# Vincenzo Aquilanti's Autobiography: A Narrative of My Voyages in Science

## Prologue

*I trust and believe that the time spent in this voyage. .. will produce its full worth in Natural History; and it appears to me the doing what little one can to increase the general stock of knowledge is as respectable an object of life, as one can in any likelihood pursue.* Charles Darwin, *Voyage Of The Beagle,* 1799.

This is an account of the sequence of events that allowed me to follow the evolution of some aspects of science in the last five decades. I feel fortunate that I was able to be a witness of a time where scientists were given the unprecedented privilege of observing directly how atoms and molecules behave at the microscopic level. This possibility of looking at the atomic world from such a viewpoint represents a change in perspective of the greatest importance that twentieth century science left as a legacy to the curiosities and capabilities of the scientists of the new millennium.

Until a century ago, one's perception of atoms and molecules came only from macroscopic observations, resulting from spatial and temporal averagings over microscopic structures and transformations, and the molecular world was considered not directly observable. This is not so anymore. Single ions, atoms, and molecules can now be followed in their flights in beams and "seen" as pulses on detectors or as traces on oscilloscopes. One of the major achievements of the early twentieth century was the clarification of how atoms and molecules, in their apparently random motion, happen to combine in order to form the structures whereby matter presents itself to us. Quantum mechanics provided the language for the detailed description. It was a main contribution of later years to foster the basic understanding of how matter evolves, providing the experimental and theoretical tools for the study of chemical transformations from a dynamical viewpoint.

My parents came to Rome from two towns in the Viterbo Province in the North East of upper Latium, the old Etruscan land. My family name is reminiscent of the Latin (and Italian) word Aquila (Eagle) typical of Etruscan origins; these precursors of the Roman civilization are reported to have read auspices for the future in the flight of birds. I can say that this is the beginning of my looking at my exploration in science as a voyage of an eagle. The two towns were only a few kilometers apart from each other and only one hundred kilometers away from Rome where they eventually met and married. One hundred kilometers may not look very far now, but this was a large distance, especially from a cultural viewpoint, for peasants at that time, when in order to survive they had to leave their landlords' farms for the big city.

My mother, Argia Del Vecchio (1897−1993), had come to Italy's capital as a teenager during the years of World War I to be trained as a seamstress, a job she kept until marriage. My father, Giovanni Battista Aquilanti (1899−1964), in 1917 - when he was only 18 - had been sent as an Italian Air Force service man to the war front in the Alps. The good thing for him was that he was given the chance to make acquaintance with motor engines for cars and airplanes, so that when he returned, after moving with his family to the capital city, he was employed as a driver and mechanic in the Rome Province Authority.

I was born in Rome as my parents' only child on December 12, 1939, under the Sagittarius sign - I do not attach any prophetic meaning to this fact, but I find it suggestive of the recurrent theme of arrows, to be expanded below. That was the time of the outbreak of World War II. So just a few months after I was born, in spite of his age (he was then over forty), my father had to serve in the Italian Air Force, again as maintenance man for airplane engines. This unfortunate event turned by chance into a lucky one; he was sent to the Viterbo Air Force Base, a few miles from where his family originated, resulting in my mother and a six-month old self also moving there, and permitting the three of us to survive those hard war years in a familiar environment.

## The Coming-of-Age Years

Of the numerous relatives of my family (several emigrated to the United States and France), I was the first one who, thanks to my parents' sacrifices and favorable circumstances, was given the opportunity to attain a University education. The apartment building to which we came back after the war and where I grew up was still standing in spite of the heavy bombings hitting the northern edge of Rome where it was located. The location turned out to be propitious, because a prestigious high school that I could attend was within walking distance. It was a "Liceo Classico", so I received a solid preparation in literature, history, Latin, and ancient Greek. Science was given only a limited space in the curriculum. However, a modern-minded philosophy professor emphasized the role and beauty of scientific thought, and I had an inspirational teacher in mathematics and physics, Maria Maiorana. She was the sister of the famous theoretical physicist of the Enrico Fermi entourage, Ettore Maiorana, who had mysteriously disappeared in 1938.

The University of Rome was fortunately also within walking distance of my home. In the late 1950s, reconstruction of that part of the city after the heavy bombing was practically complete. The Istituto di Fisica was world renowned, mostly because of the heritage of the Fermi school. However, in 1958 I started my undergraduate studies in chemistry, a discipline which in those years enjoyed particular attention from industrial perspectives, which were associated with the rise of the National Oil Company. When its president, Enrico Mattei, died in a controversial airplane crash in 1961, Italian ambitions for a role in oil and chemical world markets suddenly fell, shrinking dramatically job opportunities in the chemical industry and perhaps preventing me from becoming a chemist in a factory.

