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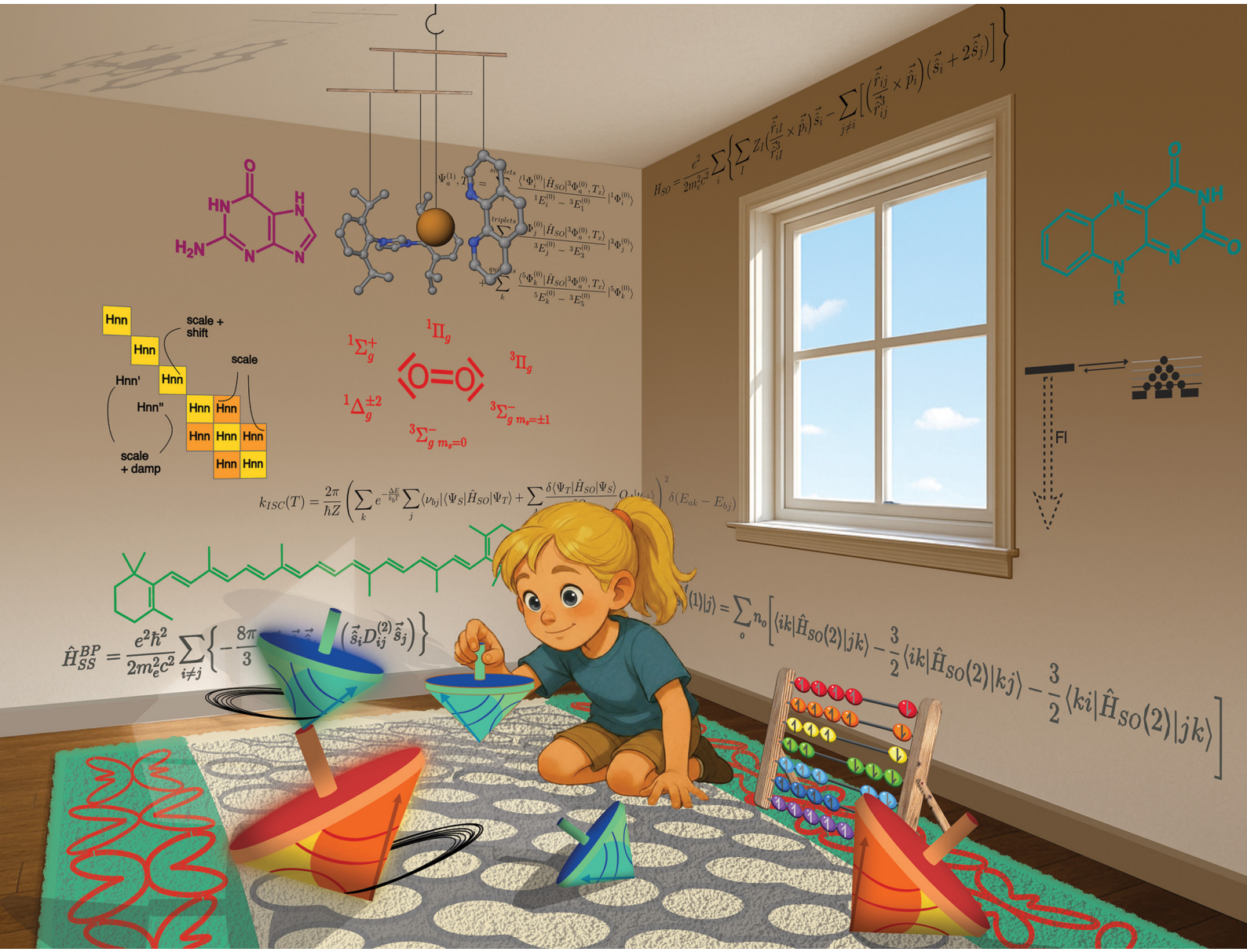

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ROYAL SOCIETY OF CHEMISTRY

EDITORIAL

Shirin Faraji *et al.*

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The role of electron spin in molecular photochemical and photophysical processes: theory and experiment†

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This themed issue of *Physical Chemistry Chemical Physics* is dedicated to Professor Christel Maria Marian (Christel) on the occasion of her 70th birthday, celebrating her immense contributions to the field of Theoretical and Computational Chemistry over several decades. Her remarkable work has not only enriched our understanding of molecular photochemical and photophysical processes but has also fostered a vibrant community within chemistry in Germany and Europe.

