"Multiple-" versus "multi-" photon absorption in the theory of resonant ionization

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The author has identified his result for resonant ionization by the simultaneous absorption of two photons by a ground-state electron [Phys. Rev. A **17**, 659 (1978)] with the high-laser-power large-intermediate-state ionization rate result derived by Eberly and co-workers using a steady-state rate theory. This result gives $R\sigma_{22}$ for all power levels considered, where R is the one-photon ionization rate for the intermediate state and σ_{22} is its steady-state population factor. The result can be cast in this form, but it is found that σ_{22} must be much less than σ_{11}, the ground-state population factor. Thus the resonant process can be described by a rate limit for conserving energy by simultaneous absorption only when the ground-state population factor remains unity to order Ω^2/R^2, where Ω is the Rabi rate for the bound-bound transition. In other words, the simultaneous and sequential processes are physically equivalent in this limit.

In a previous paper[1] (I) I presented a rate-theoretic description of the resonant ionization of an atom by the simultaneous absorption of two photons by a ground-state electron. That result depends on the assumption that the laser bandwidth is very narrow, implying single-mode conditions, such that the atomic interaction with the classical radiation field can be assumed to be proportional to a δ function in frequency space [Eq. (3b) of I]. This δ function is given by the Fourier integral representation of the time-dependent interaction with the field, in which the Fourier integral can be used if one ignores the effect of transients due to its sudden switching on.[2] The Fourier integral is evaluated by treating as constant the slow time variation of the field amplitude, defined for a given experiment by a pulse shape function. In an adiabatic following approximation[3] the slowly varying amplitude can then be defined as a function of the time required for a given pulse to propagate through a focal volume containing the target.[4]

The conservation theorem that two photons be simultaneously absorbed by a ground-state electron is the same as that obtained in second-order perturbation theory for the nonresonant process. However, in our result the infinity at the real level has been removed by solving an integral equation very near the infinity. This equation describes the shifting and broadening of the level by the *virtual processes* of ionization and recombination and of emission and reabsorption. This simultaneity precludes the possibility of "Rabi broadening" in the intermediate state due to the *real processes* of emission and reabsorption ("Rabi cycling" of the atomic population between the ground and intermediate states). Simultaneity also precludes the possibility of sequential ("multiple") photon absorption leading to "resonance ionization" from a saturated intermediate state.[5] The theory of the latter phenomenon must be based on an analysis of the probabilities for populating two bound levels lying below an ionization continuum. Below, we show that the simultaneous theory of I predicts a level-two population which is small compared to unity. The sequential process, on the other hand, is based on the assumption of a significant level one to level two population shift by one-photon excitation and the subsequent one-photon ionization of the level-two population.

We show that the two theories give the *same* result when the level-two population is small compared to the level-one population. That is, we obtain the interesting result that the sequential two-photon rate $R\sigma_{22}$ (level-two one-photon ionization rate R times the level-two population factor σ_{22}) is equal to the level-one simultaneous rate R_2, when $\sigma_{22} \ll 1$. Thus simultaneous and sequential two-photon ionization are physically equivalent in this limit.

A theory of two-photon sequential or "multiple" resonant ionization has been derived in a rate limit by Eberly and co-workers.[3,6] This result depends on the assumption that a time-independent probability for populating the levels of an atom can be calculated by making a pair of adiabatic approximations to the Liouville or Bloch equations[7] for the density matrix ρ. Then, the two-photon rate is calculated[3,6] by weighting the one-photon ionization rate of the resonant (second) level by the population factor for this level.

The first of the two adiabatic approximations is discussed and examined numerically against the exact solution of the Bloch equations by Ackerhalt and Shore.[7] This approximation was proposed by Wilcox and Lamb[8] and involves setting the time derivatives of the off-diagonal elements of ρ equal to zero, based on their rapid relaxation to steady-state values. This leads to diagonal elements of

ρ, the densities of atoms per quantum state, which are good time averages of the exact densities under the conditions discussed in Ref. 7 (principally that the detuning from resonance be small). The second adiabatic approximation is introduced by de Meijere and Eberly[3] and examined further by Eberly and O'Neil.[6] This approximation involves the further setting of the time derivatives of the diagonal density matrix elements equal to zero, then solving for the resulting time-independent elements. These are then used, in adiabatic following, to evaluate the original time derivatives of the atomic densities (diagonal elements of ρ) to obtain a decay law for the bound states of the atom.