As a matter of fact, I was motivated by my background to move toward pure research and particularly toward the physical foundations of chemistry. As an undergraduate I joined Gian Gualberto Volpi's group in the Istituto Chimico. The two "Istituti" were (and still are) facing each other in what is now known as La Sapienza Campus, and continuous exchanges took place by simply crossing the street between them.

In the second floor of the Istituto Chimico, under the direction of Vincenzo Caglioti, the Professor of General and Inorganic Chemistry, an ample spectrum of activities was being pursued, and research associates from the Italian CNR (the National Research Council) and CNEN (the National Council of Nuclear Energy) worked together with the university staff in a very lively and productive atmosphere.

Volpi, who was then in his thirties, had contributed with the physicists across the street to the exploit of the first mass

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spectrometer built in Italy for pioneer work on gas kinetics. After a two-year postdoctoral work at Harvard with G.B. Kistiakowsky, he had set up a dynamic group of post docs including two physicists, Anna Giardini and Andrea Galli, and a chemist, Fernando Zocchi, using prototypical mass spectrometers for problems in gas transport properties and gas kinetics. A vivid chronicle of those years was written in 1999 by Volpi and a physicist, Giovanni Boato, in Ann. Rev. Phys. Chem. 1999, 50, 23−50. I wrote recently an account of Anna Giardini's role(Phys. Scr. 2008, 78, 050401 (10pp)).

Ion−molecule reactions in the gas phase were a challenge in those years, only two or three laboratories in the world being engaged in this type of research. Entering the group, I was given a problem in radiolysis (the effect of X-rays on methane), a paradigm for the new science of radiation chemistry. This problem was of importance for CNEN and of interest to Volpi and his team as possible mechanisms involving ion−molecule reactions. These were being investigated by ingenious modifications of mass spectrometry sources, to reach almost atmospheric pressures, high enough to favor occurrence of reactive encounters. I learned that chemists do not necessarily have to deal with test tubes but may also have the challenge of planning, building, and repairing their instrumentations in environments similar to machine and electronic shops.

For my thesis work, I used mass spectrometry and gas chromatography as analytical tools. Gas chromatography was then a new technique introduced by analytical chemists but was going soon to become a precious instrument in the hands of gas kineticists. The extensive analysis of products (mainly hydrogen and a series of hydrocarbons) from irradiations of mixtures of methane with rare gases as selective energy and ionization agents allowed me to emphasize the until then neglected role of ions in the chemistry of gases induced by radiation. The results that were obtained for my laurea thesis in 1963 led to my first scientific paper, which appeared in 1965 as a single author in *The Journal of Physical Chemistry*.

In the Italian system, the *laurea* is roughly comparable to a Master's degree in most modern Universities, and the doctoral degree had not yet been introduced. After the laurea, fellowships from different sources were available for research activities, and I received one from CNEN, which later (1967) hired me to continue to work on Volpi's team on high pressure mass spectrometry and on mechanisms of ion−molecule reactions. This work can be considered as a precursor (by two decades) to the electron spray and MALDI techniques. We proved how ions were inducing even gas phase polymerizations. Characterization of gas phase proton transfer processes and of the role of energy transfer was my other major achievement of those years.

## The Harvard Interlude

In 1967, I left for the U.S.A. to join Dudley Herschbach's group at Harvard and was given a postdoc status in view of the papers already published by me. Gian Gualberto and Dudley knew each other since the late 1950s, and we thought it mandatory to testify about the breaking news on the wonders of applying molecular beam techniques to the unveiling of the detailed dynamics of chemical reactions. The highlight of the Harvard times was the immersion in the lively environment of apparatus builders with high level colleagues as postdocs (Yuan T. Lee among them, who was going to share the Nobel Prize with Dudley eighteen years later) and especially brilliant graduate students.

Importantly, I had the good fortune that Dudley assigned me his student Roger Anderson as a collaborator. Roger is a few years younger than I am, but from the first days at Harvard he acted for me as a travel companion, not only into the secrets of electronic and machine shops, but also into the basic quantum mechanical apparatus specifically needed in chemical dynamics. Since then, in spite of the distance between Italy and California (since 1968 he has been at the Santa Cruz Campus of the University of California) we have continued working together on various projects on themes whose roots can be traced back to those times.

