p).$$

After some algebra, Eqs. (14) are reduced to a set of first-order differential equations.

$$\left\{(p^2 - \alpha_{N-1}^2)\frac{d}{dp} + 2[(l_{N-1}+1)p-1]\right\}$$
$$\times y(l_{N-1}, L \,|p, E_p)$$
$$= 2(-1)^{(l_{N-1}+1)} \int_0^\infty R_{WL}(k, r) r^{(l_{N-1}+3)}$$
$$\times e^{-pr} dr, \quad (17a)$$

$$\left\{(p^2 - \alpha_{N-2}^2)\frac{d}{dp} + 2[(l_{N-2}+1)p-1]\right\}$$
$$\times y(l_{N-2}, l_{N-1}, L \,|p, E_p)$$
$$= -2\left(\frac{d}{dp}\right)^{l_{N-2}-l_{N-1}+2} y(l_{N-1}, L \,|p, E_p), \quad (17b)$$

$$\cdots$$

$$\left\{(p^2 - \alpha_1^2)\frac{d}{dp} + 2[(l_1+1)p-1]\right\}$$
$$\times y(l_1, l_2, \cdots, l_{N-1}, L \,|p, E_p)$$
$$= -2\left(\frac{d}{dp}\right)^{l_1-l_2+2}$$
$$\times y(l_2, l_3, \cdots, l_{N-1}, L \,|p, E_p). \quad (17c)$$

The quantity on the right-hand side of Eq. (17a) has been previously computed by Zernik,[9] whose result will be used to solve the set of equations (17).

As a consequence of the definition in Eq. (15) $S(l_j, l_{j+1}, \cdots, l_{N-1}, L \,|p, E_p)$ and all its derivatives are finite for all p such that $\mathrm{Re}\, p > 0$. With the condition $(E_g + jE_p) < 0$, an initial value of $y(l_j, l_{j+1}, \cdots, l_{N-1}, L \,|p, E_p)$ is simply determined at the positive value $p = \alpha_j$ for which the coefficient of $(d/dp)y(l_j, l_{j+1}, \cdots, l_{N-1}, L \,|p, E_p)$ vanishes.

The unique solution $y(l_1, l_2, \cdots, l_{N-1}, L \,|p, E_p)$ which is correct, has to be analytic. Knowledge of of it is sufficient to calculate the quantity $\mathcal{P}(l_1, l_2, \cdots, l_{N-1}, L \,|E_p)$.

Making use of Eqs. (8) and (15) and the general expression for $R(n, l \,|r)$, one finds

$$P(l_1, l_2, \cdots, l_{N-1}, L \,|E_p)$$

$$= (-1)^l \frac{1}{(2l+1)!} \left\{\frac{(n+l)!}{(n-l-1)!2n}\right\}^{\frac{1}{2}} \left(\frac{2}{n}\right)^{l+\frac{3}{2}}$$

$$\times \left\{{}_1F_1\left[-(n-l-1), (2l+2), \left(-2p\frac{d}{dp}\right)\right]\right.$$

$$\times \left(\frac{d}{dp}\right)^{l-l_1+2}$$

$$\times y(l_1, l_2, \cdots, l_{N-1}, L \,|p, E_p)\Big\}_{p=1/n}. \quad (18)$$

In integrating over the solid angle $\Omega(\beta, \gamma)$ and averaging over the orbital quantum numbers, the total cross section per electron for each shell may be derived.

Finally, the result is

$$\sigma_n = 4\pi^2 \alpha a^2 E_p \left(\frac{I}{I_0}\right)^{N-1} \frac{1}{n^2} \sum_{l=0}^{n-1} \frac{1}{2l+1} \left| \sum_{m=-l}^{+l} \right.$$

$$\times \{A(l)\delta(l_1, l+1) + B(l)\delta(l_1, l-1)\}$$

$$\times \{A(l_1)\delta(l_2, l_1+1) + B(l_1)\delta(l_2, l_1-1)\} \cdots$$

$$\times \{A(l_{N-1})\delta(L, l_{N-1}+1)$$

$$+ B(l_{N-1})\delta(L, l_{N-1}-1)\}$$

$$\times \mathcal{P}(l_1, l_2, \cdots, l_{N-1}, L \,|E_p) \Big|^2. \quad (19)$$

Since the solution of the set of differential equations (17) must be analytic, a standard method based on Taylor series will be developed for numerical computations.

