

# Renormalised Perturbation Theory of Resonant Multiphoton Ionisation

*K. Unnikrishnan*

Department of Theoretical Physics, Research School of Physical Sciences and Engineering, Australian National University, Canberra, ACT 0200, Australia.

## *Abstract*

Perturbation theory of multiphoton ionisation due to a classical electromagnetic field is modified to allow for intermediate resonances with bound states. Complex energies, generally associated with resonances, do not enter into this formalism. For a monochromatic field of frequency  $\nu$ , a constant ionisation rate can then be defined unambiguously and only such continuum states are excited which correspond to the absorption of energy in integral multiples of  $h\nu$ . As an application, differential and total cross sections for the two-photon ionisation of hydrogen, for frequencies below the  $n = 3$  resonance region, are obtained in closed form. Existing data for generalised cross sections, calculated numerically using the complex coordinate method, are in good agreement with the present results. Finally, the mean fractional ionisation resulting from a pulse of finite duration is estimated on the basis of the associated power spectrum. For short pulses, the time dependence of ionisation exhibits a departure from that expected of a time-independent rate.

## 1. Introduction

Owing to a breakdown of the perturbation theory of transitions due to an electromagnetic field when intermediate resonances with bound states occur, theoretical studies of resonant multiphoton ionisation (RMPI) generally rely on the notion that this phenomenon can be looked upon as the decay of a nonstationary state with a complex quasi-energy, engendered by a non-Hermitian Hamiltonian, which is either phenomenological (Beers and Armstrong 1975; Holt *et al.* 1983) or constructed more formally (Faisal and Moloney 1981; Maquet *et al.* 1983). Inherent in these formulations, as well as the resolvent operator formalism (Gontier and Trahin 1979; Faisal 1987), is the assumption that the interaction is turned on at time  $t = 0$  and never switched off. Therefore, what these calculations actually yield are the time-dependent occupation amplitudes of the dressed states of the total (atom+field) Hamiltonian. On the other hand, if ionisation is considered to be a transition from a bound state to a continuum state of the atomic Hamiltonian under the influence of a transient electromagnetic field, time-dependent  $S$ -matrix theory should be appropriate to describe this process. However, as mentioned earlier, in the vicinity of an intermediate resonance, the most common means of evaluating the  $S$  matrix, viz. perturbation theory, breaks down even for a weak perturbation. We have shown recently (Unnikrishnan 1993) that, in the absence of a continuous spectrum, Floquet theory can be adapted to prove that, for a monochromatic field of angular frequency  $\omega$ , the only

nonvanishing  $S$ -matrix elements correspond to the absorption of energy in multiples of  $h\omega$ , and that the amplitudes for such transitions can be expressed in terms of certain parameters which may be calculated nonperturbatively. Transitions to a continuum, however, present a peculiar problem, because of the fact that it is, in general, impossible to find an exact solution of the Schrödinger equation for an atom in an electromagnetic field, which reduces to a bound state in the absence of the interaction. In fact, the eigenenergy corresponding to the unperturbed initial (bound) state becomes complex, so that the resulting eigenvector cannot belong to the usual Hilbert space. (A discussion of this and related issues may be found in Prigogine 1992; see also Sudarshan 1994.) However, it is also well known (Heitler 1954) that the interpretation of the imaginary part of the energy as a decay rate, on which the non-Hermitian Hamiltonian methods ultimately depend, is valid only in the limit when this part is much smaller than the real part. Since, in perturbation theory, the imaginary part arises from terms with vanishing denominators in the *continuum* sector of the spectrum, it is reasonable to expect that as long as the continuum is treated to lowest order in perturbation theory, an  $S$ -matrix approach should be feasible and also that the rates thus obtained should agree with those estimated from the imaginary part of a complex energy, whenever a transition rate can be defined at all. This paper presents such an  $S$ -matrix approach to RMPI which involves no complex energies and is free from divergences.

In the following section, we first describe in some detail a simple formalism applicable to two-photon ionisation in the presence of a one-photon resonance. The resulting expression for the transition amplitude is then shown to be derivable from Floquet theory under certain approximations. This immediately leads to an extension of the formalism to include any number of bound states exactly and the treatment of RMPI of any order. Using the simpler formalism, closed-form expressions for two-photon ionisation cross sections for hydrogen in the frequency range below the  $n = 3$  resonance are presented and evaluated as a function of  $\omega$  to show the resonance structure near  $\omega = 3/8$ . (Atomic units are used in this work.) In the non-resonance region, these expressions reduce to those of standard second order perturbation theory, while near resonance they reproduce previous numerical results based on the complex energy approach quite well. Finally, the average fractional ionisation at the end of a rectangular pulse of duration  $T$  is estimated on the basis of the associated power spectrum, which displays a nonexponential behaviour for small  $T$ , but agrees with the usual exponential buildup resulting from a constant ionisation rate corresponding to the mean frequency, after several Rabi periods.

