

Calculation of matrix elements for mixed extreme-ultraviolet–infrared two-photon above-threshold ionization of argon

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Abstract

We present calculations of two-photon matrix elements for two-photon two-colour ionization. We focus on ionization processes that use one infrared and one extreme-ultraviolet photon. The paper describes a novel algorithm used for the calculation of radial matrix elements, and also of radial phase shifts of continuum states.

1. Introduction

Recent applications of two-photon ionization in the diagnostics of ultra-short extreme-ultraviolet (XUV) pulses [1] have revived interest in the calculation of atomic phase shifts in the perturbative regime. The theory required for obtaining such phase shifts was developed in the early 1980s [2, 3], when it was applied to a number of atoms that were obvious one-electron systems (hydrogen, alkalis). Although these methods are applications of well established low-order perturbation theory, naive application of the latter leads to divergencies when some of the virtual intermediate states are in the atomic continuum. In this case the multi-photon process is known as ATI, for above-threshold ionization [4]. Special techniques had to be developed to handle these divergencies. Due to rapid advances in laser development, and the resulting increase in experimentally accessible light intensities, interest in perturbative methods faded in the late 1980s, so some of the more advanced perturbative methods [5] have hardly received any attention in the literature.

Large-scale numerical simulations, solving the time-dependent Schrödinger equation on a grid, have shown that the single-active-electron model is also capable of providing a very accurate description of ionization of noble gases [6]. At first glance this seems rather strange, since noble gases contain many equivalent electrons in their active shell. A rationalization for this observation could be that, due to the high ionization potential (and even higher second ionization potential) all excited states in the physically relevant energy range are singly excited states, consisting of one electron that is weakly bound to a core that is virtually indistinguishable from the ion. In these states correlation between the outer and inner electrons is rather weak.

Furthermore, the time scales of the motion of inner and outer electrons is so different that the dominant part of this correlation is an almost adiabatic adaptation of the induced dipole moment in the core. This part of the correlation can be incorporated into the model without destroying the single-electron character, by a slight modification of the electron–ion interaction potential.

On the space spanned by the ground state and singly excited states the strong correlation that occurs within the ground state or ion core then simply shows up as an overall factor appearing in all transitions involving the ground state. In the lowest order this factor only affects total rates, and proper choice of the potential can provide the SAE model with a ground state that reproduces this overall factor. It is thus not as surprising as it seems that SAE models employing an empirically fitted potential approximate noble gas atoms quite well.

In this paper we present results of a calculation of two-colour two-photon ionization of argon, when ionization takes place with one XUV photon (capable of single-photon ionization) and one 800 nm photon. This is the process that was used in [1] for characterization of the XUV pulse. In addition, a full description of the perturbative method (which was hitherto only described shortly in the rather inaccessible [5]) is given.

2. Second-order perturbation theory

In second-order perturbation theory, transition rates between an initial state $|i\rangle$ and a final state $|f\rangle$ are derived from the two-photon matrix element

$$M_{if} = \langle f | D_2 (E - H)^{-1} D_1 | i \rangle \quad (1)$$

where $D_j = F_j \cdot r$ are the dipole operators of the involved fields F_j , H the Hamiltonian of the unperturbed atom, and $E = E_0 + \omega_1$ is the energy of the virtual intermediate state (atomic units $e = m_e = \hbar = 1$ are used throughout). Textbook treatment often proceeds by expansion of the resolvent operator $R(E) = (E - H)^{-1}$ on the (complete) set of eigenstates $|k\rangle$ of H :

$$R(E) = \sum_k \frac{|k\rangle\langle k|}{E - E_k}. \quad (2)$$

As we will see below this summation can be avoided in practice, but equation (2) shows that we might expect problems if one of the eigenstates (say $|k_0\rangle$) has an energy exactly equal to E . If E falls in the continuous spectrum of H , the sum should be read as an integral. There is then always a k_0 in the integration domain at which the integrand has a $1/x$ -type singularity. Integration through such a singularity involves cancellation of diverging contributions of opposite sign, with an undetermined result.

