

Table of Contents

Foreword	xiii
Introduction	xv
Chapter 1. Introduction: Representations of Electron-Lattice Bonds	1
1.1. Introduction	1
1.2. Quantum mechanics: some basics	2
1.2.1. The wave equation in solids: from Maxwell's to Schrödinger's equation via the de Broglie hypothesis	2
1.2.2. Form of progressive and stationary wave functions for an electron with known energy (E)	4
1.2.3. Important properties of linear operators	4
1.3. Bonds in solids: a free electron as the zero order approximation for a weak bond; and strong bonds	6
1.3.1. The free electron: approximation to the zero order	6
1.3.2. Weak bonds	7
1.3.3. Strong bonds	8
1.3.4. Choosing between approximations for weak and strong bonds	9
1.4. Complementary material: basic evidence for the appearance of bands in solids	10
1.4.1. Basic solutions for narrow potential wells	10
1.4.2. Solutions for two neighboring narrow potential wells	14
Chapter 2. The Free Electron and State Density Functions	17
2.1. Overview of the free electron	17
2.1.1. The model	17
2.1.2. Parameters to be determined: state density functions in k or energy spaces	17

2.2. Study of the stationary regime of small scale (enabling the establishment of nodes at extremities) symmetric wells (1D model)	19
2.2.1. Preliminary remarks	19
2.2.2. Form of stationary wave functions for thin symmetric wells with width (L) equal to several inter-atomic distances ($L \approx a$), associated with fixed boundary conditions (FBC)	19
2.2.3. Study of energy	21
2.2.4. State density function (or “density of states”) in k space.	22
2.3. Study of the stationary regime for asymmetric wells (1D model with $L \approx a$ favoring the establishment of a stationary regime with nodes at extremities	23
2.4. Solutions that favor propagation: wide potential wells where $L \approx 1$ mm, i.e. several orders greater than inter-atomic distances	24
2.4.1. Wave function	24
2.4.2. Study of energy	26
2.4.3. Study of the state density function in k space	27
2.5. State density function represented in energy space for free electrons in a 1D system	27
2.5.1. Stationary solution for FBC	29
2.5.2. Progressive solutions for progressive boundary conditions (PBC) .	30
2.5.3. Conclusion: comparing the number of calculated states for FBC and PBC.	30
2.6. From electrons in a 3D system (potential box)	32
2.6.1. Form of the wave functions	32
2.6.2. Expression for the state density functions in k space	35
2.6.3. Expression for the state density functions in energy space.	37
2.7. Problems	40
2.7.1. Problem 1: the function $Z(E)$ in 1D	41
2.7.2. Problem 2: diffusion length at the metal-vacuum interface	42
2.7.3. Problem 3: 2D media: state density function and the behavior of the Fermi energy as a function of temperature for a metallic state	44
2.7.4. Problem 4: Fermi energy of a 3D conductor	47
2.7.5. Problem 5: establishing the state density function via reasoning in moment or k spaces	49
2.7.6. Problem 6: general equations for the state density functions expressed in reciprocal (k) space or in energy space	50
Chapter 3. The Origin of Band Structures within the Weak Band Approximation	55
3.1. Bloch function	55
3.1.1. Introduction: effect of a cosinusoidal lattice potential	55
3.1.2. Properties of a Hamiltonian of a semi-free electron.	56
3.1.3. The form of proper functions	57