## 2. Formalism

Consider a single active electron in a potential  $W(\mathbf{r})$  with a Hamiltonian  $H_0 = p^2/2 + W$  having both discrete and continuum eigenstates  $\phi_a$  such that  $H_0\phi_a = \epsilon_a\phi_a$ . Let the adiabatically switched electromagnetic field be represented, in the dipole approximation, by  $\mathbf{E} = \mathbf{E}_0 \exp(-\eta|t|)\cos\omega t$  (with  $\eta$  ultimately tending to zero), so that the interaction potential may be written as

$$V(t) = 2V e^{-\eta|t|} \cos\omega t, \quad V = \frac{\mathbf{E}_0 \cdot \mathbf{r}}{2}. \quad (1)$$

As in Unnikrishnan (1993), we look for an 'in' state  $\psi_i$  evolving from the initial (discrete) state  $\phi_i \exp(-i\epsilon_i t)$  of the general form

$$\psi_i = e^{-i(\epsilon_i + \Delta_i e^{-\eta|t|})t} [\phi_i + e^{-\eta|t|} \{F_i(\mathbf{r}, t) - \phi_i\}], \quad (2)$$

satisfying the Schrödinger equation

$$i\dot{\psi}_i = [H_0 + V(t)]\psi_i, \quad (3)$$

where  $F_i$  can be chosen (Unnikrishnan 1993) to be the solution of (3) in the limit  $\eta \rightarrow 0$  such that  $F_i \rightarrow \phi_i$  as  $V \rightarrow 0$ . As mentioned earlier, since  $H_0$  has a continuous spectrum, such a solution will not generally exist (Prigogine 1992). However, we shall show that, if the coupling to the continuum is weak enough to be treated by perturbation theory, one can construct solutions possessing the above property. [This is analogous to the case of the ordinary (d.c.) Stark effect in hydrogen, where the Schrödinger equation admits of no true bound states since the potential  $Ez + 1/r$  has no lower bound as  $z \rightarrow -\infty$ , though one can construct such states in any order of perturbation theory.] The essence of the proposed method is quite simply brought out by considering the case of a two-photon transition to the continuum when resonance with a bound state is possible with the absorption of one photon.

### (2a) Intermediate Resonance in Two-photon Ionisation

In the absence of any resonance, one may expand an eigenfunction  $\psi$  of the total Hamiltonian as

$$\psi = \sum_{r=1}^{\infty} a_r(t) e^{-i\epsilon_r t} \phi_r \quad (4)$$

(where the summation also includes an integration over the continuum), and determine  $a_r$  by perturbation theory. To take into account the possibility of a resonance between two levels, say  $\phi_1$  and  $\phi_2$ , we first determine  $a_1$  and  $a_2$  nonperturbatively and then use them to calculate  $a_r$ ,  $r \geq 3$ , by perturbation theory. This procedure has been successfully employed to study electron-atom scattering in a laser field (Unnikrishnan 1988) in a similar situation. In the range of intensity where a perturbative treatment of the continuum is reasonable, the two resonant bound states can be treated using the rotating wave approximation (RWA). The required pair of solutions for  $a_1$  and  $a_2$  which ensures that  $\psi \rightarrow \phi_1 \exp(-i\epsilon_1 t)$  as  $V \rightarrow 0$  may then be written as

$$a_1 = \alpha e^{-i\Delta_1 t}, \quad (5)$$

$$a_2 = \beta e^{-i(\epsilon_1 + \Delta_1 + \omega - \epsilon_2)t}, \quad (6)$$

where

$$\alpha = \sqrt{\frac{\Omega - \epsilon}{2\Omega}}, \quad \beta = -\sqrt{\frac{\epsilon + \Omega}{2\Omega}}, \quad \Delta_1 = -\frac{\epsilon + \Omega}{2}, \quad \epsilon < 0, \quad (7a)$$

$$\alpha = \sqrt{\frac{\Omega + \epsilon}{2\Omega}}, \quad \beta = \sqrt{\frac{\Omega - \epsilon}{2\Omega}}, \quad \Delta_1 = \frac{\Omega - \epsilon}{2}, \quad \epsilon > 0, \quad (7b)$$

$$\epsilon = \omega - (\epsilon_2 - \epsilon_1), \quad \Omega = \sqrt{\epsilon^2 + 4|V_{12}|^2},$$

and  $V_{nk} = \langle \phi_n | V | \phi_k \rangle$ . Using the zeroth order approximation  $a_m^{(0)} \equiv 0$ ,  $m \geq 3$ , perturbation theory then gives

$$a_m^{(1)} = -2i \int_{-\infty}^t dt [a_1 e^{i\epsilon_{m1}t} V_{m1} + a_2 e^{i\epsilon_{m2}t} V_{m2}] \cos \omega t, \quad (8)$$

where  $\epsilon_{mn} = \epsilon_m - \epsilon_n$ . Substituting for  $a_1$  and  $a_2$  from (5) and (6), we get

$$a_m^{(1)} = \alpha \frac{V_{m1} e^{-i(\omega + \Delta_1 + \epsilon_1 - \epsilon_m)t}}{\omega + \Delta_1 + \epsilon_1 - \epsilon_m} + \beta \frac{V_{m2} e^{-i(2\omega + \Delta_1 + \epsilon_1 - \epsilon_m)t}}{2\omega + \Delta_1 + \epsilon_1 - \epsilon_m}. \quad (9)$$

Since, according to the discussion in the previous section, the function  $F_1$  of (2), with  $i = 1$ , is related to the  $\psi$  of (4) through

$$\psi = e^{-i(\epsilon_1 + \Delta_1)t} F_1, \quad (10)$$

then  $F_1$ , correct to the first order, is given by

$$F_1^{(1)} = \alpha \phi_1 + \beta e^{-i\omega t} \phi_2 + \sum_{m \geq 3} \left[ \frac{\alpha V_{m1} e^{-i\omega t}}{\omega + \Delta_1 + \epsilon_1 - \epsilon_m} + \frac{\beta V_{m2} e^{-2i\omega t}}{2\omega + \Delta_1 + \epsilon_1 - \epsilon_m} \right] \phi_m. \quad (11)$$

(It might be worth pointing out here that, since the resonant levels are treated nonperturbatively, the term 'order' only refers to couplings with the remaining states.) The  $S$ -matrix element for ionisation to a continuum specified by momentum  $\mathbf{k}$  may now be calculated by using (1), (2) and (11) in

$$S_{k1} = -i \lim_{\eta \rightarrow 0} \int_{-\infty}^{\infty} e^{-i\epsilon_k t} dt \langle \phi_k | V(t) | \psi_1 \rangle, \quad (12)$$

where  $\epsilon_k = \frac{1}{2}k^2$ .

