atoms

MDPI

Editorial

"Atoms" Special Issue (Electron Scattering in Gases—From Cross Sections to Plasma Modeling)

Grzegorz P. Karwasz

Institute of Physics, Uniwersytet Mikołaja Kopernika w Toruniu, 87 100 Torun, Poland; karwasz@fizyka.umk.pl

Experimental studies of electron scattering in gases, under the name of "cathode rays", started before the "official" discovery of the electron by J. J. Thompson (in 1897). At the beginning of the XXth century, experiments on electron scattering contributed to the formulation of modern, wave-like quantum mechanics; the minimum of the cross sections in Ar, Kr, Xe, now known as the Ramsauer–Townsend's effect (see [1] and references therein), cannot be explained even within "old" quantum mechanics. An explosion of the interest in atomic processes started with the advent of space flights. Dr Donald Rapp, the co-author of one of the most accurate measurements of electron-impact ionization of molecules [2], wrote the following in February 2021: "I didn't realize it at the time, but I had the best possible position one could imagine. I was given a laboratory, a lab assistant, association with several co-workers, and a budget. And I could work on anything I chose, provided it had at least a distant relationship to the ionosphere." Today, cross sections for electron (and positron) scattering are needed, not only to understand the atomic processes in planetary nebula and atmospheres of the solar system, but first of all to model plasma processes for numerous implementations, from semiconductor industries to thermonuclear reactors.

In this volume, we present a "cross-section" of different approaches, applications and processes, from industrial plasmas [3,4] to molecules of biological interest [5–7]; from experiments at ultra-low temperatures [8,9] to processes relevant for thermonuclear synthesis [10]. Thanks to a global response to the invitation, this volume hosts in an equilibrated manner the experimental aspects [6,8,9], ab-initio theories [7,10–12] and semi-empirical approaches [13–16], both for electron and positron scattering [11,15–17].

In principle, the more detailed our knowledge is of cross sections, the more precise modeling of plasma parameters can be carried out, but only in principle. Mohr et al. [3] stress that calculations of cross sections, in particular for the formation of neutral fragments and radicals in electron collisions, are time consuming. Therefore, even if the present methods, such as UK R-Matrix codes, are highly versatile, for chemical processes well-targeted modeling must be planned. Mohr et al. present an example of such an approach for the SF_6/O_2 mixtures used in semiconductor etching. The cross sections for the two "input" gases are known, but for the SOF_x species, which may be formed in the plasma, they are not known. The authors evaluate the unknown ionization and dissociation cross sections and then estimate the densities of electrons and radicals. The validity of this approach resides in the economizing computer (and man) power needed to model real situations in plasma reactors.

Chung et al. [4] apply cross sections to optical diagnostics of argon plasma. They assume the corona model, i.e., no collisional interaction between excited states, and no cascading in the de-excitation. The model includes numerous processes, such as stimulated absorption, collisional de-excitation, quenching of metastables on walls etc. More than 20,000 optical transitions are accounted for (primarily from NIST, LXCAT and other databases, and from different theories). Six models, based on alternative datasets, are compared with the authors' experiments with capacitively and inductively coupled plasma. The corona model applies somewhat better to the second type of reactor. Chung et al. show

Citation: Karwasz, G.P. "Atoms" Special Issue (Electron Scattering in Gases—From Cross Sections to Plasma Modeling). *Atoms* **2022**, *10*, 54. https://doi.org/10.3390/atoms10020054

Received: 5 May 2022
Accepted: 26 May 2022
Published: 27 May 2022

that the present knowledge of cross sections is vast, but other processes, such as quenching and recombination on walls, should be included to obtain more successful modeling.

