PART TWO

BEYOND MONODETERMINANTAL MO THEORY

INTRODUCTION

In the first part of this work, we applied MOVB theory to problems which, in principle, are "within" either EHMO (which does not include electron-electron interaction effects) or SCF-MO (which imperfectly accounts for interelectronic repulsion) theory in order to demonstrate the conceptual potency of the approach. In this second part, we focus our attention to problems which are "soluble" only at the SCF-MO-CI level, in order to demonstrate that the fundamental VB and MOVB theoretical concepts developed earlier are sufficient for dealing with any kind of problem. In the treatment of regular atomic arrays with one AO per atom, VB theory is simple enough so that it can replace MOVB theory as a qualitative tool. In this spirit, we begin with a discussion of the concept of the Frontier Configuration, which is the foundation of qualitative VB theory, and we develop the VB theory of molecular spin selection and weak binding (e.g., F_2), two problems which are treatable only at the level of SCF-MO-CI theory. Subsequently, we show that a general understanding of anticooperativity can be achieved by VB or MOVB theory and we discuss the problem of sigma-pi hybridization which is treatable only at the level of SCF-MO-CI theory. Finally, we use MOVB theory in order to explore the stereochemical consequences of weak binding (which are evident only at the level of SCF-MO-CI theory) and in order to make qualitative predictions of "correlation effects" in MO theory.