With the aid of equations (13) and (14) of Unnikrishnan (1993), we then get the  $S$ -matrix element corresponding to the absorption of two photons as

$$S_{k1}^{(2)} = -2\pi i T_{k1}^{(2)} \delta(\epsilon_k - \epsilon_1 - 2\omega), \quad (13)$$

$$T_{\mathbf{k}1}^{(2)} = - \left[ \alpha \sum_{m \geq 3} \frac{V_{\mathbf{k}m} V_{m1}}{\epsilon_m - \epsilon_1 - \omega - \Delta_1} - \beta V_{\mathbf{k}2} \right]. \quad (14)$$

The differential cross section for the emission of an electron per unit solid angle around  $\mathbf{k}$  may now be calculated as in conventional perturbation theory. We know that, according to second order perturbation theory, the formula corresponding to (14) above is

$$T_{\mathbf{k}1}^{(2)} = -(E_0/2)^2 \tilde{M}, \quad (15a)$$

$$\tilde{M} = - \sum_m \frac{(\hat{\mathbf{E}}_0 \cdot \mathbf{r})_{\mathbf{k}m} (\hat{\mathbf{E}}_0 \cdot \mathbf{r})_{m1}}{\epsilon_m - \epsilon_1 - \omega}, \quad (15b)$$

and that the differential cross section is given by (Zernik 1964)

$$\frac{d\sigma}{d\Omega} = \frac{I}{4\pi c I_0} |\tilde{M}|^2 k\omega (a_0^2/\text{sr}), \quad (16)$$

where  $I$  is the intensity in  $\text{W cm}^{-2}$ ,  $I_0 = 7.019 \times 10^{16} \text{ W cm}^{-2}$ ,  $c = 137$  and  $a_0$  is the Bohr radius. Since (13) has the same *form* as in second order perturbation theory, (16) also gives the differential cross section in the present case, with  $|\tilde{M}|$  replaced by

$$|M| = \left| \alpha \sum_{m \geq 3} \frac{(\hat{\mathbf{E}}_0 \cdot \mathbf{r})_{\mathbf{k}m} (\hat{\mathbf{E}}_0 \cdot \mathbf{r})_{m1}}{\epsilon_m - \epsilon_1 - \omega - \Delta_1} - \frac{4\beta}{E_0^2} V_{\mathbf{k}2} \right|. \quad (17)$$

Notice that, since  $\alpha$  and  $\beta$  are intensity-dependent, the cross section is no longer proportional to  $I$ . Calculation of cross sections using the above formulae is carried out in Section 3 for hydrogen. Before that, we shall show how (14) may be derived on the basis of the Floquet theory of the  $S$  matrix, since this paves the way for further generalisation.

### (2b) Connection with Floquet Theory

According to the Floquet theory of the  $S$ -matrix (Unnikrishnan 1993), if the function  $F_a(\mathbf{r}, t)$  corresponding to the reference state  $\phi_a$  can be expressed as

$$F_a = \sum_n e^{-in\omega t} \sum_\mu \alpha_{n\mu}^a \phi_\mu, \quad (18)$$

the amplitude for the transition  $\phi_i \rightarrow \phi_f$  with the absorption of  $n$  photons is given by

$$T_{fi}^{(n)} = (\Delta_i - \Delta_f) \alpha_{0f}^{f*} \alpha_{nf}^i, \quad \epsilon_f = \epsilon_i + n\omega. \quad (19)$$

Now, equation (11) for  $F_1$  is indeed of the same form as (18), but does not contain all the leading terms in  $\exp(-2i\omega t)$ . The first term on the right-hand side of (9) also contributes in the next order, which is readily calculated just as  $a_m^{(1)}$ . Collecting these terms, we get finally

$$\alpha_{2k}^1 = \frac{1}{2\omega + \Delta_1 + \epsilon_1 - \epsilon_k} \left[ \alpha \sum_{m \geq 3} \frac{V_{km} V_{m1}}{\omega + \Delta_1 + \epsilon_1 - \epsilon_m} + \beta V_{k2} \right]. \quad (20)$$

In the spirit of perturbation theory, we now set  $\alpha_{0f}^f = 1$  and  $\Delta_f = 0$ , where  $f$  denotes the final continuum state. (This is equivalent to the assumption that, if we start with the continuum state, its level shift and depletion due to the interaction with the field are negligible.) Equations (19) and (20), together with the energy conservation condition  $\epsilon_k = \epsilon_1 + 2\omega$ , then yield (14).

