CHAPTER ONE

Analysis of Crystal and Electronic Structures

1.1 Introduction

It is an important subject of research in chemistry, physics and materials science to study how physical properties of molecules, solids and surfaces are related to their atom arrangements. Understanding this structure-property correlation requires the knowledge of how the electronic structure of a given system depends on its geometrical structure (*Figure 1.1*). To pursue this line of research, one needs to learn how crystal structures are described in crystallography and how electronic structures of molecules and solids are discussed in electronic structure theory. In addition, it is necessary to have computer programs for analyzing crystal structures and for performing electronic structure calculations.

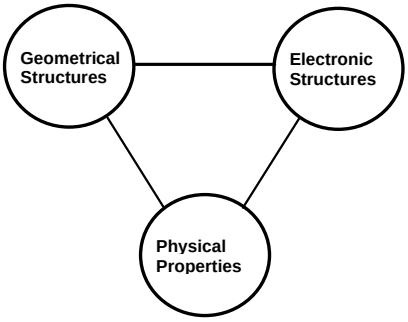

Figure 1.1. Three essential components of structure-property correlation analysis.

Even with appropriate computer programs in hand, one may still find it difficult to begin the process of a structure-property correlation study, because available programs may be forbidding to those unfamiliar with the theories and software logic employed in writing them. Consequently, there has been a need to produce user-friendly programs for those who are minimally acquainted with the basic concepts of crystallography and electronic structure theory. For the past several years the authors of this book have worked on producing such programs to be used with Personal Computers (PC's). This endeavor led to the program package *CAESAR*, which stands for *Crystal And Electronic Structure AnalyzeR*.

The *CAESAR* package consists of 15 application programs, which are divided into five groups. The names of these programs and their primary functions are as follows:

Group 1:

- *Builder:* Program for crystal structure analysis and visualization.

Group 2:

- *MC:* Program for calculating electronic structures of molecules.
- *MP:* Program for analyzing and displaying results of running *MC*.
- *NEWMI:* Program for preparing an input file for *MC*.

Group 3:

- *BC:* Program for calculating electronic structures of solids as a function of wave vector k for a selected set of wave vector points.
- *NEWBI:* Program for preparing an input file for *BC*.
- *PC:* Program for calculating properties of solids, namely, Fermi level, band dispersion relation, density of state (DOS), projected density of state (PDOS), and crystal orbital overlap population (COOP).
- *PP:* Program for analyzing and displaying results of running *PC*.
- *NEWPI:* Program for preparing an input file for *PC*.

Group 4:

- *FC:* Program for calculating Fermi surfaces of normal metallic solids.
- *FP:* Program for analyzing and displaying results of running *FC*.
- *NEWFI:* Program for preparing an input file for *FC*.

Group 5:

- *DC:* Program for calculating partial and total electron density plots of a solid and a layered structure on a cross-section plane. Scanning tunneling microscopy (STM)

and atomic force microscopy (AFM) images are simulated by partial and total electron density plots, respectively.

- *DP:* Program for analyzing and displaying results of running *DC*.

- *NEWDI:* Program for preparing an input file for *DC*.

1.2 Extended Hückel method of electronic structure calculations

To calculate the electronic structure of a molecule or a solid, one must decide what level of electronic structure theory to employ. This decision is dictated by the nature of the answers users seek from calculations and by the availability of computer programs and computing resources. If the objective of calculations is to produce quantitative numbers to compare with experiment, first principles methods should be used. If the objective is to obtain a qualitative structure-property correlation to be tested by further experiments, a semi-empirical method can be adequate.

In the *CAESAR* package, electronic structures of molecules, solids and layered surfaces are represented as linear combinations of valence atomic orbitals using the extended Hückel method.[1,2] The method of linear combination of atomic orbitals is also known as the tight binding method because atomic orbitals used for basis sets are obtained from electronic structure calculations for atoms. Namely, they represent tightly bound states of atoms in contrast to plane waves describing free electrons. The extended Hückel tight binding (EHTB) method has been used over the last three and half decades in analyzing electronic structures of molecules, solids and surfaces in conjunction with the concept of orbital interaction (i.e., overlap, symmetry, perturbation, electronegativity, etc.).[3] In such qualitative studies, one usually finds a working hypothesis as to what atomic and geometrical features of a system might be important for the electronic structure responsible for its physical properties. To test such a hypothesis, it is often necessary to repeat electronic structure calculations by varying the geometrical parameters as well as the orbital parameters of atoms for EHTB calculations.