Closer inspection of the theory reveals that the boundary conditions on the problem are decisive. In ionization, the wavefunction must consist of outgoing, rather than incoming waves. This is automatically achieved by starting at $t = -\infty$ with a bound state $|i\rangle$ in the absence of the light, and turning on the latter infinitesimally slowly. A convenient turn-on would be exponential, $F(t) = e^{\eta t} e^{-i\omega t} = e^{-i(\omega+i\eta)t}$, and is thus seen to be equivalent to having an infinitesimal imaginary part to the photon energy. The quantity we are after is thus

$$\lim_{\eta \downarrow 0} R(E + i\eta) = \text{pv} \frac{1}{E - H} - i\pi \delta(E - H), \quad (3)$$

where pv prescribes principal-value integration, and δ represents the Dirac delta function. The atomic eigenfunctions can all be chosen to be real, so the principal-value contribution describes the real part of the matrix element, and the delta-function contribution the imaginary part. The two-photon matrix element thus becomes complex,

$$M_{if} = \langle f | D_2 \text{pv}(E - H)^{-1} D_1 | i \rangle - i\pi \langle f | D_2 | k_0 \rangle \langle k_0 | D_1 | i \rangle. \quad (4)$$

The first term still contains an integral over the continuum, which is now uniquely determined by the principal-value prescription, while the second term is a simple product of single-photon matrix elements.

The formal sum over intermediate states runs over all quantum numbers, radial n (or E) as well as angular ℓ and m . For atoms in the dipole approximation, severe selection rules with respect to the angular quantum numbers apply. With linear polarization (to which we will limit ourselves in the remainder of this paper), the matrix elements of D are only non-zero if $\Delta\ell = \pm 1$ and $\Delta m = 0$. So in practice only very few ℓ and m contribute to the sum over intermediate states. This is different for the radial dimension, where there are no selection rules at all.

Thus, the total sum can be split in a few terms $M_{\ell m}$ with each a well-defined ℓ, m in the intermediate state. Since the angular dependence of all intermediate states is then the same, it can be factored out and the angular integrations can be done analytically (for each transition between angular momentum $\ell - 1$ and ℓ in the pathway this produces a factor $c_{\ell-1,\ell}^m = \sqrt{(\ell^2 - m^2)/(4\ell^2 - 1)}$). In each $M_{\ell m}$ the atomic Hamiltonian can be represented by a simple ordinary (second-order) differential operator with respect to r :

$$H_\ell = -\frac{1}{2}\partial_r^2 + V(r) + \frac{\ell(\ell+1)}{2r^2}. \quad (5)$$

(Note that this operator is different for each ℓ .) The partial sums can thus be obtained as a simple radial matrix element

$$M_{\ell m} = \langle f|r(E - H_\ell)^{-1}r|i\rangle = \langle f|r|\Psi\rangle, \quad (6)$$

between the final state and an auxiliary wavefunction

$$|\Psi\rangle = (E - H_\ell)^{-1}r|i\rangle. \quad (7)$$

This latter equation is equivalent to the ordinary differential equation

$$(E - H_\ell)|\Psi\rangle = r|i\rangle, \quad (8)$$

which can be solved for Ψ by straightforward (one-dimensional) numerical integration (using a multistep method) starting from the boundary condition $\Psi(r) = 0$ at $r = 0$. This way of evaluating the sum over states is known as the Dalgarno-Lewis method [7].

If $E < 0$, the virtual intermediate level is in the bound-state part of the spectrum, and solutions to the differential equation diverge exponentially for $r \rightarrow \infty$ except for one choice of the initial slope of $\Psi(r)$ at $r = 0$. The computer quickly hunts down the required initial slope through a bisection process, based on whether the trial solutions to equation (8) diverge to $+\infty$ or $-\infty$. In the ATI case, $E > 0$, all solutions oscillate, no matter what the initial slope was. The boundary condition at $r \rightarrow \infty$ should be such that Ψ represents an outgoing exponential wave. Such a wave has its real and imaginary parts oscillating 90° out of phase. Since equation (8) is an inhomogeneous linear differential equation, its solutions differ by a solution of the corresponding homogeneous equation, i.e. by a multiple of the continuum eigenfunction $|k_0\rangle$ at the virtual-intermediate energy. The imaginary part of Ψ is also proportional to $|k_0\rangle$. To obtain the principal-value (real) part, we should look for the solution to the inhomogeneous equation that is 90° out of phase with it. Because adding two oscillations that are 90° out of phase can only increase the amplitude, this is also the solution that has the smallest asymptotic amplitude, and this latter property is used in the search process for the correct initial slope.