Some of these themes emerged unexpectedly in disguise. In making drawings for the charge-exchange fast atom ion source, my sketches for the machine shop were based on the projection rule for three-dimensional objects that I had learned in Rome; at Harvard, people in the machine shop were puzzled and claimed the pieces would not fit. After some debate, we discovered that different conventions are used for technical drawings in the machine shops on the two sides of the Atlantic. They were based on presenting an object either as its front view as seen by an observer, or as its back view projected on a mirror. The two conventions lead to three-dimensional constructions of opposed. .. chirality! Unexpectedly, the moral of this story would have served as a track on a set of problems that have interested me and are still under my attention, as we will see below.

Roger and I built an apparatus named Dawn (a woman's name was used to baptize machines, following the tradition of previous Dudley's creations, like Bertha) and dedicated to explore increasing collision energy ranges, accelerating alkali atoms up to the KeV range by resonant charge exchange, and having them colliding with various simple targets. This leads to electronic excitation, measured by emission spectra. New important words entered into my personal jargon (nonadiabatic transition, curve crossing, etc.). Many hints came both on the experimental possibilities of crossing two beams and revealing light coming from their encounter and on the theoretical challenge of the intriguing questions that make the atomic and molecular world a wonderful testing ground for the frontier between classical and quantum behavior.

As Dudley is often quoted to have said, "*Watch what electrons do, nuclei will follow*". The understanding of how essentially classical tardy objects as nuclei obey to unpredictable elusive tiny chaps like electrons is basic to modern chemistry, leading to the development of fascinating theoretical tools, loosely referred to as "semiclassical mechanics".

On a personal note, in Boston I had the opportunity of spending several Sundays at lunch with my uncle, my mother's brother, who had emigrated to the United States in 1913. He also, like my father, was a soldier in World War I, but on the U.S. side. In fact, being an expert on horse maintenance, soon after he landed on American ground he was made a U.S. citizen much faster than usual, even if he was unable to understand or speak English. In 1914, he was sent back to Europe at the Ardenne front, where he was seriously wounded.

## The Early Perugia Years. One, Two, Three Beams

Back to Italy in late 1968, I moved directly from Rome to Perugia, a town 100 miles north, again in the old Etruscan land and location of an ancient University. There, Volpi had been appointed to a chair in the meantime. He established his group with Giorgio Liuti, Emilio Luzzatti, and myself, soon joined by Franco Vecchiocattivi, who had just graduated in Rome with Anna Giardini and Aldo Mele.

Volpi's personal Holy Grail was to study the basic foundations of chemical reactions. His natural characters should have

been hydrogen, nitrogen, oxygen atoms. We started to build an apparatus just to test the properties of such a type of atomic beams; it was named Amalasunta after an Italian queen from the XII Century. This apparatus is still operating in the expert hands of Fernando Pirani, later joined by David Cappelletti and bold legions of students. It has been modified, dismantled, and rebuilt so many times that looking at old pictures and comparing them with the present status, it can hardly be recognized, having had many new lives, like an *Araba Phoenix*, or more simply like a cat.

Amalasunta's multifaceted manifestations of alternative lives were still to come and her long life will be accounted for later. Accompanying her early developments, I suggested to Gian Gualberto, Giorgio, and Franco to undertake a smaller enterprise, along the line of the Harvard Dawn, but, exploiting our previous experience in Rome, crossing ionic and atomic beams. We mainly used alkali ions and alkali atoms, looking at emitted light in the visible and near-ultraviolet spectral ranges. For a few years, this apparatus (named Barbarella as a follower of Amalasunta in alphabetical order, and attended in later times by students like Bruno Brunetti, Piero Casavecchia, Fausto Elisei, and Gaia Grossi) unveiled interference and polarization effects, revealing wonderfully the "semiclassical" nature of atomic and molecular processes. The achievements strongly reinforced my never spent passion for theory in the direction of how angular momenta (rotational, orbital, and spin) couple and how they decouple, particularly when they are large; another motif on the theme of vectors as arrows and of their combinations in search of targets.

A parentheses on the progress of the laboratory and of the people involved. Gaia, who had become my wife since 1971 will appear often again in this narrative being not only a life companion but also a colleague in the Department of Chemistry and a collaborator in exciting research enterprises. Franco and Bruno joined the late, much missed Roberto Candori in the building and development of a third machine, named Carolina, as a crossed beam apparatus where autoionizing collisions and similar phenomena were studied. They still are being studied with the current contributions of Stefano Falcinelli and Pietro Candori (Roberto's son), who also form the team of the group for regular excursions with Franco and Fernando to investigate light-matter interaction problems at the Trieste synchrotron facility. For some years now, Bruno has moved competently and with creative spirit into applications of chemistry for art preservation, joining the successful group of Antonio Sgamellotti, a colleague (and friend for 50 years!) whose career happened to more or less develop along parallel lines with mine. We started together as students in Rome and then after some detours are sharing twin chairs of General and Inorganic Chemistry, occupying with our two groups the corresponding floor of the Chemistry Department. Piero and Fausto are now professors in Physical Chemistry in the same Department.

