Forward

Alessandro Bencini: A Choice Antinomy

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ABSTRACT

Alessandro Bencini was a relevant scientist. He was considered an acknowledged leader in the interpretation of magnetic and spectral properties of transition metal complexes. However in the last twenty-five years of his life his research activity was essentially devoted to the computational application of quantum chemistry to paramagnetic systems. The merits and the limits of this choice are here discussed in the framework of the evolution of scientific achievements in the field. It is here stressed out, that Alessandro Bencini was the founder of the laboratory of quantum chemistry in Florence, which, as far paramagnetic systems are considered, is nowadays a cutting-edge example in the specific sector.

KEYWORDS: molecular magnetism; quantum chemistry; transition metals; computational chemistry

Friends are like stars: they always shine when the rest is darkness. I warmly thank you, Federico Totti, for giving me the possibility to remember a true friend, who left this world too early. Also because I would like Vittoria, his beloved little girl, to have the chance to know something more about the father who knew too little.

Alessandro Bencini was one of my students in 1973 when he was attending the fourth year at university. We used to live in the same borough in Florence and we often met outside the academic environment. At the time of graduation, he would walk around with a copy of the Griffith or Messiah under his arm at night and day, summer and winter, in the sun and in rain, even when we ran our dogs along the river. His father, graduated in mathematics and director of the Military Geographical Institute, was a really refined man. I have always thought that his father's cultural legacy influenced deeply Sandro's choices, so much so that although he was attending one of the most prestigious classical high schools in the city, he denied the humanistic contents of the teachings received, preferring those subjects such as mathematics, physics and sciences, which in such schools had a secondary importance. Perhaps for this reason the concepts associated to reductionism and supervenience, ontology and epistemology—the latter he always confused with gnoseology—never aroused his interest. As far as the paternal refinement is concerned, I must acknowledge that he instead gave it a personal

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elaboration, giving proof of that creationism we will talk about later. He kept many aspects of it, even if his shyness did not allow him to highlight them, an aspect of his character which he alternated with an invective approach towards the world. Unfortunately, his mum was irreversibly ill and this must have seriously affected his early education. It should be considered that he was profoundly honest, extremely serious about what he considered to be important, about his whole study, while he tended to avoid intrigue and his attitude would suggest a similarity with a Lutheran of Max Weber more than reminding the complaining and tall-talking son of the Council of Trent. But above all he showed a great generosity, displayed with naturalness and joy, so in contrast with Dawkins's selfish gene, although, as it happens with all the generous people, this features was sometimes source of sullenness and discontent.

When in 1943 the Faculty of Chemistry of the University of Florence became seat of the German command, almost all that was kept inside was smuggled. One of the two devices that were left there was a magnetic scale, whose weight of a few tonnes probably made it not so desirable to seize as spoils of war. In support of this statement it must be considered that the rails of the tram that passed not far away were also left. At that time the interest of chemistry scholars was focused on the study of diamagnetism, although the outcomes of the research did not raise—and never have—great excitement in the minds of those who were committed to such enquiries. While the colleagues of chemistry and physics insisted in such a disheartening activity, a then young assistant, Luigi Sacconi, had a revolutionary idea, which was to use the surviving scale in order to study paramagnetism, which led him to an interest in the chemistry of the compounds of 3d elements. This was the beginning of the inorganic chemistry school of Florence and more specifically of LAMM (Magnetic Materials Laboratory), that, founded many years later by Dante Gatteschi, is nowadays, under the direction of Roberta Sessoli, a cutting-edge example in the specific sector.

The meeting between Sandro and Dante Gatteschi occurred in the early 70s. Sandro had a remarkable talent for laboratory synthesis, but Dante Gatteschi’s interest, shared by Sandro, limited this activity to excel in the kitchen, as it is typical of several chemists. At the time the rationalization of the magnetic and spectroscopic properties of the complexes of transition metals represented a considerable challenge for chemists, considering the limitations associated with the technology of the time and the possibility of application of complex theories. However, the ligand field theory (LFT), which was the easiest applicable theory back then, enabled to rationalize the experimental data obtained from visible spectra, magnetism and EPR spectra. The LFT, it must be reminded, only takes into consideration the correlation between valence electrons, that are as a matter of fact d electrons, without taking into account any possible correlation with the other electrons existing on the molecule. If we want a more sophisticated description we need to introduce relativistic factors,

