Relativistic and retardation effects in the two–photon ionization of hydrogen–like ions

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Abstract. The non–resonant two–photon ionization of hydrogen–like ions is studied in second–order perturbation theory, based on Dirac’s equation. To carry out the summation over the complete Coulomb spectrum, a Green’s function approach has been applied to the computation of the ionization cross sections. Exact second–order relativistic cross sections are compared with data as obtained from a relativistic long–wavelength approximation as well as from the scaling of nonrelativistic results. For high–Z ions, the relativistic wave function contraction may lower the two–photon ionization cross sections by a factor of two or more, while retardation effects appear less pronounced but still give rise to non-negligible contributions.

1. Introduction

The multi–photon ionization of atoms has been widely studied during the last few decades. While, however, most previous atomic experiments focused on the multi–photon ionization of the valence–shell electrons of the alkaline metal and group I elements (Jaouen et al 1984, Antoine et al 1996), theoretical investigations—instead—often dealt with the excitation and ionization of low–Z, hydrogen– and helium–like ions, owing to their simplicity (Karule et al 1985, Maquet et al 1998). With the recent progress in the development and set–up of coherent light sources in the EUV and x–ray domain, such as the various free–electron lasers, it now become much more likely that two– and multi–photon processes can be observed also for the inner–shell electrons of medium and heavy elements in the near future (Kornberg et al 2002). Since, generally, a relativistic theory is needed to describe such elements, a primary interest in studying multi–photon processes may concern first the importance of relativistic effects along the hydrogen isoelectronic sequence. In the past, similar investigations have been carried out only for the decay of the 2s1/2 metastable level (Santos et al 2001) as well as for the two–photon excitation from the 1s ground states of hydrogen–like ions (Szymanowski et al 1997). To the best of our knowledge, however, no attempt has been made so far to explore two– and multi–photon processes for medium and high–Z ions by means of a relativistic theory.

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In this paper, we consider the two–photon ionization of hydrogen–like ions in second–order perturbation theory, based on Dirac’s equation. To obtain the total ionization cross sections, a Green’s function approach is applied in section 2 to perform the summation over the complete hydrogen spectrum appropriately. Using such an approach, cross sections for the two–photon ionization of the 1s ground state of hydrogen–like ions are calculated for nuclear charges in the range \( Z = 1, \ldots, 100 \) in order to explore both, the relativistic contraction of the wave functions as well as those effects which arise from the higher multipoles in the decomposition of the radiation field, i. e. the so–called retardation effects. Section 3 later, provides a comparison of the cross sections from the relativistic theory (as obtained in two different approximations) as well as from the scaling of non-relativistic results. Finally, a few conclusions are given in section 4.

2. Two-photon ionization cross section. Perturbative treatment

In second–order perturbation theory, the two–photon ionization cross section \( \sigma_2 \) is given by (Laplanche et al. 1976)

\[
\sigma_2 = \frac{8\pi^3\alpha^2}{E_i^2} \left| \sum_{\nu} \frac{\langle \psi_f | p \cdot u_{\lambda} e^{i k_2 \cdot r} | \psi_{\nu} \rangle \langle \psi_{\nu} | p \cdot u_{\lambda} e^{i k_1 \cdot r} | \psi_i \rangle}{E_{\nu} - E_i - E_\gamma} \right|^2, \tag{1}
\]

where \((\psi_i, E_i), (\psi_{\nu}, E_\nu)\) and \((\psi_f, E_f)\) denote the wave functions and the energies of the initial, intermediate and final atomic states, respectively ‡. In this expression, as usual, the electron–photon interaction is described in terms of the transition operator \( p \cdot u_{\lambda} e^{i k \cdot r} \) which includes the momentum \( p \) of the electron and the photon wave \( u_{\lambda} e^{i k \cdot r} \).

As appropriate for laser experiments, here and in the following we assume that both photons have equal wave vectors \( k_1 = k_2 = k \) and equal helicities \( \lambda_1 = \lambda_2 = \lambda = \pm 1 \), i. e. that they have the same circular polarization. Then, the energy \( E_f = E_i + 2E_\gamma \) of the emitted electron simply follows from the energy conservation and is given by the energy of the initial state and twice the photon energy \( E_\gamma \).

