Cesare Pisani: a life in science

The scientific activity of Cesare Pisani is so strictly interwoven with mine, that I have chosen to present it from a personal point of view. I have adopted the same criterion for selecting some references from his rich production.

In 1968, when I was a third-year undergraduate student, I started to attend lectures and seminars at the Laboratory directed by prof. Franco Ricca, whose main activity was the experimental investigation of gas-surface interactions in ultra-high-vacuum which was a frontier of physical chemistry at that time. That same year Cesare Pisani was invited by Franco to join the group and had come to Torino with his wife Flavia and their three children. In fact, his collaboration with Franco had started some time before, while Cesare was working at SAES Getters, a top level high-vacuum industry in Milan, where he had acquired skill and expertise in various aspects of surface science [1]. At the same time Carla Roetti was also beginning her collaboration with the group after graduating in chemistry with Franco. In these very early years of computers, Cesare introduced collaborators and students to programming and simulation techniques. I remember my first experiences in 1970-71, while working at my thesis under Ricca’s supervision, in modeling the adsorption of rare gases at the surface of graphite and rare-gas crystalline surfaces using Lennard-Jones type potentials [2]. The codes were written by Cesare and Carla, and we were running them at computer centers here and there, where and when we could get access, often only during the nights.

In those years (1969-1974) the role of simulation as a support of the experimental activity was increasing constantly, and became for us the dominant activity after Franco Ricca became full professor of Theoretical Chemistry, and decided to stop the experimental activity [3] and to create a theoretical chemistry group in Torino. A long period of intense study followed, aimed at acquiring a background in theoretical chemistry and solid state physics that could both be proposed to the Chemistry students, and provide the necessary background for starting an independent scientific activity in this area. I (as with many other students or post-docs) like to keep a relic of my formative years, and to use it for refreshing some parts of my background, the handwritten notes of courses and seminars prepared in those years by Franco and Cesare. In the 1973-76 years, after my degree and my military service, I obtained short range grants from various sources, and I worked day by day, shoulder to shoulder with Cesare and Carla on different simulation projects, where in all cases we were implementing related computer codes. That period was extremely useful and creative for me, and I had the opportunity to learn mathematics, physics, computer science and, more generally, a rigorous scientific method from Cesare. Our first programming experiences, concerning codes for the atomistic description of surfaces and solids [4], and then their semiempirical (Extended Hückel, CNDO) extension [5], provided an excellent training for our more ambitious subsequent projects.

In 1973, during a six-month sabbatical leave spent with Prof. Grimley at the Liverpool University, Cesare became interested in the problem of local defects in crystals, and in its treatment via Green function techniques [6]. He formulated an original approach for this purpose [7], leading eventually to the “Embed” project, which will parallel a large part of Cesare’s scientific life.
However such a scheme requires, as a preliminary step, the availability of the quantum-mechanical solution of the perfect infinite system. For this reason, in 1976, Cesare, Carla and myself decided to start a very ambitious project, namely the construction of an ab initio Hartree-Fock (HF) code in a basis of Gaussian type functions (GTF) for the treatment of periodic systems. At that time, with the adsorption problem in mind, the objective was to be able to describe the graphite monolayer, and later, possibly, other substrates. Cesare reformulated the basic equations (early proposals from other groups existed, notably that by Euwema et al). We started then to construct our code, CRYSTAL, by exploiting the GAUSSIAN70 integral package, which was free-access at that time. It took about four years hard work before obtaining the first results concerning the total energy and band structure of graphite. The corresponding papers appeared in 1980 [8,9]; in the same years alternative strategies were being formulated, in particular the LDA-plane-waves-pseudopotential scheme, that dominated the scientific arena for about 20 years, for instance in M. Cohen’s implementation. It is interesting to notice that the HF-GTF approach, which requires more sophisticated techniques and has been considered for many years a sort of exotic exercise, is receiving in these last years an increasing interest, and its use is being introduced in nearly all the most diffuse periodic ab initio plane-wave codes.

