MULTIPHOTON TRANSITIONS TO AN EXCITED LEVEL OF THE HYDROGEN ATOM

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Multiphoton transitions to a degenerate level of the hydrogen atom induced by intense laser radiation of a given frequency ω and an additional light source of variable frequency Ω are considered. The laser radiation perturbs the degenerate level and determines the parameter of the theory of multiphoton transitions. The dependence of the transition probability on the statistical properties of the radiation is established. An "inhibition" of the resonance absorption of the light of frequency Ω by the laser radiation is predicted.

MULTIPHOTON ionization of atoms (see, for example, [1]) has recently been investigated in detail. Multiphoton transitions (with the number of photons greater than two) in the discrete spectrum of atoms has been studied in less detail. On the other hand, the development of methods of multiphoton spectroscopy may turn out to be fruitful, for example, in order to obtain information about the basic parameters which determine the "resonances"[2] associated with multiphoton ionization of atoms.

Multiphoton transitions in the hydrogen atom are of special interest since the well-known l-degeneracy of the energy levels is realized in it. In this connection the contribution of the electron-photon interaction to the expansion parameter which determines the probability of a multiphoton transition may turn out to be much larger than in the case of hydrogen-like atoms. Multiphoton transitions from the ground state of the hydrogen atom to the level $n = 2$ will be investigated below. Since the laser frequency ω is usually fixed, in order to achieve a transition we introduce into consideration, in accordance with the fundamental idea of multiphoton spectroscopy, an additional source of radiation with a variable frequency Ω of generation.

Let us consider the Hamiltonian of a hydrogen atom interacting with stationary laser radiation. We expand the vector potential $\mathbf{A}$ in a series with respect to the normal coordinates. We go over to the representation of second quantization for both the photon and electron subsystems. In the dipole approximation the operator $\hat{H}'$ describing the interaction of the electron with the radiation has the form[2]

$$\hat{H}' = \frac{ie_0}{c}\sum_{i,j,\varkappa}\sqrt{\frac{\omega_\varkappa}{2}}\,(\mathbf{A}_\varkappa\mathbf{r})_{ij}\,(b^+_{-\varkappa} - b_\varkappa)\,a_i^+a_j. \tag{1}$$

Here we have introduced the notation

$$\mathbf{A}_\varkappa = c\sqrt{\frac{4\pi\hbar}{L^3}}\,e^{i\varkappa\mathbf{r}}\,\mathbf{e}_\varkappa$$

($\mathbf{e}_\kappa$ is a unit polarization vector); $b^+_{-\kappa}$ and b_κ are Bose operators for the photons; a_i^+ and a_j are Fermi creation and annihilation operators in the i-th and j-th states of the atom; e_0 is the electron charge; c is the velocity of light; L^3 is the volume of quantization. The total Hamiltonian is given by

$$\hat{H} = \hat{H}_0 + \hat{H}',$$
$$\hat{H}_0 = \sum_i \varepsilon_i a_i^+a_i + \sum_\varkappa \hbar\omega_\varkappa\,(b_\varkappa^+b_\varkappa + 1/2), \tag{2}$$

where ϵ_i denotes the energy of the i-th state of an electron in the hydrogen atom.

Let us consider the case of a single laser mode of Z-polarization. We assume that the frequency of the laser does not coincide with any of the eigenfrequencies of the atom. For simplicity we shall confine our attention to taking account of the electron-photon interaction only for the level $n = 2$.[1)] In the dipole approximation the matrix element between the following states (nlm) will differ from zero: $\alpha(200)$ and $\beta(210)$. Thus

$$\hat{H}' = i\hat{B}_{\alpha\beta}(b^+ - b),$$
$$\hat{B}_{\alpha\beta} \equiv v_{\alpha\beta}a_\alpha{}^+a_\beta + v_{\beta\alpha}a_\beta{}^+a_\alpha,$$
$$v_{\alpha\beta} = v_{\beta\alpha} = 3e_0a_0L^{-3/2}\sqrt{2\pi\hbar\omega}. \tag{3}$$

Here a_0 denotes the Bohr radius.