3.2. Mathieu's equation	59
3.2.1. Form of Mathieu's equation.	59
3.2.2. Wave function in accordance with Mathieu's equation	59
3.2.3. Energy calculation	63
3.2.4. Direct calculation of energy when $k = \pm \frac{\pi}{a}$	64
3.3. The band structure.	66
3.3.1. Representing $E = f(k)$ for a free electron: a reminder	66
3.3.2. Effect of a cosinusoidal lattice potential on the form of wave function and energy	67
3.3.3. Generalization: effect of a periodic non-ideally cosinusoidal potential	69
3.4. Alternative presentation of the origin of band systems via the perturbation method	70
3.4.1. Problem treated by the perturbation method	70
3.4.2. Physical origin of forbidden bands.	71
3.4.3. Results given by the perturbation theory	74
3.4.4. Conclusion	77
3.5. Complementary material: the main equation	79
3.5.1. Fourier series development for wave function and potential	79
3.5.2. Schrödinger equation.	80
3.5.3. Solution	81
3.6. Problems	81
3.6.1. Problem 1: a brief justification of the Bloch theorem.	81
3.6.2. Problem 2: comparison of $E(k)$ curves for free and semi-free electrons in a representation of reduced zones	84
Chapter 4. Properties of Semi-Free Electrons, Insulators, Semiconductors, Metals and Superlattices	87
4.1. Effective mass (m^*)	87
4.1.1. Equation for electron movement in a band: crystal momentum . .	87
4.1.2. Expression for effective mass	89
4.1.3. Sign and variation in the effective mass as a function of k . . .	90
4.1.4. Magnitude of effective mass close to a discontinuity	93
4.2. The concept of holes	93
4.2.1. Filling bands and electronic conduction.	93
4.2.2. Definition of a hole	94
4.3. Expression for energy states close to the band extremum as a function of the effective mass	96
4.3.1. Energy at a band limit via the Maclaurin development (in $k = kn = n \frac{\pi}{a}$)	96
4.4. Distinguishing insulators, semiconductors, metals and semi-metals .	97

4.4.1. Required functions	97
4.4.2. Dealing with overlapping energy bands	97
4.4.3. Permitted band populations	98
4.5. Semi-free electrons in the particular case of super lattices	107
4.6. Problems	116
4.6.1. Problem 1: horizontal tangent at the zone limit ($k \approx \pi/a$) of the dispersion curve	116
4.6.2. Problem 2: scale of m^* in the neighborhood of energy discontinuities	117
4.6.3. Problem 3: study of $E_F(T)$	122
Chapter 5. Crystalline Structure, Reciprocal Lattices and Brillouin Zones	123
5.1. Periodic lattices	123
5.1.1. Definitions: direct lattice	123
5.1.2. Wigner-Seitz cell	125
5.2. Locating reciprocal planes	125
5.2.1. Reciprocal planes: definitions and properties	125
5.2.2. Reciprocal planes: location using Miller indices	125
5.3. Conditions for maximum diffusion by a crystal (Laue conditions)	128
5.3.1. Problem parameters	128
5.3.2. Wave diffused by a node located by $\vec{\rho}_{m,n,p} = m \cdot \vec{a} + n \cdot \vec{b} + p \cdot \vec{c}$	129
5.4. Reciprocal lattice	133
5.4.1. Definition and properties of a reciprocal lattice	133
5.4.2. Application: Ewald construction of a beam diffracted by a reciprocal lattice	134
5.5. Brillouin zones	135
5.5.1. Definition	135
5.5.2. Physical significance of Brillouin zone limits	135
5.5.3. Successive Brillouin zones	137
5.6. Particular properties	137
5.6.1. Properties of $\vec{G}_{h,k,l}$ and relation to the direct lattice	137
5.6.2. A crystallographic definition of reciprocal lattice	139
5.6.3. Equivalence between the condition for maximum diffusion and Bragg's law	139
5.7. Example determinations of Brillouin zones and reduced zones	141
5.7.1. Example 1: 3D lattice	141
5.7.2. Example 2: 2D lattice	143
5.7.3. Example 3: 1D lattice with lattice repeat unit (a) such that the base vector in the direct lattice is \vec{a}	145
5.8. Importance of the reciprocal lattice and electron filling of Brillouin zones by electrons in insulators, semiconductors and metals	146
5.8.1. Benefits of considering electrons in reciprocal lattices	146