Three papers discuss "edge-cutting" experiments in electron scattering. Ptasińska [5] presents a review on the role of very-low (below few V) electrons in radiation damage of living cells. The experiments (on molecules in gas phase) showed that low-energy electrons are resonantly captured by DNA constituents (sugars or nucleobases), via a dissociative attachment (DA) process. The experiments detected negatively charged fragments produced in such a dissociation. However, the DA mechanism with DNA does not explain the high lethality of ionizing radiation (electrons from ionization events are the main product of radiation slowing-down processes). In living cells, it is probably the water molecule, which via a resonant electron capture, produces OH and H radicals that together with solvated electrons "kill approximately 70% of cells". Therefore, Ptasińska proposes new experiments aiming to detect "the missing part" of the radiation damage, i.e., neutral radicals.

Collisions of electrons with nano-droplets is the conceptual pathway leading from scattering on single atoms to studies of condensed matter; single scattering events occur in the "bulk-like" environment. Liquid helium droplets are able to capture atoms and molecules, clusters may form inside them and the spectroscopy of cold molecules inside a neutral matrix is possible. Laimer et al. [9] used a tandem mass spectrometer to study the collision of electrically charged He droplets with electrons with variable energy (0–120 eV). By changing the energy of the first electron beam, from 40 eV to 30 eV, positively or negatively charged droplets, with up to 100 million He atoms, can be produced. For positively charged droplets and 22.5 eV collision energy, Laimer et al. observed predominantly a reduction in the charge, while for 120 eV, an increase in the charge was observed (i.e., additional ionization). Laimer et al. discuss several reaction channels, such as Penning ionization in the collision of two metastable He atoms, or electron detachment (combined with the ionization) in the collision of a metastable anion with a metastable He atom. Reactions, probably, undergo via resonant-like processes.

Helium, differently from Ar, Kr and Xe, does not show Ramsauer–Townend minimum in the integral elastic (and momentum transfer) cross sections. Borghesani [8] measured the drift velocities of electrons in moderately dense (up to 10 MPa) helium. Drift conditions (temperature, gas densities and the electric field) have been chosen to evidence the different regimes of scattering, including the low-field region where scattering is well approximated by a rigid-sphere model and the intermediate region where a bubble of solvated electron moves in the electrical field. The paper is an excellent matching between quantum and classical physics.

García-Abenza et al. [6] carried out a critical evaluation using recent data by Song et al. [18] for electron scattering on H_2O. Their methodology, which is "capable of delivering the most accurate datasets", combines both the theory (event-by-event Monte Carlo simulation and Geant4DNA code) and the experiment (the transmission of magnetically confined electrons in gas cell). The independent-atoms model was used to extend differential cross sections for elastic and inelastic scattering into angles that are not measurable in angular-distribution experiments (below 10° and above 130°). The comparison of the simulations with the transmission-current experiment shows that, particularly at high collision energies, more insight is needed into the differential cross sections, especially for inelastic processes with small energy losses.

In this context, the prototype of the so-called magnetic-angle changer spectrometer, projected by Kłosowski and Piwiński [19] to measure differential cross sections in a wide angular range, is particularly interesting. The device consists of as many as 30 pairs of circular wires arranged into coils. The task was to maintain the bending magnetic field low (below 1 mT), in order to avoid the influence of that field on the configurations/populations of metastable atoms in the region of scattering. Numerical simulations show that the spectrometer should allow measurements in the low-angle range, down to 0°. Above 60°, the spectrometer introduces a quite large (of few degrees) angular spread of the incident electron beam, which limits its use.

Total cross sections, which comprise elastic and inelastic processes (rotational, vibrational and electronic excitation, and ionization), are easily measured (see [1]), but are quite difficult to be calculated. Uddin et al. [20] calculated the total cross section for electron scattering (6–5000 eV energy) on butanol and pentanol isomers. They used spherical complex optical potential in which the static (Hartree–Fock), exchange (Hara's) and polarization potentials constitute the real part, and the energy-dependent, imaginary part is responsible for the "absorption" (i.e., electronic excitation and ionization) processes. For butan-1-ol, the comparison with experiments is possible as both the integral elastic and the total cross sections match the measurements well. The cross sections for different isomers (five within the pentanol and four within butanol group) show some differences only in the low energy range (below 20 eV).

