

## Foreword

I still remember the day when I first looked at the large accordion-folded sheets that a noisy dot-matrix spewed forth, sheets that contained the output of an extended *Hückel* calculation on pyridazine, pyrimidine, and pyrazine. The wave functions emerged as a  $28 \times 28$  matrix, running across several pages; one had to scan down a long column to assign symmetries to the levels and see where in the molecules the largest coefficients were.

In the MOs of these diazines I was naturally looking for two lone pairs more or less localized at N. Every chemist expected to see them; I was a chemist. I already knew from a pyridine calculation that the lone pairs weren't as localized as I thought they would be. In the diazine series I expected to see the lone pairs split by a lot in energy in pyridazine, due to lone-pair–lone-pair overlap, less so in pyrimidine, still less in pyrazine. No different from anyone else, I was thinking the problem through in a “through-space” direct overlap way.

Pyridazine followed expectations. Pyrimidine was a bit of a surprise – the gap between the lone pairs was larger than I expected. But the real shock was pyrazine – the 1,4-diazine – the gap between the two mainly-N-localized orbitals was not tiny, but a few eV. And the “wrong” combination, the antisymmetric one, was lower in energy! “Wrong” because from the perspective of through-space interactions I expected the symmetric combination lower – not that I would have expected any significant interaction between two orbitals 2.8 Å apart, and pointing away from each other.

I couldn't even get that result into my 1964 paper on  $\sigma$  orbitals in azines; friends didn't believe it. And while the result perplexed me, it took the slow building of confidence in orbital interaction diagrams, and my own rediscovery of qualitative perturbation theory (both clearly arising from the fertile interaction with *R. B. Woodward*) before I could hazard a simple, symmetry- and overlap-based explanation for that pyrazine finding. You will find it in a chapter in this book.

The purpose of telling this story is not solipsistic. What you see in this wonderful book is theory and experiment at the nexus of maximal understanding. It is where the authors of this book and I were fortunate enough to be in our scientific journey. And it is where contemporary quantum chemistry is not. Yet it is a place of the intellect to where I am confident electronic structure theory in chemistry must eventually wend its way.

We are in the age of simulation. Bigger and better calculations, winding their way through a maze of functionals, basis sets, and ways of including correlation, give an observable to almost any desired degree of accuracy. With little explanation – none from the

computer, of course, little from the man or woman guiding the computer. If you want the same observable for a slightly modified molecule, a methyl replacing a hydrogen, the prescription is to go back into the computer. It's as if there were an uncertainty principle relating chemical understanding and computational accuracy. There are exceptions, but by and large the complexity of what one has to do to get, say, an electronic spectrum, right, and the psychology of human-machine interactions militate against accepting simple, qualitative explanations. Such as the ones you will find in this book.

Meanwhile, our graduate students and undergraduates desperately crave understanding, not numbers. Actually, so do their teachers. So what we teach is just that simple orbital argument, the perturbation-theory-based mechanics of interacting orbitals. The students lap it up, for the desire to understand is so strong!

The disjunction that these students, now become professionals, face when they turn to today's computational theoretical chemist for assistance in their research, may be traumatic. People don't write about this moment of collision of simple (true, often too simple), learned explanations with calculations; there is no place for describing that emotional experience in our papers. But I see the traces, papered over, as I read the literature. And I smile as I see them.

This volume provides true understanding, which is the best thing one can say of any book. The book reaches at every point for a conciliation of three threads: (a) the best electronic structure computations of the day; (b) the experimental tools by which one can probe interaction, foremost among them photoelectron and electronic spectroscopy; and (c) qualitative (yet quantifiable) molecular-orbital-based reasoning. In doing so, this book's rehearsal of a journey of understanding that goes back decades is also a signpost for the future. For there will surely come a time, and there will come theoreticians for that time, who will do state-of-the-art calculations not just for the numbers. Instead bright young people will, one day, use their computers' rich harvest and infinite potentialities for probing alternative realities intelligently, as a numerical laboratory. Not just for rationalizing or predicting an observable, but for building chemical understanding. I am confident that the path to understanding set forth in this volume will survive in that future.

*Roald Hoffmann*