



# Ions, electrons, coincidences and dynamics

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 Raimund Feifel, \*<sup>a</sup> Majdi Hochlaf \*<sup>b</sup> and Stephen Price \*<sup>c</sup>

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When we, as Guest Editors, discussed the assembly of a themed collection of *PCCP* to celebrate the 80th birthday of Professor John H. D. Eland, we envisaged a wide-ranging volume with articles involving studies of all aspects of ionisation and associated phenomena. We felt such an inclusive issue could highlight the dramatic increase in the sophistication with which we can now probe the ionisation of atoms, molecules and clusters due to recent developments in experimental and theoretical techniques. Such developments have been driven, in part, by the availability of new technologies, such as position-sensitive detection, synchrotron radiation, high-power lasers, VUV and X-ray free electron lasers, and increasing computing power. These advances have provided a step-change in our understanding of the physics and chemistry associated with ionisation and the consequences of ionisation in diverse environments, such as astrophysics, plasma physics, combustion science and biology. This progress has also, of course, been driven by fruitful collaborations between experimentalists and theoreticians

to disentangle the complex and enmeshed processes that occur when atoms, molecules and clusters are ionised. We hope that readers opening (almost certainly virtually!) this volume will agree that the number and quality of the articles both meet our initial vision, and also show the worldwide esteem in which John is held in our field.

Working in Europe, the USA, then returning to Oxford, followed by sabbaticals/guest professorships in Japan and again Europe, John Eland's contribution to physical chemistry and molecular physics is extensive. He displays an enviable talent for conceiving and commissioning new high-vacuum experiments to study high-energy photochemistry, focusing on ionisation-induced phenomena and dynamics. His development of a huge variety of coincidence experiments (with a huge variety of acronyms) to probe single and multiple ionisation has both transformed our understanding of this field and also provided tools that are now employed by many investigators. In recognition of his scientific contributions, John was elected as a Fellow of the Royal Society (FRS) in 2006. This date also marked John's move to an emeritus position at Oxford. However, this purely notional "retirement" has marked an escalation in John's collaborations and productivity. He has on-going projects involving colleagues worldwide, many of whom are represented in this volume. He has recently published (2018) a book

on double ionisation,<sup>1</sup> a text following on from his classic book on *Photoelectron Spectroscopy*.<sup>2</sup> Indeed, in recognition of his continuing and internationally-leading contribution to our field, John was awarded an Honorary Doctorate from the University of Gothenburg in 2019.

Considering one of John's major interests, multiple ionisation, this themed edition shows us just how far our understanding has developed since John's first investigations of double photoionisation.<sup>3</sup> In this volume, we find reports of both sophisticated multi-particle coincidence experiments to probe the formation of multiply charged atoms<sup>†</sup> and the application of a variety of imaging methodologies to probe singly and multiply charged ions formed by (i) synchrotron radiation sources,<sup>‡</sup> (ii) impact of ionic projectiles,<sup>§</sup> (iii) laser ionisation,<sup>¶</sup> (iv) ultrafast laser pulses,<sup>||</sup> (v) X-ray free-electron laser pulses\*\*

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<sup>§</sup> <https://doi.org/10.1039/D2CP02194C> and <https://doi.org/10.1039/D2CP02458F>
<sup>¶</sup> <https://doi.org/10.1039/D2CP02449G> and <https://doi.org/10.1039/D2CP02101C>
<sup>||</sup> <https://doi.org/10.1039/D2CP03089F> and <https://doi.org/10.1039/D2CP01684B>
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<sup>a</sup> Department of Physics, University of Gothenburg, Origovägen 6 B, 41296 Gothenburg, Sweden.  
E-mail: [raimund.feifel@physics.gu.se](mailto:raimund.feifel@physics.gu.se)
<sup>b</sup> Université Gustave Eiffel, COSYS/IMSE, 5 Bd Descartes 77454, Champs sur Marne, France.  
E-mail: [majdi.hochlaf@univ-eiffel.fr](mailto:majdi.hochlaf@univ-eiffel.fr)
<sup>c</sup> Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, UK.  
E-mail: [s.d.price@ucl.ac.uk](mailto:s.d.price@ucl.ac.uk)

and (vi) energetic electrons.†† Indeed, several papers reflect the current interest in (multiply) charged ion formation *via* (multiple) ionisation and the resurgence of covariance analysis.‡‡ The application of coincidence techniques, developed to probe small molecules, to larger, biologically pertinent, species is also reviewed in this issue.§§ New multi-particle experimental techniques are also well represented; for example, the use of Coulomb explosion imaging to determine molecular structure.¶¶

Full understanding of ionisation phenomena almost always requires collaboration with theoreticians, who can determine structural properties and energy profiles using post-Hartree–Fock approaches or advanced density functional theory.|||| Indeed, John Eland has initiated many such collaborations over his career. The accuracy of such determinations may now reach 0.01 eV when computing ionisation energies.\*\*\* Faster and less costly computation, without a notable reduction in accuracy, can use explicitly correlated methods. To go beyond this requires the very costly CCSDT and/or CCSDTQ methodologies.††† Such high computational accuracy complements state-of-the-art experimental determinations.‡‡‡ The high-energy processes forming (multiply) charged molecular species can also involve electronic excited

states. Here, multi-reference configuration computations§§§ or time-dependent density functional theory¶¶¶ are required. Full interpretation of experimental spectra often requires the computation of band intensities. For rigid molecules, this is straightforward, but it is still challenging to treat large amplitude motions and/or floppy molecules,|||| and a fully quantum mechanical approach for bimolecular reactions is still a goal.\*\*\*\*

We feel this issue highlights key strengths of the chemical physics community. Firstly, the ability to rapidly incorporate new developments in technology in the design of novel and incisive new investigations; for example, short-pulse laser ionisation, multi-particle imaging detection, Born–Oppenheimer molecular dynamics simulations†††† and composite theoretical approaches.‡‡‡‡ But, secondly, we also see the imagination to take fundamental advances and realise their power when applied in a different context; for example, the development of imaging experiments and the use of electron–nuclear (“beyond Born–Oppenheimer”) methods to directly observe electronic and nuclear motions§§§§ together with the behaviour of molecules under strong-field dynamics.¶¶¶¶

In his preface to the first edition of his book *Photoelectron Spectroscopy*,<sup>4</sup> John

Eland remarked that new scientific techniques “require an incubation period in the hands of specialist physicists and physical chemists” before making their way into wider fields of chemistry and physics. The papers in this volume show that this pipeline of experimental and computational techniques, developed to probe specific problems associated with ionisation phenomena, but which are then adopted far more widely, is still flowing freely. The editors thank all the contributors for allowing us to realize our initial vision.

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¶¶¶ <https://doi.org/10.1039/D2CP02383K>

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