The starting point for Refs. 3 and 6 can be taken to be Eqs. (8) and (9) of Ref. 7 for the two-level atom *after* the Wilcox-Lamb approximation has been made. Also the difference and sum, respectively, of Eqs. (25) and (26) of Ref. 3 are

$$\dot{\rho}_{11} = R_s(\rho_{22} - \rho_{11}) \tag{1a}$$

$$\dot{\rho}_{22} = -R_s(\rho_{22} - \rho_{11}) - R\rho_{22}\ , \tag{1b}$$

where R is the one-photon ionization rate of level two and R_s is a transition rate based on the substitution of the off-diagonal elements ρ_{12} and ρ_{21} into the original right-hand sides of the equations for ρ_{11} and ρ_{22}. Neglecting the collisional and spontaneous decay widths relative to R, it is

$$R_s = \frac{R\Omega^2/4}{[\Delta^2 + (R/2)^2]}\ , \tag{2}$$

where Ω is the Rabi rate for the bound-bound transition and Δ is the detuning (including the light shift) from resonance. The ionization rate for the bound levels follows from the addition of Eqs. 1,

$$\dot{\rho}_{11} + \dot{\rho}_{22} = -R\dot{\rho}_{22}. \tag{3}$$

Eberly and co-workers[3,6] set $\dot{\rho}_{22}$ equal to zero in Eq. (1b), obtaining for the probability of populating level-two:

$$\sigma_{22} = \rho_{22}/N = \frac{R_s}{(2R_s + R)} = \frac{\Omega^2/4}{[\Delta^2 + (R/2)^2 + \Omega^2/2]}\ , \tag{4}$$

subject to the condition that $\rho_{11} + \rho_{22} = N$, the total density of atoms in the bound levels. Thus from Eqs. (3) and (4) the ionization rate for the bound levels is $R\sigma_{22}$ (the one-photon rate for level-two times the steady-state probability for populating this level).

Equation(4)is based on the assumption that the relaxation rate of ρ_{jj} to steady-state values is much faster than the ionization rate leading to population depletion; thus the field cannot be ultra strong. Although not discussed in Refs. 3 and 6, it is clear that Eqs. (1), on using the constraint that $\rho_{11} + \rho_{22} = N$, appear to lead to different results for the steady-state densities. Setting the left-hand side of Eq. (1a) equal to zero leads to the statement $\rho_{11} = \rho_{22} = N/2$, while performing this operation in Eq. (1b) leads to Eq. (4). It is clear, however, that the result from Eq. (1a) is a special case, when $\Omega^2/2 \gg [\Delta^2 + (R/2)^2]$, of the general result given by Eq. (4).

The rate for the ionization of the ground level by the simultaneous absorption of two photons has been given in I. It is the integrated cross section times F, the flux [see Eq. (13) of I]. A little manipulation (Appendix) shows that it is given by

$$R_2 = \frac{R\Omega^2/4}{[\Delta^2 + (R/2)^2]}\ . \tag{5}$$

At this level of approximation R_2 is equal to R_s [Eq. (2)] or level one decays by two-photon ionization at the same rate at which excitation occurs from level one to level two.

We note that $R_2 = R\sigma_{22}$, when σ_{22} is evaluated in the limit[9] $(R/2)^2 \gg \frac{1}{2}\Omega^2$. Thus, to order Ω^2/R^2, σ_{11} is unity on resonance ($\Delta = 0$). This result tells us that simultaneous and sequential two-photon ionization are physically equivalent processes when the level-two one-photon ionization rate is sufficiently large that the level-one to level-two population shift is no larger than Ω^2/R^2.

It remains to identify the high-power assumption in the derivation of R_2 of I. From Eqs. (2), (4b), (8), and (14a) of I, we note that the response state leading to two-photon absorption is a p state having the form

$$\psi_1(\vec{r}, t) = a_{2p}(t)\psi_{2p}(\vec{r})e^{-i\omega_2 t}\ , \tag{6}$$

where

$$a_{2p}(t) = \frac{\frac{1}{2}\Omega e^{i(\omega_2 - \omega_1 - \omega)t}}{[\Delta - iR/2]}\ . \tag{7}$$

Thus the probability for populating level two is

$$|a_{2p}|^2 = \frac{\Omega^2/4}{[\Delta^2 + (R/2)^2]}\ . \tag{8}$$

As pointed out in I, the δ-function form of the interaction in frequency space [see the first term on the right-hand side (rhs) of Eq. (7b) of I] implies that the wave function could be written in the forms given by Eqs. (8) and (9) of I. It is the inverse Fourier transformation of Eq. (8) [see Eq. (2)] whose absorptive part [first term on the rhs of Eq. (8)] leads to a probability amplitude given by Eq. (7) above, in which the Rabi broadening

contribution is missing from the denominator [contrast Eqs. (4) and (8) of the present paper].

Thus the divergence at $\omega_{1s}+\omega_p=\omega_{2p}$ can be removed by the solution of an integral [Eq. 10(a) of I]; yet the above identification of R_2 (derived from this solution very near the divergence) with $R\sigma_{22}$ for small σ_{22} from the steady-state theory has revealed that this solution does not have a general validity. This is obvious from Eq. (8) above, where $|a_{2p}|^2$ is meaningless if $\Omega > R$ and, from the above identification with $R\sigma_{22}=R(\Omega^2/R^2)$, is reliable only when $\frac{1}{2}\Omega^2 \ll (R/2)^2$. We can trace the implicit high-power assumption to the original *ansatz* [Eq. (1a) of I], in which the source (first term of the rhs) is proportional to $\delta(\omega-\omega_{1s})$. Thus the $1s$ state can be broadened only through the first and third terms on the rhs of Eq. (9) of I for $j=0$ (the second term contains no $1s$ contribution [see Eq. (A3) of I for $\omega_i=\omega_{1s}$]). These terms are of higher order in the intensity, however, than the linear dependence exhibited by Rabi ($\frac{1}{2}\Omega^2$) broadening.