The generalisation of the formalism to treat any number of bound states nonperturbatively is now obvious. Let us expand  $F_1$  as

$$F_1 = \sum_{n=-\infty}^{\infty} e^{-in\omega t} \sum_{\mu \in B} \alpha_{n\mu} \phi_{\mu} + \sum_{\nu \notin B} e^{i(\epsilon_1 + \Delta_1)t} a_{\nu}(t) e^{-ie\nu t} \phi_{\nu}, \quad (21)$$

where  $B$  represents all the bound states of interest. If we neglect the second term on the right-hand side,  $\alpha_{n\mu}$  and  $\Delta_1$  may be calculated without any further approximation, as described in Unnikrishnan (1993). In the zeroth order, we have  $\alpha_{\nu}^{(0)} \equiv 0$ . Higher orders can be calculated as before using perturbation theory, and it may be verified that the resulting expression for  $F_1$  will have the required form (equation 18). The transition amplitude from  $\phi_1$  to  $\phi_k$  is then given by  $\Delta_1 \alpha_{nk}$ , for  $\phi_k$  such that  $\epsilon_k = \epsilon_1 + n\omega$ .

### 3. Two-photon Ionisation of Hydrogen

We may now use the results of Section 2a to express the two-photon ionisation cross section of hydrogen for frequencies across the 1s–2p resonance ( $\omega = 3/8$ ), but below the next ( $n = 3$ ) resonance, in closed form. Though this can be done retaining the level shift  $\Delta_1$  in the denominator of the first term on the right of (17), in the intensity range where this simplified approach is valid,  $\Delta_1$  will be much less than  $(\epsilon_{m_1} - \omega)$  for all  $m \geq 3$ , and hence may be safely dropped. This facilitates the use of the analytical results of Klarsfeld (1969) with only minor modifications, as described below. Klarsfeld has evaluated the second order matrix element in the radiation gauge which, in the dipole approximation, is

$$M_{k1}^{K\ell} = \sum_{m \geq 2} \frac{\langle k | \hat{A}_0 \cdot \mathbf{p} | m \rangle \langle m | \hat{A} \cdot \mathbf{p} | 1 \rangle}{\epsilon_m - \epsilon_1 - \omega}, \quad (22)$$

where  $\mathbf{A}_0 = c\mathbf{E}_0/\omega$ . The transition matrix element in this gauge, corresponding to (15a), is given by

$$T_{k1}^{K\ell} = \frac{A_0^2}{c^2} M_{k1}^{K\ell}. \quad (23)$$

Since the on-the-energy shell  $T$ -matrix elements are gauge-invariant (e.g. Peticolas *et al.* 1968), comparison of equations (15a) and (15b) with (22) and (23) enables us to rewrite (17) (neglecting  $\Delta_1$ ) as

$$|M| = \left| \alpha \left[ \frac{M_{\mathbf{k}_1}^{K\ell}}{\omega^2} - \frac{\langle \mathbf{k} | \hat{\mathbf{E}}_0 \cdot \mathbf{r} | 2p_0 \rangle \langle 2p_0 | \hat{\mathbf{E}}_0 \cdot \mathbf{r} | 1 \rangle}{\epsilon_2 - \epsilon_1 - \omega} \right] - \frac{2\beta}{E_0} \langle \mathbf{k} | \hat{\mathbf{E}}_0 \cdot \mathbf{r} | 2 \rangle \right|. \quad (24)$$

Here  $M_{\mathbf{k}_1}^{K\ell}$  is already available in closed form (Klarsfeld 1969), and it is straightforward to evaluate the remaining matrix elements analytically. The final expressions are given below in terms of the following parameters (all quantities in a.u.):

$$x = 2\omega, \quad \xi = (1 - x)^{-1/2}, \quad \eta = (2x - 1)^{-1/2},$$

$$z = \frac{1 - \xi}{1 + \xi} e^{i\phi}, \quad \phi = 2 \tan^{-1}(\xi/\eta),$$

$$C = 2^7 \sqrt{\pi} e^{\pi\eta/2} \Gamma(1 - i\eta), \quad \cos \theta = \hat{\mathbf{E}}_0 \cdot \hat{\mathbf{k}},$$

$$M_{\mathbf{k}_1}^{K\ell} = -C \left[ A + \frac{\xi^2}{\eta^2} R \cos^2 \theta \right], \quad (25)$$

$$A = \xi x^{-2} e^{-\eta\phi} e^{i\phi} (2 - \xi)^{-1} (1 + \xi)^{-4} F_1(2 - \xi; 3 + i\eta, 1 - i\eta, 3 - \xi; z, z^*), \quad (25a)$$

$$\begin{aligned} R = & 2x^{-3} \xi^{-2} e^{-\eta\phi} (2 - \xi)^{-1} (1 + \xi)^{-4} (1 - i\eta)(2 - i\eta) \\ & \times \left[ F_1(2 - \xi; 3 + i\eta; 3 - i\eta; 3 - \xi; z, z^*) - \left( \frac{1 - \xi}{1 + \xi} \right)^2 \left( \frac{2 - \xi}{4 - \xi} \right) \right. \\ & \left. \times F_1(4 - \xi; 3 + i\eta, 3 - i\eta; 5 - \xi; z, z^*) \right], \quad (25b) \end{aligned}$$

$$\langle 2p_0 | \hat{\mathbf{E}}_0 \cdot \mathbf{r} | 1 \rangle = 2^{15/2} / 3^5, \quad (26)$$

$$\langle \mathbf{k} | \hat{\mathbf{E}}_0 \cdot \mathbf{r} | 2p_0 \rangle = C(\mathcal{A} + \mathcal{B} \cos^2 \theta), \quad (27)$$

$$\mathcal{A} = \frac{\sqrt{2}(2k - i)^2}{(1 + 4k^2)^4} \exp\left( -\frac{1}{k} \tan^{-1} \frac{k}{-k^2 + \frac{1}{4}} \right), \quad (27a)$$