but actually the spectroscopic and magnetic properties of the transition metal compounds can be satisfactorily interpreted by determining the lower-energy external electronic levels. In fact the properties are determined only by the thermally populated states and both the EPR and the dependence of the magnetization on the temperature and on the magnetic field can be easily interpreted. From a pragmatic point of view the real Hamiltonian operator describing the system can be simplified if there is no orbital degeneration in the ground state, with the so-called spin Hamiltonian, which is in fact operating only on the system of electronic levels that are thermally populated. In this case, the LFT has the advantage that most experimental data can be quantitatively rationalized and simulated using a limited set of parameters. This procedure does not require the need for excessively long and sophisticated calculations. The problem is that the number of these parameters increases considerably when the symmetry of the molecule is lowered and in this case it is increasingly difficult to obtain a univocal set of parameters, which allow to analyze a molecular system with sufficient accuracy. Moreover, charge transfer transitions and couplings of electronic and nuclear motions cannot be simulated.

The collaboration with Dante Gatteschi was extremely successful, culminating with the interpretation and correct description of the electronic properties of homo- and hetero-dinuclear complexes, which made Sandro an acknowledged leader in the reference field. The book “Electron Paramagnetic Resonance of Exchange Coupled Systems” of which he is co-author represents the epitome of his youth scientific activity [1]. But the transition from mononuclear to dinuclear ones naturally implied the subsequent transition to magnetically interacting polynuclear compounds.

Dante Gatteschi placed it as the foundation of the experimental study of molecular magnetic materials, a branch of chemistry that over the years has had a growing success, which having as its object the study of extended bi- and tri-dimensional systems, presented an enormous complexity due to the frustration of spin. The great result that Dante and his collaborators obtained was that, beyond its complexity, the so-called emergent properties of a collection of interacting paramagnetic centres could be anticipated *a priori* and justified using an appropriate representation model [2,3]. The general conclusion, which for thirty years has constituted the postulate to be adopted in the study of magnetic materials for a multitude of researchers, was therefore that the limit of the problem lay in the choice of the model of representation, a choice that is often limited by the need for approximation and simplification.

Sandro instead devoted himself to the computational application of quantum chemistry to paramagnetic systems. The availability of ever more powerful and sophisticated means of calculation justified this choice, which in fact was not something new, since, from Pythagoras onwards, mathematics has always been the dominant means of explaining

phenomenology, so much so that it survived in our way of thinking in the vision that Plato has left us as a legacy, given that, as Bohr argued, it provides the easiest way to teach the ignorant.

We have never argued in over thirty years of sincere friendship, except in 2008 when we did it fiercely. At that time, I was guest editor of the special issue of a scientific review [4], whose editorial board had decided to celebrate Dante Gatteschi, who had been Sandro's master, mentor and guarantor. I had received over one hundred twenty papers from the international scientific community, but nothing from Sandro and the deadline had already expired. When I asked him how long I should wait, he told me that he intended not to write anything. I called him to my office, closed the door and told him what I thought of him on a human level. I still see him staring into space while he was telling me that it was useless for him to write something, so it made no sense. All his activity was reduced to the exercise of mere numerical calculations of which the literature was full. At that time Umberto Eco had still not anticipated that Facebook and the other forums had allowed the "invasion of idiots" (sic). But the heart of the matter was the same: since computers were cheap and programs were easy to find, literature was overrun with computational chemistry papers written by people who didn't understand what they were doing. The sector, in Sandro's Lutheran perspective, was ridiculed and in retrospect it was logical that it was. Perfect, I told him, why don't you write it since you have the competence to do it? And he went away grumbling, but a few days later he gave me the most beautiful work [5] of his life, which I still judge to be characterized by a clearness of expression and essential understanding (in an alchemical sense), which is very rarely found in scientific works. I hope Dante appreciated it.

Years later this episode leads me to a reflection and several times I have wondered if that uneasy situation is better reflected by Plato's *Phaedrus* or *Parmenides*. But perhaps the juxtaposition is too noble, besides the fact that these dialogue are defined as dialectical or of an old age, a status that for non-exciting reasons of age also characterizes my current writings as well. The first answer that came to my mind was obvious: Sandro had developed a culture he had passed on to some students, such as Federico Totti, who is enthusiastically carrying on his work, and all the students who had worked with him. Thanks to his initial effort, in Florence a group still exists where this culture survives and has evolved. This from the standpoint of academic teleological ethics leads the discussion to a conclusion: the teacher or the master played his part, leaving his mark, as the seed planted and watered by Sandro has given the result that everyone can see.

