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LETTER TO THE EDITOR

Resonance two-photon ionisation with ultrashort laser pulses

D L Andrews

Departments of Mathematics and Chemistry, University College London, Gower Street, London WC1E 6BT, England

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Abstract. An expression is derived for the amount of two-photon ionisation produced by sub-nanosecond laser pulses under resonance conditions. On this time scale damping effects can be neglected and the ionisation probability becomes proportional to the cube of the pulse duration. A similar prediction for resonance multiphoton processes of higher order leads to a qualitative agreement with recent experimental observations. Finally, it is demonstrated that the same result can be obtained from a simple analysis of a two-step model.

Recently, much attention has been focused on theoretical and experimental studies of multiphoton ionisation: see for example the review by Lambropoulos (1976). One aspect of particular interest has been the behaviour under resonance conditions (Fedorov and Kazakov 1977), where the photon energy $\hbar\omega$, or an integral multiple of $\hbar\omega$, equals the difference in energy between two bound states of the atom. Selection of an incident frequency which satisfies such a condition can often result in a substantial enhancement of the ionisation probability. The conventional theory of resonance involves consideration of damping processes which limit this enhancement and give a width to the atomic energy levels. Since it is typically associated with the nanosecond time scale, the damping plays an important role even in studies using pulses of about 10^{-8} s from a Q-switched laser. However, the situation is quite different when picosecond pulses from a mode-locked laser are employed; in this case the damping is likely to be relatively unimportant.

In this letter the theory of resonance ionisation with ultrashort pulses is developed using the framework of quantum electrodynamics. Taking the simple example of a two-photon process, it is demonstrated that even when damping is completely disregarded, the resonance transition probability is still finite and has a cubic dependence on the pulse duration; higher order multiphoton processes are expected to exhibit similar behaviour. The results indicate that the amount of ionisation should be *smaller* for picosecond pulses than is predicted by the conventional theory. This accords with recent experimental observations (Lompre *et al* 1976, 1977).

Let us consider the process where an atomic electron is promoted from an initial state $|i\rangle$ to a continuum state $|k\rangle$ through absorption of two photons of frequency ω, the transition proceeding through an intermediate bound state $|r\rangle$ which satisfies the condition

$$\omega_{ri} \equiv \omega_r - \omega_i = \omega. \tag{1}$$

The Hamiltonian for the system comprising the atom and the field may be written as

$$H = H_0 + H_{\text{int}} \tag{2}$$

$$H_0 = H_{\text{atom}} + H_{\text{rad}}. \tag{3}$$

We take the electric dipole approximation for H_{int}, i.e.

$$H_{\text{int}} = -\boldsymbol{\mu}.\boldsymbol{e}^{\perp} \tag{4}$$

and assume that this interaction may be treated as a perturbation on the basis eigenstates of H_0. The initial state of the system, with n photons in the incident radiation mode, is represented by $|i;n\rangle$; the resonant intermediate state is $|r;(n-1)\rangle$ and the final state $|k;(n-2)\rangle$. The two-photon ionisation probability at time t, if the laser pulse first impinges on the atom at time $t = 0$, is given by

$$P(t) = \int |c(t)|^2 \rho_k \, \mathrm{d}E_k \tag{5}$$

where ρ_k is the density of states around the continuum energy level E_k, and

$$c(t) = \langle (n-2);k|U(t,0)|i;n\rangle. \tag{6}$$

The time-evolution operator $U(t,0)$ is expressible as the series

$$U(t,0) = 1 + \sum_{n=1}^{\infty} \left(\frac{1}{\mathrm{i}\hbar}\right)^n \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \ldots \int_0^{t_{n-1}} \mathrm{d}t_n \, \tilde{H}_{\text{int}}(t_1)\tilde{H}_{\text{int}}(t_2)\ldots\tilde{H}_{\text{int}}(t_n) \tag{7}$$

with

$$\tilde{H}_{\text{int}}(t) = \exp(\mathrm{i}H_0 t/\hbar)\, H_{\text{int}} \exp(-\mathrm{i}H_0 t/\hbar). \tag{8}$$