$$\mathcal{B} = \frac{2\sqrt{2}(k-i)(2k-i)}{(1+4k^2)^4}. \quad (27b)$$

Using these in (24), we may express  $|M|$  as

$$|M| = C(A_1 + A_2 \cos^2\theta), \quad (28)$$

$$A_1 = \frac{\alpha A}{\omega^2} - \mathcal{A} \left( \beta + \alpha \frac{2^{10}\sqrt{2}}{3^5} \frac{\xi^2}{4 - \xi^2} \right), \quad (28a)$$

$$A_2 = \frac{\alpha \xi^2 R}{\eta^2 \omega^2} - \mathcal{B} \left( \beta + \alpha \frac{2^{10}\sqrt{2}}{3^5} \frac{\xi^2}{4 - \xi^2} \right), \quad (28b)$$

Replacing  $|\tilde{M}|$  in (16) by  $|M|$ , we may express the differential cross section in the same form as in second order perturbation theory (Klarsfeld 1970) as

$$\frac{d\sigma}{d\Omega} = (\tilde{A} + \tilde{B} \cos^2\theta + \tilde{C} \cos^4\theta) I(a_0^2/\text{sr}), \quad (29)$$

where  $\cos\theta = \hat{\mathbf{E}} \cdot \mathbf{k}$  and the new (intensity-dependent) coefficients are given by

$$\tilde{A} = K|A_1|^2, \quad \tilde{B} = 2K \operatorname{Re}(A_1^* A_2),$$

$$\tilde{C} = K|A_2|^2 \quad \text{and} \quad K = \frac{2^{13}\pi\omega}{cI_0(1 - e^{-2\pi\eta})}.$$

Integrating over the angles, the total cross section is then given by

$$\sigma = 4\pi \left( \tilde{A} + \frac{\tilde{B}}{3} + \frac{\tilde{C}}{5} \right) I(a_0^2). \quad (30)$$

For comparison with existing data, one may also calculate the generalised cross section, which is independent of the intensity in lowest order perturbation theory (e.g. Faisal 1987), from

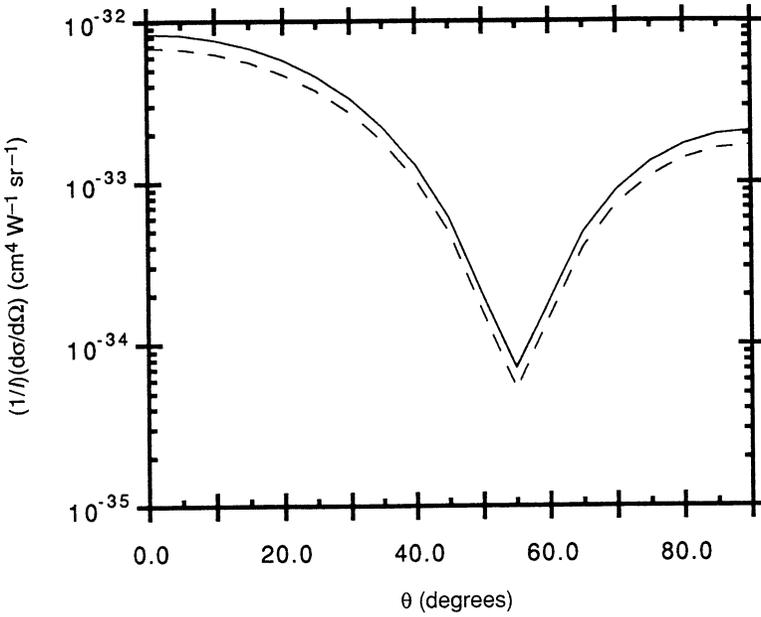
$$\sigma_G = \frac{\sigma\omega}{I} (\text{a.u.}) = \frac{\sigma\omega}{I} \times 4.36 \times 10^{-18} \text{cm}^4 \text{s}. \quad (31)$$

Calculations using the above equations have been carried out for  $0.3 \leq \omega \leq 0.41$ , i.e. in the frequency range where the only resonance of consequence is due to

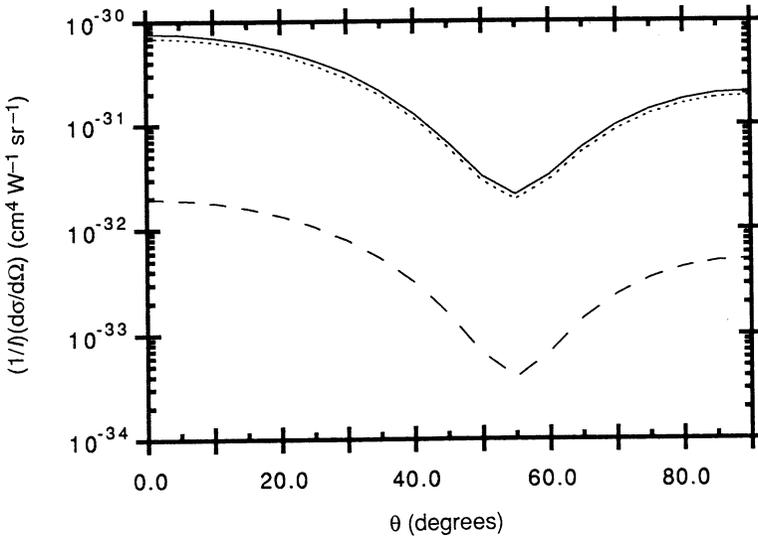
the 2p state. [It may be explicitly verified that the residues of the first and second terms on the right of (24) at the common pole  $\omega = \frac{3}{8}$  cancel exactly, so that  $M$  has no singularity at this point, i.e. the perturbation theory has been 'renormalised' Faisal (1987).] Values of the coefficients governing the differential cross section are given in Table 1, for several wavelengths around the 1s-2p resonance, extending up to the nonresonance region. The values labelled 'a' are from Klarsfeld (1970) and represent second order perturbation theory. [As is evident from equations (25) and (28), the functional dependence on  $\cos\theta$  is the same in both cases.] Entries marked 'b' and 'c' refer to the present work and represent the low and high intensity regimes respectively. The last column gives the total cross section per unit intensity. As expected, far away from resonance, the three calculations are in reasonable agreement with one another and as exact resonance is approached, deviations from standard perturbation theory set in sooner, the higher the intensity. Variation of the differential cross section per unit intensity, which is independent of the intensity in second order perturbation theory, with the scattering angle  $\theta$ , is illustrated in Figs 1 and 2 at  $\omega = 0.36$  and  $\omega = 0.374$ , respectively. [As is clear from (29) the differential cross section is symmetric about  $\theta = 90^\circ$ .] No other comparable data for differential cross sections in the resonance region could be found in the literature.