On the other hand, as regards the state of discomfort in which he found himself, I do not allow myself to infer judgments even today, also because I am fortunate enough to consider myself a bad psychologist. However, if we take into account what Hans Primas wrote [6], who is one of the most important experts of Quantum Chemistry, who died recently, in the

introduction to his famous text on the subject, flattening one's professional activity exclusively on calculation, as Sandro had done for many years, almost always involves signs of paranoia, as can be clearly seen from the exaggerated and exorbitant respect that the lovers of this subject have towards the compartmentalization and computers. I totally agree with it, although I may add all the smartphone enthusiasts, along with the depressing image they offer daily in showing their isolationist regression. This is because—Primas goes on—the separation between science and philosophy has led to the triumph of the so-called realistic view of the world, which is characterized by the total blindness of many experts in assessing the demand for immanent abstraction in the nature of modern science. As a matter of fact, I would like to conclude by thinking about Sandro, that the opium war, which saw England undermining the institutional foundations of the Chinese empire, had taught him nothing. But this can be considered a secondary fact, because the point is a different one.

Sandro was a chemist and the importance of chemistry in the history of scientific thought had its roots precisely in the fact that it had shown that the properties of substances depended on the nature of the atoms that constituted them and on their way of mutual interaction, rather than on macroscopic parameters of a general nature such as those used in classical physics such as mass, length or temperature. This specificity, such as that shown for example by emission and absorption spectra, had led to the introduction of the concept of operator, to the development of quantum mechanics (Prigogine defines Stael's revenge) and therefore to the creation of that field that has changed our modern life, including the aforementioned smartphones, Facebook and the invasion of idiots. It had provided chemists with the method to rationalize the object of their study with particular reference to the understanding of the interactions between the different types of atoms. In other words, quantum mechanics had provided chemists with the universal basis for understanding their research area and at the same time the most powerful linear method for analyzing, rationalizing and predicting molecular interactions, as well as the reactivity of individual chemical agents.

The basic problem therefore lies in finding the answer to the question: can chemistry be reduced to quantum chemistry? The question is deliberately specific, but it can be formulated in a more general sense just to please the adepts of physicalism. In a philosophical perspective the correct question is whether it makes sense to think that quantum mechanics actually contains all the necessary and sufficient concepts both from an ontological and an epistemological point of view in order to define a reductionist process that leads molecular chemistry to be an expression of quantum mechanics itself [7–10]. In a few words, by translating using a more popular language style, is it correct to think, as many have thought starting from Dirac, Putnam, Reichenbach (but, I like to emphasize, not Heisenberg and Bohr), that chemistry is nothing more than an APP of

quantum mechanics? My answer is simple: obviously not, because those who make these assertions have not understood what chemistry is and what quantum mechanics is. This simply because it has no importance that the silver lapis with which Botticelli painted the fine hair of the seventeen-year-old Simonetta Cattaneo in the Spring and the Birth of Venus is made up of atoms with a centered or compact hexagonal body lattice.

