

Parallelized Procedure for the Determination of the Fully Differential Cross Section for $(\gamma, 2e)$ Photo-Double Ionization of N_2 Molecule

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The double ionization by a single polarized photon is one of the principle experimental means to study the electronic structure of atoms and molecules and to probe electron-electron correlation, which is the main factor which causes double ionization of a target [1]. An abundant literature is available for the particular case of $(\gamma, 2e)$ photo-double ionization, where the two ejected electrons are detected in coincidence, specially for the helium and rare gas targets [2, 3]. In the case of diatomic targets, theoretical results for the multiply differential cross section (MDCS) are relatively less frequent. However an experimental detection of the ejected electrons from stable, naturally existing diatomic targets like H_2 , or N_2 is quite similar to that of atoms, like helium.

The aim of the present work is to give the first MDCS of $(\gamma, 2e)$ photo-double ionization of diatomic nitrogen using a parallelized FORTRAN procedure. To our knowledge no such data exist, in spite of the large interest on the molecular dication in astrophysics and plasma science, dications being very abundant in the ionosphere of many planets and in interstellar clouds. In this work we extend the procedure we have recently applied [4] to the MDCS evaluation of the $(e, 3e)$ double ionization of N_2 and H_2 where we have used the two center double continuum function [5]. This has given a better agreement with the experimental results on the $(e, 3e - 1)$ double ionization of hydrogen molecule [6], and have shown that the introduction of the electron-electron correlation in the final state is necessary.

Theory

The MDCS of the detection of the two ejected electrons from a diatomic molecule is fivefold, and is given by

$$\begin{aligned} \sigma^{(5)}(\boldsymbol{\rho}) &= \frac{d^5\sigma}{d\Omega_\rho d\Omega_1 d\Omega_2 d(k_1^2/2) d(k_2^2/2)} \\ &= \frac{4\pi^2\alpha}{\omega} |T_{fi}|^2, \end{aligned} \quad (1)$$

where $d\Omega_1$, $d\Omega_2$ and $d\Omega_\rho$, are respectively the elements of the solid angles for the orientations of the

ejected electrons, $\boldsymbol{\rho}$ represents the internuclear axis, k_1 and k_2 are the moduli of the wave vectors of the ejected electrons, $\alpha = 7.29735 \times 10^{-3}$ is the fine-structure constant and ω is the photon frequency. In the case of randomly oriented targets, we must pass to the fourfold differential cross section (FDCS) by integrating over all possible and equally probable directions of the molecule in space

$$\sigma^{(4)} = \frac{1}{4\pi} \int d\Omega_\rho \sigma^{(5)}(\vec{\rho}). \quad (2)$$

The conservation of the energy for fixed internuclear distance ρ gives

$$E_f = E_1 + E_2 = E_i + \omega, \quad (3)$$

where $E_1 = k_1^2/2$, $E_2 = k_2^2/2$ represent respectively the energies of the ejected electrons. E_i represents the energy needed to free the two bound electrons in N_2 . We define the transition matrix element

$$T_{fi} = \int d\vec{r}_1 \int d\vec{r}_2 \bar{\chi}_f(\vec{r}_1, \vec{r}_2) V \varphi_i(\vec{r}_1, \vec{r}_2). \quad (4)$$

Here V is given in the velocity gauge by $V = \vec{\epsilon}(\vec{\nabla}_{r_1} + \vec{\nabla}_{r_2})$ with $\vec{\epsilon}$ representing the polarization vector for the photon, and \vec{r}_j , ($j = 1, 2$) refer to the positions of the bound (ejected) electrons.

The final state symmetrized wave function describing the state of the two equivalent ejected electrons coming from the same molecular orbit is written in the following form

$$\begin{aligned} \chi_f(\vec{r}_1, \vec{r}_2) &= 2^{-1/2} \\ &\times (\phi_f(\vec{k}_1, \vec{r}_1, \vec{k}_2, \vec{r}_2) + \phi_f(\vec{k}_1, \vec{r}_2, \vec{k}_2, \vec{r}_1)). \end{aligned} \quad (5)$$