3. The asymptotic amplitude and phase

In a short-range potential continuum radial wavefunctions become harmonic oscillations (i.e. phase-shifted sine waves) in the region where the potential vanishes. Coulomb waves, on

the other hand, converge to harmonic behaviour only very slowly (and their phase never really does, but diverges logarithmically). It is thus impractical to estimate the asymptotic amplitude from integrating to large r , and instead we resort to the following ‘magical trick’ [5].

The function $\Psi(r)$ asymptotically approaches a homogeneous solution (since the inhomogeneous part in equation (8) decays exponentially), and obeys

$$\Psi'' = -Q(r)\Psi, \quad (9)$$

with $Q(r) = Q_r = 2(E - V(r))$. Let us define the quantity $A(r)$ as

$$A(r) = Q_r^{1/2}\Psi^2(r) + Q_r^{-1/2}(\Psi'(r))^2. \quad (10)$$

We then have

$$A_\infty = A(r) + \int_r^\infty \partial_r A(r) dr = A(r) + B(r). \quad (11)$$

Since

$$\begin{aligned} \partial_r A(r) &= \frac{1}{2}(Q_r^{-1/2}Q'_r\Psi^2(r) + 4Q_r^{1/2}\Psi(r)\Psi'(r) - Q_r^{-3/2}Q'_r(\Psi'(r))^2 + 4Q_r^{-1/2}\Psi'(r)\Psi''(r)) \\ &= \frac{1}{2}(Q_r^{-1/2}Q'_r\Psi^2(r) + 4Q_r^{1/2}\Psi(r)\Psi'(r) \\ &\quad - Q_r^{-3/2}Q'_r(\Psi'(r))^2 - 4Q_r^{1/2}\Psi'(r)\Psi(r)) \\ &= \frac{1}{2}(Q_r^{-1/2}Q'_r\Psi^2(r) - Q_r^{-3/2}Q'_r(\Psi'(r))^2) \\ &= \frac{1}{2}(-\Psi(r)\Psi''(r) - (\Psi'(r))^2)Q_r^{-3/2}Q'_r, \end{aligned} \quad (12)$$

(where we used equation (9) twice) we can do the integral in equation (11) by parts:

$$B(r) = -\frac{1}{2}Q_r^{-3/2}Q'_r\Psi(r)\Psi'(r)|_r^\infty + \frac{1}{2}\int_r^\infty \Psi(r)\Psi'(r)(Q_r^{-3/2}Q'_r)' dr. \quad (13)$$

The integrand in the last term of equation (13) decays very rapidly (as r^{-3} in the Coulomb case), so that neglecting it only produces an error that decreases rapidly with r . The function Q and all its derivatives are asymptotically known as simple analytical functions, so a rapidly converging estimate of A_∞ , using $A(r)$ as defined by equation (10) and the stock term of $B(r)$ from equation (13), is easily evaluated from the numerically determined $\Psi(r)$ and $\Psi'(r)$. From A_∞ we can of course obtain an estimate of the asymptotic amplitude Ψ_∞ through applying equation (10) in a maximum of Ψ at asymptotically far r :

$$A_\infty = Q_\infty^{1/2}\Psi_\infty^2. \quad (14)$$

In the same spirit, we also calculated the asymptotic radial phase shift:

$$\delta_l(E) = \arctan\left(\frac{\Psi'}{Q_r^{1/2}\Psi}\right) - C(r), \pmod{2\pi},$$

where the counter-term

$$C(r) = \frac{1}{\sqrt{2E}}(u + \ln(2Er + 1 + u)) - 2\sqrt{l(l+1)}\left(\arctan\frac{2Er + u}{\sqrt{2El(l+1)}} - \frac{\pi}{2}\right),$$

with $u = \sqrt{4E^2r^2 + 4Er - 2El(l+1)}$, cancels the linear and the logarithmic divergent terms in the phase, such that at the infinity only the constant term is left.

