A brief review of the origin and development of the self-consistent field-\(X\alpha\)-Dirac-scattered-wave (SCF-\(X\alpha\)-DSW) molecular orbital method is presented. The DSW scheme is the fully relativistic counterpart of the SCF-\(X\alpha\)-SW method, which, in turn, is the molecular analog of the Korringa-Kohn-Rostoker energy band calculation technique. Since the SCF-\(X\alpha\)-SW method follows the same approximations as the nonrelativistic SW method, it suffers from the same severe limitations. However, it incorporates all relativistic effects within the one-electron local exchange framework, yielding four-component wave functions that transform according to the double point group of the given system. Selected DSW results are reviewed to illustrate chronologically the development of the method, and to demonstrate its strength as well as limitations. These examples include molecules \(I_2\) and \(UF_6\), small metal clusters and their use in modeling chemisorption, and cluster complexes of the quasi one-dimensional conductor KCP. They represent the classes of problems where SW calculations will continue to provide useful information. The method should be viewed as complementary to traditional quantum chemical approaches for those calculations where high quality \textit{ab initio} computations are currently unfeasible.
I. INTRODUCTION

The multiple-scattering or scattered-wave (SW) approach to determining electronic structures of molecules and solids has, in recent years, proven its utilities in many areas of inorganic chemistry and solid-state physics. Combined with the local density approximation for the exchange potential, which effectively reduces the many-electron problem to a much more manageable one-electron one, the SW method becomes a very attractive computational procedure whereby useful information about electronic properties can be obtained. The first derivation of energy band structure using this technique was given by Korringa (1). Subsequently Kohn and Rostoker (2) employed a variational approach with the Green's function technique and arrived at identical results. This so-called KKR method for calculating electronic energy band structure of crystalline solids is similar to the augmented-plane-wave (APW) scheme reported earlier by Slater (3). In fact, their equivalence has been extensively studied by Ziman (4), LLoyd (5), Slater (6), and Johnson (7).

The generalization of the SW technique for finite polyatomic systems with no translational invariance was suggested by Slater (8) and subsequently developed by Johnson (9). Numerous applications to molecules and clusters followed, which can be found in review articles by Johnson (10-12), Connolly (13), Weinberger and Schwarz (14), Rösch (15), Messmer (16), and most recently Case (17). The self-consistent-field-Xα-scattered-wave (SCF-Xα-SW) method, as it is popularly called, has not, and most probably will not replace traditional quantum chemical methods for computing molecular orbitals (MO). However, largely because of its computational tractability, both in bases representation and in numerical procedures, the SCF-Xα-SW method is more suitable in establishing bonding trends for elements across the rows as well as down the columns of the periodic table. Furthermore, molecular properties calculations requiring knowledge of continuum or scattering states (18,19) can be accomplished with reasonable accuracy and with little extra effort. It should be noted that the method suffers from several serious limitations. The principal ones are the local exchange potential and the muffin-tin (MT) approximation, which are discussed at length in Case's review (17). Despite these disadvantages, the inherent flexibility of the method overwhelmingly justifies its extension to the relativistic domain, where systems containing heavy elements can be treated more realistically.

Extension of the SW scheme to include relativistic effects has been explored by many authors (see reviews by Pyykkö (20) and Case (17)). Two approaches have been used. The first employs a simplified Dirac radial equation excluding the spin-orbit term and solves the secular problem in the framework of the non-relativistic SW formalism (21-26). This approach is essentially the one-component