Here

$$\begin{aligned} \phi_f(\vec{k}_1, \vec{r}_1, \vec{k}_2, \vec{r}_2) &= v(k_{12}) T(\vec{k}_1, \vec{r}_1) T(\vec{k}_2, \vec{r}_2) \\ &\times {}_1F_1\left(\iota\alpha_{12}, 1, -\iota(k_{12}r_{12} + \vec{k}_{12}\vec{r}_{12})\right) \end{aligned} \quad (6)$$

in which we have introduced the electron-electron correlation [7] $\vec{r}_{12} = \vec{r}_1 - \vec{r}_2$, and

$$v(k_{12}) = \exp(-\pi\alpha_{12}/2) \Gamma(1 - \iota\alpha_{12}) \quad (7)$$

represents the Gamow factor with $\alpha_{12} = (2k_{12})^{-1}$, $\vec{k}_{12} = (\vec{k}_1 - \vec{k}_2)/2$. The final state wave

function satisfies the ortho-normality condition in the sense

$$\begin{aligned} & \langle \phi_f(\vec{k}_1, \vec{r}_1, \vec{k}_2, \vec{r}_2) | \phi_f(\vec{k}'_1, \vec{r}_1, \vec{k}'_2, \vec{r}_2) \rangle \\ & = \delta(\vec{k}_1 - \vec{k}'_1) \delta(\vec{k}_2 - \vec{k}'_2). \end{aligned} \quad (8)$$

In equation (6), the one electron two center continuum (TCC) wave function [5] is given by

$$\begin{aligned} T(\vec{k}_i, \vec{r}_j) &= \frac{\exp(-\pi\alpha_i) (\Gamma(1 - \alpha_i))^2 \exp(i\vec{k}_i \vec{r}_j)}{(2\pi)^{3/2}} \\ & \times \prod_{l=a}^b {}_1F_1(\alpha_i, 1, -\iota(k_i r_{jl} + \vec{k}_i \vec{r}_{jl})), \end{aligned} \quad (9)$$

It describes a slow electron in the field of two Coulomb centers. Here

$$\alpha_i = -1/k_i, \quad \vec{r}_{ja} = \vec{r}_j + \vec{\rho}/2, \quad \vec{r}_{jb} = \vec{r}_j - \vec{\rho}/2. \quad (10)$$

The space coordinates of the wave functions are defined in the molecular frame of reference, whose origin is fixed on the center of mass of the molecule and whose z -axis is parallel to the internuclear vector $\vec{\rho}$ of constant modulus.

The initial ground state configuration of N_2 is given by [8]:

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4. \quad (11)$$

The molecular orbitals σ_g , σ_u and π_u -type mentioned above are constructed by linear combinations of the double Slater type $1s$, $1s'$, $2s$, $2s'$, $2p$, $2p'$ and single Slater type $3d$ atomic orbitals [8] for the internuclear distance $\rho = 2.0675$ a.u. We consider an ionization from the $3\sigma_g^2$ state

$$\varphi_i(\mathbf{r}_1, \mathbf{r}_2) = 3\sigma_g(\mathbf{r}_1)3\sigma_g(\mathbf{r}_2), \quad (12)$$

where the $3\sigma_g$ is the molecular orbital with one effective electron.

An algorithm for rapid calculation of the ${}_1F_1(a, b, ix)$

Let us consider the confluent hypergeometric function $y(x) = {}_1F_1(a, b, ix)$ with complex parameters a , b and argument x on the finite interval $x \in [0, x_{\max}]$. This function satisfies the Kummer's equation

$$x \frac{d^2 y(x)}{dx^2} + (b - ix) \frac{dy(x)}{dx} - \iota a y(x) = 0. \quad (13)$$

The main idea of the algorithm is to use a predetermined values of $y(x)$ and their derivatives on the set of points $\{x_i = h i\}_{i=0}^N$ with step $h = x_{\max}/N$. For the interval $x \in [0, x_{\max}]$, the Taylor series gives

$$y(x) \approx \bar{y}(x) = \sum_{i=0}^n \frac{1}{i!} \left. \frac{d^i y(x)}{dx^i} \right|_{x=x_{i_o}} (x - x_{i_o})^i \quad (14)$$

The optimal point x_{i_o} is defined from the condition $\min_{0 \leq i \leq N} |x - x_i|$. From here we obtain $i_o = [x/h + 1/2]$, and $|x - x_{i_o}| \leq h/2$, where $[x]$ designates the integer part of x .

High-order derivatives of $y(x)$ are calculated by the relation

$$\frac{d^n y(x)}{dx^n} = \iota^n \frac{\Gamma(b) \Gamma(a+n)}{\Gamma(a) \Gamma(b+n)} {}_1F_1(a+n, b+n, ix). \quad (15)$$

Also if $x_i > 2$, the high-order derivatives of $y(x_i)$ can be expressed via the recurrence formula:

$$\begin{aligned} x \frac{d^n y(x)}{dx^n} + (b+n-2-ix) \frac{d^{n-1} y(x)}{dx^{n-1}} \\ - \iota(a+n-2) \frac{d^{n-2} y(x)}{dx^{n-2}} = 0, \quad n \geq 2, \end{aligned} \quad (16)$$

which obtained from Eq. (13). In this case needed only numerical values of $y(x_i)$ and its first derivative.

