

Preface

One of the earliest books about the qualitative theory of the electronic structure of molecules—*Valence Theory* by John Murrell, Sid Kettle and John Tedder (1965)—was a collaborative project by a physical chemist, an inorganic chemist and an organic chemist, all from the Department of Chemistry at the University of Sheffield. The very idea of scientists with such disparate backgrounds co-operating on such a venture seems scarcely credible today. I have been teaching quantum chemistry for forty years at all levels; from introductory courses for medical students to graduate lectures for Ph.D. chemists and physicists. During that time there has been a gradual movement away from the idea that there can be a qualitative theory which can be accepted and used by all branches of chemistry (or even by a wider consensus). An amusing example is provided by the concept of a dative bond: for contemporary organic chemists such a thing does not exist, yet much of modern inorganic chemistry is dominated by the idea.

Organic chemists have, over the years, either abandoned the idea of a quantum-based theory or have used the nomenclature of quantum theory to develop a series of rules which no longer refer to the physical laws which underlie chemical phenomena.

Inorganic chemists have, in general, been hampered by their history. The idea that the bonding in transition-metal molecules is ionic and only needs “correcting” for quantum-mechanical effects, together with the use of symmetry-adapted MOs for this correction have prevented the growth of a qualitative theory of the wealth of novel electronic structures to be found in inorganic molecules.

Physical chemists, who are in the best position to provide common ground, have unfortunately remained aloof from these difficulties, concentrating instead on quantitative methods and, in extreme cases, insisting

that there is no such thing as a chemical bond, only calculated electron distributions!

In this work I have tried to explain things in terms of the interactions amongst charged particles; something which, if it *has* been attempted before, has not been tried for many decades. The first two or three chapters are devoted to providing the basis for the simplest and most commonly-used prescriptions for an orbital *description* of the electronic structure of molecules. Of course, explanations can only go back so far and have to stop somewhere. What I have attempted is to present a theory of valence which is based on the idea that the factors which shape molecules and their interactions are based on two main sources: experimental observations and the laws of nature—electrostatic interactions between particles and Schrödinger’s mechanics—and not rules of thumb involving atomic orbitals. Some of the things I have said are controversial and others are stated without proof because of the nature of this work. A more thorough case for the relationship between probability and the interpretation of orbitals is to be found in my *Probability and Schrödinger’s Mechanics* (World Scientific, 2002) and the technical support for the computational methods used are given in *Handbook of Computational Quantum Chemistry* (Dover, 2005).

David B Cook Sheffield 2007