III. NUMERICAL RESULTS

The transition rate σ_n/I^{N-1} has been evaluated as a function of radiation wavelength. For the multiphoton ionization of hydrogen atoms in ground state, the results can be seen in Figs. 1–7. These graphs correspond to the simultaneous absorption of two photons to eight photons. For radiations whose wavelengths are equal to integer multiples of those relative to the Lyman lines, the dispersion curves show some peaks arising from the resonant structure of the quantity $V(l_1, l_2, \cdots, l_{N-1}, L \,|r, E_p)$. Since the damping corrections to the perturbation theory results have been neglected, the amplitudes of these peaks remain indeterminate. However, the calculations give correct results far from resonances.
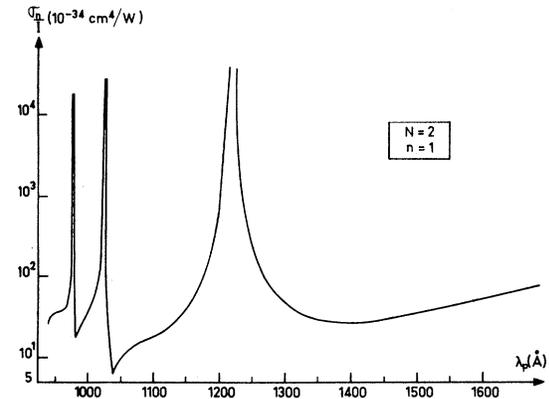

FIG. 1. Two-photon ionization cross section of hydrogen atom in ground state per unit intensity σ_n/I, versus the wavelength λ_p of the incident light.
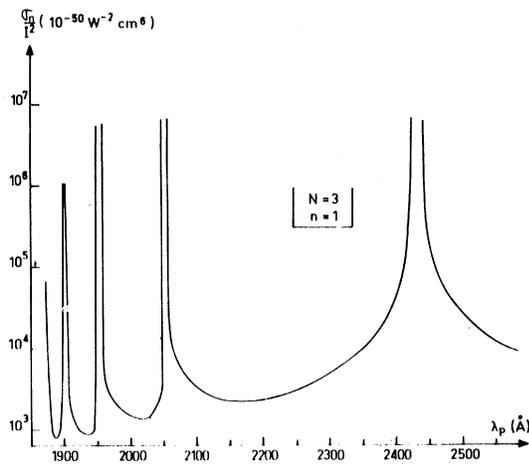
$\frac{\sigma_n}{I^2}$ (10^{-50} W^{-2} cm^6)

FIG. 2. Dispersion rate σ_n/I^2 for the three-photon ionization of H in ground state versus the wavelength λ_p of the incident light.
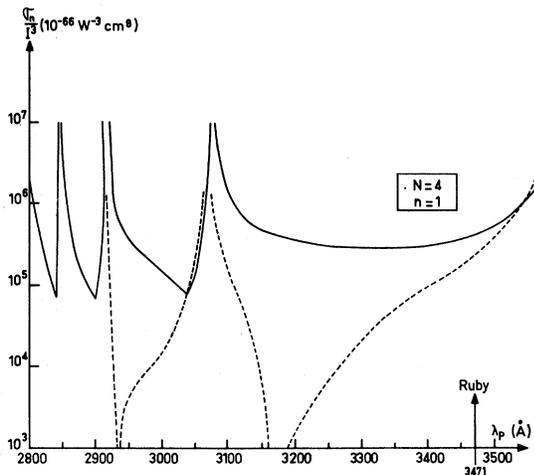
$\frac{\sigma_n}{I^3}$ (10^{-66} W^{-3} cm^8)

FIG. 3. Dispersion rate σ_n/I^3 for four-photon ionization of H in ground state. The value $\lambda_p = 3471$ Å corresponds to the second harmonic of the ruby laser light. Presently calculated—solid lines; results obtained by Bebb and Gold (Ref. 12)—dashed lines.
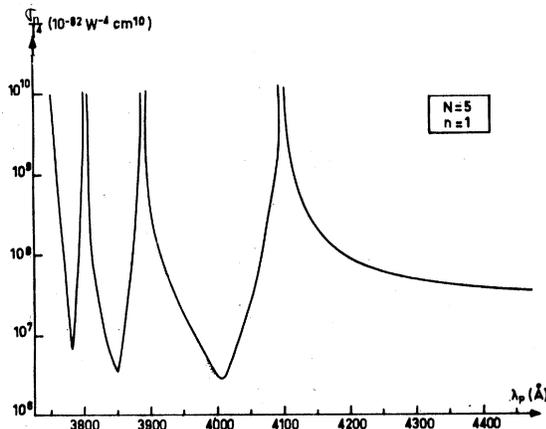
$\frac{\sigma_n}{I^4}$ (10^{-82} W^{-4} cm^{10})