4. Handling divergent integrals

Since the auxiliary function Ψ and the final state f both have continuum character, it is necessary to calculate the dipole matrix element between continuum functions. This amounts to integrating the product of two oscillating functions and a factor r , which produces a diverging, oscillating integrand. Again, this divergence is regularized by first considering finite η and then taking the limit $\eta \downarrow 0$. For finite η the complex part in $Q(r)$ endows Ψ with some exponential decay, and this is good enough to compensate any power of r . If $g(r)$ is an oscillating function with (asymptotic) period L (and possibly polynomially diverging amplitude), then

$$I_\eta = \int_0^\infty g(r)e^{-\eta r} dr \quad (15)$$

exists for any $\eta > 0$. The integral is invariant under a shift of the integration variable,

$$I_\eta = e^{-\eta L/2} \int_{-L/2}^\infty g(r + L/2)e^{-\eta r} dr. \quad (16)$$

Any linear combination of equations (15) and (16) would also do, i.e. if $w_1 + w_2 = 1$ then

$$I_\eta = \int_{-\infty}^\infty (w_1 g(r) + w_2 e^{-\eta L/2} g(r + L/2))e^{-\eta r} dr \quad (17)$$

(where $g(r)$ for $r < 0$ is defined to be 0 for more compact notation of the integrals). But $g(r + L/2)$ oscillates asymptotically 180° out of phase with $g(r)$, and so if we pick $w_1 = w_2 = 0.5$ these terms have the tendency to cancel each other. This cancellation reduces the divergence of the integrand, and if this divergence is reduced enough then both the left- and right-hand side of equation (17) are well defined for $\eta = 0$. Taking the limit $\eta \downarrow 0$ then becomes a trivial substitution:

$$I_0 = \lim_{\eta \downarrow 0} I_\eta = 0.5 \int_{-\infty}^\infty (g(r) + g(r + L/2)) dr. \quad (18)$$

The approach sketched above can be generalized to any moving-average filter W ,

$$(Wg)(r) = \sum_{j=1}^N w_j g(r + \alpha_j): \quad (19)$$

as long as $\sum w_j = 1$, applying such a moving-average filter to the integrand will not change the integral. By choosing a filter W with a zero of high multiplicity at the asymptotic wavevector of the integrand, the filtered result can be made to approach zero very quickly with increasing r , even when the original integrand diverged. For a Coulomb potential the local wavevector approaches the asymptotic wavevector as $1/r$, so each zero at the asymptotic wavevector speeds up the asymptotic decay by one power of r .

In practice, the wavefunctions are calculated on an equidistant grid, and the shifts α_j should be multiples of the grid spacing δr . Due to this restriction, shifts of exactly half the period are usually not possible, and W needs at least three terms (i.e. $N = 3$) with real w_j to provide an exact zero (of multiplicity 1) at the desired wavevector. The shifts are chosen as $\alpha_j = (j - 1)L/4$ rounded up to a multiple of δr , so that all w_j can be of the same sign (which is good for numerical stability). To create a zero of order n this simple filter of order 1 is simply applied n times (so that its transmission is raised to the power n). We use $n = 6-8$, checking if the results have converged with respect to n .

If a matrix element is calculated between two outgoing waves with momenta k_1 and k_2 , the only oscillation left in the integrand has wavevector $k_1 - k_2$. The asymptotic k is easily calculated from the respective energy. For historical reasons our code treats real and imaginary

Table 1. The m -independent radial parts ($l_i l_f$) of the matrix elements.

