

Esteemed Rector Magnificus,
President of the Board of Trustees of the University of Girona,
Esteemed Authorities,
Professors, Students and Members of the University Staff,
Ladies and Gentlemen,

It is a great honor for me to receive the doctorate honoris causa from your university. For several reasons.

One of the reasons is the special place that Catalunya has held for me since a long time. I think contacts started in the nineties when Dr. Miquel Sola, now professor Miquel Sola, spent time as a postdoc in Amsterdam. I spent three summer periods as an Iberdrola Fellow at the Universita Autònoma de Barcelona, being hosted by professors Joan Bertran, Mariona Sodupe and Vicenç Branchadell, renewing also contacts with the Theoretical and Computational Chemistry group of the University of Girona at that time. The contacts have not been limited to Universita Autònoma de Barcelona or Girona, I remember memorable visits to Tarragona and to the University of Barcelona. I cannot record all contacts, but I should mention that since that time a strong connection with the Netherlands has built up over the years, with many fruitful exchanges.

Another reason to enjoy this award, apart from the personal honor it brings to me, is the tribute it constitutes to the field of science I am involved with, and am representing today, namely chemistry. It is a truism that science in general, and chemistry and physics in particular, have shaped our modern world. Maybe I should include biology, and then in its wake also medical science, but let me note a bit chauvinistically that biochemistry has hugely impacted biology and medicine. It is not only the technical achievements of the natural sciences that have impacted our lives. Their influence is much broader and deeper. They shape our culture and our outlook on life. They also are a source of beauty. Chemistry offers the beauty of chemical structures. I just have to mention the DNA molecule, with its intricate double helix

structure. And chemistry is a creative art. It creates many new beautiful structures, never before realized in nature.

On this occasion, however, I want to stress the lesson science teaches us about our mental outlook. Given that this award is in chemistry, in particular in theoretical chemistry, and then in the subfield of density functional theory, I think it is appropriate to highlight the role of open mindedness, the lack of prejudice, the flexibility of mind to adopt new paradigms, even when not yet completely established. In science, any preconception runs the risk of being thoroughly demolished. It appears that all obvious conceptions in whatever field one is interested in, are bound to be dispelled by further investigation.

By way of example, before I focus on theoretical chemistry, let me remind you of a very well known but actually very esoteric problem, that the most famous scientist ever has set himself. This most famous scientist is Einstein, you will agree. The question he struggled with is: can anything go faster than light? Isn't that an irritating question at a time the highest speeds were achieved by trains running ca. 100 km per hour, compared to the speed of light of 300 000 km per second? I am afraid a grant application by Einstein would not have been rated high at "usefulness for society".

Now we all know that Einsteins results have revealed staggering insights in such fundamental issues as the nature of space and time. But also position determination with GPS needs Einsteins theory of relativity. The utterly useful and very widely employed GPS devices that serve as the everyday navigation equipment in our automobiles rely on the theory of relativity! GPS has also revolutionized navigation at sea. Sextants and celestial navigation are not even taught any more at maritime schools! Often, the more fundamental insights are, the more revolutionary useful they prove to be. The lesson is: never reject a notion or question off-hand, however irritating or esoteric it may seem, be open minded and unprejudiced.

Let me focus then on chemistry, and to make a long story short, on my own field of the theory of chemical bonding and structure. Let me start with the

picture of bonding by electron pairs as developed by Gilbert Lewis (Figure 1), which I think every high-school student will remember from his chemistry classes. In the first decades of the twentieth century Lewis pictured chemical bonds as arising from electron pairs (Figure 2), and the remaining electrons pairing up in so-called lone pairs. This model rationalized a large number of known facts. In the first place the predominance of compounds with an even number of electrons. In the second place the explanation within this model of the valences of the elements when combined with the rule that an atom tries to collect 8 electrons (the octet rule). But of course there is also something ridiculous in this theory: why would negatively charged electrons, which according to electrostatics will repel each other, get together to form a bond? Moreover, just at the time Lewis was developing these ideas, the Bohr theory of the hydrogen atom, which pictures electrons as fast moving particles circling the atomic nucleus, like planets are circling the sun, was astonishingly successful in predicting quantitatively the spectra of the H atom. In a sense Bohr's model marks the beginning of the efforts that would lead, about a decade later, to quantum mechanics. Quantum mechanics is one of the two great theories of physics to emerge in the twentieth century, and from the physics side there was only ridicule and contempt for Lewis's model. And not only from physics. Also many physical chemists felt that Lewis's electron pair theory was too simplistic, the basis of electronic structure theory should rest firmly in the quantum theoretical treatment of the motions of the electrons. This may have cost Lewis the Nobel prize, he is often referred to as the most famous and deserving chemist who never got the Prize. But we should recognize that Lewis has had enormous impact in chemistry. His concepts were so useful and such an excellent basis for theorizing about bonding in molecules that even today every chemist knows what Lewis structures are. Much of his thinking, for instance his generalization of the concepts of acidity and basicity, to donation and acceptance of electron pairs, are now fully vindicated by quantum chemistry. Lewis is another example that we should beware of hasty condemnation and be open minded and unprejudiced.