**Table 1. Differential cross section parameters (equation 29) and total cross section per unit intensity for two-photon ionisation of hydrogen: a, second order perturbation theory; b and c, renormalised perturbation theory at intensity  $I = 8.77 \times 10^9$  and  $5.48 \times 10^{12}$  W cm $^{-2}$  respectively (numbers in parentheses represent power of ten)**

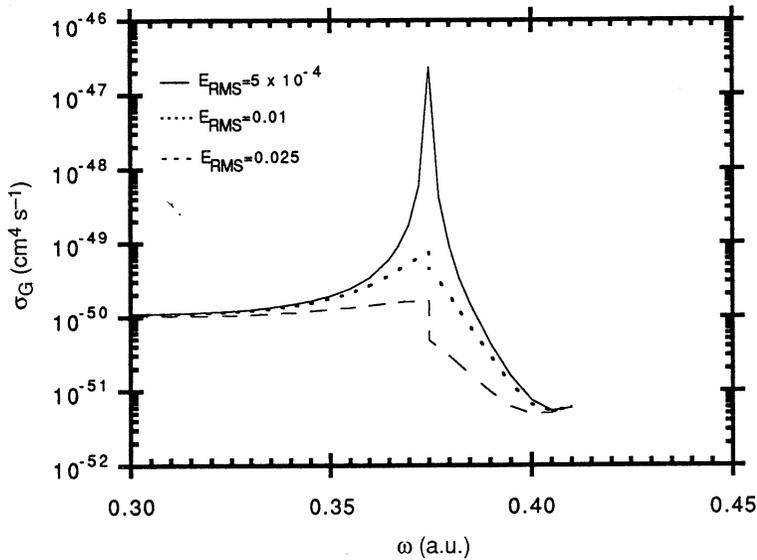
$\lambda$ (Å)		$\tilde{A}$	$\tilde{B}$	$\tilde{C}$	$\sigma/I$ (cm $^4$ W $^{-1}$ )
1122	a	2.310 (-35)	-3.113 (-35)	5.709 (-35)	3.034 (-34)
	b	2.311 (-35)	-3.115 (-35)	5.712 (-35)	3.035 (-34)
	c	2.290 (-35)	-3.642 (-35)	6.545 (-35)	2.998 (-34)
1200	a	5.616 (-33)	-2.790 (-32)	4.152 (-32)	5.803 (-32)
	b	5.591 (-33)	-2.778 (-32)	4.133 (-32)	5.778 (-32)
	c	1.412 (-33)	-6.642 (-33)	9.870 (-33)	1.473 (-32)
1210	b	5.310 (-32)	-2.771 (-31)	4.146 (-31)	5.486 (-31)
	c	2.595 (-33)	-1.281 (-32)	1.916 (-32)	2.710 (-32)
1215	b	1.385 (-29)	-7.361 (-30)	1.104 (-29)	1.431 (-29)
	c	3.372 (-33)	-1.694 (-32)	2.539 (-32)	3.526 (-32)
1220	b	1.129 (-31)	-6.109 (-31)	9.178 (-31)	1.167 (-30)
	c	5.037 (-33)	-2.805 (-32)	4.214 (-32)	5.170 (-32)
1230	b	1.336 (-32)	-7.418 (-32)	1.118 (-30)	1.382 (-31)
	c	3.868 (-32)	-2.184 (-32)	3.290 (-32)	3.982 (-32)
1250	b	3.419 (-33)	-1.967 (-32)	2.977 (-32)	3.542 (-32)
	c	2.317 (-33)	-1.341 (-32)	2.029 (-32)	2.394 (-32)
1300	a	1.239 (-33)	-7.413 (-33)	1.126 (-32)	1.283 (-32)
	b	1.240 (-33)	-7.415 (-33)	1.127 (-32)	1.283 (-32)
	c	1.147 (-33)	-6.868 (-33)	1.043 (-32)	1.186 (-32)
1450	a	8.307 (-34)	-4.948 (-33)	7.372 (-33)	8.240 (-33)
	b	8.309 (-34)	-4.950 (-33)	7.375 (-33)	8.243 (-33)
	c	8.217 (-34)	-4.893 (-33)	7.288 (-33)	8.146 (-33)
1700	a	1.230 (-33)	-6.592 (-33)	8.907 (-33)	1.024 (-32)
	b	1.231 (-33)	-6.594 (-33)	8.910 (-33)	1.024 (-32)
	c	1.226 (-33)	-6.568 (-33)	8.872 (-33)	1.020 (-32)



**Fig. 1.** Differential cross section per unit intensity as a function of the scattering angle at  $\omega = 0.36$ . Full curve, second order perturbation theory; dashed curve, renormalised theory at  $I = 5.48 \times 10^{12} \text{ W cm}^{-2}$ .