The probability of absorption by an atom per unit time of light of a frequency Ω lying within the interval between Ω and $\Omega + d\Omega$, of intensity $\mathscr{L}(\Omega)$, and of polarization Z is determined by the Fourier transform of the correlation function of the dipole moment operators:[3]

$$dW = \frac{2\pi}{\hbar^2 c}\mathscr{L}(\Omega)\int_{-\infty}^{+\infty}\mathscr{K}(t)\,e^{-i\Omega t}\,dt\,d\Omega, \tag{4}$$

$$\mathscr{K}(t) = \sum_{i,j,i_1,j_1} d_{ji}{}^*\,d_{i_1j_1}\,\mathscr{K}_{iji_1j_1}(t),$$
$$\mathscr{K}_{iji_1j_1}(t) = \langle\langle a_i{}^+a_j\,|\,a_{i_1}{}^+(t)\,a_{j_1}(t)\rangle\rangle. \tag{5}$$

Here

$$d_{ji} = e_0\int\psi_j^*(z)\,z\,\psi_i\,dv,\quad a(t) = e^{i\hat{H}t/\hbar}\,a\,e^{-i\hat{H}t/\hbar},$$

and the symbol $\langle\langle\ldots\rangle\rangle$ denotes statistical averaging over the initial state of the system (atom + laser radiation).

To a high degree of accuracy (in the concentrations) one can neglect the contribution of excited states of the atoms to the absorption and consider only transitions

1) One can neglect the influence of the laser radiation on the ground state energy level of the hydrogen atom since, as it is not difficult to verify, the corresponding Stark correction is negligible.

from the ground state. Since the ground state $a_s^+|0\rangle$ of hydrogen in the chosen model is not perturbed by the laser radiation, the atomic and field variables factor so that to the accepted degree of accuracy

$$\mathcal{K}_{iji_1j_1}(t) = \mathrm{Sp}\,\{\rho_f \langle 0|\, a_s a_i^+ a_j e^{i\hat{H}t/\hbar} a_{i_1}{}^+ a_{j_1} e^{-i\hat{H}t/\hbar} a_s^+ \,|0\rangle\}. \qquad (6)$$

Here ρ_f is the statistical operator which describes the electromagnetic field of the laser. The subsequent calculation is carried out exactly.

Inside the trace sign in formula (6) we perform a canonical "shifting" transformation with the aid of the unitary operator:

$$\hat{U} = \exp\left\{\frac{i}{\hbar\omega}\hat{B}_{\alpha\beta}(b^+ + b)\right\}. \qquad (7)$$

It is not difficult to verify that

$$\hat{U}\hat{H}\hat{U}^{-1} = \hat{H}_0 - \frac{1}{\hbar\omega}\hat{B}_{\alpha\beta}^2. \qquad (8)$$

Formula (6) takes the form

$$\mathcal{K}_{iji_1j_1}(t) = \mathrm{Sp}\left\{\rho_f \sum_{\nu_1\nu_2} R^{(1)}_{sij\nu_1}(t) R^{(2)}_{\nu_1\nu_2}(t) R^{(s)}_{\nu_2 i_1 j_1 s}(t)\right\}. \qquad (9)$$

Here the following notation has been introduced:

$$R^{(1)}_{sij\nu_1}(t) = \left\langle 0\right| a_s a_i^+ a_j \exp\left\{-\frac{it}{\hbar}\left(\sum_i \varepsilon_i a_i^+ a_i - \frac{\hat{B}_{\alpha\beta}^2}{\hbar\omega}\right)\right\} a_{\nu_1}^+ \left|0\right\rangle,$$

$$R^{(2)}_{\nu_1\nu_2}(t) = \langle 0|\, a_{\nu_1} \hat{U}^+(0)\hat{U}(t) a_{\nu_2}^+ |0\rangle,$$

$$\hat{U}(t) = e^{i\omega t b^+ b}\hat{U} e^{-i\omega t b^+ b},$$

$$R^{(3)}_{\nu_2 i_1 j_1 s}(t) = \left\langle 0\right| a_{\nu_2} a_{i_1}^+ a_{j_1} \exp\left\{-\frac{it}{\hbar}\left(\sum_i \varepsilon_i a_i^+ a_i - \frac{\hat{B}_{\alpha\beta}^2}{\hbar\omega}\right)\right\} U^+(t) U(0) a_s^+ \left|0\right\rangle. \qquad (10)$$