1.2.1 Strengths and weaknesses of the EHTB method

In the EHTB method [4] the exact form of the Hamiltonian is not specified, but the matrix representation of the Hamiltonian in atomic orbital basis is constructed semi-empirically (see *Section 4.3*). Since this approximation is crude, the EHTB method has several drawbacks that first principles methods do not have. For precisely the same reason, however, the EHTB method possesses a few advantages that first principles computational methods cannot match. Since the *CAESAR* package employs the EHTB method for electronic structure calculations, it is important to appraise its strengths and weaknesses in order that improper uses of EHTB calculations should be avoided.

Unlike first principles calculations, EHTB calculations are not designed to predict the optimum structure of a molecule or a crystal. For systems of known geometry, EHTB calculations have been indispensable in uncovering the structure-property relationships for discrete molecules [3] and solid state materials [5] and in explaining STM and AFM images.[6] These studies reveal that approximate electronic structures obtained by ETHB calculations are mostly adequate for structure-property correlation analysis, although they may not provide quantitative predictions. The relevance of EHTB calculations lies in this role of facilitating the search for structure-property correlations. When used in conjunction with the concept of orbital interaction,[3] EHTB calculations have been instrumental in discovering a number of qualitative concepts useful for thinking about the electronic properties of materials, e.g., fragment orbitals,[3] orbital correlation diagrams,[3] through-space and through-bond interactions,[3,7] and isolobal analogy [3,8] for molecular systems, a band orbital picture of magnetic insulating state,[5a,9] an orbital-mixing view of electronic phase transitions in metals,[5c,10] hidden Fermi surface nesting [5c,11] for solid state materials, and tip-force induced local stiffness variation [6,12] in STM and AFM.

The energy levels and orbitals that EHTB calculations generate for a system do not depend on the number of electrons the system has, because the EHTB method neglects electron-electron repulsion. Consequently, unlike first principles methods, the EHTB method does not provide a correct way of describing the relative energies of different electronic states available for a given system. For example, consider a molecular system that has two electrons to fill its two energy levels. The ground state of this system can be a singlet state (in which the lower-lying level is doubly occupied) or a triplet state (in which the two levels are each singly occupied with the same spin). In EHTB calculations the total energy of a system is given by the sum of its occupied orbital energies. Thus EHTB calculations predict that the singlet state is always more stable than the triplet state, in disagreement with experiment. However, it is important to recognize that EHTB calculations do provide the information concerning when such a failure is likely to occur. The essential effect of electron-electron repulsion is to make the double occupancy of an orbital energetically unfavorable. Therefore, the triplet state becomes more stable than the singlet state if the energy difference between the two orbitals is small enough (see *Section 4.6.1*). Thus when EHTB calculations for a molecule lead to a small HOMO-LUMO gap, one must note that the system may adopt a triplet state as the ground state.

It is important to note the solid-state counterpart of the above observation.[8] When the unit cell of a solid contains an odd number of electrons, the highest-occupied band of this system becomes half filled. If electron-electron repulsion is neglected, the levels of the bottom half of the band are each doubly filled, and those of the top half are each empty, thereby leading to a metallic state. Thus EHTB calculations predict that a system with a partially filled band is always metallic, in conflict with experiment. This is again a serious failure, if results of EHTB calculations are taken blindly. However, EHTB calculations do provide the information concerning when such a failure is likely to occur. For a system with a partially filled band, a magnetic insulating state may become more stable than the metallic state, when the width of the partially filled band is narrow (*Section 4.6.1*). The metallic and magnetic insulating states are similar in that they possess a partially filled band, but they differ in the way the band levels are occupied. In a magnetic insulating state, a partially filled band has all its band levels singly filled.[8] Therefore, when EHTB calculations for a system lead to narrow partially filled bands, one must consider the possibility that its ground state is magnetic insulating rather than metallic.

The fact that EHTB calculations do not depend on the number of electrons in a system gives rise to advantages that first principles methods cannot provide: (1) EHTB calculations are simple and fast. Consequently, EHTB calculations can be used to study those molecular and extended solids that contain so many atoms (in a unit cell for solids) that first principles calculations are impossible to apply. The simplicity of the EHTB method does not necessarily mean that the electronic structures it generates are unreliable. The usefulness of any calculation, be it first principles or semi-empirical, rests ultimately on the test of whether the calculated results are consistent with experimental observations and provide insight into experimental problems under question. EHTB calculations carried out for a variety of materials over the past three and half decades manifest that EHTB calculations are useful.[5,6,10] (2) EHTB calculations for a complex system can be approximated by those for the relevant part of the system. For example, in the organic conducting salt k-(BEDT-TTF)$_2$Cu(NCS)$_2$, the layers of the (BEDT-TTF)$_2^+$ cations alternate with layers of the Cu(NCS)$_2^-$ anions.[5f-h] It is the cation layers that are largely responsible for the transport properties of the salt, and the cation layers are separated by the anion layers. Therefore, for the purpose of studying the transport properties of the k-(BEDT-TTF)$_2$Cu(NCS)$_2$ salt, the electronic band structure of the salt can be well approximated by that of an isolated cation layer. Such an approximation greatly simplifies the computational task and has been widely applied to a variety of organic conducting salts.[5f-h] In a similar manner, for the purpose of studying the transport properties of the hexagonal alkali tungsten bronze A_xWO_3 (A = K, Rb, Cs; $x < 1/3$), the electronic band structure of this bronze can be approximated by that of the WO_3^{x-} lattice.[13] In EHTB calculations, these kinds of approximations are valid, and as a consequence simplify the task of calculations enormously.

