Sequential two-photon double ionization of noble gas atoms

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Abstract. We develop a formalism which describes sequential two-photon double ionization (TPDI) of a closed-shell atom. We apply this formalism to calculate the angular asymmetry parameters of TPDI of the Ne $2p$ and Ar $3p$ valence subshells Comparison with the latest experimental data is made.

PACS numbers: 42.50.Hz 32.80.-t 32.80Fb

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In recent years, strong field ionization of noble gas atoms have been studied extensively using the Free electron LASer at Hamburg (FLASH). Wabnitz *et al* (2005) studied multiple ionization of Ar and Xe atoms at the photon energy of $\omega = 13$ eV. Moshammer *et al* (2007) reported few-photon multiple ionization of Ne and Ar at $\omega = 38.8$ eV. Sorokin *et al* (2007) mesaured direct, sequential, and resonant multi-photon ionization and excitation processes in Ne at $\omega = 42.8$ eV. Using an alternative high harmonic generation technique, Benis *et al* (2006) observed two-photon double ionization of Ar and Kr atoms by a superposition of harmonics. Besides the total ionization rate, the latest experiments are aiming to obtain various differential cross-sections. Very recently, Braune *et al* (2007) reported the angular anisotropy β parameters in sequential two-photon double ionization of Ne at 47.5 eV and Ar at 38 eV. Recoil ion momentum resolved measurements of Moshammer (2007) on Ne at 45 eV can also be interpreted in terms of these β parameters.

On the theoretical side, little have been done so far to support these angular resolved measurements. The only related work is a calculation of Kazansky & Kabachnik (2006) who reported the angular distributions of the Auger $2p$ and $3d$ electrons in Ar and Kr in coincidence with photoelectrons in femto- and attosecond pulse regimes.

In the meantime, the theoretical framework to evaluate the β parameters in TPDI of noble gases can be readily developed. The works of Jacobs & Burke (1972) and Dill *et al* (1975) provided two alternative formulations for the β_2 parameters for one-photon single-electron ionization of an arbitrary atomic target. The only missing link with the present measurements of β parameters in sequential TPDI of noble gases is coupling of the angular momenta of two photons, two photoelectrons and two residual ions. This coupling can be worked out using the graphical angular momentum summation technique provided, i.e. by Varshalovich *et al* (1988).

In the present communication, we perform this task and derive the expressions for the $\beta 2$ parameters in sequential TPDI of a closed-shell atomic target. We use these expressions to evaluate the angular anisotropy parameters for TPDI of the outer valence subshells of Ne and Ar in a wide photon energy range. We make a comparison of the calculated parameters with available experimental data at few selected photon energies.

We illustrate our graphical method by first deriving well known expressions of the β parameter in one-photon single-electron ionization of an arbitrary atomic target. We write the matrix element of the dipole operator between the initial and final many-electron states using notations of Sobelman (1972) in which we omit the spin variables:

$$\langle l_0^n\, L_0 M_0 \mid D \mid l_0^{n-1}[L_a]\; l\, LM\rangle = \sqrt{n}\; G_{L_a}^{L_0}\; (-1)^{L-M} \langle l_0^n\, L_0 \parallel D \parallel l_0^{n-1}[L_a]\; l\, L\rangle \qquad (1)$$

Here $G_{L_a}^{L_0}$ is a fractional parentage coefficient. The expression for the reduced dipole matrix element is given by Chen *et al* (2003):

$$\langle l_0^n\, L_0 \parallel D \parallel l_0^{n-1}[L_a]\; l\, L\rangle = \sqrt{\frac{n}{2}}\; G_{L_a}^{L_0}\; \hat{L}_0 \hat{L}\; (-1)^{L+L_a+l_0+1} \times \left\{ \begin{array}{ccc} 1 & L_0 & L \\ L_a & l & l_0 \end{array} \right\} \langle \nu_0 \| \; d \; \| \; \nu \rangle \qquad (2)$$

where the one-electron reduced dipole matrix element is defined according to Amusia (1990):

$$\langle \nu_0 \| \; d \; \| \; \nu \rangle = (-1)^{l>} \sqrt{l_>} \int r^2 \, dr R_{n_0 l_0}(r) R_{kl}(r) \; . \tag{3}$$

Here $l >$ is greater of l_0 and l. For a closed-shell system, the factor preceding the one-electron reduced dipole matrix element in Equation (2) is equal to one.