The leading contribution to (6) comes from the $n = 2$ term in (7), and by introducing a complete set of states between $\tilde{H}_{\text{int}}(t_1)$ and $\tilde{H}_{\text{int}}(t_2)$ and retaining only the dominant resonance term, we obtain

$$c(t) \simeq -\frac{1}{\hbar^2} \int_0^t \mathrm{d}t_1 \langle (n-2);k|\exp(\mathrm{i}H_0 t/\hbar) H_{\text{int}} \exp(-\mathrm{i}H_0 t/\hbar)|r;(n-1)\rangle$$
$$\times \int_0^{t_1} \mathrm{d}t_2 \langle (n-1);r|\exp(\mathrm{i}H_0 t/\hbar) H_{\text{int}} \exp(-\mathrm{i}H_0 t/\hbar)|i;n\rangle. \tag{9}$$

After performing the time integrations and calculating the matrix elements of H_{int} using the usual mode expansions for the electric field, we find

$$|c(t)|^2 \simeq \frac{4\pi^2 I^2}{\hbar^4 c^2} |\boldsymbol{\mu}^{kr}.\boldsymbol{e}|^2 |\boldsymbol{\mu}^{ri}.\boldsymbol{e}|^2 f(\omega', t). \tag{10}$$

Here I is the irradiance of the incident light, $\boldsymbol{e}$ is the polarisation vector and

$$\omega' \equiv \omega_{ki} - 2\omega. \tag{11}$$

The function $f(\omega', t)$, given by

$$f(\omega', t) = \frac{1}{\omega'^4}(2 + \omega'^2 t^2 - 2\cos\omega' t - 2\omega' t \sin\omega' t) \tag{12}$$

here plays a role similar to that of the function $(1 - \cos\omega' t)/\omega'^2$ in the conventional

treatment of non-resonant two-photon absorption. Both functions have an ω' dependence which peaks strongly at the origin, with a peak width inversely proportional to t; also both functions rapidly tend to zero outside this region. Thus when t becomes large compared to an optical cycle, $|c(t)|^2$ only makes significant contributions to (5) when

$$E_k \simeq \hbar(\omega_i + 2\omega) \tag{13}$$

and hence the limits of the integral can be extended to $\pm\infty$ in the usual way with μ^{kr} and ρ_k evaluated at $\omega' = 0$ and taken outside the integral. The result for the ionisation probability is then found to display a cubic dependence on the pulse duration t:

$$P(t) \simeq \frac{8\pi^3 I^2 t^3}{3\hbar^3 c^2} |\boldsymbol{\mu}^{kr} \cdot \boldsymbol{e}|^2 |\boldsymbol{\mu}^{ri} \cdot \boldsymbol{e}|^2 \rho_k. \tag{14}$$

By similar methods the resonance ionisation probability for higher order processes can also be shown to vary with t^3 (see also Fedorov and Kazakov 1977).

The result (14) differs from the expression derived from the usual damping theory by a factor $\Gamma^2 t^2/12$, where Γ is the half-width of the Lorentzian line shape. We can therefore conclude that the amount of ionisation produced by a picosecond pulse at the resonant frequency is appreciably less than the conventional theory allows, and also less than should be expected from a longer pulse of the same frequency, polarisation and intensity. Such observations are borne out by recent experimental studies (Lompre *et al* 1976, 1977).

We conclude by noting that (14) can also be obtained from a calculation of the probability for *sequential* two-photon ionisation. Since the first transition is between the discrete levels $|i\rangle$ and $|r\rangle$, the corresponding transition probability is quadratic in time:

$$P_{ri}(t) = \frac{2\pi I t^2}{\hbar^2 c} |\boldsymbol{\mu}^{ri} \cdot \boldsymbol{e}|^2. \tag{15}$$

As the second transition $|k\rangle \leftarrow |r\rangle$ goes into the continuum, however, its transition probability is given by the usual Fermi rule,

$$P_{kr}(t) = \frac{4\pi^2 I t}{\hbar c} |\boldsymbol{\mu}^{kr} \cdot \boldsymbol{e}|^2 \rho_k. \tag{16}$$

Since other excitation and decay channels play a relatively unimportant role, they can to a good approximation be disregarded, so that the probability for the overall transition $|k\rangle \leftarrow |i\rangle$ is given by the formula

$$P_{ki}(t) = \int_0^t \dot{P}_{kr}(\tau) P_{ri}(\tau)\, \mathrm{d}\tau \tag{17}$$

which reproduces equation (14). The fact that this same result is obtained reflects the assumption of a single channel in which the transition to the continuum provides the only escape route from the intermediate state; a more general analysis of the rate equations would lead to a result giving (14) as a first approximation. Although this discussion has concerned absorption of two photons from the same radiation mode, analogous results can be expected if the two photons have different polarisations.

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