It has been Linus Pauling (Figure 3) who has done an admirable job of tying in quantum mechanics with Lewis's ideas, even before computers were powerful

enough to actually perform quantum mechanical calculations on the motions of the electrons. He realized that even without computation one can give chemists a feeling for the relative importance of quantum mechanical effects by considering what he called "resonance" among various electronic structures. These contributions, also called valence bond structures, translate into simple pictures the quantum mechanical superposition principle (Figure 4). Many chemists who never studied quantum mechanics in any depth, and would think of it as a rather esoteric physical theory, were as a matter of fact practicing quantum mechanical concepts in their daily thinking and talking about the structures and reactivity of their compounds. I am ashamed to admit that as a young theoretical chemist I have made the error of ridiculing Lewis's and Pauling's models with their "unphysical" electron pairs, and the arrows indicating how these pairs might hop around in order to create other contributing resonance structures. So modesty is something that has to be acquired. We should be open minded and modest enough to keep in mind that what seems at first sight to be absurd and contrary to accepted wisdom may eventually turn out to contain a lot of truth.

Lewis and Pauling created a paper and pencil method for judging bonding and structures of compounds. But when computers became sufficiently powerful, it became possible to actually carry out the complicated and time-consuming calculations that are necessary to solve the quantum mechanical equations with sufficient accuracy. Sufficient accuracy was denoted "chemical accuracy", something like 0.1 kcal/mol in the energy. That would make it possible to actually do "chemistry on the computer" or "in silico". This development started slowly in the fifties and then made great leaps in the subsequent decades, mostly through the astonishing improvements in computer technology. Expectations (in my opinion unrealistic) were very high that eventually, maybe even soon, reducing chemistry to a computational science might become a reality. There was also a clear paradigm: calculations should be done "*ab initio*", that is by solving the equations purely by mathematical and numerical methods, without empirical parameters. We may use the picture of Thomas Kuhn, who distinguished periods of "normal science" and "scientific revolutions". In our case then, the paradigm was given, no scientific

revolution would be needed. We could envisage a period of "normal science" where theoretical chemists would work hard on the given task of developing increasingly sophisticated and efficient techniques of solving the given equations. They would eventually reach the holy grail of "chemical accuracy". As Kuhn describes, scientists usually enjoy such normal science. The goal is clear, it is easy to see who makes the smartest contributions to solving the set problem. All efforts can be directed towards developing methods to solve the given problem. No need to waste time and energy on debates about the underlying science or the goals to be reached. However, the downside is that the scientists no longer are so modest as to recognize that maybe the chosen path is not the right one, or at least not the only one. They may hate colleagues who will doubt the accepted paradigm, with a professional and sometimes even personal hatred.

This is what happened when in the seventies and eighties a new paradigm was provided in our science by the advent of density functional theory. We give it the acronym DFT. This is not the place to go into any detail about this theory. Let me just note that it provided a great simplification of the equations to be solved. The big drawback was the absence of a simple straightforward path to the exact solutions. In theory DFT did afford exact solutions. But often "in theory" is almost a euphemism for "not in practice". That is also to some extent the case with DFT, but not completely. It has not been made exact, by no means, but it is sufficiently accurate to be eminently useful. My career has entirely revolved around this particular approach. DFT has become thoroughly successful, by now maybe 90% of all quantum chemical calculations are DFT calculations. But the initial reception of DFT was utterly hostile. How did a small group of theoretical chemists dare to challenge the path forward that had been chosen by the very large majority of theoretical chemists, namely *ab initio* calculations? If I look back on my career, I like to divide it into two halves: the first twenty years (seventies and eighties) I was met, as a DFT practitioner and developer, with scorn and contempt. I remember a conference, organized by two well known professors in our field, in the mid eighties, where I was invited as a speaker. But they were harassing me so much at that meeting, that afterwards their students invited me to

dinner, telling me how embarrassed they were by this treatment. That is an illustration of the danger that old and established scientists are in. They may get too much entrenched in their pet theories and methods and may start to consider anything else as an aberration. It is also a beautiful illustration that, fortunately, young people tend to be much more open minded. That I am receiving this doctorate honoris causa today I consider a great honor for me personally, but at the same time I think it is recognition of the importance of the scientific revolution that has led to the predominance of DFT in our field, in particular for large systems.

But what I want to single out most is that again we see demonstrated that as scientists, we should never be rigid and prejudiced. We should be rigorous in our proofs and deductions, but that is a different matter. Things may always turn out to be just the opposite of what we think. Actually, they very often do. The *ab initio* approach looked so admirably clear and rigorous, while DFT was, and still is, far from straightforward and indeed somewhat muddled. Many people do not fully understand it, and there is still much to be criticized. But it has provided an enormous boost to the application of quantum chemical methods in chemistry. When I started my scientific career, most of the chemistry professors at my university, and surely at other universities as well, would question any "chemical relevance" of the theoretical chemists, with their penchant for mathematics and physics and computer work. That attitude amongst experimental colleagues has totally disappeared. They now enjoy to have computational input to their work. That is almost hundred percent owing to DFT.

So DFT is my last and telling example of the great virtue and even necessity in science to be open minded and without prejudice. It gives me great joy and satisfaction that this award underlines how this principle can lead, as so often in history, to unexpected and important progress.

Thank you for your attention.

Evert Jan Baerends,
Girona, May 9, 2019