The ionization of atoms and molecules, at least in the case of electron collisions, has rather vast experimental coverage. This allows us to test different theoretical and semi-empirical approaches, which, in turn, allow us to predict cross sections for species inaccessible for direct measurements, such as highly charged ions [10], molecular metastables [15] or metals [14].

Campeanu and Whelan [11] calculated triple differential cross sections (TDCS) both for positron and electron scattering on inert gases. The comparison between electrons and positrons allows one to test the exchange effects. Differential cross sections, and particularly those measured in coincidence experiments, bring much more information on the scattering processes than integral values. Campeanu and Whelan concentrated on scattering geometries in which the impinging electron loses more than half its energy, so the recoil effects of the nucleus are significant. Additionally, they modified the kinematics of scattering in order to identify possible role of distortion, post-collision interaction and interference effects. For electron scattering on helium and neon, the theoretical TDCS, different scattering geometries agree very well with the experiments. The paper shows the importance of few-body effects in the ionization process, including the interference effects for non-coplanar geometries and multiple scattering at high energies.

Laricchiuta et al. [21] applied the Binary-Encouter Bethe (BEB) approach to calculate the ionization cross section of the N_2 ($A\ ^3\Sigma_u^+$), CO ($a\ ^3\Pi$) and H_2 ($c\ ^3\Pi_u$) and ($a\ ^3\Sigma_g^+$ metastables. Orbital energies needed as the input data to BEB were obtained from the unrestricted Hartree–Fock approach. The N_2 metastable state is long-lived (2.4 s), so its presence significantly changes the kinetics of nitrogen discharges. Laricchiuta et al.'s results suggest that available experimental determinations may be underestimated by a factor of two. In turn, H_2 metastables show even higher total ionization cross sections, up to about 10×10^{-16} cm^2 at their maxima.

A similar model, derived from the BEB approach, has been applied by Franz et al. [15] for positron ionization of diatomic molecules. In the high energy limit, according to the Born approximation, positron and electron-scattering cross sections should merge. This has been theoretically and experimentally proved for H_2 at energies above 100 eV (see a recent review [22]) but is still uncertain for heavier targets. In particular, in the case of positron scattering and in the energy range between 10–100 eV, a high contribution comes from the formation of the bound electron-positron state (positronium), which leaves the target molecule in the ionized state, making the experimental distinction difficult. The two cases, ionization by electrons and positrons, should show different threshold dependences; after the ionization, the two electrons fly in the opposite directions (in the first case) or in the same direction (for the electron–positron pair). The BEB approach by Franz et al. takes into account these differences. For H_2 and N_2, the results with the "correct" threshold law reproduce the experimental data very well. The agreement is worse for O_2 and CO, but it can be also caused by uncertainties in experiments.

Golyatina and Maiorov [14] discuss integral ionization cross sections. They propose a simple, three-parameter power-like fit, deriving from early (1912) Thomson's formula. The authors make a vast review of experiments for as many as 28 atomic targets, starting from hydrogen to platinum and uranium, including noble gases and transitions metals. For

the targets that received somewhat better experimental (and theoretical) coverage, such as alkali metals, the quality of the fit may be judged as good. However, as in the case of positron-impact ionization, more experiments are also needed for the electron ionization of metal vapors.

Two contributions discuss the vibrational excitation. This subject needs new approaches, as the simplified Born approximation works well only in some cases, such as the excitation of infrared-active modes. Ayouz et al. [7] present results for vibrational excitation (and de-excitation) of three modes in H_2O by electron impact, while Poveda et al. [17] demonstrate the excitation of the $\nu = 0 \rightarrow 1$ mode in H_2 by positron impact.