Born in Bad Münstereifel in 1954, Christel pursued her studies in chemistry at the universities of Cologne and Bonn, where she obtained her "Diploma," equivalent to an MSc degree, in 1977. Already then, she was drawn to topics centered around spin–orbit coupling. The scientific course of Christel's career was set during her PhD (1977–1980) at the Chemistry Department of the Rheinische Friedrich-Wilhelms-Universität (RFWU) Bonn, under the mentorship of Prof. Sigrid D. Peyerimhoff, during which she worked on the spin–orbit and spin–spin coupling between multi-reference determinant configuration interaction (MRD-CI) wavefunctions. This work laid the foundation for one of her future main research directions. After half a year of parental leave, Christel became a scientific assistant (later scientific associate) within the same institute until 1986. Following her postdoctoral work (1986–1988) at the Theoretical Physics Department of Stockholm University, where she focused on the theoretical spectroscopy of diatomic heavy transition metal compounds, she returned to Bonn as an assistant professor, completing her habilitation in 1991. After various short stays as deputy professor and senior scientist, eventually Christel joined Heinrich-Heine-University Düsseldorf (HHU) as Chair for Theoretical Chemistry in 2001, where she is still today as senior professor.

Throughout her distinguished career, Christel has played a pivotal role in advancing theoretical and computational excited-state electronic structure methods, focusing particularly on multi-reference methods and spin-forbidden processes that are crucial for understanding light-responsive molecules. These methods have applications ranging from physical and materials sciences to organic and inorganic, as well as biological chemistry. Therefore, Christel holds great international prestige not only among theoretical and computational chemists but also within a much broader scientific community that includes organic, inorganic, physical, and biological chemists. Her creativity in generating models with high predictive power has contributed to the development of novel chemical species and materials, thus promoting a very fruitful interplay between theory and experiment. This synergistic approach is reflected in her cross-disciplinary publications. Her scientific profile is exceptional and well known; therefore, there is no need to discuss in detail her many achievements and impressive bibliometric data. Instead, let us emphasize the significant impact and wide range of her scientific production, which includes over 250 research papers (Web of Science: *H*-index 53), more than 12 book chapters and monographs, and four scientific software packages.

Today, Christel's combined density functional theory and multireference configuration interaction (DFT/MRCI) methods for computing spin–orbit coupling, spin–spin coupling, and vibronic couplings have become essential tools for describing excited-state processes and related properties. A wide scientific community uses these methods to understand and predict many photo-induced chemical processes. This is critically important for advancing transformative technologies utilizing light, such as solar energy harvesting, photopharmacology, photo-responsive materials, and green chemistry. These achievements are also reflected in numerous prestigious awards and elected memberships, including her election as a

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† In honor of the 70th birthday of Christel Marian.

member of the North-Rhine Westphalian Academy of Sciences and Arts (2014) and the International Academy of Quantum Molecular Sciences (2024), to name a few.

Her research group has been, and continues to be, engaged in various central themes that have significantly advanced the fields of photochemistry, materials science, and theoretical chemistry. Their pioneering work encompasses a range of topics, including intersystem crossing (ISC), DNA photochemistry, organic light-emitting diodes (OLEDs), thermally activated delayed fluorescence (TADF), transition metal complexes, excitation energy transfer (EET), and flavin and carotenoid photochemistry and photophysics. This editorial reflects on the foundational research and impactful findings that have shaped our understanding and application of these complex systems.