If $h < 0.5$, the double precision accuracy $|y(x) - \bar{y}(x)| \leq \epsilon = 2 \cdot 10^{-16}$ is usually achieved at $n < 20$.

For the beforehand calculated values of $y(x)$ and their derivatives on the set of points $\{x_i\}_{i=0}^N$, we used the Fortran code CONHYP [9].

Numerical integration details

The corresponding (2D+6D) integrals are calculated using the adaptive subdivision algorithm, and it has a loop that contains four steps:

- i) determination of a new subdivision of the integration region,
- ii) applying the basic rule to any new subregions,
- iii) combining new results from step ii) to the previous results and
- iv) checking the convergence.

For p -processors parallelization of above algorithm we used the Single list algorithm:

```
p-sect region  $[a_1, b_1] \times [a_2, b_2] \times \dots \times [a_d, b_d]$ 
do parallel
  apply integration rule to subregions
end do parallel
do while (error >  $\epsilon$ ) and (number of rule evaluations  $\leq N_{\max}$ )
  SUBREGION SELECTION
  do parallel
    compute new subregion limits
    apply cubature rule to new subregions
  end do parallel
  do parallel
    remove old subregions from list
    add new subregions to list
    update integral approximation and error estimate
```

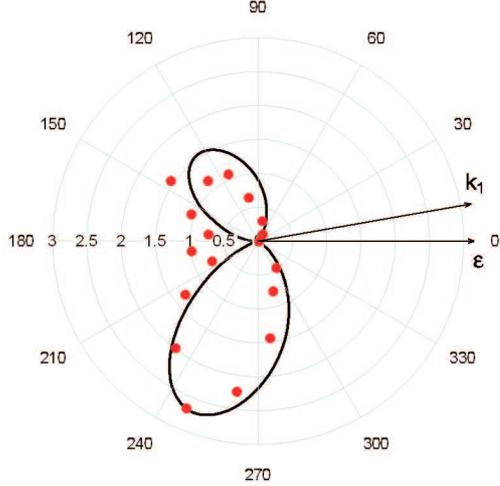


Figure 1: The variation, in polar representation, of the FDCS, scaled by 10^5 , of the double-photo ionization of H_2 in the velocity gauge obtained by the Turbiner- Guevara wave function [10]. Polar angle represents the θ_2 of the ejected electron. Here $E_1 = E_2 = 12.5$ eV and $\theta_1 = 10^\circ$. The experimental data are from [11].

end do parallel

end do

Our p -processors parallel calculations are approximately 0.8 p times faster than single processor.

Results and Discussion

In what follows we take the propagation of the linearly polarized photon in the x direction and that the polarization vector $\vec{\epsilon}$ parallel to the z axis of the laboratory frame. The orientation of the internuclear axis, which will be considered as fixed during the ionization process, will be given by the polar θ_ρ and azimuthal φ_ρ angles with respect to the laboratory frame.

Once we have tested our procedure on hydrogen molecule and observed that it produces, quite well, the experimental results (see figure 1), we pass to the photo-double ionization of N_2 . Here also we will consider the photo-double ionization of N_2 as a vertical transition from the fundamental electronic state of the neutral target at its equilibrium internuclear distance to the fundamental $^1\Sigma_g$ state of the residual N_2^{2+} dication. The case of the photo double ionization to the neighboring $^3\Pi_u$ final state of N_2^{2+} , which should contribute to the results in experiments, which have low energy resolution and cannot distinguish between the the two possible events (see [12, 13]). The present work is a first tentative to tackle the photo-double ionization of N_2 by the correlated TCC function. We will apply, at this stage, the wave function described in section The-