Using these notations, we can write the differential, with respect to the photoelectron momentum, cross-section as

$$\frac{d\sigma}{d\boldsymbol{k}} = \frac{1}{2L_0+1} \sum_{M_0} \left| \sum_{\substack{LM \\ lm}} \hat{L} (-1)^{L+L_a+l} \right. \tag{4}$$
$$\left. \begin{pmatrix} L & 1 & L_0 \\ -M & \mu & M_0 \end{pmatrix} \begin{pmatrix} L_a & l & L \\ M_a & m & -M \end{pmatrix} D_{lL} Y_{lm}(\hat{\boldsymbol{k}}) \right|^2$$

Here $\mu = 0, 1$ is associated with the linear and circular polarizations, respectively. The hat-symbol denotes $\hat{L} = \sqrt{2L+1}$. Following Jacobs & Burke (1972), we introduce in Equation (4) a shortcut for the phase-modulated and normalized dipole matrix element:

$$D_{lL} \equiv 2\pi (\omega/c)^{1/2} \exp(l\pi/2 + \delta_l) \langle l_0^n \, L_0 \; \| \, D \, \| \; l_0^{n-1} [L_a] \; l \, L \rangle \tag{5}$$

The product of two spherical harmonics in Equation (4) can be transformed using the Clebsch-Gordan series given by Eq. (5.6.9) (Equation (9) of Section 5.6) of Varshalovich *et al* (1988)

$$Y_{lm}(\hat{\boldsymbol{k}}) Y_{l'm'}(\hat{\boldsymbol{k}}) = \frac{1}{4\pi} \hat{l} \hat{l}' \sum_{JM_J} \hat{J}^2 \begin{pmatrix} l & l' & J \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & l' & J \\ m & m' & -M_J \end{pmatrix} Y_{JM_J}(\hat{\boldsymbol{k}}) \tag{6}$$

Thus, Equation (4) contains the sum of five $3j$ symbols running over six angular momentum projections which can be exhibited graphically by the left diagram of Figure 1

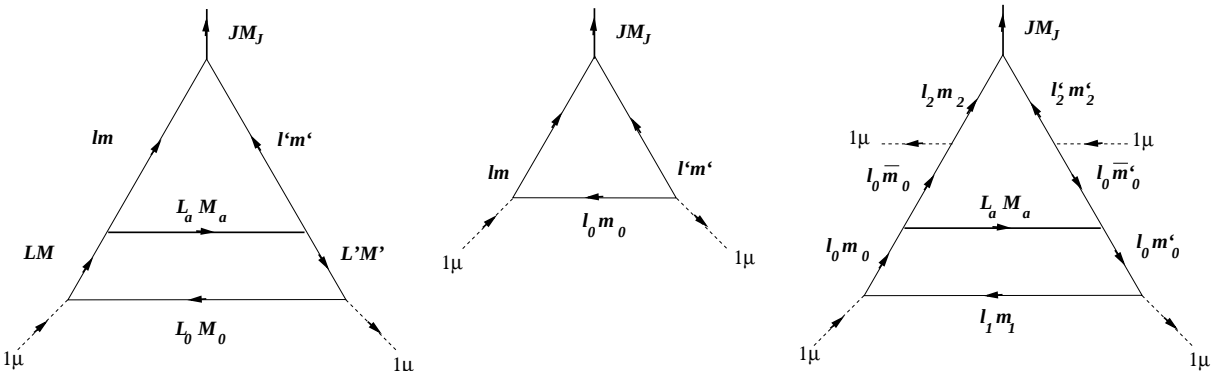

Figure 1. Angular momentum coupling schemes for one-photon single ionization (left and center) and two-photon double ionization (right). The vertex denotes a $3j$ symbol. The sign of the angular momentum projection is indicated by the arrow, incoming with the plus sign and outgoing with the minus sign.