Christel's research has greatly enhanced our comprehension of intersystem crossing, the non-radiative transition between electronic states of different multiplicities. Since 1977, Christel's major research focus has been directed towards the development of methods and programs for spin–orbit coupling (zero-field splitting, phosphorescence rates, intersystem crossing rates), electronic spin–spin coupling, spin-rotational coupling, g-tensors, and spin–vibronic coupling. Her work explains how molecules with high triplet quantum yields and long triplet lifetimes can serve as effective sensitizers in photochemical reactions. Notably, her group challenged the common belief that only direct spin–orbit coupling between $\pi\pi^*$ and $n\pi^*$ states leads to fast ISC, revealing the importance of vibronic coupling in environments such as polar protic solvents. The group's investigations into the xanthone family of dyes exemplify their approach to understanding how ISC rate constants and triplet quantum yields are influenced by solvent interactions. Their innovative methodologies include the VIBES approach for computing temperature-dependent vibronic spectra and rate constants and the SPOCK (Spin–Orbit Coupling Kit) and SPOILER (Spin–Orbit Interaction Linear Response) methods, which enable the comprehensive investigation of spin–orbit coupling effects. Additionally, the electronic spin–spin coupling method (SPOCK.SISTER) provides insights into spin interactions that significantly influence excited-state behavior.

From 1995 to 2008, as an active member of the Collaborative Research Center 408 ''Inorganic solids without translational symmetry - synthesis, structure and modeling'', Christel made significant contributions to two key research areas. In the field of inorganic solids without translational symmetry, her work focuses on modeling amorphous ceramic materials and their molecular precursor reactions. By parameterizing force fields and investigating structure–property relationships, she provides fundamental insights into the formation and behavior of these complex materials, which are crucial for applications in catalysis, coatings, and high-performance ceramics. Additionally, in drug discovery, she has contributed to developing scoring functions for flexible docking, improving the accuracy of computational methods for predicting how drugs bind to protein targets. Her research enhances the efficiency of virtual screening by accounting for protein flexibility, ultimately aiding in the design of more effective and potent pharmaceuticals.

Another research direction that became Christel's focus from 2002 to 2015 was understanding the spectroscopy and excited-state dynamics of nucleic acid bases, particularly adenine. One of her most cited papers, ''A New Pathway for the Rapid Decay of Electronically Excited Adenine'', introduces a novel non-radiative relaxation mechanism, demonstrating how adenine undergoes ultrafast internal conversion *via* a previously unrecognized conical intersection. This insight is crucial for explaining the exceptional photostability of DNA, as it reveals how adenine efficiently dissipates excess electronic energy and minimizes UV-induced damage. Through several combined theoretical and experimental studies, she has also investigated the effects of protonation and chemical modifications, such as acetylation, on the electronic properties and spectral behavior of adenine, providing insights into its behavior in biologically relevant environments. Additionally, her work incorporates spin–orbit coupling effects in the analysis of excited-state decay pathways, illuminating the role of intersystem crossing in energy dissipation. Collectively, her findings bridge fundamental quantum chemistry with experimental molecular biology, advancing our knowledge of excited-state pathways and the photophysical properties of nucleic acid bases, with important implications for DNA damage mechanisms and drug design.

Christel has been a pivotal figure in the field of molecular responses to electronic excitation since 2005, when she began leading the Collaborative Research Center 663 ''Molecular Response to Electronic Excitation''. She initiated a new research direction focused on enhancing the fluorescence quantum yield and lifetime of flavin chromophores through rational design. Her innovative approach included the computer-aided design of fluorinated flavin derivatives that modulate intersystem crossing and fluorescence, optimizing their properties for applications in biochemical sensors. Additionally, her investigations into the dual photochemical reaction pathways in flavin-based LOV (Light, Oxygen, or Voltage) domains, utilizing combined quantum mechanics and molecular mechanics (QM/MM) methods, provided critical insights into light-driven processes. She explored the photophysics of flavin derivatives that absorb in the blue-green region, identifying thioflavins as potential cofactors for photoswitches, and examined the differences in photophysical behavior between gas phase and aqueous solutions. Expanding her research to carotenoids, she has conducted theoretical studies on the low-lying excited states of β-carotene isomers and the spectroscopic properties of phenolic and quinoid carotenoids, employing multireference methods to deepen the understanding of their photophysical behavior. Her work on the photophysics of carotenoids, intersystem crossing rates of keto-amino cytosine, spin–orbit coupling in keto-porphyrins, and the electronic spectra of various

tautomeric forms of cytosine further underscores her commitment to advancing the field of molecular photophysics through an integrated approach combining theoretical and experimental techniques.