I recognize that my point of view is partial, as is the case on the other hand with an admirer of Wittgenstein and Simone Weil. On the other hand, I strongly believe that the history of chemistry has been and still is determined by the laboratory results obtained by chemists and not by others, and that the fascination of this field consists fundamentally in the ability to sculpt one's will in the matter, even if they are not able to control the properties of a collection of molecules, nor to predict the effect of dimensionality on the properties of the same collection. This leads to the promotion of a significant interest in the characterization of nanoscopic or mesoscopic particle systems. But it is still true that Michael Faraday's conception of chemistry, which in fact ignored the atomistic theories of school teacher Dalton, has always had a certain validity for me. So why there is someone who asks the question if chemistry can be reduced to an expression of quantum mechanics and why there are people who continue to think that the calculation, as a new avatar with its purifying descent, can nullify and make the laboratory experiment obsolete, which in fact characterizes the imperfect nature of the human factor in its interaction with the outside? The answer largely lies in the fact that the philosophy of science, which triumphs in the Anglo-Saxon world, was written by the followers of logical positivism, that is by Schlik, Carnap, Neurath, Hempel and Reichenbach, who once members of the Vienna and Berlin Circles then mostly moved to the US when the Nazi Party rose to power (Schlik was assassinated by a Nazi student, but this event, given his political ideas, would not have worried Sandro that much). All these people had experienced the birth of quantum mechanics and, being deeply fascinated, formed a class of disciples who identified the philosophy of science with theoretical physics, however ignoring the ambiguity of meaning that the word "physics" had developed in its temporal evolution. This misconception is quite common in the academic world and in simple minds it leads to the conclusion that chemistry is only an exercise in quantum mechanics. But as we will discuss later, this point of view has its own limitation in positivism and can be harmful to someone who does not have a simple mind. Perhaps this is the origin of the paranoia that Sandro showed, since, being very intelligent and competent, he understood the limit of his own work more than any other.

If we must listen to Paul Feyerabend, the philosopher of epistemological anarchism, positivism describes things are as they appear: all that is to be done is to observe and order them.

But it must be remembered that Heraclitus and Parmenides had already strongly criticized this way of thinking ("Knowing a lot of things—

writes Heraclitus—does not give you the reason for their being"). This is what actually happens when, for example, technology provides you with tools that increase the accuracy of the calculation, but in fact they do not allow you to distinguish whether the calculation simulates abstract or real entities. Moreover, even realism—Feyerabend continues—which states that things are not what they appear to be, but that there is always an underlying reality that the scientist must understand, does not allow an improvement of the perspective in an absolute sense. The path to follow is rather structuralism, which involves dividing knowledge into domains consisting of elements that are consistent with each other. Dante Gatteschi, Roberta Sessoli, Andrea Caneschi and the other members of LAMM in Florence, to limit the discussion to this sub-microcosm, have followed this path unlike Sandro, who despite having started it, abandoned it.

The spirit of chemistry lies in the study of the constitution of matter and its transformations and there are different methods to represent the object of their study. All these methods have limitations and chemists are aware of them, but they do not worry about distinguishing between an absolute or an operational method. This is because, excuse my banality, in the manipulation of the matter an effective approach is always necessary, regardless of the absolute truth formulated by a law that governs the hidden variables of nature. They are limited to the determination of the microscopic constituents of the product of their synthesis in order to improve a knowledge that allows them to synthesize other compounds. From this perspective the knowledge of the constituents is only a means or if you want a tool that allows them to verify the potential of nature. Therefore it is indifferent for a chemist to interpret the properties of a compound in one way rather than another, when these properties must be examined in a context that has its own reference in other chemical compounds and that this context cannot be defined according to the canons of physics or biology, but only from chemical ones. This is the meaning of the structural approach that sees the experiment and the calculation, considered as tools, in separate domains. And this is the great difference between chemistry and theoretical physics given the different knowledge goals that the two subjects have. However, this fundamental difference escapes many, especially when looking at an aseptic computer with too much veneration.

It is evident that conceptually from a chemical point of view the contribution brought by quantum mechanics is extremely important but limited, despite what many supporters of physicalism claim. Starting from the middle of the last century it has been pointed out that the macroscopic properties of matter are the resultant of the properties of the structural properties of the single constituents and their mutual interactions. The structural properties of the single constituents are usually determined experimentally through the X-ray diffraction but nevertheless the Hamiltonian that describes the system does not contain any terms related to the structure of the molecules. It happens the same in the case of ethanol

and dimethyl ether, which have the same brute formula but have very different physical and chemical properties, and for example, in the case of benzene, it is compatible with the structure of seven different compounds. As a result quantum mechanics does not provide any information on the symmetry of the molecule, nor does it justify the existence of chiral compounds. In addition to this, while molecular geometry is described by a set of observable parameters, the algebra of observables in quantum mechanics does not contain any observable parameters. Finally, the nuclei and the electrons are in entangled states and this situation remains independently of the reciprocal geometric relations. In other words, as Wolley observed more than forty years ago [11], the analysis of the properties of molecules requires several concepts that cannot be inspired by quantum mechanics. Now, if reduction means that the properties of something are necessary and sufficient to define the properties of another thing, the answer to the question of whether the chemical properties of a certain substance can be deduced or simply derived in a reductionist way from the laws of quantum mechanics, the answer can only be negative. It would be like formulating a theory of relativity without the observer.