The sum can be readily evaluated using Eq. (12.1.13) of Varshalovich *et al* (1988) which leads to the standard photoelectron angular distribution $d\sigma/d\boldsymbol{k} = (4\pi)^{-1}d\sigma/dE[1+\beta_2 P_2(\cos\theta)]$ with $\beta_2 = A_2/A_0$ where the coefficients A_J are given for linear polarization ($\mu = 0$) by the following expression:

$$A_J = \frac{(-1)^{L_a+L_0}}{2L_0+1}\hat{J}^2 \sum_{\substack{LL' \\ ll'}} \hat{l}\hat{l}'\hat{L}\hat{L}' \times \begin{pmatrix} J & l & l' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} J & 1 & 1 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} J & 1 & 1 \\ L_0 & L & L' \end{Bmatrix} \begin{Bmatrix} J & l & l' \\ L_a & L' & L \end{Bmatrix} Re\{D_{lL}D^*_{l'L'}\}$$

Equation (7) is equivalent to Eqs. (3)-(4) by Jacobs & Burke (1972) †

When the electron-ion interaction is isotropic, we can neglect the effect of the total spherical symmetry of the ionized atom on the photoelectron and factor out the explicit L-dependence of the dipole matrix elements from Equations (2) and (5):

$$D_{lL} \equiv d_l\ \hat{L}\hat{L}_0(-1)^L \begin{Bmatrix} 1 & L_0 & L \\ L_a & l & l_0 \end{Bmatrix} \tag{7}$$

The sum over the total angular momenta L, L' can now be carried over using successively Eqs. (12.2.18) and (12.2.7) of Varshalovich *et al* (1988). This finally leads to

$$A_J = \frac{1}{2l_0+1}\hat{J}^2 \sum_{l,l'=l_0\pm1} \hat{l}\hat{l}' \begin{pmatrix} J & l & l' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} J & 1 & 1 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} 1 & 1 & J \\ l & l' & l_0 \end{Bmatrix} Re\{d_l\, d^*_{l'}\} \tag{8}$$

The asymmetry parameter $\beta_2 = A_2/A_0$ derived from Equation (8) does not contain atomic or ionic quantum numbers. The fractional parentage coefficient occur both in A_0 and A_2 and cancels out. Thus the β_2 parameter can be expressed solely through one-electron quantum numbers. This result can be obtained straightforwardly if we consider the photoionization in the independent electron approximation and describe it by the angular momentum coupling scheme exhibited by the center diagram of Figure 1. This is a well-known result (see e.g. (Dill *et al* 1975)) which explains the success of the Cooper-Zare independent-electron model (Cooper & Zare 1969).

Now we extend our formalism to the case of two-photon two-electron ionization. The cross-section of the sequential TPDI process can be written as

$$\frac{d\sigma}{d\boldsymbol{k}_1 d\boldsymbol{k}_2} = \frac{1}{2L_0+1} \sum_{M_0 M_a} \Bigg| \sum_{L_i M_i} \sum_{\substack{L_1 M_1 \\ l_1 m_1}} \sum_{\substack{L_2 M_2 \\ l_2 m_2}} \tag{9}$$

$$(-1)^{L_1+L_i+l_1} \begin{pmatrix} L_1 & 1 & L_0 \\ -M_1 & \mu & M_0 \end{pmatrix} \begin{pmatrix} L_i & l_1 & L_1 \\ M_i & m_1 & -M_1 \end{pmatrix} D_{l_1 L_1}\, Y_{l_1 m_1}(\boldsymbol{k}_1)$$

$$(-1)^{L_2+L_a+l_2} \begin{pmatrix} L_2 & 1 & L_i \\ -M_2 & \mu & M_i \end{pmatrix} \begin{pmatrix} L_a & l_2 & L_2 \\ M_a & m_2 & -M_2 \end{pmatrix} D_{l_2 L_2}\, Y_{l_2 m_2}(\boldsymbol{k}_2) \Bigg|^2$$

† Notations of Jacobs & Burke (1972) are ambiguous as the angular momenta of the atom and the ion are both denoted by the same symbol. When unambiguous notations are employed, the equivalence of the original equations and the present Equation (7) becomes evident