Ayouz et al. [7] used the fixed-nuclei reactace matrix, obtained numerically from the UK molecular R-Matrix code (UKRMol) with the Quantemol-N system. The calculation for the equilibrium geometry predicts the following 4 resonances: 2 narrow at 7.8 eV and 10 eV and 2 wider at 6.7 eV and 11 eV. The calculated excitation cross sections agree well with the recent "recommended" values [18] up to 4 eV. At higher energies, the resonant scattering increases significantly (by a factor of two, as compared to the theory) the vibrational excitation. For the stretching modes, different theories systematically underestimate the experiment. The choice of different orbital basis sets does not improve this discrepancy. Ayouz et al. hypothesized two possible reasons for this discrepancy, one physical, another numerical, including the capturing of the incoming electron into the molecule in the excited vibrational state and/or the underestimation of the polarization interactions in the close-coupling approach.

The vibrational excitation by positron impact, as in CF_4, follows the Born approximation. However, the annihilation rate for positrons colliding with molecules possessing numerous vibrational models, such as complex hydrocarbons, [23] shows sharp resonant enhancements just below the threshold for vibrational modes (we call them "Surko resonances"). Poveda et al. [17] used a wave-packet dynamics for the vibrational $\nu = 0 \rightarrow 1$ excitation of H_2 molecules by positron impact. They used well-established molecular parameters of the molecule (the internuclear distance and the polarizability), and a cut-off polarization. The model reproduces the experimental determination very well in the range from the threshold up to 3 eV. The same model with much higher polariziability values gives a sharp threshold peak, but does not change the cross sections at higher (1–3 eV) energies. This may be a valid indication for the explanation of "Surko" resonances, and links to the discussion of the vibrational excitation in H_2O.

Applications of atomic physics in thermonuclear plasmas require knowledge of cross sections for "exotic" systems, including heavy atoms and highly charged ions, for scattering energies up to tens of keV. The present volume brings two such contributions. Khandker et al. [12] calculated differential, integral elastic, momentum transfer, viscosity, total inelastic and grand total cross sections, together with spin polarization parameters for electron and positron scattering on Rn atoms and ions of radon isonuclear series (up to Rn^{+86}), in the energy range from 1 eV to 1 MeV. A short range complex optical potential has been used; for charged particles, this potential is supplemented by the Coulomb interaction; the Dirac partial wave analysis has been employed. Differential cross sections for electron scattering show phenomena related to the interference between partial waves (i.e., Ramsauer minima) at energies as high as 2000 eV. The absorption potential is particularly important at intermediate energies, up to 500 eV, decreasing elastic scattering by a factor of two. For positron scattering, the influence of the absorption potential persists up to 50 keV. Above 10 keV, the positron and electron scattering cross sections coincide.

Electron-impact excitations of dipole-allowed transitions in the extreme UV range of Xe^{+7}–Xe^{+10} ions were calculated by Sahoo and Sharma [10]. Cross sections for 9, 18, 75 and 57 transitions for Xe^{+7}, Xe^{+8}, Xe^{+9} and Xe^{+10} ions, respectively, have been calculated. The multi-configuration Dirac–Fock method with QED corrections was used for the atomic structure calculations. Cross sections were calculated in the relativistic distorted-wave approach. Generally, the energy levels and transition rates agree well with the available experiments and theories. Transitions that involve the change in the spin have lower

cross sections than spin-conserving transitions. Sahoo and Sharma also give the fitting formula for the cross sections, including in the low energy range, a series of powers of energy (somewhat resembling the fit of the ionization cross sections by Golyatina and Mayorov [14]), and the Bethe–Born formula at high energies. Rate coefficients are given for electron temperatures from 5 to 100 eV.