A calculation according to the formulas (10) gives

$$R^{(1)}_{sij\nu_1}(t) = \delta_{is}\,\delta_{j\nu_1}(\delta_{\nu_1\alpha} + \delta_{\nu_1\beta})\exp\left\{\frac{it}{\hbar}\left(\varepsilon_{\nu_1} - \frac{v_{\alpha\beta}^2}{\hbar\omega}\right)\right\};$$

$$R^{(3)}_{\nu_2 i_1 j_1 s}(t) = \delta_{j_1 s}\,\delta_{i_1\nu_2}(\delta_{\nu_2\alpha} + \delta_{\nu_2\beta})\exp\left\{-\frac{i\varepsilon_s}{\hbar}t\right\} \qquad (11)$$

(δ_{ij} is the Kronecker delta).

Expression (9) takes the form

$$\mathcal{K}_{iji_1j_1}(t) = \delta_{is}\,\delta_{j\nu_1}\,\delta_{j_1 s}\,\delta_{i\nu_2}(\delta_{\nu_1\alpha} + \delta_{\nu_1\beta})(\delta_{\nu_2\alpha} + \delta_{\nu_2\beta})\exp\left\{\frac{it}{\hbar}\left(\varepsilon_{\nu_1} - \varepsilon_s - \frac{v_{\alpha\beta}^2}{\hbar\omega}\right)\right\} K_{\nu_1\nu_2}(t), \qquad (12)$$

where the notation is defined by

$$K_{\nu_1\nu_2}(t) = \langle 0|\, a_{\nu_1}\hat{\Phi}(t) a_{\nu_2}^+ |0\rangle,$$
$$\hat{\Phi}(t) = \mathrm{Sp}\,\{\rho_f \hat{U}^+(0)\hat{U}(t)\}. \qquad (13)$$

Let us use the $\mathcal{P}$-representation for the density operator ρ_f:[4]

$$\rho_f = \int \mathcal{P}(|\xi|)\,|\xi\rangle\langle\xi|\,d^2\xi \qquad (14)$$

Here $\mathcal{P}(|\xi|)$ is the Glauber weight function for a steady-state source of radiation, and ξ is the complex eigenvalue of the photon annihilation operator:

$$b|\xi\rangle = \xi|\xi\rangle. \qquad (15)$$

According to the methods of Glauber,[4] in order to calculate the average value of an operator $A(b^+, b)$ it is necessary to bring it into normal (N) form for the operators b^+ and b. In the expression NA the Fock operators b^+ and b must be replaced, respectively, by ξ^+ and ξ, and the result is integrated term-by-term with the weight function $\mathcal{P}$. It is not difficult to show that

$$\hat{U}^+(0)\hat{U}(t) = N\exp\left\{-\frac{i\hat{B}_{\alpha\beta}}{\hbar\omega}(1 - e^{i\omega t})b^+\right\}$$
$$\times\exp\left\{-\frac{i\hat{B}_{\alpha\beta}}{\hbar\omega}(1 - e^{-i\omega t})b\right\}\exp\left\{-\frac{B_{\alpha\beta}^2}{\hbar^2\omega^2}(1 - e^{i\omega t})\right\}. \qquad (16)$$

Let us consider the evaluation of $K_{\nu_1\nu_2}(t)$ for two types of weight functions.

A. A continuously operating, stabilized laser:[4]

$$\mathcal{P}(|\xi|) \equiv \mathcal{P}_\delta(|\xi|) = \frac{1}{2\pi\sqrt{\bar{n}}}\,\delta(|\xi| - \sqrt{\bar{n}}).$$

Here $\bar{n}$ denotes the average number of photons in the mode, and $\delta(\alpha)$ is the Dirac delta function. We find

$$\hat{\Phi}^{(\delta)}(t) = J_0\left(\frac{4\hat{B}_{\alpha\beta}}{\hbar\omega}\sqrt{\bar{n}}\sin\frac{\omega t}{2}\right)\exp\left\{\frac{-\hat{B}_{\alpha\beta}^2}{\hbar^2\omega^2}(1 - e^{i\omega t})\right\}. \qquad (18)$$

(Here and below the superscript (δ) indicates the type of $\mathcal{P}$-function.) $J_0(x)$ is the Bessel function of zero order.