2.1. Green’s function method

Apart from the usual integration over the spatial coordinates, the evaluation of the transition amplitude in in Eq. (1) also requires a summation over the complete spectrum of the (hydrogen) ion. Obviously, this summation includes the sum over all discrete states as well as an integration over continuum. In particular the second part, i. e. the integration over the continuum, is rather difficult to carry out in practice since it implies the computation of free–free electronic transitions. An alternative to carrying out the summation over the spectrum explicitly in the transition amplitude is given by a change

‡ Here and in the following, we use Hartree atomic units. Since the two–photon ionization cross section \( \sigma_2 \) has the dimension length\(^4 \times \) time, it can easily be converted also to other units such as cm\(^4 \cdot \) sec by using the conversion factor \( 1.89679 \times 10^{-50} \).
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in the sequence of summation and integration from
\[ \int \int d\mathbf{r} \, dE_\nu \text{ to } \int \int dE_\nu \, d\mathbf{r} \text{.} \]
Then, the summation over the complete hydrogen spectrum can be replaced by the Coulomb Green’s function (Swainson and Drake, 1991)
\[ G_E(\mathbf{r}, \mathbf{r}') = \sum_\nu \int \frac{|\psi_\nu(\mathbf{r})\rangle \langle \psi_\nu(\mathbf{r}')|}{E_\nu - E} \]
which is zero at the origin and tends to zero if \( r \to \infty \) or \( r' \to \infty \), respectively. This particular property of Coulomb Green’s function ensures that the second-order transition amplitudes in (1) can be evaluated even if the continuum wavefunctions \( \psi_f \) remains oscillating at large \( r \).

Using the Green’s function (2), the ionization cross section (1) can be re-written in the form (Maquet et al. 1998)
\[ \sigma_2 = \frac{8\pi^3\alpha^2}{E_\gamma^2} \left| \langle \psi_f | \mathbf{p} \cdot \mathbf{u}_\lambda e^{i\mathbf{k} \cdot \mathbf{r}} G_{E_i+E_\gamma}(\mathbf{r}, \mathbf{r}') \mathbf{p}' \cdot \mathbf{u}_\lambda e^{i\mathbf{k}' \cdot \mathbf{r}'} | \psi_i \rangle \right|^2, \]
including a new double integration over \( \mathbf{r} \) and \( \mathbf{r}' \). For hydrogen–like ions, the Coulomb–Green’s functions \( G_E(\mathbf{r}, \mathbf{r}') \) are known analytically, both within the nonrelativistic as well as the relativistic theory. Based on the Dirac–Hamiltonian with a hydrogen potential, \( H_D = c\alpha \cdot \mathbf{p} + \beta mc^2 - Z/r \), a radial–angular representation of the relativistic Coulomb–Green’s function was given earlier by Swainson and Drake (1991). In the evaluation of matrix elements, such a representation allows for the analytic integration over all angles by using the techniques of Racah’s algebra, while the radial integration has—often—to be carried out numerically.

2.2. Multipole expansion of the photon wave

To evaluate the angular part of the transition amplitude in expression (3), of course, we need first to represent the photon wave in terms of its electric and magnetic multipole fields (Rose 1957)
\[ \mathbf{u}_\lambda e^{i\mathbf{k} \cdot \mathbf{r}} = \sqrt{2\pi} \sum_{L=1}^{\infty} i^L \sqrt{2L+1} \left( A_L^{(m)} + i\lambda A_L^{(e)} \right), \]
where, for the sake of simplicity, we have taken the quantization axis, i. e. the \( z \)-axis, along the photon momenta \( \mathbf{k} \). For a proper radial–angular representation of all Coulomb wave and Green’s functions, then, the transition amplitude can be reduced to a (finite) sum of products of the type angular coefficient \( \times \) radial integral, in dependence on the number of multipoles and on further approximations which are made for the (coupling of the) radiation field. In our computations, the angular coefficients were obtained algebraically, using the RACAH program (Fritzsche 1997, Fritzsche et al. 2001). For the radial integrals, in contrast, we applied the procedures from the GREENS library (Koval and Fritzsche 2003). Owing to the structure of the radial Green’s function (matrix) this implies a double integration over a 2–dimensional area in \( 0 \leq r < \infty \) and \( 0 \leq r' \leq \infty \), for which an adaptive numerical integration algorithm with a user–defined precision was developed. This algorithm is based on the Gauss–Legendre quadrature and has been implemented as well in the GREENS library.
3. Results and discussion

3.1. Relativistic Z-scaling rule

Different approximations can be applied to investigate the two–photon ionization of hydrogen–like ions, in dependence on the photon frequency and the nuclear charge. In nonrelativistic quantum theory, for instance, the total non–resonant cross section in the long–wavelength approximation is known to scale down like

$$\sigma_2(Z, E_\gamma \cdot Z^2) = \frac{1}{Z^6} \cdot \sigma_2(Z = 1, E_\gamma),$$