At the end of the seventies Ricca had become more and more involved in scientific projects of general interest, such as the organization of a Natural Science Museum in Torino, or the creation of a pioneering Regional Computer Center to be used by the Public Administration and the University, so that Cesare took in practice the leadership of the group. The subsequent decade (1980-1990) was devoted to the application of the CRYSTAL code to a variety of problems of surface science and solid state physics, and to its generalization, standardization, and improvement [10-14]. Let me mention a few examples of this activity: soon, we realized that the computational scheme was sufficiently general to permit the investigation also of 3D and 1D systems; further generalization to 0D systems allowed comparisons between molecules and molecular crystals; the large variety of space, slab and polymer symmetries suggested to code general input routines; the need of disk space (we are in the eighties!) for storing the bielectronic files, and the reduced speed of the machines imposed the full exploitation of point symmetry; the problem of the long range electrostatic interactions (Madelung problem) required a new formulation which exploited the many interesting features of the GTF basis set; a new integral package for treating d and f functions had to be coded. Many of these problems have been solved thanks to the extraordinary qualities (scientific, computational, human) of Vic Saunders, who became “the fourth person” of the group, starting a collaboration that lasted for more than two decades, until his retirement in 2003. In 1988 the CRYSTAL project had reached a well defined steady state, with the distribution, through QCPE (Quantum Chemistry Program Exchange) of the first public version of the code (CRYSTAL88 was the first ab initio code for the study of the electronic structure of crystalline solids publicly available), and the parallel publication of the corresponding theory in a book of the Lecture Notes in Chemistry series [15]. A generation of undergraduate students, PhD and post-docs were introduced in those years to solid state, quantum chemistry and simulation, and provided important contributions to the CRYSTAL development. In this activity Cesare was particularly interested, as he always preferred to “restart from the pencil”, to study new problems and to formulate new proposals rather than doing the systematic and often boring work that transforms a prototype code in its public standard version. This curiosity had brought him to explore the possibility of studying disordered systems with ab initio tools [16], the use of diagrammatic techniques for correlation and the Green function reformulation of many solid state problems. While Dovesi, Roetti, Saunders and many other collaborators continued the development of the CRYSTAL code which would eventually bring to five other public versions, in 1992, 1995, 1998, 2003 and 2006, Cesare decided that times were ripe for a new adventure, the implementation of an ab initio code for local defects using the perfect solution generated by CRYSTAL: the EMBED code.
The EMBED formal scheme is presented in a series of papers by Cesare and Furio Corà (his main collaborator on this project) [17,18]; further important boost was given to the project by Uwe Birkenheuer, Silvia Casassa and Roberto Nada, which permitted to set up a first public version of EMBED in 1996 (the second and last one appeared in 2003).

In the same year another volume in Lecture Notes in Chemistry was published, Cesare acting as editor [19], with contributions from many international collaborators invited in Torino for a simulation School. Many other simulation Schools will follow, one or two every year, in Torino or in other places such as Pau (France), Barcelona (Spain), London; in all of them Cesare was one of the most appreciated teachers, as documented by the clear lectures still available. Starting from the mid-eighties, when some of the tools implemented in the group became sufficiently ripe, a very large number of scientific interactions of different nature took place in Torino (up to twenty visitors per year for periods longer than a week), or in the different places he was visiting: frequently Pau (France), Konstanz, Paris.

Important recent contributions to surface science, simulation of zeolites, defects in bulk materials are documented in Cesare’s bibliography [20-23]. Most of these applications were performed with EMBED, which was recognized in the scientific literature as the most successful code of this kind. However, partly due to the limited human resources available, partly due to some inherent difficulties, EMBED was unable to result an effective alternative to other more standard but increasingly more efficient ab initio approaches to the problem of defects in crystals: supercell periodic schemes and multi-level cluster approaches may provide in fact high quality information with much lower entry levels. So he decided to stop his activity in this direction, although with some regret.

From the beginning of this century, Cesare was following with increasing interest the rapid evolution of the correlation techniques in the molecular context, mainly related to the local approach and to the density fitting techniques, features that were particularly suited for large molecular systems and, in perspective, for crystalline solids; for this purpose, the availability in CRYSTAL of Wannier functions, generated with an original scheme implemented by C.M. Zicovich Wilson, appeared to provide an ideal reference [24]. The CRYSCOR project was so started, relying on a collaboration between the Torino group and that of Martin Schütz (one of the main authors of the MOLPRO code) at the Regensburg University. Five years intense work in the two groups (involving Lorenzo Maschio, Silvia Casassa, Denis Usyvat and others) resulted in the implementation of a computer code which is becoming progressively more robust, and will be distributed during 2009. CRYSCOR uses the CRYSTAL wave function and evaluates the MP2 energy (for the moment being) of any insulating system in 1D, 2D and 3D [25-27]. So Cesare is retiring in the same moment in which his last “son” is becoming adult, and soon will be a standard for comparison in solid state physics.

The papers presented in this volume, written by scientists and groups that had the opportunity to work with Cesare during his long activity, represent a sort of summary of the many scientific problems and areas in which Cesare has been active and gave important, illuminating contributions. All the authors are also, or mainly, Cesare’s friends, because working with him in all cases means to have and keep friendly relations with him. In nearly forty years of side by side work it happened very frequently to have different opinions, but I must admit that it has been impossible to argue with him.

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