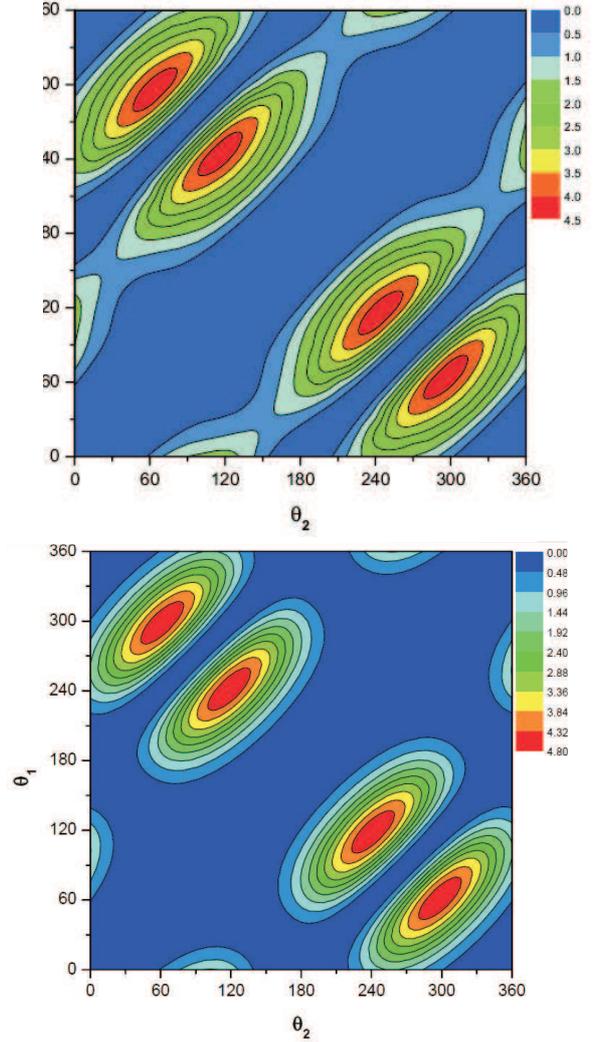


Figure 2: On the top: color scale representation of the variation of the TDCS in atomic units Eq. (2), scaled by 10^4 , of the photo-double ionization of the $3\sigma_g$ level of N_2 obtained by the velocity gauge in terms the two ejection angles θ_1 and θ_2 . Here $E_1 = E_2 = 10$ eV, and the vectors \mathbf{k}_1 , \mathbf{k}_2 , ϵ lie in the same plane. On the bottom: the equivalent representation obtained by the Gaussian parametrization fit.

ory, which is constructed by Hartree-Fock diatomic orbital (see Eq. (12)). Higher quality wave functions including the electron-electron separation r_{12} are more difficult to obtain, and their application is much more time consuming. We will undertake this work in a future paper. Our results will be compared to those obtained by the best fit of the following Gaussian parametrization formula [14]

$$f(\theta_1, \theta_2) = a (\cos(\theta_1) + \cos(\theta_2))^2 \times \exp \left[-4 \ln(2) \frac{(\theta_{12} - 180^\circ)^2}{\Gamma^2} \right]. \quad (17)$$

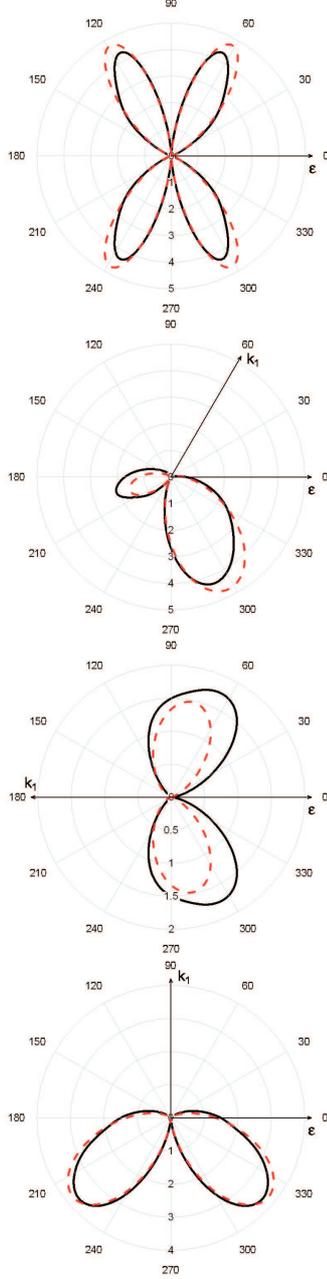


Figure 3: Polar representation of the variation of the TDCS (see fig. 2). The solid line represents the results obtained by Eq. (2). The dashed line those obtained by the Gaussian parameterization. Left-top: $\theta_1 = 2\pi - \theta_2$, right-top: $\theta_1 = 60^\circ$, left-bottom: $\theta_1 = 180^\circ$, right-bottom: $\theta_1 = 90^\circ$.