1.2.2 Parameters of the EHTB method

In EHTB calculations, one should pay attention to the parameters of the basis atomic orbitals used to construct the Hamiltonian and overlap matrix elements. In the EHTB method only valence electrons are considered, and valence atomic orbitals are approximated by Slater type orbitals (STO's). To fully specify the matrix elements for a given system, one needs the exponents and the valence state ionization potentials (VSIP's) of all the valence STO's present in the unit cell. These values for most chemical elements are stored in the data base of the *CAESAR* package (see *Section 5.2.2*), and one can inspect and modify them before proceeding with electronic structure calculations. These orbital parameters stored in the data base should be regarded as providing a starting point for the process of electronic structure analysis.

When results of EHTB calculations for a molecule or a solid of known structure are not consistent with the physical properties of the molecule or the solid, one should consider two possible sources leading to this disagreement. (1) The failure is caused by the assumptions inherent in any electronic structure theory. For example, because of electron-electron repulsion, the lowest possible spin state of a molecules may not be the ground state, and the metallic state of a solid may be less stable than the corresponding magnetic insulating state. In this case, one should consider an alternative way of filling the calculated energy levels with electrons so as to generate a high-spin state for a molecule and a magnetic insulating state for a solid and should attempt to extract, from results of EHTB calculations, useful information needed to go beyond a one-electron electronic structure theory. (2) The failure is not caused by the assumptions of electronic structure theory but originates from the use of EHTB approximations. In this case, it is important to analyze the source of the failure from the viewpoint of the atomic parameters employed, modify the parameters appropriately, and repeat calculations. This task is not difficult, if one becomes familiar with the concept of orbital interaction.[3] In spirit, this process is not different from what one does with first principles calculations. For example, when a chosen basis set or correlation level does not give correct results, one tries another basis set or correlation level. First principles methods are based on rigorous theoretical and mathematical formulations, but their actual calculations do include approximations.

1.3 General features of *CAESAR*

To analyze how the electronic structure of a solid is related to its crystal structure, it is essential to know the geometrical details of the solid. For this purpose, it is desirable to instantly display the crystal structure from any view angle, quickly identify the atoms of the crystal displayed on the screen, and interactively extract information about the local environment (e.g., interatomic distances, bond angles and dihedral angles) of any atom displayed on the screen. These tasks are carried out by the *Builder* program in the *CAESAR* package. An input for this program is constructed interactively by using the *Define Crystal Structure* program of *Builder*. This structure analysis generates a *filenam.CI* file that contains the structural information about a solid or a molecule to be studied in terms of electronic structure calculations.

The electronic structure of a molecule is obtained by performing molecular orbital (MO) calculations using the program *MC*. An input file, *filename.MI*, for *MC* is generated interactively by using the *NEWMI* program. Results of MO calculations are analyzed interactively by using the *MP* program.

Analysis of the electronic structure of a solid proceeds in three steps: (1) The electronic band structure of a solid are calculated as a function of wave vector k (see Section 4.4) for a selected set of wave vector points by using the program *BC*. This requires an input file, *filename.BI*, which is generated interactively using the program *NEWBI* and a structure file, *filename.CI*. (2) To analyze results of the electronic band structure calculations, the program *PC* is run with an input file, *filename.PI*, which is generated interactively using the program *NEWPI*. (3) Finally, results of running the *PC* program are displayed and analyzed interactively using the program *PP*.

When a solid under examination is a normal metal, the user may wish to study its Fermi surface. For this purpose, the program *FC* is run with an input file, *filename.FI*, which is generated interactively by using the program *NEWFI*. Results of running the *FC* program are displayed and analyzed interactively by using the *FP* program.

Partial and total electron density plots on a cross-section plane of a solid, or a layered structure designed to simulate a particular surface of a solid, are calculated by using the *DC* program. Atomic-

and molecular-resolution STM and AFM images of a layered structure are respectively described by its partial and total electron density plots calculated on a cross-section plane that is parallel to and lies above the surface at a certain distance. A required input, *filename.DI*, is generated interactively by using the *NEWDI* program and a *filename.CI* file that contains the structural information about a solid and a layered structure. Results of running the *DC* program are displayed and analyzed interactively by using the *DP* program.

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