Table of Contents ix

5.8.2. Example of electron filling of Brillouin zones in simple structures: determination of behaviors of insulators, semiconductors and metals	146
5.9. The Fermi surface: construction of surfaces and properties	149
5.9.1. Definition	149
5.9.2. Form of the free electron Fermi surface	149
5.9.3. Evolution of semi-free electron Fermi surfaces	150
5.9.4. Relation between Fermi surfaces and dispersion curves	152
5.10. Conclusion. Filling Fermi surfaces and the distinctions between insulators, semiconductors and metals	154
5.10.1. Distribution of semi-free electrons at absolute zero	154
5.10.2. Consequences for metals, insulators/semiconductors and semi-metals	155
5.11. Problems	156
5.11.1. Problem 1: simple square lattice	156
5.11.2. Problem 2: linear chain and a square lattice	157
5.11.3. Problem 3: rectangular lattice	162
Chapter 6. Electronic Properties of Copper and Silicon	173
6.1. Introduction	173
6.2. Direct and reciprocal lattices of the fcc structure	173
6.2.1. Direct lattice	173
6.2.2. Reciprocal lattice	175
6.3. Brillouin zone for the fcc structure	178
6.3.1. Geometrical form	178
6.3.2. Calculation of the volume of the Brillouin zone	179
6.3.3. Filling the Brillouin zone for a fcc structure	180
6.4. Copper and alloy formation	181
6.4.1. Electronic properties of copper	181
6.4.2. Filling the Brillouin zone and solubility rules	181
6.4.3. Copper alloys	184
6.5. Silicon	185
6.5.1. The silicon crystal	185
6.5.2. Conduction in silicon	185
6.5.3. The silicon band structure	186
6.5.4. Conclusion	189
6.6. Problems	190
6.6.1. Problem 1: the cubic centered (cc) structure	190
6.6.2. Problem 2: state density in the silicon conduction band	194
Chapter 7. Strong Bonds in One Dimension	199
7.1. Atomic and molecular orbitals	199
7.1.1. s- and p-type orbitals	199
7.1.2. Molecular orbitals	204

x Solid-State Physics for Electronics

7.1.3. σ - and π -bonds	209
7.1.4. Conclusion	210
7.2. Form of the wave function in strong bonds: Floquet's theorem	210
7.2.1. Form of the resulting potential	210
7.2.2. Form of the wave function	212
7.2.3. Effect of potential periodicity on the form of the wave function and Floquet's theorem	213
7.3. Energy of a 1D system	215
7.3.1. Mathematical resolution in 1D where $x \equiv r$	215
7.3.2. Calculation by integration of energy for a chain of N atoms	217
7.3.3. Note 1: physical significance in terms of $(E_0 - \alpha)$ and β	220
7.3.4. Note 2: simplified calculation of the energy	222
7.3.5. Note 3: conditions for the appearance of permitted and forbidden bands	223
7.4. 1D and distorted AB crystals	224
7.4.1. AB crystal	224
7.4.2. Distorted chain	226
7.5. State density function and applications: the Peierls metal-insulator transition	228
7.5.1. Determination of the state density functions	228
7.5.2. Zone filling and the Peierls metal–insulator transition	230
7.5.3. Principle of the calculation of E_{relax} (for a distorted chain)	232
7.6. Practical example of a periodic atomic chain: concrete calculations of wave functions, energy levels, state density functions and band filling .	233
7.6.1. Range of variation in k	233
7.6.2. Representation of energy and state density function for $N = 8$. . .	234
7.6.3. The wave function for bonding and anti-bonding states	235
7.6.4. Generalization to any type of state in an atomic chain	239
7.7. Conclusion	239
7.8. Problems	241
7.8.1. Problem 1: complementary study of a chain of s-type atoms where $N = 8$	241
7.8.2. Problem 2: general representation of the states of a chain of σ -s-orbitals (s-orbitals giving σ -overlap) and a chain of σ -p-orbitals .	243
7.8.3. Problem 3: chains containing both σ -s- and σ -p-orbitals	246
7.8.4. Problem 4: atomic chain with π -type overlapping of p-type orbitals: π -p- and π^* -p-orbitals	247
Chapter 8. Strong Bonds in Three Dimensions: Band Structure of Diamond and Silicon	249
8.1. Extending the permitted band from 1D to 3D for a lattice of atoms associated with single s-orbital nodes (basic cubic system, centered cubic, etc.)	250