FIG. 4. Dispersion rate σ_n/I^4 for five-photon ionization of H in ground state versus the wavelength λ_p of the incident light.
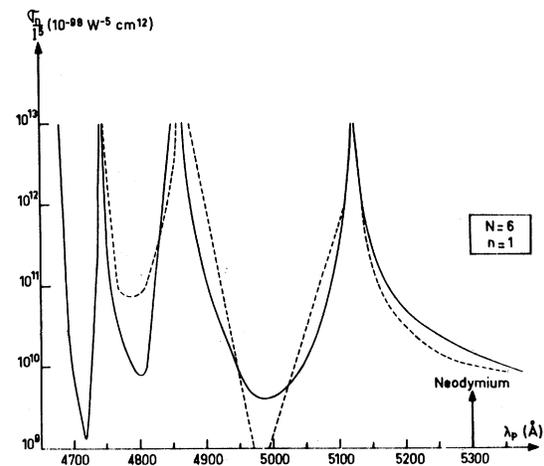
$\frac{\sigma_n}{I^5}$ (10^{-98} W^{-5} cm^{12})

FIG. 5. Dispersion rate σ_n/I^5 for six-photon ionization of H in ground state. The value $\lambda_p = 5300$ Å corresponds to the second-harmonic of the neodymium laser light. Presently calculated—solid lines; results obtained by Bebb and Gold (Ref. 12)—dashed lines.
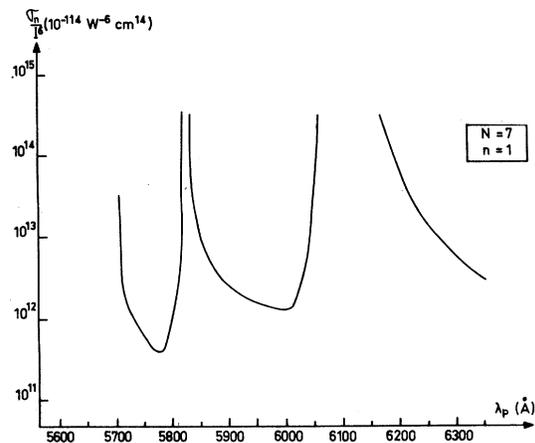
$\frac{\sigma_n}{I^6}$ (10^{-114} W^{-6} cm^{14})

FIG. 6. Dispersion rate σ_n/I^6 for seven-photon ionization of H in ground state versus the wavelength λ_p of the incident light.
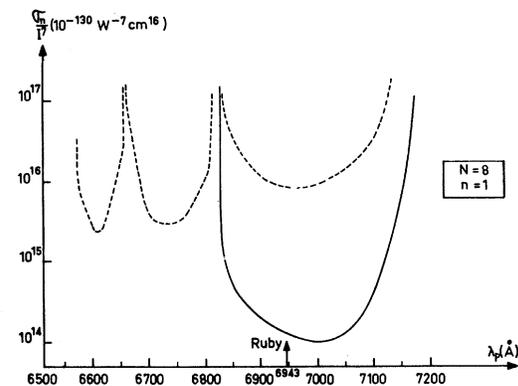
$\frac{\sigma_n}{I^7}$ (10^{-130} W^{-7} cm^{16})

FIG. 7. Dispersion rate σ_n/I^7 for eight-photon ionization of H in ground state. The value $\lambda_p = 6943$ Å corresponds to the wavelength of the ruby laser light. Presently calculated—solid lines; results obtained by Bebb and Gold (Ref. 12)—dashed lines.