**Fig. 2.** Differential cross section per unit intensity as a function of the scattering angle at  $\omega = 0.374$ . Full curve, second order perturbation theory; dotted curve, renormalised theory at  $I = 8.77 \times 10^9 \text{ W cm}^{-2}$ ; and dashed curve, renormalised theory at  $I = 5.48 \times 10^{12} \text{ W cm}^{-2}$ .



**Fig. 3.** Generalised cross sections for two-photon ionisation of hydrogen as a function of the photon angular frequency  $\omega$ , for the three values of  $E_{\text{RMS}} = E_0/\sqrt{2}$  (a.u.) shown.

Fig. 3 shows  $\sigma_G$  as a function of  $\omega$  for three field amplitudes,  $E_{\text{RMS}} = 0.0005$ ,  $0.01$  and  $0.025$  where  $E_{\text{RMS}}$  is the root mean square amplitude,  $E_{\text{RMS}} = E_0/\sqrt{2}$ . Maquet *et al.* (1983) have also estimated  $\sigma_G$  numerically for these cases, from the imaginary part of the energy of the dressed  $1s$  state. A comparison with their graphical results shows that both calculations are indeed in good agreement with each other [though at  $E_{\text{RMS}} = 0.025$ , the effect of the energy shift  $\Delta_1$  is already perceptible in the results of Maquet *et al.* (1983) close to resonance, but not in the present ones, since we have neglected  $\Delta_1$  in (17) while making these calculations].

#### 4. Ionisation by a Pulse of Finite Duration

In practice, the quantity of interest is the fraction of atoms ionised at the end of a pulse which lasts for a finite time. For a strictly monochromatic radiation of frequency  $\omega$ , the transition rate  $W = \sigma I/\omega$  has the usual statistical interpretation, viz.

$$W = \lim_{N \rightarrow \infty} \frac{n}{N}, \quad (32)$$

where  $N$  is the number of atoms in the initial state, of which  $n$  are ionised per unit time. The mean fractional ionisation after time  $T$  is then given by

$$P = 1 - \exp(-WT). \quad (33)$$

Let us now consider a rectangular pulse of duration  $T_p$ , which may be represented by the function

$$\begin{aligned} f(t) &= E_0 \sin \omega_0 t, & |t| \leq T \\ &= 0, & |t| > T, \end{aligned} \quad (34)$$

where  $T = T_p/2$ . The power spectrum corresponding to this pulse can be calculated by Fourier analysing  $f(t)$  (Sommerfeld 1949):

$$f(t) = \int_0^\infty \sin \omega t b(\omega) d\omega, \quad (35a)$$

$$b(\omega) = \frac{2}{\pi} \int_0^\infty f(\xi) \sin \omega \xi d\xi. \quad (35b)$$

To simplify the algebraic expressions, we follow Sommerfeld (1949), and consider only  $T$  such that  $\omega_0 T = 2\pi n$ ,  $n = 0, 1, \dots$ . Then we have

$$b(\omega) = \frac{2\omega_0 \sin \omega T}{\pi(\omega^2 - \omega_0^2)}, \quad (36)$$

and the normalised power spectrum is given by

$$I(\omega)d\omega = |b(\omega)|^2 d\omega / \int_0^\infty |b(\omega')|^2 d\omega'. \quad (37)$$

Thus, for a pulse of radiation of frequency  $\omega_0$  which lasts for a time period  $2T$ , the average ionisation rate is

$$\bar{W} = \int_{\omega_{\min}}^{\omega_{\max}} W(\omega) I(\omega) d\omega, \quad (38)$$

where, theoretically,  $\omega_{\max} = \infty$  and  $\Omega_{\min} = 0.25$  for two-photon ionisation of hydrogen though, in practice, the range of integration can be restricted further, depending on the bandwidth of  $I(\omega)$ . The mean fractional ionisation at the end of the pulse is then

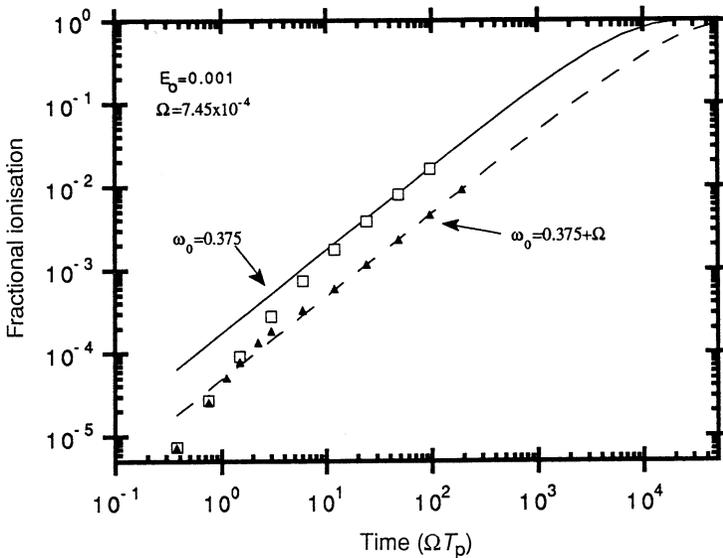
$$\bar{P} = 1 - e^{-\bar{W}T_p}. \quad (39)$$