(5)
i. e. with the sixth power of the nuclear charge, if—at the same time—the photon energy is scaled with $Z^2$ (Zernik 1964). This scaling rule for the non–resonant part of the cross section applies for all photon energies $\text{Ry}/2 \leq E_\gamma < \text{Ry}$ below of the one–photon threshold of hydrogen ($Z = 1$), where $\text{Ry} \approx 13.6 \text{ eV}$ refers to the hydrogen ground–state energy. To display the deviations of the cross sections in the different relativistic approximations from the nonrelativistic scaling, we may re–write Eq. (5) in the form

$$\sigma_2(Z, E_\gamma(Z)) = \xi(Z) \cdot \sigma_2(Z = 1, E_\gamma(Z = 1)),$$

(6)

where the photon energy $E_\gamma(Z) \equiv \varepsilon \cdot |E_{1s}(Z)/2$ now depends on the relativistic binding energy and, thus, shows a slightly more complicated $Z$–dependence than the nonrelativistic $\sim Z^2$ behaviour. As above, we may restrict ourselves to photon energies with $1 \leq \varepsilon < 2$ below of the one–photon threshold of all hydrogen ions. With this definition of $\varepsilon$, however, the interpretation of the scaling rule (6) becomes quite simple as, say, a value $\varepsilon = 1.05$ obviously specifies the photon energy so, that the total energy of the two photons together exceeds the $1s$ threshold by just 5%; a definition which can be used also in the nonrelativistic case. Thus, the net deviation between the various approximations is shown in the scaling factor $\xi(Z)$ which, in the nonrelativistic limit, is $\xi(Z) \equiv 1$.

3.2. Relativistic and retardation effects

Figure displays the scaling factor $\xi(Z)$ as function of the nuclear charge $1 \leq Z \leq 100$ for $\varepsilon = 1.05$, i. e. for a two–photon excess energy of 5 % which is well within the non–resonant region. Three different approximations are shown in this figure: Apart from the trivial nonrelativistic factor $\xi(Z) = 1$, the scaling factors are given for the relativistic long–wavelength approximation $e^{ikr} = 1$ (dashed–dotted line) as well as for the exact second–order perturbation treatment of all retardation effects (solid line). In practice, only the multipole fields up to $L_{\text{max}} = 5$ are needed in order to obtain convergence of the corresponding cross sections at about the 1% level.

When compared with the nonrelativistic decrease of the two–photon ionization cross sections, owing to the $1/Z^6$ scaling of the cross sections in Eq. (5), a further significant reduction arises for multiple and highly–charged ions mainly because of the relativistic contraction of the wave functions towards the nucleus. This contraction can lower the

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Figure 1. Dependence of the scaling factor $\xi(Z)$ on the nuclear charge $Z$ for $\varepsilon = 1.05$, i.e., for a two–photon excess energy of 5%. 1. Nonrelativistic long–wavelength approximation; 2. Relativistic long-wavelength approximation; 3. Exact relativistic second–order results.

Figure 2. Dependence of the scaling factor $\xi(Z)$ on the nuclear charge $Z$ for $\varepsilon = 1.40$. All other notations are the same as in Figure 1.
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Cross sections easily by a factor of two or more in the high–Z domain. The incorporation of higher multipoles beyond the E1–E1 dipole approximation, in contrast, contributes even for large values of $Z \sim 100$ only to $\leq 5\%$ for photon energies near the two–photon threshold. Somewhat larger retardation effects, however, are found for higher photon energies. For a two–photon excess energy of, say, 40\% above the threshold [cf. Figure 2], the retarded two–photon cross sections (solid line) are now larger than the cross sections in the long–wavelength approximation with deviation up to about 30\% at the high–Z end of the sequence. The behaviour of the retarded cross sections with respect to the long–wavelength approximation clearly shows the importance of higher multipoles which, otherwise, are usually seen only in angle–differential measurements (Surzhykov et al 2002).

4. Conclusion

In conclusion, the non–resonant two–photon ionization of hydrogen–like ions has been studied in detail within the relativistic theory. Emphasize was placed, in particular, on the relativistic contraction of the wave functions as well as on the retardation in the cross sections which arise from higher multipoles of the radiation field. However, our computations also showed that a Green’s function approach may provide a reliable access to second–order properties other than the total two–photon ionization cross sections. Investigations on the angle–differential emission of electrons as well as the two–photon decay of few–electron ions are currently under work.

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