In order to evaluate $K_{\nu_1\nu_2}(t)$ we shall use a representation of the Bessel function in the form of a series, and we also expand the exponential appearing in formula (18) in a series. Terms having the structure

$$\sum_{m=0}^{\infty}\sum_{n=0}^{\infty}\frac{(-1)^m}{(m!)^2 n!}\left(2\sqrt{\bar{n}}\sin\frac{\omega t}{2}\right)^{2m}(e^{i\omega t} - 1)^n\left(\frac{v_{\alpha\beta}}{\hbar\omega}\right)^{2(m+n)}$$
$$\times\delta_{\nu_1\nu_2}\{\langle 0|\, a_\alpha(a_\alpha^+ a_\beta a_\beta^+ a_\alpha)^{m+n} a_\alpha^+ |0\rangle\,\delta_{\nu_1\alpha}$$
$$+ \langle 0|\, a_\beta(a_\beta^+ a_\alpha a_\alpha^+ a_\beta)^{m+n} a_\beta^+ |0\rangle\,\delta_{\nu_1\beta}\}. \qquad (19)$$

will be different from zero. Finally we find

$$K^{(\delta)}_{\nu_1\nu_2}(t) = J_0\left\{\rho_1\sin\frac{\omega t}{2}\right\}\exp\{(e^{i\omega t} - 1)\rho_0\}\,\delta_{\nu_1\nu_2}(\delta_{\nu_1\alpha} + \delta_{\nu_1\beta}). \qquad (20)$$

Here the notation is given by

$$\rho_1 = \frac{4v_{\alpha\beta}}{\hbar\omega}\sqrt{\bar{n}}, \qquad \rho_0 = \frac{v_{\alpha\beta}^2}{\hbar^2\omega^2}. \qquad (21)$$

B. A Gaussian source of radiation (for example, a laser operating below threshold). The weight function has the form

$$\mathcal{P}_G(|\xi|) = \frac{1}{\pi\bar{n}}\exp\left\{-\frac{|\xi|^2}{\bar{n}}\right\}. \qquad (22)$$

A calculation gives

$$\hat{\Phi}^{(G)}(t) = \exp\left\{-\frac{2\hat{B}_{\alpha\beta}^2}{\hbar^2\omega^2}\bar{n}(1 - \cos\omega t)\right\},$$

$$\mathcal{K}^{(G)}_{\nu_1\nu_2}(t) = \exp\{-{}^1/_8\rho_1^2(1 - \cos\omega t)\}\,\delta_{\nu_1\nu_2}(\delta_{\nu_1\alpha} + \delta_{\nu_1\beta}). \qquad (23)$$

With the aid of the formulas obtained above, let us determine the probabilities $dW^{(G)}$ and $dW^{(\delta)}$. We find

$$\mathcal{K}^{(\delta)}(t) = d_{s\alpha}^2\exp\left\{\frac{i}{\hbar}(\varepsilon_\alpha - \varepsilon_s)t\right\}J_0\left(\rho_1\sin\frac{\omega t}{2}\right)\exp\{\rho_0(e^{i\omega t} - 1)\}. \qquad (24)$$

Let us use the expansion[6]

$$J_0\left(\rho_1\sin\frac{\omega t}{2}\right) = J_0^2\left(\frac{\rho_1}{2}\right) + 2\sum_{k=1}^{\infty}J_k^2\left(\frac{\rho_1}{2}\right)\cos k\omega t. \qquad (25)$$

We note that as $L^3 \to \infty$, $\rho_0 \to 0$ while ρ_1 remains finite ($\rho_1 \sim \bar{n}/L^3$, $\bar{n} = L^3 N_0$, where N_0 is the number of photons in 1 cm^3).