In practice though,  $I(\omega)$  can be obtained in closed form from (36) and (37),  $\bar{W}$  has to be determined by quadrature, and the exact expression for  $I(\omega)$  is not well-suited for this purpose, being highly oscillatory. Now, as shown by Sommerfeld (1949),  $I(\omega)$  has a smooth envelope, whose full width at half maximum (FWHM) is equal to  $2\sqrt{2}/T$ . We may therefore approximate the power spectrum by a Gaussian distribution, having the same FWHM, i.e.

$$I(\omega) = \frac{1}{\sqrt{2\pi\sigma_1^2}} e^{-(\omega-\omega_0)^2/2\sigma_1^2}, \quad (40)$$

$$\sigma_1 = \frac{\text{FWHM}}{2.355} = \frac{1.201}{T}. \quad (41)$$

It is readily verified that, in the important region  $(\omega - \omega_0)T \ll 1$ , where  $b(\omega)$  is large, the exact expression is well represented by a Gaussian with  $\sigma_1 = \sqrt{1.5}/T$ , which agrees well with (41).



**Fig. 4.** Ionisation as a function of pulse length  $T_p$ . Curves represent values expected on the basis of a constant rate  $W(\omega_0)$ ; points refer to the full calculation.

The fractional ionisation  $\bar{P}$  calculated in this manner is shown in Fig. 4 as a function of  $T_p$  in units of the Rabi frequency  $\Omega$  at resonance. The field amplitude is chosen to be  $E_0 = 0.001$ , which corresponds to an intensity of  $3.51 \times 10^{10} \text{ W cm}^{-2}$ . Two situations are illustrated,  $\omega_0 = 0.375$  (exact resonance, open squares) and  $\omega_0 = 0.375 + \Omega$  (off-resonance, solid triangles). In each case, the ionisation due to a strictly monochromatic field of frequency  $\omega_0$  [given by  $P = 1 - \exp\{-W(\omega_0)T_p\}$ ] is also shown as full line and broken curves respectively. Using a phenomenological model having only the two resonant states and a non-Hermitian Hamiltonian, Holt *et al.* (1983) have also estimated the ionisation probability for the same field parameters. However, what they actually calculated was the time dependent probability that the two bound states are not occupied in the presence of the full interaction, whereas Fig. 4 shows the mean fraction of the initial atoms that are left in the ionised state after the radiation is switched off. The time development shown in Fig. 4 is therefore not quite the same as that predicted by Holt *et al.* (1983), though in both cases the approach to saturation is faster at resonance. In the initial stages, the ionisation is seen to be less than that predicted by a time-independent rate  $W(\omega_0)$ . The latter holds good after about 20 Rabi periods. At exact resonance,  $\bar{P}$  approaches  $P$  from below, while in the off-resonance case,  $\bar{P}$  first exceeds  $P$  at  $\Omega T_p \approx 2$  before finally approaching  $P$ . This behaviour can be understood by referring to Fig. 3. At exact resonance,  $W$  is maximum and therefore any spread in the frequency can only decrease the ionisation rate. In the other case, however,  $W$  increases towards resonance and

decreases away from it, so that depending on the bandwidth,  $\bar{P}$  may be more or less than  $P$ .

In conclusion, the formalism developed in this work provides a natural extension of the conventional perturbation theory, which allows for intermediate resonances with bound states. The only restriction is that the coupling to the continuum should be small enough for it to be treated perturbatively which, in any case, is a requisite for a constant transition rate to exist. It is worth stressing here that, saturation due to a sufficiently long pulse is always possible, even if the ionisation rate is small.

## References

- Beers, B. L., and Armstrong, L. Jr (1975). *Phys. Rev.* A **12**, 2447.  
Faisal, F. H. M. (1987). 'Theory of Multiphoton Processes' (Plenum: New York).  
Faisal, F. H. M., and Moloney, J. V. (1981). *J. Phys.* B **14**, 3603.  
Gontier, Y., and Trahin, M. (1979). *Phys. Rev.* A **19**, 264.  
Heitler, W. (1954). 'The Quantum Theory of Radiation' (Clarendon: Oxford).  
Holt, C. R., Raymer, M. G., and Reinhardt, W. P. (1983). *Phys. Rev.* A **27**, 2971.  
Klarsfeld, S. (1969). *Lett. Nuovo Cimento* **2**, 548.  
Klarsfeld, S. (1970). *Lett. Nuovo Cimento* **3**, 395.  
Maquet, A., Chu, S. I., and Reinhardt, W. P. (1983). *Phys. Rev.* A **27**, 2946.  
Peticolas, W. L., Norris, R., and Rieckhoff, K. E. (1968). *J. Chem. Phys.* **42**, 4164.  
Prigogine, I. (1992). *Phys. Reports* **219**, 93.  
Sommerfeld, A. (1949) 'Partial Differential Equations in Physics', p. 298 (Academic: New York).  
Sudarshan, E. C. G. (1994). *Phys. Rev.* A **50**, 2006.  
Unnikrishnan, K. (1988). *Phys. Rev.* A **38**, 2317.  
Unnikrishnan, K. (1993). *Phys. Rev.* A **48**, 4539.  
Zernik, W. (1964). *Phys. Rev.* **135**, A 51.

Manuscript received 26 April, accepted 23 May 1995