Frankly, I believe that Sandro's choice was positive because it has allowed the improvement of specific skills in the field of quantum chemistry, especially as regards the problems of the paramagnetic molecule in the diluted state, in other words the molecule isolated from the others. The validity of his work lies in the fact that today there is still a group in the Department of Chemistry in Florence which, under the direction of Federico Totti, is successfully developing it. Moreover, I think it was negative because it did not allow him to broaden his horizons. Indeed, while he was struggling with a pyramid of approximations and perturbations, the rest of the LAMM members under the impulse of Dante first and of Roberta Sessoli with Andrea Caneschi then and of all the other members began to cultivate the principles of systemic thought in the field of magnetism. This thought [12–14] that derived from Aristotle and the Pythagorean school, had been taken up by Bogdanov (the one who had translated the Capital by Marx into Russian) at the beginning of the last century, and later by von Bertalanffy with the classic “General Theory of Systems” [15], which made it possible to rationalize the structure-property dichotomy for each scientific discipline. In chemistry these concepts had been set out by introducing the definitions of “supramolecularity” [16] and “cooperativity” [17] that constitute the pillars of the chemistry of materials, which is systems that present extensive interactions. This choice has allowed LAMM to obtain a series of awards and successes worldwide, earning the reputation of a cutting-edge laboratory. In practice the single molecule magnets properties exhibited by some mesoscopic molecular systems provide the basis for bridging the quantum world with the classical one [18]. But perhaps Sandro had never read “Diderot’s Egg” which, with the creation of the Encyclopedie, contrasted with the linear monism of the various Galileo, Newton and Laplace. What a shame:

perhaps he would have been fascinated and would not have felt frustrated in carrying out his praiseworthy research.

CONFLICTS OF INTEREST

The author declares that there is no conflicts of interest.

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REFERENCES

1. Bencini A, Gatteschi D. Electron Paramagnetic Resonance of Exchange Coupled Systems. Berlin Heidelberg (Germany): Springer Verlag; 1990.
2. Gatteschi D, Kahn O, Miller JS, Palacio F. Magnetic Molecular Materials. Dordrecht (The Netherlands): Kluwer; 1991. (NATO ASI Series, vol. 198).
3. Gatteschi D, Sessoli R, Villain J. Molecular Nanomagnets. Oxford (UK): Oxford University Press; 2006.
4. Dei A, editor. Protagonists in Chemistry: Dante Gatteschi [special issue]. Inorg Chim Acta. 2008;361:3339-4166.
5. Bencini A. Some considerations of the proper use of computational tools in transition metal chemistry. Inorg Chim Acta. 2008;361:3820-31.
6. Primas H. Chemistry, Quantum Mechanics and Reductionism. New ed. Berlin Heidelberg (Germany): Springer Verlag; 2013.
7. Schummer J. The Philosophy of Chemistry. Endeavour. 2003;27:37-41.
8. Bishop RC. Patching Chemistry and Physics together. Philos Sci. 2005;72: 710-22.
9. Bishop RC, Atmanspacher H. Contextual emergence in the description of properties. Found Phys. 2006;36:1753-77.
10. Scerri ER. Collected paper on Philosophy of Chemistry. London (UK): Imperial College Press; 2008.
11. Woolley R. Quantum Theory and Molecular Structure. Adv Phys. 1976;25: 27-52.
12. Checkland P. Systems Thinking, System Practice. New York (NY, US): John Wiley; 1981.
13. Emery FE, editor. Systems Thinking: Selected Readings. New York (NY, US): Penguin; 1969.
14. Johnson SB. Emergence: The Connected Lives of Ants, Brains, Cities. New York (NY, US): Scribner; 2001.
15. Von Bertalanffy L. General Systems Theory. New York (NY, US): Braziller; 1968.
16. Lehn JM. Supramolecular Chemistry. Weinheim (Germany): Wiley-VCH; 1995.
17. Kahn O. Molecular Magnetism. Weinheim (Germany): Wiley-VCH; 1993.

18. Dei A. Molecular Magnetism: a philosophical perspective from a biased point of view. Inorg Chim Acta. 2008;361:3344-55.

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