The integration over t in formula (4) is elementary to perform with the aid of formulas (24) and (25). We find

$$dW^{(\delta)} = M(\Omega) \sum_{k=0}^{\infty} J_k^2\left(\frac{\rho_1}{2}\right)\delta\left(\frac{\varepsilon_\alpha-\varepsilon_s}{\hbar}-\Omega-k\omega\right)d\Omega. \quad (26)$$

Here

$$M(\Omega) = \frac{4\pi^2}{\hbar^2 c} d_{s\alpha}{}^2 \mathscr{L}(\Omega).$$

$J_k(x)$ denotes a Bessel function.

$dW^{(G)}$ is determined in similar fashion:

$$dW^{(G)} = M(\Omega)\exp\left(\frac{-\rho_1^2}{8}\right)\sum_{h=0}^{\infty} I_h\left(\frac{\rho_1^2}{8}\right)\delta\left(\frac{\varepsilon_\alpha-\varepsilon_s}{\hbar}-\Omega-k\omega\right)d\Omega, \quad (27)$$

$I_k(x)$ denotes a modified Bessel function. Formulas (26) and (27) have the typical structure which describes multiphoton processes. In the absence of laser radiation $\rho_1 = 0$ and only one term out of the sum is left which does not vanish for $k = 0$ ($J_0(0) = 1$, $I_0(0) = 1$). In this connection formulas (26) and (27) go over into the well-known expression for the probability of one-photon absorption of a quantum $\hbar\Omega$ by a hydrogen atom.

If the frequency Ω varies within the interval from Ω_0 to $\Omega_0 + \Delta\Omega_0$, then for the integral transition probabilities we find

$$W^{(\delta)} = M(\Omega_0) J^2_{[k_0]}\left(\frac{\rho_1}{2}\right),$$

$$W^{(G)} = M(\Omega_0)\exp\left(-\frac{\rho_1^2}{8}\right) I_{[k_0]}\left(\frac{\rho_1^2}{8}\right). \quad (28)$$

Here $[k_0]$ denotes the integer part of the number k_0:

$$k_0\omega = (\varepsilon_\alpha - \varepsilon_s)/\hbar - \Omega_0.$$

The parameter ρ_1 appearing in expressions (28) has the form

$$\rho_1 = \frac{12\sqrt{2\pi}\, e_0}{\sqrt{\hbar\omega}} a_0 \sqrt{N_0}. \quad (29)$$

At photon densities N_0 for which $\rho_1 \ll 1$ we find

$$W^{(\delta)} \cong \frac{M(\Omega_0)}{[[k_0]!]^2}\left(\frac{\rho_1^2}{16}\right)^{[k_0]},$$

$$W^{(G)} \cong \frac{M(\Omega_0)}{[k_0]!}\left(\frac{\rho_1^2}{16}\right)^{[k_0]}. \quad (30)$$

It immediately follows from formula (30) that

$$W^{(G)} = [k_0]!\, W^{(\delta)}.$$

In other words, the transition probability (for the same intensity of radiation) is, in the case of a Gaussian source, $[k_0]!$ times larger than in the case of a source with a δ-shaped $\mathscr{F}$-function. Since in an experiment the intensity of a Gaussian source is usually not large, this result is of rather theoretical interest. (For the case of two-photon transitions the indicated problem has been extensively discussed in the literature.[5,7])

Let us denote by $W^{(r)}$ the probability for the absorption of a quantum Ω in the absence of laser radiation under the exact resonance condition, $\Omega = (\epsilon_\alpha - \epsilon_s)/\hbar$. The corresponding probability $W^{(\delta)}$ for the absorption of a quantum Ω in the presence of the laser beam has the form