Table of Contents xi

8.1.1. Permitted energy in 3D: dispersion and equi-energy curves	250
8.1.2. Expression for the band width	255
8.1.3. Expressions for the effective mass and mobility.	257
8.2. Structure of diamond: covalent bonds and their hybridization	258
8.2.1. The structure of diamond	258
8.2.2. Hybridization of atomic orbitals	259
8.2.3. sp^3 Hybridization	262
8.3. Molecular model of a 3D covalent crystal (atoms in sp^3 -hybridization states at lattice nodes)	268
8.3.1. Conditions	268
8.3.2. Independent bonds: effect of single coupling between neighboring atoms and formation of molecular orbitals	272
8.3.3. Coupling of molecular orbitals: band formation.	273
8.4. Complementary in-depth study: determination of the silicon band structure using the strong bond method.	275
8.4.1. Atomic wave functions and structures.	275
8.4.2. Wave functions in crystals and equations with proper values for a strong bond approximation	278
8.4.3. Band structure	282
8.4.4. Conclusion	287
8.5. Problems	287
8.5.1. Problem 1: strong bonds in a square 2D lattice	287
8.5.2. Problem 2: strong bonds in a cubic centered or face centered lattices	294
Chapter 9. Limits to Classical Band Theory: Amorphous Media	301
9.1. Evolution of the band scheme due to structural defects (vacancies, dangling bonds and chain ends) and localized bands	301
9.2. Hubbard bands and electronic repulsions. The Mott metal–insulator transition	303
9.2.1. Introduction	303
9.2.2. Model	304
9.2.3. The Mott metal–insulator transition: estimation of transition criteria	307
9.2.4. Additional material: examples of the existence and inexistence of Mott–Hubbard transitions	309
9.3. Effect of geometric disorder and the Anderson localization	311
9.3.1. Introduction	311
9.3.2. Limits of band theory application and the Ioffe–Regel conditions .	312
9.3.3. Anderson localization	314
9.3.4. Localized states and conductivity. The Anderson metal-insulator transition	319
9.4. Conclusion	322

9.5. Problems	324
9.5.1. Additional information and Problem 1 on the Mott transition: insulator–metal transition in phosphorus doped silicon	324
9.5.2. Problem 2: transport via states outside of permitted bands in low mobility media	331
Chapter 10. The Principal Quasi-Particles in Material Physics	335
10.1. Introduction	335
10.2. Lattice vibrations: phonons	336
10.2.1. Introduction	336
10.2.2. Oscillations within a linear chain of atoms	337
10.2.3. Oscillations within a diatomic and 1D chain	343
10.2.4. Vibrations of a 3D crystal	347
10.2.5. Energy of a vibrational mode	348
10.2.6. Phonons	350
10.2.7. Conclusion	351
10.3. Polarons	352
10.3.1. Introduction: definition and origin	352
10.3.2. The various polarons	352
10.3.3. Dielectric polarons	354
10.3.4. Polarons in molecular crystals	357
10.3.5. Energy spectrum of the small polaron in molecular solids	361
10.4. Excitons	364
10.4.1. Physical origin	364
10.4.2. Wannier and charge transfer excitons	365
10.4.3. Frenkel excitons	367
10.5. Plasmons	368
10.5.1. Basic definition	368
10.5.2. Dielectric response of an electronic gas: optical plasma	368
10.5.3. Plasmons	372
10.6. Problems	373
10.6.1. Problem 1: enumeration of vibration modes (phonon modes)	373
10.6.2. Problem 2: polaritons	375
Bibliography	385
Index	387