Here we adopt the following angular momentum coupling scheme:

$$l_0^n[L_0] + \gamma \rightarrow l_0^{n-1}[L_i] + k_1 l_1\} \, L_1 \quad , \quad l_0^{n-1}[L_i] + \gamma \rightarrow l_0^{n-2}[L_a] + k_2 l_2\} \, L_2$$

By integrating Equation (9) over $d\boldsymbol{k}_1$ and employing the Clebsch-Gordan series (6), we end up with the expression containing the sum of nine $3j$-symbols running over eleven angular momentum projections. This sum can be exhibited by a triangular diagram similar to the one on the left of Figure 1 but with a larger number of "ladder steps". Varshalovich *et al* (1988) does not provide a direct summation formula for this case. Nevertheless, the summation can be carried over using reduction formulae (12.1.10) and (12.1.11) which reduce the number of ladder steps by one. As a result, the angular distribution of the photoelectron is given by the Legendre polynomial expansion $d\sigma/d\boldsymbol{k}_2 = (4\pi)^{-1} d\sigma/dE_2[1 + \beta_2 P_2(\cos\theta_2) + \beta_4 P_4(\cos\theta_2)]$ where the angular anisotropy coefficients $\beta_J = A_J/A_0$ can be derived from the following coefficients:

$$A_J = \hat{J}^2 \sum_{l_1 l_2 l_2'} (-1)^{L_0+L_a+l_1} \hat{l}_2 \hat{l}_2' \sum_{\substack{L_1 L_1' \\ L_2 L_2'}} \sum_{L_i L_i'} \begin{pmatrix} l_2 & l_2' & J \\ 0 & 0 & 0 \end{pmatrix} Re\{\mathcal{D}_{l_1 l_2 \, L_1 L_2} \mathcal{D}^*_{l_1 l_2' \, L_1' L_2'}\}$$
$$\begin{Bmatrix} L_2 & L_2' & J \\ l_2' & l_2 & L_a \end{Bmatrix} \sum_{KK'} \hat{K}^2 \hat{K}'^2 (-1)^{K+K'} \begin{pmatrix} 1 & K & 1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & K' & 1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} K & K' & J \\ 0 & 0 & 0 \end{pmatrix}$$
$$\begin{Bmatrix} 1 & 1 & K \\ L_1 & L_1' & L_0 \end{Bmatrix} \begin{Bmatrix} L_i & L_i' & K \\ L_1' & L_1 & l_1 \end{Bmatrix} \begin{Bmatrix} K & L_i' & L_i \\ K' & 1 & 1 \\ J & L_2' & L_2 \end{Bmatrix} \qquad (10)$$

Here we denoted $\mathcal{D}_{l_1 l_2 \, L_1 L_2} = D_{l_1 L_1} D_{l_2 L_2}$ for brevity of notations and set $\mu = 0$.

For a closed atomic shell, $L_0 = 0$ and $L_i = L_i' = l_0$, $L_1 = L_1' = 1$. Further simplification of Equation (10) can be achieved if we neglect the dependence of the wave function of the second photoelectron on the total angular momentum L_2. Then the explicit L_2 dependence of the matrix element $D_{l_2 L_2}$ can be factored out using Equation (7) and the summation over L_2, L_2' can be carried over. This leads to the anisotropy parameters $\beta_J = A_J/A_0$ which can be extracted from the following coefficients:

$$A_J = \hat{J}^2 \sum_{l_1 l_2 l_2'} (-1)^{l_1+l_2+l_2'} \hat{l}_2 \hat{l}_2' \begin{pmatrix} l_2 & l_2' & J \\ 0 & 0 & 0 \end{pmatrix} |d_{l_1}|^2 Re\{d_{l_2} d^*_{l_2'}\}$$
$$\sum_{KK'} \hat{K}^2 \hat{K}'^2 (-1)^{K'} \begin{pmatrix} 1 & K & 1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & K' & 1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} K & K' & J \\ 0 & 0 & 0 \end{pmatrix}$$
$$\begin{Bmatrix} 1 & 1 & K \\ l_0 & l_0 & l_1 \end{Bmatrix} \begin{Bmatrix} l_0 & l_0 & K \\ l_0 & l_0 & L_a \end{Bmatrix} \begin{Bmatrix} K & l_0 & l_0 \\ K' & 1 & 1 \\ J & l_2 & l_2 \end{Bmatrix} \qquad (11)$$

As in the case of Equation (8), the β parameters extracted from Equation (11) do not contain the ionic or atomic quantum numbers except for the total angular momentum of the doubly charged ion L_a. Equation (11) can be derived straightforwardly if we consider an independent electron TPDI process in which the angular momenta of the two holes

couple to the total angular momentum L_a. This process is exhibited graphically by the right diagram of Figure 1.