The opposite, i.e., near-to-zero, energy range is "attacked" by Fedus, who re-proposes the modified-effective range theory. This is a semi-empirical approach that allows one to relate the integral elastic, differential elastic and momentum transfer cross sections in the very low energy range. As in this energy range only few partial waves contribute significantly to scattering, the method uses few fitting parameters, such as the zero-energy cross section (i.e., the scattering length) and the effective range. In the MERT fit used in the past both by experimentalists and theoreticians, these were cross section developed into series of power of energy. As a consequence, the applicability of the fit was limited to energies below 1 eV. A modification that consists of the development not of cross sections but of phase shifts [24] allowed one to extend the applicability of MERT up to the threshold for inelastic processes, both for positron and electron scattering. Fedus re-analyses experimental cross sections, both from beam and swarm experiments, in five noble gases (He-Xe). Fedus gives MERT parameters, together with their uncertainties, for single experimental sets of data, as well as for the whole ensemble of data. For He and Ne, Fedus additionally applies the hard-sphere model, similar to the work of Borghesani [8]. The model with radii of the hard spheres obtained from MERT analysis reproduces the phase shift for the s, p, d waves up to 1–3 eV, in pretty good agreement with other theories.

The volume concludes with our contribution [16] that proposes the re-opening of the discussion on some possible "invariance" parameters in electron and positron scattering. All the contributions of this volume relate total and partial cross sections to other atomic/molecular parameters. The question is if all these cross sections are somehow inter-related, i.e., if the rise of the ionization cross section is dependent on the decreasing of the elastic cross section. The absorption model by Khandker et al. [12] would suggest so. However, even this volume shows that the low and high energy ranges are treated separately, both in experiments and in theories. Can we "sew" back the energy ranges, and consider the total (i.e., elastic and inelastic) cross sections in the "whole" energy range, from zero to infinity? Can we further relate such an integral part of the total cross section with other molecular parameters, such as the total number of electrons or polarizability? For our study conducted for electron and positron scattering on molecules that received sufficient experimental coverage, N_2, CO_2, CH_4, CF_4 would suggest some relations, but they are still far from being conclusive.

We hope that this volume may constitute a short but useful overview of the scientific approaches and interests in electron and positron scattering and plasma applications, as portrayed in December 2021.

Funding: This research received no external funding.

Conflicts of Interest: The author declares no conflict of interest.

References

1. Zecca, A.; Karwasz, G.P.; Brusa, R.S. One century of experiments on electron-atom and molecule scattering: A critical review of integral cross-sections. *Rev. Nuovo Cim.* **1996**, *19*, 3. [CrossRef]
2. Rapp, D.; Englander-Golden, P. Total Cross Sections for Ionization and Attachment in Gases by Electron Impact. I. Positive Ionization. *J. Chem. Phys.* **1965**, *43*, 1464. [CrossRef]
3. Mohr, S.; Tudorovskaya, M.; Hanicinec, M.; Tennyson, J. Targeted Cross-Section Calculations for Plasma Simulations. *Atoms* **2021**, *9*, 85. [CrossRef]
4. Chung, H.-K.; Song, M.-Y.; Kwon, J.-W.; Lee, M.-G.; Park, J.; Bae, N.; Song, J.; Kim, G.-H.; Dipti; Ralchenko, Y. Population Kinetics Modeling of Low-Temperature Argon Plasma. *Atoms* **2021**, *9*, 100. [CrossRef]
5. Ptasinska, S. A Missing Puzzle in Dissociative Electron Attachment to Biomolecules: The Detection of Radicals. *Atoms* **2021**, *9*, 77. [CrossRef]

