

## CHAPTER I

### INTRODUCTION



The electronic energy band structures of solids have been the subject of intensive experimental and theoretical study. A good knowledge of the electronic band structure is essential for a detailed understanding of the electrical, magnetic, optical and other properties of a solid, be it a metal, a semiconductor or an insulator. However, reliable results of the electronic band structures of metals have become available only in the last ten to fifteen years because of the development of new technique and the refinement of earlier methods.

There are a variety of experimental and theoretical methods available for studying the electronic properties of metals. Experimental informations are obtained from, among others, Fermi surface experiments<sup>1</sup>, photoemission studies<sup>2</sup> and optical studies<sup>3</sup>. On the theoretical side there are many

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<sup>1</sup> M. Saffren, in *The Fermi Surface*, edited by W.A. Harrison and M.B. Webb, John Wiley & Sons, Inc., New York, 1960.

<sup>2</sup> D.E. Eastman and W.F. Krolikowski, Physical Review Letters, **21**, 623 (1968).

<sup>3</sup> J.C. Phillips, *Solid State Physics*, Vol. 18, 55 (1966).

methods<sup>4</sup> available for making band structure calculations, such as the cellular method, the tight-binding method, the orthogonalized-plane-wave method, the augmented-plane-wave method, and the Korringa-Kohn-Rostoker or Green function method.

These theoretical and experimental techniques have been applied to many metallic systems, of which copper is one of the technologically important noble and transition metals. Of more immediate concern to us is the basic interest in the challenge to delineate and to calculate the band structure of the noble and transition metals, whose valence electrons consist of two groups — the conduction- and the d-electrons — which have rather different behaviors but are intimately related through hybridization. Furthermore, high precision experimental information on copper is also available to test the theoretical calculations.

Among the many methods that have been proposed for the calculation of electronic band structure from a given crystal potential, two have proved to be practical for their ability to yield quantitatively accurate results, either along lines of symmetry in  $\vec{k}$ -space or at general  $\vec{k}$ . These two are the augmented-plane-wave (APW) method proposed by Slater<sup>5</sup> and the

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<sup>4</sup> J. Callaway, "Energy Band Theory" Academic Press, New York, 1964.

<sup>5</sup> J.C. Slater, "Wave Functions in a Periodic Potential." Physical Review B, 51, 846-851 (1966).

Green function or KKR method developed by Korringa<sup>6</sup>, Kohn and Rostoker<sup>7</sup>. Burdick<sup>8</sup> and Segall<sup>9</sup> used respectively the APW method and the KKR method to calculate the energy bands of copper. However, there are difficulties with these two methods. One of these is that the secular determinant is implicit, as well as explicit, functions of the energy. The radial wave equation must be solved within the muffin-tin spheres and the secular determinant must be evaluated for each energy over a selected range. The energy eigenvalue is then determined as the energy for which the determinant goes to zero. To accomplish this, heavy computational efforts are required.

After 1965, a different approach, the so-called interpolation schemes, has been developed independently and at the same time by L. Hodges and H. Ehrenreich<sup>10,11</sup> and by

<sup>6</sup> J. Korringa, "On the Calculation of the Energy of a Bloch Wave in the Metal," Physica, XIII, 392-400 (1947).

<sup>7</sup> W. Kohn and N. Rostoker, "Solution of the Schrödinger Equation in Periodic Lattices with an Application to Metallic Lithium," Physical Review B, 94, 1111-1120 (1954).

<sup>8</sup> G.A. Burdick, "Energy Band Structure of Copper." Physical Review B, 129, 138-150 (1967).

<sup>9</sup> B. Segall, "Fermi Surface and Energy Bands of Copper." Physical Review B, 125, 109-122 (1962).

<sup>10</sup> L. Hodges, "Interpolation Scheme for Band Structure of Noble and Transition Metals: Ferromagnetism and Neutron Diffraction in Nickel." Ph.D. Thesis, Harvard University, Cambridge, Massachusetts, 1966 (Unpublished).

F.M. Mueller<sup>12</sup> and J.C. Phillips, respectively. This approach provides a highly efficient tool for obtaining extensive band structure information with substantial saving in computational effort. Its advantage lies in the successful treatment of the band structure in terms of rather elementary calculations which help to provide an understanding into the physical processes involved. Furthermore, this approach yields an easy means for the incorporation of and comparison with many different types of experimental information.

The principle behind the two interpolation schemes can be briefly described as follows. In Hodges' scheme, the conduction bands are treated in a free-electron-like approximation with pseudopotential parameters, while the d bands are treated in the tight-binding approximation, with the overlap integrals represented by adjustable parameters. The hybridization integrals are further parametrized by  $\vec{k}$ -dependent functions. In Mueller's scheme, the orthogonalization of conduction and d functions is explicitly included. The conduction bands were treated by the

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<sup>11</sup> L. Hodges, H. Ehrenreich, and N.D. Lang, "Interpolation Scheme for Band Structure of Noble and Transition Metals: Ferromagnetism and Neutron Diffraction in Ni." Physical Review B, 152, 505-526 (1966).

<sup>12</sup> F.M. Mueller, "A Combined Interpolation Scheme for Transition and Noble Metals." Physical Review B, 153, 659-669 (1967).

orthogonalized-plane-wave approach<sup>13</sup>. The d band treatment rather resembled that in Hodges' approach.

The simplicity and applicability of the interpolation schemes have been convincingly demonstrated, even for the complicated band structures of noble and transition metals, particularly for those of Cu and Ni. The interpolated bands, obtained by using only a small number of parameters, resembled very closely that given by first-principles band calculations. For instance, Hodges and Mueller could both fit the APW bands for paramagnetic Cu with root-mean-squares deviations of the order of 0.1 eV. The interpolation schemes have been widely applied to many problems in the quantum structure of metals, such as the determination of accurate fits to observed Fermi surfaces<sup>14</sup> and the calculation of direct interband optical spectra<sup>15</sup>.

However, there has been no exhaustive comparison of the working of the two interpolation schemes. The present thesis is devoted to a study of the Hodges scheme and the Mueller scheme comparatively, by using the case of Cu in the

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<sup>13</sup> C. Herring, "A New Method for Calculating Wave Functions in Crystals." Physical Review B, 57, 1169-1177 (1940).

<sup>14</sup> E.I. Zornberg and F.M. Mueller, "Fermi Surface of Copper." Physical Review B, 151, 557-560 (1966).

<sup>15</sup> F.M. Mueller and J.C. Phillips, "Electronic Spectrum of Crystalline Copper." Physical Review B, 157, 600-607 (1967).

paramagnetic state as an example. Detailed comparisons will be made for relative accuracy, computational ease and economy of the two schemes. Then the more desirable features from each of these two schemes will be incorporated into a new hybrid scheme. It is hoped that this new scheme will proved to be the optimum scheme for providing electronic energy band structures in the interpolation approach.

Chapter II discusses the general framework of the interpolation scheme we employ. This hybrid scheme includes a combination of desirable features found in both Hodges' and Mueller's schemes.

Chapter III presents the explicit extraction of the interpolation parameters by fitting with energy eigenvalues from first-principles band calculations at points of high symmetry in the Brillouin zone.

Chapter IV discusses the computation process and the results in detail, including a comparison of the accuracy, efficiency and economy of the working of the two schemes.