Transition	(psp)	(pdp)	(pdf)
11 + IR	218.61 - $i\pi$ 12	98.85 - $i\pi$ 131.71	-105.92 + $i\pi$ 300.93
13 + IR	184.21 - $i\pi$ 23.20	228.06 - $i\pi$ 100.71	-109.65 + $i\pi$ 204.17
15 + IR	158.12 - $i\pi$ 28.15	239.46 - $i\pi$ 64.57	-69.98 + $i\pi$ 145.4
17 + IR	137.63 - $i\pi$ 29.74	216.63 - $i\pi$ 37.66	-39.08 + $i\pi$ 104.49
13 - IR	89.16 - $i\pi$ 36.48	61.55 - $i\pi$ 178.13	-14.76 + $i\pi$ 89.25
15 - IR	89.79 - $i\pi$ 36.02	196.89 - $i\pi$ 114.78	-17.47 + $i\pi$ 82.34
17 - IR	86.06 - $i\pi$ 34.67	208.93 - $i\pi$ 68.41	-11.3 + $i\pi$ 67.71
19 - IR	80.78 - $i\pi$ 34.07	179.56 - $i\pi$ 38.23	-4.73 + $i\pi$ 52.10

parts of the wavefunctions separately. In this case, the wavefunctions at a certain energy can contain both incoming and outgoing waves, so oscillations at $k_1 + k_2$ have to be filtered out as well.

5. Results

We applied the described method to a one-electron system with a potential

$$V(r) = (1 + 5.4e^{-r} + 11.6e^{-3.682r})/r. \quad (20)$$

This potential produces a very good fit of its eigenenergies to the (configuration-averaged) experimental energies of the argon singly excited states. In addition, it produces the correct binding energies of all K, L and M-shell electrons, and has the physically expected behaviour as $r \downarrow 0$ and as $r \rightarrow \infty$. It is the same potential that has been used very successfully as a starting point for time-dependent calculations [8].

Since the peaks in the electron spectra of [1] are all due to ejection of 3p electrons, we have to take account of the degeneracy of this shell. Separate calculations are done for $m = 0$ and ± 1 electrons; in the latter case, only intermediate d states can contribute. In all cases the final state can be p or f continuum. Also, when $m = 0$ the pathway through s intermediates contributes to matrix elements of the final p wave. The radial functions are the same irrespective of m ; it is only the angular factors that differ. The contributions for $m = 1$ and -1 are identical.

All pathways leading from the same initial state to the same final state are added to produce the total (complex) matrix element for this process. For the two-colour process this includes pathways that differ in the order of photon absorption, and thus have their $R(E)$ taken at a different intermediate energy. At the light frequencies we consider, absorbing the infrared photon first does not bring the system into the continuum, and thus does not contribute to the imaginary part of the matrix element. (The contribution of this pathway is small anyway, due to the small polarizability of the ground state.) Radial parts of matrix elements M_{if} are presented in table 1 for all transitions of interest in the experiment described in [1] (namely, involving odd harmonics 11–19 of the 800 nm laser). For each pair of states $(i, f) \equiv (l_i m, l_f m)$ corresponding to one transition (where $l_i = 1$, and $l_f = 1$ or 3), the angular parts c_{xx}^m and the radial ones ($l_i l_f$) give

$$\tilde{M}_{if} = \sum_V c_{l_i l_f}^m c_{l_f l_i}^m (l_i l_f),$$

where the sum is over the intermediate states; see figure 1 for clarity. The final M_{if} equals $\tilde{M}_{if} F_2 F_1$, where F_1 and F_2 are the two electric fields involved.

When multiple harmonics are present in addition to the fundamental, sum and difference processes can lead to the same final state (11 + IR and 13 - IR contribute together to

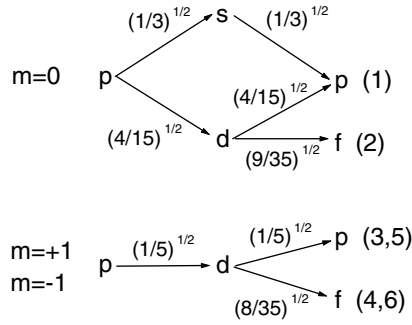


Figure 1. Scheme of the six processes $i \rightarrow f$, occurring between the ground state of Ar, 3p, and the same final energy in the continuum, via two-photon ionization. The value of $c_{ll'}^m$ is given for each transition $l \rightarrow l'$.