We use Equation (11) to evaluate the β_J parameters of TPDI of Ne $2p$ and Ar $3p$ valence subshells. Isotropy of the system containing the doubly charged ionic core and the photoelectron, which is essential for application of Equation (11), can be judged, at least partly, from the properties of the discrete excited states of this system reflected in the spacing of the energy levels of the singly charged ion. Inspection of the Ne II energy levels (Moore 1949) shows that $2p^4[L_aS_a]nl\}LS$ manifold is indeed governed by the quantum numbers L_aS_a and depend very weakly on LS. This is less so in Ar II. Therefore the present Ar results should be treated as qualitative rather than quantitative. More accurate calculation using Equation (10) is needed to get the Ar β-parameters on the same level of accuracy as for Ne.

In practical computations, we obtain the one-electron dipole matrix elements for the neutral atom d_{l_1} running the RPAE computer code (Amusia & Chernysheva 1997). The random phase approximation with exchange (RPAE) provides a very accurate description of single-photon one-electron ionization processes in noble gas atoms (Amusia & Cherepkov 1975). The β_2 parameters derived from the RPAE dipole matrix elements using Equation (8) are in excellent agreement with experimental data of Braune *et al* (2007). For Ne at 47.5 eV, $\beta_2 = 0.98$ as compared with experimental value of 1.00. For Ar at 38 eV, $\beta_2 = 1.84$ as compared with experimental value of 1.88.

In principle, the RPAE method can be modified to describe ionization of an open np^5 shell (Cherepkov & Chernysheva 1977). This, however, would require an explicit account for anisotropy of the ionized system which we neglect when substituting Equation (10) with Equation (11). Therefore, we opted for a less computationally demanding Hartree-Fock method when calculating the one-electron dipole matrix elements d_{l_2} for the singly charged ion. The radial orbitals $R_{n_0l_0}$ and R_{kl} entering Equation (3) are calculated using the self-consisted and frozen-core Hartree-Fock codes, respectively (Chernysheva *et al* 1976, Chernysheva *et al* 1979).

Results of our computations are shown in Figure 2 for Ne (left) and Ar (right). On the same figure we indicate the numerical values of the experimental anisotropy parameters $\beta_2 = 0.74$, $\beta_4 = -0.5$ for Ne at 47.5 eV and $\beta_2 = 1.82$, $\beta_4 = -0.14$ for Ar at 38 eV as reported by Braune *et al* (2007) for the ^3P final state of the doubly charged ion. These results are in fair agreement with the present calculation. However, more experimental data across a wider photon energy range are clear needed to gauge the quality of the present theoretical model and its numerical implementation.

It is noteworthy that the β_2 parameters depend weakly on the symmetry of the doubly charged ion. Conversely, the β_4 parameters demonstrate a very strong dependence with very small absolute values for ^1D state and relatively large in magnitude and opposite in sign values for ^3P and ^1S states. This behavior can be understood from Equation (11). The statistical average $\sum_{L_a}(2L_a+1)A_J$ is proportional to δ_{K0} which eliminates the coefficients A_4 and reduces A_0 to single-photon one-electron value (8). Although the statistical average does not apply directly to the ratio A_J/A_0,