A fourth machine of the group was built by Piero when he returned from his time as a postdoc with Yuan Lee. He was assisted by Gian Gualberto and later notably by Nadia Balucani with help from students and postdocs. This machine, although it remained unnamed (no proposal with a name starting with a D obtained a consensus), turned out to be highly successful and continues to be extremely productive.

The Amalasunta configuration in the meantime had turned out to be ideal for unprecedented accurate integral elastic scattering cross section measurements. Its unique features were the velocity selection resolution (to within a few percent), the very narrow angular resolution within the "true" uncertainty-principle limit, and the possibility of absolute target pressure and scattering length calibration. Under lucky circumstances, the observation of a semiclassical effect, the "glory" (the name originates from an analogous phenomenon in physical optics, in turn reminiscent of a signature of holiness) was another Holy Grail, which allowed us to measure detailed features of intermolecular forces. This allowed us to establish an ample phenomenology, including typically all the five rare-gases, the ubiquitous diatomic molecules (hydrogen, oxygen, nitrogen), small hydrocarbons, and providing ingredients for thermodynamical and statistical mechanics modeling of high pressure gases and atmospheres.

## Opening Shells: Experimental and Theoretical Tools

The late 1970s and the early 1980s saw on Amalasunta an unexpectedly serendipitous twist, in part propitiated by my enduring insistence on open shell atoms, carrying spin and angular momentum, which I had been watching through analysis of light emission in Dawn and Barbarella.

Fine structure and polarization effects are signatures that atoms are not just microscopic balls. Because of anisotropies of electron distributions, those having an open shell exhibit specific orientational properties, just like the small arrows used in the vector notation as indicators of directions.

Actually the role of electronic open shells in every day chemistry, as well as in that of planetary and interstellar environment, is overwhelming, and the natural venerable way for its characterization is through magnetic selection. In the 1960s, elaborated voluminous Stern-Gerlach devices have been built and used by physicists like Joerg Reuss in Nijmegen, Netherlands, and Christoph Schlier in Freiburg, Germany. In 1971, Christoph had just dismissed using his large magnet, so returning by car from a conference in Central Germany my just married wife Gaia, Bruno Brunetti, and myself took this piece of metal with strange wires for electric connections and copper tubing for cooling water. We had to smuggle it across the Alps through the Germany-Swiss border first, and the Swiss-Italian border later. Fortunately, having had a good lunch with Christoph and his group in the Black Forest, we went through the two borders so late at night and so early in the morning, respectively, that we had no careful control from the sleepy toll-watchers. Otherwise we would have presumably been in trouble trying to explain what that fearful object was for.

Indeed what that object turned out to be for was not only for analyzing internal angular momentum (spin and orbital) states of a series of atoms of paramount importance, such as fluorine, chlorine, oxygen, sulfur, but also as a unique device for studying the features of their interactions, introducing in our quiver the additional arrow of electronic anisotropy.

Those years (mid-1970s) had seen increasing attraction by chemists on the use of computers. Antonio Laganà had been involved in his *laurea* thesis with the Sgamellotti's group for electronic structure calculations. I invited him as an instructor for the General Chemistry course that I was teaching then (and still am, as a full professor since 1980). Because of my interests in alkali atoms and ions, we started our collaborations with one-electron pseudopotential calculations of alkali atom wave functions.

My main theoretical interests were however always focused on collision theory, and in particular on understanding elastic and reactive processes through quantum mechanics, or possibly through suitable semiclassical approaches that would satisfactorily mimic the quantum behavior. With Gaia, I (and our one year old son Giovanni and our daughter Francesca "in prepara-

tion") spent the summer of 1977 at Oxford. There, we enjoyed the hospitality of Mark Child, amplifying considerably our knowledge of semiclassical mechanics but especially of the quantum mechanical angular momentum theory, which was going to represent what in my opinion was the most insightful tool that I have ever possessed to tackle the problems that I had ahead.

