

This book describes modern thinking about the electronic structure and properties of crystalline and non-crystalline materials in a form that is readily accessible to undergraduates in materials science, physics, and chemistry. In recent years the dominant role of the local atomic environment in controlling electronic structure and properties of materials has been recognized. The 'real-space' approach to electronic structure that this recognition has spawned runs through the book, and provides a coherent framework in which to study perfect and defective crystals and non-crystalline materials. This is the approach that those who have been worried by the conventional preoccupation with perfect crystals and band theory have been waiting for. The reciprocal space approach, exemplified in band theory, is also developed and powerful links between the two approaches are shown. Modern, first principles calculations, based on density functional theory, are now predictive tools in materials science and they are introduced and illustrated with relevant examples. Throughout this book the mathematical complexity is kept to a bare minimum. This book provides a unique introduction to current understanding and predictive modelling of electronic structure and properties in today's materials.

**Adrian Sutton** is a University Lecturer in Materials Science at Oxford University and a Fellow of Linacre College.

The cover shows a snapshot of the electronic charge density of a chlorine molecule dissociating on a silicon (111) surface as computed self-consistently in density functional theory by A. De Vita, M. J. Gillan, D. King-Smith, M. C. Payne, and I. Stich.

OXFORD UNIVERSITY PRESS





<b>1. Introduction</b>	<b>1</b>
Aims of the book	1
The 'universal' equation of state for metals	1
Structure maps	9
The hydrogen atom	9
Metals, semiconductors, and insulators	20
References	20
<b>2. The diatomic molecule</b>	<b>21</b>
Review of bras, kets, and all that	21
A homonuclear diatomic molecule: the hydrogen molecule	25
A heteronuclear diatomic molecule	32
Electronegativity	34
Bond energy and bond order	35
Reference	37
<b>3. From the finite to the infinite</b>	<b>38</b>
Chain molecules and $k$ -space	38
Bond order in an infinite system	52
The density of states: total and local	58
Band energy and bond energy	63
The moments theorem	66
The binary AB alloy	72
References	73
<b>4. Into two and three dimensions</b>	<b>74</b>
Solids as giant molecules	74
The square lattice	74
The cubic lattice	78
Brillouin zones for the f.c.c and b.c.c. lattices	78
Equation of motion of an electron under an external force	80
Holes	84
The Fermi surface	87
The density of states in two- and three-dimensional crystals	88
The density matrix, bond order, and bond energy	92
The moments theorem applied to two- and three-dimensional crystals	97



<b>5. Band gaps: origins and consequences</b>	<b>101</b>
Introduction	101
Infinite linear chain with two s states per atom	103
Energy gap in a binary AB alloy linear chain crystal	106
Peierls distortions	107
Metals, insulators, and the metallic bond	109
<b>6. s-p bonding—a case study in silicon</b>	<b>112</b>
s-p bonding	112
s-p bonding between two silicon atoms	113
Angular dependence of s-p and p-p hopping integrals	116
sp hybrids	117
Simple models of the electronic structure of tetrahedrally bonded silicon	122
The band structure of silicon in a minimal atomic basis set	124
The bond order and bond energy in silicon in a minimal atomic basis set	127
References	131
<b>7. Free electron theory</b>	<b>132</b>
Introduction to free electron theory	132
The free electron approximation	133
Electrons in a box	135
Density of states	138
Free electron bands and LCAO bands	139
The nearly free electron model	144
The pseudopotential	151
Screening	153
Exchange and correlation	155
References	157
<b>8. Properties of free electron metals</b>	<b>158</b>
Fermi-Dirac statistics	158
Contact potential	159
Electronic specific heat	160
Electrical conductivity of metals	162
Thermal conductivity of metals	164
The Wiedemann-Franz law	164
The Hall effect	165
The cohesive energy of simple metals and its volume dependence	166
Structural energy differences	169
Reference	171



<b>9. The transition metals</b>	<b>172</b>
The transition metals	172
The Friedel model	174
The Friedel model in the second moment approximation	175
Finnis–Sinclair potentials for computer simulations of transition metals	179
d–d bonding	183
Changes in crystal structure across the transition metal series	187
Bonding in metallic alloys	189
References	193
<b>10. Structural stability of compounds</b>	<b>194</b>
Hybridization and crystal structural stability	194
Atomic factors influencing the structures of compounds	197
Structure maps	198
Applications of structure maps	201
References	203
<b>11. Introduction to modern quantitative theory</b>	<b>204</b>
Modern quantitative predictions of crystal structure and stability	204
The Born–Oppenheimer approximation	205
Outline of density functional theory	205
Applications	209
References	214
<b>12. Where band theory breaks down</b>	<b>215</b>
Electrons in noncrystalline materials	215
The energy gap in amorphous silicon	219
Electron localization	221
Polarons	222
Anderson localization	224
Metal–insulator transitions, or, what is a metal?	225
References	235
<b>Problems</b>	<b>236</b>
<b>Sample examination questions</b>	<b>250</b>
<b>Index</b>	<b>257</b>