It is now interesting to compare our numerical values with the Bebb-Gold data[12] obtained in replacing the infinite sums by a limited number of dominant terms. Our dispersion curves (solid lines) exhibit some changes with respect to the dashed lines which represent the approximation. In particular, the position of every minimum is removed and the corresponding wavelength is shifted. Significant discrepancies, which can become as high as several orders of magnitude for $N = 4$, 6, and 8, are observed in Figs. 3, 5, and 7. This is not very surprising, since for higher-order processes the contribution arising from every neglected state[12] does not seem to be small.

IV. CONCLUSION

From the previous remarks, it has been concluded that the contribution due to states far from energies $(E_g + jE_p)$ to the intermediate-state sums must not be considered as negligible.

There is another reason why the approximation discussed is not suitable. In a rigorous treatment of absorption processes, the lower-order damping corrections must be taken into account. They provide an energy shift and a broadening of the resonance lines. Because of the sensitivity of the $V(l_1, l_2, \cdots, l_{N-1}, L \mid r, E_p)$ functions to small modifica-tions of the energy levels, the calculations require a much greater accuracy, chiefly, for the summations of the near-resonant terms which belong to the part of the spectrum where the density of states becomes important.

Although experimental measurements, using atomic hydrogen beams, seem to be possible, it does not appear that any observations have been published to date.

However, investigations of this gas would be of particular interest for two reasons. First, being the simplest of the atoms, hydrogen can furnish clear information on the ionization processes and provide a correct starting point for a study of more complicated atoms. Second, since hydrogenic wave functions are the only well-known eigenfunctions, computations may be expected to be more accurate than for rare gases or alkalis. These reasons justify the present calculations.

[1] R. G. Meyerand and A. F. Haught, Phys. Rev. Letters 13, 7 (1964).

[2] R. G. Tomlinson, Phys. Rev. Letters 14, 489 (1965).

[3] J. L. Hall, E. J. Robinson, and L. M. Branscomb, Phys. Rev. Letters 14, 1013 (1965); J. L. Hall in IEEE J. Quantum Electron. 2, 21 (1966).

[4] G. S. Voronov, G. A. Delone, and N. B. Delone, Zh. Eksperim. i Teor. Fiz. 51, 1660 (1966) [English transl.: Soviet Phys.—JETP 24, 1122 (1967)]; T. M. Barhudarova, G. S. Voronov, G. A. Delone, N. B. Delone, and N. K. Martakova, in Proceedings of the Eighth International Conference on Phenomena in Ionized Gases (Springer-Verlag, Vienna, 1967).

[5] M. Berry, Y. Durand, P. Nelson, and P. Veyrie, Compt. Rend. 259, 2401 (1964).

[6] M. Goeppert-Mayer, Ann. Phys. (Leipzig) 9, 273 (1931).

[7] L. V. Keldysh, Zh. Eksperim. i Teor. Fiz. 47, 1945 (1964) [English transl.: Soviet Phys.—JETP 20, 1307 (1965)].

[8] S. Geltman, Phys. Letters 4, 168 (1963); 19, 616 (1965); E. J. Robinson and S. Geltman, Phys. Rev. 153, 4 (1967).

[9] W. Zernik, Phys. Rev. 51, A135 (1964); W. Zernik and R. W. Klopfenstein, J. Math. Phys. 6, 262 (1965).

[10] A. M. Perelomov, V. S. Popov, and M. V. Terent'ev, Zh. Eksperim. i Teor. Fiz. 50, 1393 (1965) [English transl.: Soviet Phys.—JETP 23, 924 (1966)].

[11] P. Nelson, Compt. Rend. 261, 3089 (1965); P. Nelson and P. Veyrie, ibid. 262, 1337 (1966).

[12] H. B. Bebb and A. Gold, Phys. Rev. 143, 1 (1966); H. B. Bebb, ibid. 149, 25 (1966); 153, 23 (1967).

[13] A. Dalgarno and J. T. Lewis, Proc. Roy. Soc. (London) A233, 70 (1955); A. Dalgarno, Rev. Mod. Phys. 35, 522 (1963).

[14] C. Schwartz, Ann. Phys. (N.Y.) 6, 156 (1959); C. Schwartz and J. J. Tieman, Ann. Phys. (N.Y.) 6, 178 (1959).

[15] H. A. Bethe and E. Salpeter, Quantum Mechanics of One and Two Electron Atoms (Academic Press Inc., New York, 1957).

[16] G. Breit and H. A. Bethe, Phys. Rev. 93, 888 (1954).