## Arrows and Targets

We have left behind the account of the important developments coming from the laboratory. An illustration of those times is my caricature as a lonely "opener" of shells in the (nearly dead) sea of atomic physics (see the drawing by Peter Toennies for his concluding remarks at a Molecular Beam Symposium in Freiburg, Germany in 1984). Also insightful on progress in understanding atomic and molecular anisotropies is the San Sebastiano under crossed beams of archers in the Perugino painting (∼1500), see http://www.chm.unipg.it/chimgen/mb/theo2/index.html, aiming essentially at showing how an account of perspective leads to a proper description of the three-dimensional world. This basic discovery of Central Italian Renaissance suggested to us the perfect logo for the Molecular Beams Symposium that we organized in Perugia in 1989, which was later often exploited by us to emphasize analogies in setting up a crossed molecular and/or laser beam experiment to aim at targets such as the spatial features of atomic and molecular encounters in order to look into the microscopic features of stereochemistry.

Clearly, expertise on manipulating angular momenta was of course mandatory in order to understand open shell atoms, as carriers of electronic and spin type of angular momenta, as well as to characterize momentum exchanges due to their encounters. One important outcome of those years was the classifications of the ways all these angular momenta couple and decouple during collisions, inducing for example fine structure transitions. This provided a framework for the quantum mechanical treatment of both the apparently distinct experimental enterprises in which I was involved in those years, namely the measurements of anisotropies of intermolecular forces of open shell atoms from thermal energy scattering and the study of electronic energy transfer processes in superthermal collisions.

A crucial aspect that became predominant for my progress was the clear understanding that most relevant processes of interest in atomic and molecular physics and basic chemical physics lie in the semiclassical regime (recipe: "classical nuclei - quantum electrons"). So the wonders of properties of angular momentum combinatorics (the formidable 3n*j* symbols, to be later designated "spin networks") was one of the leading themes of my future research, looking especially in the regime where orbital angular momenta become large.

Simply stated, when as oftentimes in molecular motion the quantized angular momenta involved are large in units of Planck's constant, they can be considered as varying continuously, and the underlying mathematics for the proper description is that of harmonic analysis and Fourier series, while the underlying physical picture is that of vector models to represent anisotropies in the world of electrons and nuclei.

The mastering and developing of these ideas turned out to be far reaching. The orbital of a quantum mechanical electron in an open shell atom can be regarded as a microscopic anisotropic object, allowed only a limited number of spatial directions. Thus when for example two atoms interact and bind, the match gives anisotropic electronic distributions of sharply defined symmetry (the $\Sigma$, $\Pi$, $\Delta$, etc. molecular orbitals). Similarly anisotropies of larger objects, such as molecules, might well be seen as the limit of a large number of the quantized directions compatible with the vector model. I felt that it was going to be a rewarding challenge to make this intuition rigorous, and this theme has been in the background of several of my future advances in basic theory. On the other hand, it also provided the tools for developing the powerful computational approaches, which I later baptized under the general name "hyperquantization algorithm". All that turned out to provide a language for communicating with the computer, a language dealing with the discrete mathematics that its digital logic demands. In practice, the advantages are not only new insights but also savings of computing times, permitting the exact solution of otherwise formidable quantum mechanical problems.

The best exemplification comes from the application to a fundamental case study for the chemical physicists, the dynamics of the elementary chemical reaction, usually written as A + BC → AB + C. The challenge is its study as a three-body quantum mechanical problem. Felix Smith in the early 1960s and later Aron Kuppermann and others had been focusing on what was starting to be known as the hyperspherical coordinate approach to the A + BC problem. Aron is still contributing vigorously to go beyond, to cases where atoms are four, five, and so forth. Antonio Laganà did some postdoctoral work with him at Caltech.

My personal encounter with hyperspheres came rather from being introduced to the already mature work of nuclear and atomic physicists by Hubert Klar from Freiburg, Germany, with whom I collaborated on basic three body Coulomb problems. Hubert had been a postdoc of Ugo Fano, a famous Italian angular momentum guru (Racah's cousin, and Fermi's postdoc in Rome in the 1930s). In later years, Ugo was a professor in Chicago, and I was fortunate to meet him regularly in the 1990s on the occasions of his frequent stays in central Italy.

I was particularly amazed by the enormous power of exploiting the mappings by hyperspherical coordinates in hyperspaces to deal with many body problems and how matching with angular momenta techniques in these spaces provided effective, orthonormal, complete basis sets for quantum mechanical representations.