In 2015, after completing her service as the first female Dean of the Faculty of Mathematics and Natural Sciences at HHU, the combined density functional theory and multireference configuration interaction (DFT/MRCI) Hamiltonians caught Christel's attention. Beyond any doubt, she is a key contributor to the development and refinement of the DFT/MRCI method, originally devised by Stefan Grimme and Mirko Waletzke. This well-established and efficient semi-empirical quantum chemical approach is crucial for computing molecular singlet and triplet excited-state properties, particularly in extended π-systems such as polyacenes, polyenes, and carotenoids, where double excitations play a significant role. The original variant of the method faced challenges in accurately describing loosely coupled multi-chromophore systems, which are crucial in photovoltaics and metal-free OLED emitters. To address this, Christel's efforts have played a major role in redesigning and reparameterizing the DFT/MRCI Hamiltonian while preserving the fundamental principles of the method. Her contributions include the development of a spin-invariant redesigned Hamiltonian that extends the application range of DFT/MRCI to electronically excited doublet and quartet states through restricted open-shell Kohn–Sham optimization of molecular orbitals. Recently, her work has also integrated novel damping functions for off-diagonal matrix elements, significantly enhancing the method's performance on transition metal complexes. The DFT/MRCI program, featuring both the original and redesigned Hamiltonians, is now available to the academic community free of charge, facilitating further research and development in quantum chemistry. Christel's ongoing efforts ensure that DFT/MRCI remains a powerful tool for studying complex molecular systems and excited-state dynamics.

During the last 10 years, in addition to overcoming fundamental challenges in method developments, Christel's research spans several application domains, significantly advancing fields such as organic light-emitting diodes (OLEDs), thermally activated delayed fluorescence (TADF), transition metal compounds, and excitation energy transfer (EET), to name a few. In OLED technology, her work focuses on improving the efficiency and stability of light-emitting materials, particularly addressing the challenges posed by blue OLED emitters, known for rapid bleaching. By enhancing internal quantum efficiencies through the incorporation of chromophores that exhibit efficient ISC and phosphorescence, she aims to develop more stable and energy-efficient devices. Her theoretical insights provide a robust framework for predicting emission characteristics, guiding advancements in this area. Christel's exploration of TADF represents a significant breakthrough, as she investigates metal-free donor–acceptor compounds and earth-abundant metal complexes to unveil the mechanisms governing reverse intersystem crossing (rISC) and delayed fluorescence. This research optimizes TADF performance by focusing on factors such as the singlet–triplet energy gap and environmental influences, highly relevant for OLED technology. Additionally, her work on transition metal complexes addresses challenges related to relativistic effects and the multiconfigurational nature of excited states, utilizing DFT/MRCI methods to accurately predict electronic transitions in phosphorescent iridium, platinum, copper and zinc complexes, showcasing her commitment to developing efficient emitters for practical applications. In the realm of excitation energy transfer, Christel has developed a monomer transition density (MTD) approach that extends the understanding of Förster resonance energy transfer (FRET) beyond traditional models, highlighting the importance of interchromophore distances and orientation factors to improve imaging techniques and OLED efficiency.

In summary, Christel's research has left, and continues to leave, a lasting impact across multiple disciplines, advancing our understanding of complex photochemical and material systems. Her contributions not only deepen theoretical knowledge but also foster practical advancements that could lead to significant technological innovations in the future.

In addition to her research, she is a dedicated educator, having supervised over 25 PhD theses and taught numerous courses on computational, theoretical, and physical chemistry. Her engaging teaching style and the clarity of her lectures have inspired countless students and researchers alike. Through her efforts, she has established a strong international network of collaborations across more than 20 countries, fostering the development of the next generation of theoretical chemists. On a personal note, Christel's commitment to the chemistry community and her supportive, approachable attitude have made her a respected figure among colleagues and students. Her leadership, fairness, and ability to take the initiative exemplify the qualities we admire in a mentor, role model and leader. As an ambassador for theoretical and computational chemistry, she has significantly shaped the landscape of our discipline, making her truly deserving of this themed issue honoring her scientific achievements.

This themed issue includes contributions from her colleagues, students, and collaborators, reflecting the diverse and impactful research that Christel has inspired throughout her career. We hope this compilation honors her legacy and serves as a testament to her influence in the scientific community and the appreciation of the ''Geburtstagskind''.

