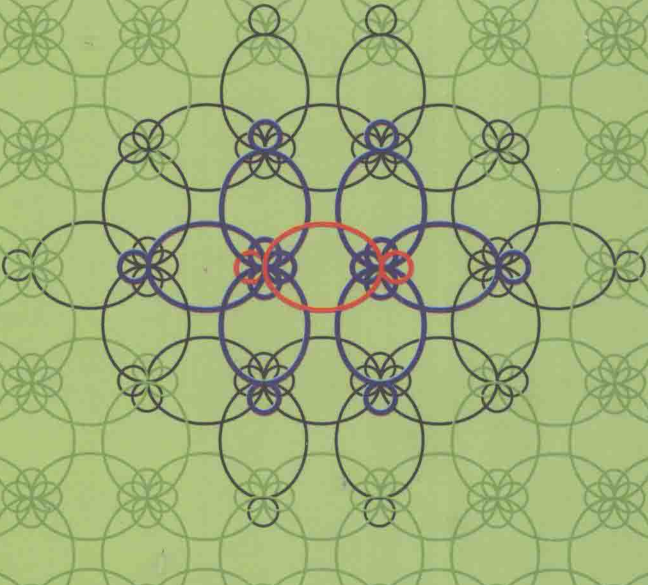
Elementary Electronic Structure

基础电子结构

Walter A. Harrison



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Preface

This text presents an account of *analytic* electronic structure, to be distinguished from *computational* electronic structure. Both are based upon a one-electron approximation, local-density theory, and the determination of the quantum-mechanical electronic states. They both seek to predict the properties of the resulting solids, or molecules on the basis of these states. In the computational mode, the minimum number of approximations are used, and numerical solutions are sought. Here we seek instead to focus on the most important aspects of the solution, making what approximations are necessary in order to proceed analytically and obtain formulae for the properties. This reducing of the problem to basics is almost always less accurate that the computational solution, but has the advantage that it displays the dependence of any property on the parameters of the system. It gives us an understanding of the property in a sense that a numerical solution, or a direct measurement, cannot.

There is a long tradition of such approximate analyses of solids, but often based upon a model of the system, designed to describe a particular property. Usually a few experimental parameters needed adjustment for each specific material. Thus spring constants for the interaction between atoms could be adjusted to fit the elastic constants. Then the vibration spectrum for the solid could be calculated and the vibrational contribution to the heat capacity could be obtained. In more chemically oriented studies, the measured elastic constants of LiCl and KCl might be interpolated to obtain the constants for NaCl since sodium lies between lithium and potassium in the periodic table.

The distinctive feature of the approach described here is that it is an approximate theory of the basic electronic structure, and consequently a

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single approximate theory of *all* of the properties of the solids. One would not know in advance whether such an approach could be accurate enough to be useful, or how much information would need to be supplied in order to estimate properties. It is turned out in fact that once the solids were understood, often on the basis of the results of major computational efforts, it was possible to estimate all of the needed parameters without further reference to the calculations or to experiment. Over a period of forty years of my own efforts, those of coworkers, and colleagues around the world, have provided the insights needed to make this possible, surprisingly often by recognizing that two very different viewpoints are simultaneously valid. Then the combination provided the needed parameters. Perhaps the clearest case of this, discussed in Chapter 1, is the recognition that the electronic states of a chain of lithium atoms can be described as a linear combination or valence s-states on the atoms (a tight-binding state), or as freely propagating electrons along a line. The consequence was that the parameters essential for the tight-binding description, the coupling between neighboring s-states, must be given in terms of the spacing d and the free-electron mass m by $-(\pi^2/8)\hbar^2/md^2$. In terms of such couplings, all other properties of the chain can be estimated. These forty years of effort have also allowed such approaches to be extended over virtually all types of solids: metals, semimetals, semiconductors, insulators, transition-metal and f-shell-metal systems. All are discussed here, as well as some molecular systems.

This book is organized much as *Electronic Structure and the Properties of Solids* , which was published by W. H. Freeman (San Francisco, 1980) and reprinted by Dover (New York, 1989) but the text is entirely new. Subsequent work has made the predictions much more accurate and general, and at the same time greatly simplified the theory. For example, by introducing more stable coupling parameters it became unnecessary to define different sets of covalent and polar energies for dielectric than for bonding properties. By introducing an algebraic overlap repulsion it became possible to write analytically the total energies, as well as dielectric properties, of semiconductors in terms of these covalent and polar energies. It was also found possible to analytically evaluate the effective interaction between atoms in simple metals in the form $Z^2e^2\cosh^2 r_c e^{-\kappa r}/r$, in terms of the empty-core pseudopotential radius r_c , greatly simplifying the estimates of many properties. Improved parameters and approximations for transition-metal systems made their study much more direct and accurate, and the theory was extended to f-shell-metal systems, including the formation of correlated electronic states in the rare earths.

In spite of the diversity of systems and materials, the approach is systematic and coherent, combining the tight-binding (or atomic) picture with the pseudopotential (or free-electron) picture. This provides parameters as we illustrated above, and conceptual bases for estimating the various properties of all of these systems.

Chapter 1 introduces almost all of the concepts and parameters needed to understand the entire range of solids and illustrates their application. The remainder of the text is like an appendix, filling in the details and expanding the treatment, with extensive tables of parameters and properties. It can be used as a text, but the coverage is so large that only a selected portion could be used in one course. For that purpose there are a limited number of problems at the end of chapters, but it is very easy to generate more by asking for estimates different properties, or different materials, than treated in the text. The list of references is extensive, but focused on the particular publications which bear directly on the analytic approach used here, and not on the more general theory of solids.

I was pleased that World Scientific would publish this text a price considerably below that of other publishers, and with this goal in mind I provided camera-ready copy. Not all readers may consider the result adequate, but I believe it can be suffered for the purposes of economy, particularly for its use as a text.

Walter A. Harrison
January, 1999
Stanford, California

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