## Occasions in Chaos

The 1980s were years when many new avenues were opened up by the debate on relationships between classical and quantum mechanics with respect to applications in molecular dynamics and chemical kinetics. Computers allowed generating potential energy surfaces by electronic structure calculations and by running batches of trajectories. How reliable were the obtained interactions and the treatments of the dynamics? One of the key issues was related to establishing how to introduce semiclassical ideas, namely quantum effects (interferences, resonances) in a classical setting, and how to assess the role of the interesting concept of chaos, so pervasive in classical mechanics (a nonlinear, approximate, theory) but elusive in quantum mechanics (a linear, better founded, theory of the microscopic world).

In the early spring of 1982, about the time our second daughter Claudia was born, I organized in Perugia an international symposium on "The Wave Particle Dualism", the occasion being the 90th birthday of Louis de Broglie (eventually he had to decline his participation because of health problems; he died in 1987). This is one of the first of the series of international conferences that our group organized in Perugia and nearby Assisi, that are particularly well-suited settings for this kind of

scientific and convivial events. It became progressively clear to me through extensive case studies that the order and the chaos of the classical description of the macroscopic world have their roots at the microscopic, quantum level on concepts like regularity of slowly ("adiabatically") changing systems and irregularity of strongly ("non-adiabatically") coupled modes. Traditional gas kinetics and statistical mechanics capitalize on this, and it is opportune to recall that the word "gas" was coined as a deformation of the primordial biblical word "chaos".

Gaia and Simona Cavalli were actively engaged in these themes. Misha Sevryuk brought in deep insights and mathematical rigor. Misha is a former student of the Russian mathematician Arnol'd and a collaborator on chemical physics of the group of Lev Rusin in Moscow. I had in those times a student, Nazzareno Re, dealing with mathematical subtleties of nonadiabatic transitions and curve crossings (he is now a professor in Chieti University and active in molecular dynamics). The results of his *laurea* thesis work later converged with those of Hiroki Nakamura's group in Okazaki, Japan, propitiating my several visits there in the 1990s.

In those years, we realized that we were actually having in our hand several ingredients that, if properly sharpened and put together, should have provided us with the frame for decisive progress for looking into quantum reactive scattering. Although extremely fascinating, the semiclassical approaches were in need of confrontation with exact quantum mechanics.

## Alignment and Hyperquantization

The topical turn came in the early 1990s. Extensive studies of the behavior of seeded beams of oxygen molecules by the Stern-Gerlach magnet convinced Fernando and David that their internal state distribution (essentially the orientation of the rotational angular momentum) was showing an unexpected behavior. It was known that under supersonic conditions, the technique of seeding, namely allowing molecules (oxygen in our first instance) to flow along streams of other gases (such as helium as a prototypical example), would lead to variation in speed (acceleration in this case) and to changes in internal state distribution (vibrational and rotational cooling in this case).

The interesting additional phenomenon was that of alignment, namely the possibility of forcing the molecule to rotate at least partially in a preferential plane. As in other cases, R. N. Zare was a pioneer in this also, and actually his precious book "Angular Momentum" (1967), with the illuminating subtitle "Understanding spatial aspects in chemistry and physics", has to be recommended as a travel companion for the aspirant explorers of the wonders of angular momentum land.

After a few years of studies of other diatomic molecules and of linear hydrocarbons, we even succeeded in proving that a disk-shaped molecule, benzene, could be made preferentially flying like a frisbee. The technique greatly amplified the application area of the molecular beam scattering method to the study of a wide variety of systems, permitting the accumulation of an extensive phenomenology of van der Waals interactions, and in particular their anisotropies, to be characterized within a coherent unifying framework. Applications are to problems and models in atmospheric and combustion chemistry, where theory and experiments provide the basic tools for their interpretation.

The theoretical apparatus had to be refined and amplified through the proper definition of coordinates based on the hyperspherical representation and of adequate basis sets based on hyperspherical harmonics. The hyperquantization algorithm could then be founded on the observation that discrete analogues of hyperspherical harmonics can be defined through the 3n*j* symbols of angular momentum theory. The development of efficient computational implementations were made possible by a postdoctoral stay of Maurice Monnerville from Jean Claude Rayez' lab in Bordeaux and now a professor in Lille, and by the continuing work of Dario De Fazio, who entered as a graduate student in 1992. Now he is still active in the group as a researcher of the Italian National Research Council.