the same intermediate peak, ‘sideband’, in the electron spectrum, for example). The ionization yield for a process (defined by the angular momentum of the photo-electron l_f , and that of the electron removed, i.e. the hole in the remaining ion l_i) is obtained by squaring the sum of all contributing transitions: $|(M_{if})_{q-1}^+ + (M_{if})_{q+1}^-|^2$, which we can write as $C_{if} + I_{if}$. C_{if} is a constant term and equals $|(M_{if})_{q-1}^+|^2 + |(M_{if})_{q+1}^-|^2$, I_{if} is the interference term and equals $(\tilde{M}_{if})_{q-1}^+ ((\tilde{M}_{if})_{q+1}^-)^* F_{q-1} F_{IR} (F_{q+1} F_{IR}^*)^* + \text{c.c.}$ I_{if} can also be written as $A_{if} \cos(2\varphi_{IR} + \varphi_{q-1} - \varphi_{q+1} + \Delta\varphi_{\text{atomic}}^{if})$, where $A_{if} = 2|(\tilde{M}_{if})_{q-1}^+| |(\tilde{M}_{if})_{q+1}^-|$, and $\Delta\varphi_{\text{atomic}}^{if} = \arg((\tilde{M}_{if})_{q-1}^+) - \arg((\tilde{M}_{if})_{q+1}^-)$ (see the table in [1]).

To calculate the total (angle integrated) ionization to all continuum states of a given final energy, the yields for all the processes are added:

$$T_{\text{sideband}} = \sum_{(i,f)} |(M_{if})_{q-1}^+ + (M_{if})_{q+1}^-|^2.$$

Then we can define

$$A_{\text{sideband}} = 2 \left| \sum_{(i,f)} (\tilde{M}_{if})_{q-1}^+ ((\tilde{M}_{if})_{q+1}^-)^* \right|, \quad \text{and}$$

$$\Delta\varphi_{\text{atomic}}^{\text{sideband}} = \arg \left(\sum_{(i,f)} (\tilde{M}_{if})_{q-1}^+ ((\tilde{M}_{if})_{q+1}^-)^* \right).$$

For non-angle-integrated measurements, (not presented in this paper) the matrix element for a process would have to be multiplied by the spherical harmonic of its final state. Processes to all final continua starting with the same 3p electron would have to be added before squaring (taking account of the radial phase shift of the states of different angular momentum with respect to each other). This then produces the angular distribution of the photo-electron from photo-ionization of that particular 3p orbital, and the contributions of all 3p orbitals have to be added after squaring:

$$T_{\text{sideband}} = \sum_i \left| \sum_f ((M_{if})_{q-1}^+ + (M_{if})_{q+1}^-) Y_{l_f}^m(\Theta, \Phi) \exp(i\delta_{l_f}^{\text{sideband}}) \right|^2,$$

where $\delta_{l_f}^{\text{sideband}}$ are the radial phase shifts of the final continuum states f used in the calculation of the matrix elements, and are given in table 2. Θ and Φ are the angles of detection with

Table 2. The l -dependent phase shifts for final continuum states p ($l_f = 1$) and f ($l_f = 3$).

Sideband	δ_p (rad)	δ_f (rad)
12IR	-6.17	-3.25
14IR	-6.12	-2.66
16IR	-6.10	-2.30
18IR	-6.10	-2.05

respect to the polarization vector¹. (The l -dependent phase shifts of the continuum waves are not included in the matrix elements, because these were calculated with real wavefunctions.)

6. Conclusions

We calculated matrix elements describing mixed-colour two-photon transitions in lowest-order perturbation theory. Various novel convergence-accelerating numerical techniques were used in the calculation. This made the results indeed converge rather quickly, and allowed us to obtain the matrix elements without significant numerical error. The values reported can thus be considered exact, for a single electron bound in the model potential. Errors could still be present due to a real argon atom not being perfectly representable by a simple potential. The potential, however, was fitted to optimally reproduce the known atomic levels, and has proved highly reliable in earlier, non-perturbative contexts of multi-photon ionization.

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¹ This result is independent of Φ .