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APPENDIX

R_2 [Eq. (5)] is defined by the parameters (in s^{-1})

$$\Omega=(8\pi F\alpha\omega)^{1/2}/E\,|\langle\psi_1|\,\hat{\rho}\cdot\vec{\nabla}|\,\psi_0\rangle|\,a_0\ , \tag{A1}$$

$$\Delta=(\omega_0-\omega_1)+\omega-(\hbar/2m_e)\Delta_r\ , \tag{A2}$$

$$R=(\hbar/m_e)\Gamma_r\ , \tag{A3}$$

where (in cm^{-2})

$$\Delta_r=-\left(\frac{8\pi F\alpha}{\omega}\right)\mathrm{Re}\sum_{n=0,2}^{2}\iint d\vec{r}\,d\vec{r}\,'\,\psi_1^*(\vec{r})(\hat{\rho}\cdot\vec{\nabla})\times g[\vec{r},\vec{r}\,';2(E_0+nE)]\times(\hat{\rho}\cdot\vec{\nabla}')\psi_1(\vec{r}\,')\ , \tag{A4}$$

$$\Gamma_r=-\left(\frac{8\pi F\alpha}{\omega}\right)\mathrm{Im}\iint d\vec{r}\,d\vec{r}\,'\,\psi_1^*(\vec{r})(\hat{\rho}\cdot\vec{\nabla})\times g[\vec{r},\vec{r}\,';2(E_0+2E)]\times(\hat{\rho}\cdot\vec{\nabla}')\psi(\vec{r}\,')\ , \tag{A5}$$

where $\psi_0(\vec{r})$ and $\psi_1(\vec{r})$ are the level-one and -two eigenstates with eigenfrequencies ω_0 and ω_1 (E_0 and E_1 in a.u.), ω is the photon frequency (E in a.u.), $\hat{\rho}$ is the unit vector in the direction of polarization of the photon, F is the flux, and g is the Green's function appropriate for the atomic field. We note the well-known relationship between the shift and width and the frequency-dependent polarizability of level two, $\alpha_1(\omega)$,

$$\lim_{\omega_0+\omega\to\omega_1}[(\hbar/m_e)\Delta_r+iR]=(8\pi F\omega/c)\alpha_1(\omega)\ , \tag{A6}$$

from which, setting $R=F\sigma_1$, where σ_1 is the level-two photoelectric cross section,

$$\sigma_1=(8\pi\omega/c)\,\mathrm{Im}\alpha_1(\omega)\ . \tag{A7}$$

After the angular integrations have been performed [for linearly polarized light and using Eq. (4a) of I], Eqs. (A1)–(A5) reduce a form already given in I. This can be recognized by setting $[I/(I_0\omega_p^2)]^{1/2}$ [see Eq. (1b) of I] equal to $[F/(F_0\omega_p)]^{1/2}$ a.u. or $(2\pi F\alpha/\omega)^{1/2}$ cm^{-1}. Then $\frac{1}{2}\Omega$ [Eq. (A1) above] reduces to the radial integral in the numerator of Eq. (14a) times $\hbar/(2m_e)$, and $\Delta-iR/2$ [Eqs. (A2) and (A3) above] reduce to the denominator of Eq. (14a) times $\hbar/(2m_e)$.

Finally we note a couple of notational errors in Eq. (A1) of I, namely, that $\frac{1}{2}k^2$ should be replaced by k^2 and the right-hand side should be multiplied by a minus sign. Also in Eq. (14c) U_{ij} and U_{1j} should be replaced by U_{1j} and U_{j1}, respectively [see Eq. (14b)]. Also, in Eq. (13) $\chi_1^{(aI)}$ should be replaced by $\chi_1^{(aI)}Y_{10}(\theta_r,\phi_r)$ [see Eqs. (4b) and (8)].

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[2]This assumption has been examined by de Meijere and Eberly (Ref. 3) and allows the initial time limit in the dynamical equations to be taken at $-\infty$ (also required in the Fourier transformation of I) rather than at 0.

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[9]It is hard to satisfy this inequality for two-photon ionization except at quite high power levels ($\sim 10^{13}$ W/cm^2) where the adiabatic assumptions of Refs. 3 and 6 may not hold. However, the theories of I and of Refs. 3 and 6 are easily generalized to four-photon resonant ionization where the inequality is satisfied at lower power levels ($\sim 10^9$ W/cm^2 for the four-photon ionization of Cs near the $6F$ resonance). For example, see M. Crance, J. Phys. B 11, 1931 (1978).