On the way over the years to a wide series of computational results on the elementary bimolecular reaction as a quantum mechanical problem, Simona, Dario, and I had the luck of extensive and pertinent collaborations. Here is a perhaps incomplete list. Regarding potential energy surfaces, we enjoyed the always precious insights of Fernando and David on long-range forces. Paolo Palmieri and Cristina Puzzarini from Bologna, and later Francesco Tarantelli from Perugia, made important contributions on electronic structure calculations. On dynamics, we have been collaborating with Antonio Aguilar, Xavier Jiménez, and José-Maria Lucas on massive calculations at the Barcelona computing facilities; with Roger Anderson (again) and José Maria Alvariño from Salamanca with his former student Jesús Aldegunde, and with Dimitris Skouteris (currently Antonio Laganà's co-worker) on the exact representation of steric effects in quantum mechanics (the "stereodirected representation for the exact scattering matrix). Lately Dimitri Sokolovski, a professor in Belfast, introduced us to the exploration of reactive scattering resonances as poles in the complex plane.

Rotating around these projects, over the years I had valid postdocs (Laurent Bonnet, again coming from Jean Claude's group and now back to Bordeaux, Andrea Simoni now in Rennes), and graduate students (Andrea Beddoni, Alessandro Volpi). Andrea Lombardi started as an undergraduate and continued as a graduate student and postdoc. He collaborated with Robert Littlejohn from Berkeley, and also regularly visited Ersin Yurtsever in Istanbul. With him we had the idea of exploiting the tools that we had refined for the quantum mechanical treatment of few body systems, in order to reformulate their classical mechanics counterpart. The purpose was that of tackling the many-body problems needed for the study of atomic and molecular clusters, extending the scope of hyperspherically based approach to the issues of the structure and dynamics of nanoaggregates. Our efforts were put into firm mathematical grounds by Misha Sevryuk, and supported by further applications in collaborations with Xavier Gadea and Florent Calvo from Toulouse, and of Jesus Rubayo and Juan Carlos Castro Palacio from Havana.

## Spin Networks and Sturmians

These developments extend to recent times. To put things into a reasonable chronological order, we have to go back in time, but it is important to note how the extensions of my collaborations also regarded the spatial dimensions involving both my visits to and visitors from various parts of the world.

Lucky encounters played a key role. I had first met Robert Littlejohn at a conference a dozen years ago. He later visited here in part also because he was attracted by the classic Roman culture. Collaborations with him through his subsequent extensive visits have led to a continuous confrontation on the most intriguing problems of the quantum mechanics of few bodies, and of semiclassical approaches, currently focused on the fascinating problem of 3n*j* symbols.

These symbols, and in general the spin networks, which are of continuous interest for us for application both in spectroscopy

and in collision theory but also are important for their role in our hyperquantization algorithm, were also under focus of a colleague from Pavia University, Annalisa Marzuoli, who is motivated by problems in quantum gravity and quantum computing. The collaborations with her, Robert, and Roger are providing further fascinating perspectives especially on understanding the classical limits of 3n*j* symbols and the associated spin networks.

We continued of course to be attracted by specific chemical problems. In the early 1990s, we were intrigued by the possibility of applying these powerful mathematical tools (hyperspherical harmonics, 3n*j* symbols) in quantum chemistry as complete orthogonal basis sets and orthogonal matrix elements. The clue happened to be the exploit of a projection into momentum space of the *n*-body Coulomb problem, extending the one devised by Fock in 1935 for the hydrogen atom. Gaia, Simona, and I had as main collaborators in this enterprise my undergraduate and doctoral students Cecilia Coletti (now a professor in Chieti) and more recently Andrea Caligiana. They worked on this topic for both their *laurea* and doctoral thesis projects. Meeting and collaborating with John Avery in Copenhagen continues to be illuminating, particularly on clarifying aspects of relationships of the configuration space counterparts of these basis sets (Sturmian Orbitals) with Slater orbitals, venerable ingredients of electronic structure theory.

## Four (and More) Bodies, Chirality

The rest of the story leads us to recent times, to current problems, and to present collaborators. As before, experiments, theory, and calculations intermingle on themes motivated from understanding spatial aspects, anisotropies, steric effects. The new keyword entering the game, although on a waiting list all these years, is "chirality".

From a theoretical viewpoint, we are after extensions of accurate quantum mechanical approaches beyond the three-center case, and formal aspects are being clarified. To the long time collaborators we have added Federico Palazzetti, Mirco Ragni, Ana Carla Bitencourt, Cristiane Ferreira as students, and Glauciete Maciel, Chelat Ramachandran, and Elango Munusamy as postdocs.