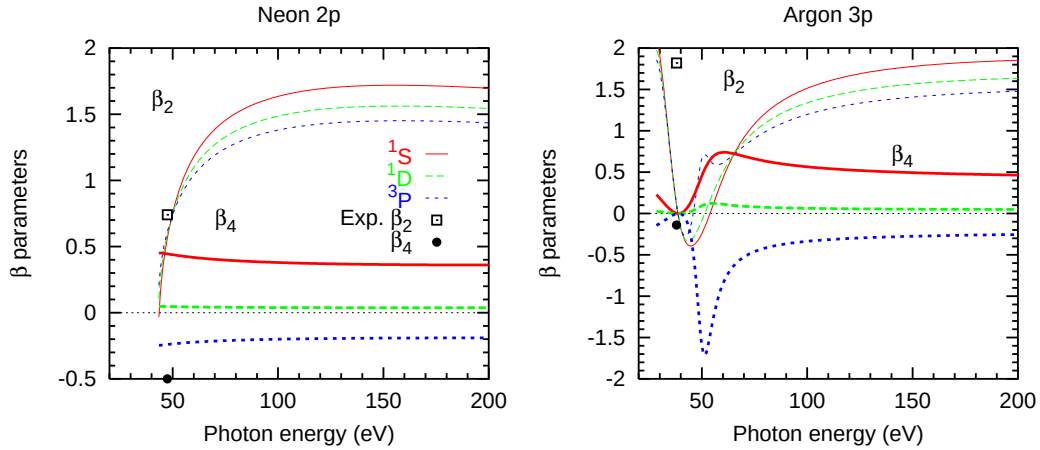

Figure 2. The angular anisotropy β-parameters for Ne (left) and Ar (right). The experimental data are from Braune *et al* (2007)

one would expect the term average value of β_4 close to zero which is indeed the case for Ne for which β_2 shows little term dependence. For Ar, β_2 shows strong term dependence near the threshold and the statistical average of β_4 deviates from zero in this photon energy range.

The author wishes to thank Markus Braune and Robert Moshammer for communicating their experimental result prior to publication

Amusia M I & Chernysheva L V 1997 *Computation of atomic processes : a handbook for the ATOM programs* Institute of Physics Pub. Bristol, UK

Amusia M Y 1990 *Atomic photoeffect* Plenum Press New York

Amusia M Y & Cherepkov N A 1975 *Case Studies in Atomic Physics* **5**, 47

Benis E P *et al* 2006 *Phys. Rev. A* **74**(5), 051402

Braune M *et al*, Reinköster A, Viefhaus J, Lohmann B & Becker U 2007 *in* 'ICPEAC XXV Abstracts' Freiburg p. Fr034

Chen Z, Cherepkov N & Msezane A Z 2003 *Phys. Rev. A* **67**(2), 024701

Cherepkov N A & Chernysheva L V 1977 *Phys. Lett. A* **60**(2), 103–105

Chernysheva L V, Cherepkov N A & Radojevic V 1976 *Comp. Phys. Comm.* **11**, 57

Chernysheva L V, Cherepkov N A & Radojevic V 1979 *Comp. Phys. Comm.* **18**, 87–100

Cooper J & Zare R N 1969. In *Lectures in Theoretical Physics* Geltman S, Mahanthappa K T & Britten W E, eds Vol. XI-C Gordon and Breach New York pp. 317–337

Dill D, Starace A F & Manson S T 1975 *Phys. Rev. A* **11**(5), 1596–1606

Jacobs V L & Burke P G 1972 *Journal of Physics B: Atomic and Molecular Physics* **5**(4), L67–L70

Kazansky A K & Kabachnik N M 2006 *Phys. Rev. A* **73**(6), 062712

Moore C E 1949 *Atomic Energy Levels* Circ. No. 467 Vol. 1, Natl. Bur. Stand. , Washington

Moshammer R 2007. private communication

Moshammer R *et al* & Ullrich J 2007 *Phys. Rev. Lett.* **98**(20), 203001

Sobelman I I 1972 *Introduction to the theory of atomic spectra* Oxford, Pergamon Press

Sorokin A A, Wellhofer M, Bobashev S V, Tiedtke K & Richter M 2007 *Phys. Rev. A* **75**(5), 051402

Varshalovich D A, Moskalev A N & Khersonskii V K 1988 *Quantum theory of angular momentum* 1st edn World Scientific Philadelphia

Wabnitz H *et al* 2005 *Phys. Rev. Lett.* **94**(2), 023001