$$W^{(\delta)} = W^{(r)} J_0^2(\rho_1/2). \quad (31)$$

As follows from formula (31), the laser radiation "modulates" the absorption of light of frequency Ω. In the absence of the laser beam $\rho_1 = 0$, $J_0(0) = 1$, and consequently $W^{(\delta)} \equiv W^{(r)}$. With switching-on of the laser source and with an increase of its intensity, the argument of the zero-order Bessel function increases and its value decreases. For sufficiently intense laser irradiation the coefficient for the absorption of light with frequency Ω may be practically "suppressed." Utilization of a carbon dioxide laser ($\omega \sim 10^{14}$ sec^{-1}) represents a favorable situation for observation of the indicated effect. At fields $F \sim 5\times10^6$ V/cm the argument $\rho_1 = 3$, $J_0^2(1.5) \simeq 0.25$, and consequently the rate of light absorption is decreased by a factor of four. It is not difficult to verify that for such fields the decay probability per unit time for the excited (n = 2) state of the hydrogen atom is $\sim 1\times10^8$ sec^{-1}, i.e., it does not exceed the value for the probability of spontaneous emission (6×10^8 sec^{-1}). (In order to estimate the probability of decay via tunneling, one should use formula (16) of article[1] in which for the factor S it is necessary to take only the first few terms of the series (18) into account).

Side by side with the absorption processes, processes involving the spontaneous emission of the frequency Ω in the presence of laser radiation of frequency ω are treated in similar fashion. In this connection

$$W^{(\delta)}_{\text{emission}} = W^{(r)}_{\text{emission}} J_0^2\left(\frac{\rho_1}{2}\right).$$

If the amplitude of the laser signal is modulated with a large period, then one would expect that the intensity of the Ω-luminescence will contain a corresponding variable signal which may be observed and amplified according to the well-known techniques associated with much weaker laser fluxes.[2)]

We note that l-degeneracy is also realized for excitons in a solid (for example, for excitons in CdS[8] a quasilinear Stark effect arises for the n = 2 level at a sufficiently large value of the field F). In this case formula (31) is applicable for qualitative estimates. Since the radius of an exciton in CdS is 30 times larger than the radius of the Bohr orbit in hydrogen, complete "inhibition" of the absorption of light of the frequency Ω is achieved in the case of a CO_2 laser for fields F $\sim 3\times10^5$ V/cm. (Since the quantity $\hbar\omega$ is an order of magnitude larger than an exciton's binding energy, its ionization by a quantum of laser radiation is unlikely.)

In conclusion we note that a factor of the type $J^2_{[k_0]}(\rho_1/2)$ reflects the fact that there is a definite probability for the participation of $[k_0]$ laser photons in the transition. (Coefficients of a type involving the square of Bessel functions are also obtained in articles [9,10] which are devoted to similar physical problems about the high-frequency Stark and Zeeman effects.) The factor $J_0^2(\rho_1/2)$ expresses the probability that real laser photons do not participate in the transition, but the contribution of virtual photons to the transition probability is appreciable. (In analogy with the well-known Debye–Waller factor in the theory of phononless lines and the Mössbauer spectrum.)

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[1] L. V. Keldysh, Zh. Eksp. Teor. Fiz. **47**, 1945 (1964) [Sov. Phys.-JETP **20**, 1307 (1965)].

[2] H. B. Bebb and A. Gold, Phys. Rev. **143**, 1 (1966).

[3] R. Barrie and R. G. Rystephanick, Can. J. Phys. **44**, 109 (1966).

[4] R. Glauber, in: Kvantovaya optika i kvantovaya radiofizika (Quantum Optics and Quantum Radiophysics) [translation], Mir, 1966.

[5] R. Guccione-Gush, H. P. Gush, and J. Van Kranendonk, Can. J. Phys. **45**, 2513 (1967).

[6] I. S. Gradshteĭn and I. M. Ryzhik, Tablitsy integralov, summ, ryadov i proizvedeniĭ (Tables of Integrals, Sums, Series, and Products), Fizmatgiz, 1962 (Engl. Transl., Academic Press, New York, 1965).

[7] S. Carusotto, G. Fornaca, and E. Polacco, Phys. Rev. **157**, 1207 (1967).

[8] Robert S. Knox, Theory of Excitons, Academic Press, New York, 1963 (Russ. Transl., Izd. Mir, 1966).

[9] D. Blochinzew, Sow. Phys. **4**, 501 (1933).

[10] M. A. Divil'kovskiĭ, Zh. Eksp. Teor. Fiz. **7**, 650 (1937).

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