6. García-Abenza, A.; Lozano, A.I.; Oller, J.C.; Blanco, F.; Gorfinkiel, J.D.; Limão-Vieira, P.; García, G. Evaluation of Recommended Cross Sections for the Simulation of Electron Tracks in Water. *Atoms* **2021**, *9*, 98. [CrossRef]
7. Ayouz, M.; Faure, A.; Tennyson, J.; Tudorovskaya, M.; Kokoouline, V. Cross Sections and Rate Coefficients for Vibrational Excitation of H_2O by Electron Impact. *Atoms* **2021**, *9*, 62. [CrossRef]
8. Borghesani, A.F. Accurate Electron Drift Mobility Measurements in Moderately Dense Helium Gas at Several Temperatures. *Atoms* **2021**, *9*, 52. [CrossRef]
9. Laimer, F.; Zappa, F.; Gruber, E.; Scheier, P. Electron Ionization of Size-Selected Positively and Negatively Charged Helium Droplets. *Atoms* **2021**, *9*, 74. [CrossRef]
10. Sahoo, A.K.; Sharma, L. Electron Impact Excitation of Extreme Ultra-Violet Transitions in $Xe7^{+}$–$Xe10^{+}$ Ions. *Atoms* **2021**, *9*, 76. [CrossRef]
11. Campeanu, R.I.; Whelan, C.T. Few Body Effects in the Electron and Positron Impact Ionization of Atoms. *Atoms* **2021**, *9*, 33. [CrossRef]
12. Khandker, M.H.; Haque, A.K.F.; Haque, M.M.; Billah, M.M.; Watabe, H.; Uddin, M.A. Relativistic Study on the Scattering of e± from Atoms and Ions of the Rn Isonuclear Series. *Atoms* **2021**, *9*, 59. [CrossRef]
13. Fedus, K. Elastic Scattering of Slow Electrons by Noble Gases—The Effective Range Theory and the Rigid Sphere Model. *Atoms* **2021**, *9*, 91. [CrossRef]
14. Golyatina, R.I.; Maiorov, S.A. Analytical Cross Section Approximation for Electron Impact Ionization of Alkali and Other Metals, Inert Gases and Hydrogen Atoms. *Atoms* **2021**, *9*, 90. [CrossRef]
15. Franz, M.; Wiciak-Pawłowska, K.; Franz, J. Binary-Encounter Model for Direct Ionization of Molecules by Positron-Impact. *Atoms* **2021**, *9*, 99. [CrossRef]
16. Carelli, F.; Fedus, K.; Karwasz, G. Total Cross Sections for Electron and Positron Scattering on Molecules: In Search of the Dispersion Relation. *Atoms* **2021**, *9*, 97. [CrossRef]
17. Poveda, L.A.; Varella, M.T.d.N.; Mohallem, J.R. Vibrational Excitation Cross-Section by Positron Impact: A Wave-Packet Dynamics Study. *Atoms* **2021**, *9*, 64. [CrossRef]
18. Song, M.-Y.; Yoon, J.-S.; Cho, H.; Karwasz, G.P.; Kokoouline, V.; Nakamura, Y.; Tennyson, J. "Recommended" cross sections for electron collisions with molecules. *Eur. Phys. J. D* **2020**, *74*, 60. [CrossRef]
19. Kłosowski, Ł.; Piwiński, M. Magnetic Angle Changer for Studies of Electronically Excited Long-Living Atomic States. *Atoms* **2021**, *9*, 71. [CrossRef]
20. Uddin, N.; Modak, P.; Antony, B. On the Electron Impact Integral Cross-Sections for Butanol and Pentanol Isomers. *Atoms* **2021**, *9*, 43. [CrossRef]
21. Laricchiuta, A.; Celiberto, R.; Colonna, G. Electron Impact Ionization of Metastable States of Diatomic Molecules. *Atoms* **2022**, *10*, 2. [CrossRef]
22. Karwasz, G.P.; Karawacki, M.; Carelli, F.; Fedus, K. Hydrogen molecule as seen in electron and positron scattering. *Mol. Phys.* **2022**, e2070087. [CrossRef]
23. Sullivan, J.P.; Gilbert, S.J.; Surko, C.M. Excitation of Molecular Vibrations by Positron Impact. *Phys. Rev. Lett.* **2001**, *86*, 1494. [CrossRef] [PubMed]
24. Idziaszek, Z.; Karwasz, G.P. Applicability of modified effective-range theory to positron-atom and positron-molecule scattering. *Phys. Rev. A* **2006**, *73*, 064701. [CrossRef]