The fitting is done by minimizing the following function with respect to the parameters a , Γ , using a comprehensive modified Newton algorithm:

$$F(a, \Gamma) = \frac{1}{37^2} \times \sum_{i,j=1}^{37} \left(\sigma^{(3)}(\theta_1^i, \theta_2^j) - f(\theta_1^i, \theta_2^j) \right)^2 \rightarrow_{a,\Gamma} \min, \quad (18)$$

$$\theta_1^i = 10^\circ(i-1), \quad \theta_2^j = 10^\circ(j-1),$$

with $\sigma^{(3)}(\theta_1^i, \theta_2^j)$ representing our calculated TDCS. The reached accuracy is 10^{-6} . This gives the best correlation factor width $\Gamma = \Gamma(E) = 1.7346 = 99.4^\circ$ and $a = a(E) = 1.2945 \times 10^{-3}$, $F(a, \Gamma) = 1.0029 \times 10^{-1}$.

We see that the diagonal of this figure $\theta_1 = \theta_2$ is an axis of symmetry, as we obtain practically the same structure on both sides of this line. We must mention here, that the perfect symmetry on the figure is obtained by employing accurate averaging integration over the molecular orientations. We next observe, that the second diagonal line defined by $\theta_1 + \theta_2 = 2\pi$ is also a symmetry axis as expected. In the same manner the lines $\theta_1 = \theta_2 \pm \pi$ have the same structure on their two sides as expected also.

On figure 3 (left-top) we observe that when $E_1 = E_2$ and $\theta_1 = 2\pi - \theta_2$ the four lobes are identical as they should be. On figure 3 (right-top) we show the variation which gives the largest lobe. This happens for $\theta_1 = 60^\circ$. Analysis of the geometries with $\theta_1 = 180^\circ$ and $\theta_1 = 90^\circ$ (see figures 3 (left-bottom and right-bottom)), corresponding in the first case to the electron with wave vector \vec{k}_1 ejected in direction of $\vec{\epsilon}$ and in the second case perpendicular to it, shows, as expected, the second geometry which puts \vec{k}_1 far from the polarization vector $\vec{\epsilon}$ to be more efficient.

Conclusions

We have determined the four fold and triple differential cross sections, corresponding respectively to the oriented and randomly oriented diatomic molecules, of the photo-double ionization of H_2 and N_2 diatomic systems, in equal ejection energy regime, by applying the correlated product of two two center continuum function, to describe the two equivalent ejected electrons, which has the advantage of showing the influence of the final state electron-electron correlation. We have applied three different initial states wave function for the fundamental state of H_2 and shown the importance of the initial state correlation and obtained quite good agreement with the experimental results. In the case of N_2 , basic Hartree-Fock diatomic orbitals are obtained and applied as a first attempt. The results verify the symmetry conditions of the TDCS and show the optimal ejection directions for an equal energy sharing geometry. The comparison with the fitted Gaussian parametrization results show some instructive deflections due to the diatomic nature of the targets. The case of unequal ejection energy, and the neighboring $^3\Pi_u$ state of N_2^{2+} , which

presents open shell configurations will be treated in a near future paper.

References

- [1] H. McGuire, *Electron Correlation and Dynamics in Atomic Collisions* (Cambridge University Press, Cambridge, UK, 1997)
- [2] P. Bolognesi et. al., *J. Phys. B*, **37** (2004) 2285.
- [3] N. Chandra, S. Sen, *Eur. Phys. J. D* **6** (1999) 457.
- [4] O. Chuluunbaatar et. al., *J. Phys. B*, **45** (2012) 015205.
- [5] O. Chuluunbaatar et al. 2008 *J. Phys. B: At. Mol. Opt. Phys.*, **41** 015204
- [6] A. Lahmam-Bennani et. al., *Phys. Rev. A*, **67** (2003) 010701.
- [7] B. Joulakian et. al., *J. Phys. B*, **25** (1992) 2863.
- [8] R.K. Nesbet, *J. Comp. Phys.*, **40** (1964) 3619.
- [9] M. Nardin et. al., *ACM Transactions on Mathematical Software* **18** (1992) 345.
- [10] A.V. Turbiner et. al. 2007 *arXiv:physics/0606120v2 [physics.atom-ph]*.
- [11] A.S. Kheifets, *Phys. Rev. A*, **71** (2005) 022704
- [12] J.H.D. Eland, *Chem. Phys.*, **294** (2003) 171.
- [13] M. Lundqvist M et.al., *J. Phys. B*, **29** (1996) 1489.
- [14] A. Huetz et. al., *J. Phys. B*, **24** (1991) 1917.