The four-body case, and in general the four-center problem in chemistry, is turning out to be very hard to tackle at a rigorous level. We have to produce the accurate benchmark information that is needed to compare approximations necessary to simplify both the numerical treatment and the exhaustive understanding of the relevant features. That would help to clarify the physical nature of the processes we are attempting to describe. Deficiencies of classical mechanics approaches in dealing, for example, with proton tunneling, is particularly serious, specifically in the molecular dynamics of interest in biochemical environments. Along this line, the four-body case is important also because it is at the level of structures of at least four bodies that one encounters the manifestation of chirality.

The intriguing set of phenomena associated with this concept have taken a large part of my recent activity from different standpoints, involving both the fundamental quantum mechanical treatment of mirror symmetry, a counterpart of time-reversal, and recent advances in the experimental and theoretical chemical physics of elementary processes of interest also in environments, such as the atmosphere and the biosphere.

Recent progress has regarded the use of quantum mechanical tools for understanding structure and processes for systems of relevance in environmental chemistry. The focus is on problems again triggered by experimental activity in this laboratory on investigations of intermolecular interactions by molecular beam scattering. For dimers of the major components of the atmosphere ($N_2$—$N_2$, $O_2$—$O_2$, $N_2$—$O_2$), experimental and phenomenologically derived potential energy surfaces have been used to compute quantum mechanically the intercluster dynamics. Daniela Ascenzi (now in Trento), Massimiliano Bartolomei (now in Madrid), Miguel de Castro (sent here by Angel Gonzalez-Ureña, and now also back in Madrid), Estela Carmona (sent by Gerardo Delgado and Pablo Villareal, and also back to Madrid) had been involved in this work in different times and roles. Rovibrational levels and wave functions have been obtained for perspective use in atmospheric modeling of radiation absorption of weakly bound complexes.

Further work has involved interactions of paramount importance, those of water. Molecular beam scattering experiments measure essentially the isotropic part of the forces, and state-of-the-art quantum chemical calculations for its complexes with rare gases yield complementary information on the interaction (specifically the anisotropies). Similar approaches and results have been pursued and obtained for $H_2S$. Collaborations here were with Brazilian colleagues, Ricardo Gargano, Patricia Barreto, and Alessandra Vilela.

Stimulated in part by the interesting problem of large amplitude vibrations, such as the chirality change transitions associated with the torsional motions around O—O and S—S bonds, a systematic series of quantum chemical studies has been undertaken on systems that play roles in the photochemistry of minor components of the atmosphere ($H_2O_2$, $H_2S_2$, and several molecules obtained by substitutions of the hydrogens by alkyl groups or halogens). Quantum chemistry has been proven to have reached the stage of resolving many previously controversial features crucial for intramolecular dynamics of these molecules (dipole moments, equilibrium geometries, heights of barriers for torsion). Quantum dynamics calculations are also performed to compute torsional levels and temperature dependence of their distributions.

These computational investigations assist the search for stereodynamical manifestations of molecular alignment and possibly of chiral discrimination. The parallel experimental effort involves collaboration on electrostatic molecular alignment between our lab and that of Toshio Kasai and co-workers in Osaka.

Another project pursued through my frequent visits there is on a chemical kinetics approach to respiration of leaves. Mass spectrometry is again the crucial technique. Experimental and theoretical advances in the observed non-Arrhenius temperature dependence on rates are also shown to be relevant for diverse fields, such as packaging for food preservation and adaptations of biosphere to climate changes.

## Epilogue

*The true voyage of discovery does not consist in the search of new landscapes but in having new eyes.*

Marcel Proust *A la recherche du temps perdu.*

At the end of this bird's eye view of my personal story, and particularly professional progress, I wonder whether my voyages can be regarded as those of an eagle-eyed person. I am also grateful for this opportunity, which has been offered to me, to put some order in accounting for developments that are due much to favorable occasions and to encounters with wonderful travel companions. Again, this refers both to my family and to my career as a teacher and as a scientist.

In retrospect, a recurrent theme that I have contributed to elaborate has been to provide full three-dimensional views on

how molecular structures transform. I see a sign of continuity with the effort of Renaissance artists to represent the world according to the new science of perspective. A dream continues to be that of succeeding in favoring or disfavoring effective molecular encounters by influencing their mutual orientations; this can be seen as a modern aspect of the science of catalysis. Indeed, most of the progress in understanding these features of the nature of elementary chemical processes, in particular that of chirality (a topic mentioned as one currently a focus of my recent interests) have to be brought within the realm of activity in stereodynamics.

These examples show how connections arise in scientific research, amplifying the scope of our investigations toward both immediate applications (such as combustion and atmospheric chemistry) and to new fields, such as astrochemistry, protobiological chemistry, ultracold chemistry. These are among the most exciting areas of research that we leave to future generations.

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