

IMPERIAL COLLEGE LONDON

**Modelling of Silicon-Germanium Alloy
Heterostructures using Double Group
Formulation of $\mathbf{k} \cdot \hat{\mathbf{p}}$ Theory**

by

Robert M. Ward

A thesis submitted in partial fulfillment for the
degree of Doctor of Philosophy

in the
Faculty of Natural Sciences
Department of Physics

May 2012

Declaration of Authorship

I, Robert M. Ward, declare that this thesis titled, ‘Modelling of Silicon-Germanium Alloy Heterostructures using Double Group Formulation of $\mathbf{k} \cdot \hat{\mathbf{p}}$ Theory’ and the work presented in it are my own. I confirm that:

- This work was done wholly or mainly while in candidature for a research degree at this University.
- Where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated.
- Where I have consulted the published work of others, this is always clearly attributed.
- Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work.
- I have acknowledged all main sources of help.
- Where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself.

Signed:

Date:

“By academic freedom I understand the right to search for truth and to publish and teach what one holds to be true”

Albert Einstein

IMPERIAL COLLEGE LONDON

Abstract

Faculty of Natural Sciences

Department of Physics

Doctor of Philosophy

by Robert M. Ward

Silicon-Germanium alloy heterostructures offer the most viable opportunity to integrate electronics with optoelectronic devices for widespread commercial application. Indeed Germanium rich devices may be designed for application around $1.5\mu\text{m}$ by preying on the direct-gap energy of 890meV . Low power optical modulators operating, under the quantum confined Stark effect, at wavelength bands used in 3^{rd} generation fibre optic communication channels are developed in this thesis from a theoretical perspective.

An investigation into strained Germanium rich quantum well structures was performed, revealing information about sub-band dispersion, joint density of states and absorption coefficient using the double group formulation of $\mathbf{k} \cdot \hat{\mathbf{p}}$ theory.

Using zone centre eigenstates as symmetrised half integer basis functions transforming according to irreps of the double group, the spin orbit interaction is incorporated into the unperturbed Hamiltonian. Along with semi-empirical input parameters available in the literature, dispersion in bulk Silicon and Germanium reveals information about hole effective masses and indirect conduction band minima in broad agreement with experimental data.

In accordance with degenerate perturbation theory; effective mass Hamiltonians, with an arbitrary quantisation axis through a canonical transformation, are constructed through a series of matrix multiplications. Retaining operator ordering allows numerical modelling of heterostructures grown on arbitrary growth planes with appropriate boundary conditions across an abrupt interface under the envelope function framework. In this thesis, the effect on the transition energy, hh_1-e_1 , by the choice of growth plane in a quantum well heterostructure is investigated.

Acknowledgements

I would like to thank Prof. Jing Zhang for his help, guidance and support for the last 3 years; not his least virtuous patience. I would also like to thank Dr. Paul Stavrinou for offering his time to help me not least in the writing of this thesis and Prof. Lesley Cohen for her support in the administration of my studentship. Also due a mention are Warren Elder who has been a great colleague and friend to work with.

Other people I couldn't have done this without are my friends and family who have put up with me for so long - not least my fiancée Aya Kamoda.

I would also like to acknowledge the EPSRC (UK) for financial support over the duration of the Ph.D.

Contents

Declaration of Authorship	2
Abstract	4
Acknowledgements	5
List of Figures	9
List of Tables	12
Abbreviations	14
Physical Constants	15
1 Introduction & Overview	17
1.1 Introduction to Electronic Structure	18
1.1.1 Many Body Hamiltonians	18
1.1.2 Self-consistent Ab-initio Techniques	20
1.1.3 Semi-empirical Methods	21
1.2 The $\mathbf{k} \cdot \hat{\mathbf{p}}$ Method	22
1.2.1 Bloch's Theorem & Brillouin zones	23
1.2.2 The Empty FCC Lattice	25
1.2.3 $\mathbf{k} \cdot \hat{\mathbf{p}}$ Perturbation	27
1.3 Introduction to Heterostructures	30
1.3.1 Pikus-Bir Hamiltonian	30
1.3.2 Envelope Function Approximation	32
1.3.3 The Quantum Well	33
1.4 Overview of the Thesis	35
2 Group Theory in Cubic Crystals	37
2.1 Finite Groups	38
2.1.1 Elements of Group Theory	38
2.1.2 Conjugacy Classes	39
2.1.3 Irreducible Representations	41
2.1.4 Character Tables	42

2.1.5	T_d and O_h Single Groups	43
2.2	Infinite Groups	46
2.2.1	3D Special Orthogonal Group; $SO(3)$	46
2.2.2	2D Special Unitary Group; $SU(2)$	49
2.2.3	T_d and O_h Double Groups	51
2.3	Reducible Tensor Operators	53
2.3.1	Multiplication Tables	53
2.3.2	Symmetrisation Procedures	54
2.4	Anti-Unitary Operators	57
2.4.1	Time Reversal Symmetry	57
2.4.2	Herring Rules without Spin	59
2.4.3	Herring Rules with Spin	60
3	Symmetrised Basis Functions	63
3.1	Single Group Basis Functions	64
3.1.1	Angular Momentum Operators	64
3.1.2	Representation Matrices I	65
3.1.3	Projection Operator Technique	67
3.2	Double Group Basis Functions	70
3.2.1	Clebsch-Gordan Coefficients	70
3.2.2	Representation Matrices II	74
3.2.3	Adapted Double Group Basis	75
3.2.4	Zinc-blende Basis Functions	78
4	Double Group Formulation of $\mathbf{k} \cdot \hat{\mathbf{p}}$ Theory	80
4.1	The $\mathbf{k} \cdot \hat{\mathbf{p}}$ Hamiltonian	81
4.1.1	Single Group Formulation	81
4.1.2	Double Group Formulation	82
4.1.3	Full Zone Bulk Band Diagrams	85
4.2	Löwdin Renormalisation	90
4.2.1	2 nd Order Perturbation Theory	90
4.2.2	DKK Effective Mass Hamiltonian	91
4.2.3	Silicon 6-Band Model	92
4.2.4	Germanium 8-Band Model	96
4.3	The Theory of Invariants	98
4.3.1	Irreducible Perturbation Components & Generator Matrices	98
4.3.2	Luttinger-Kohn Valence Band Hamiltonian	100
4.3.3	Coordinate Transformations	101
5	Extension to Strained Systems	106
5.1	Stress & Strain	107
5.1.1	Principles of Strain	107
5.1.2	Generalised Poisson Ratio	110
5.1.3	Experimental Implications	111
5.2	Band Edges in Heterostructures	112
5.2.1	Pikus-Bir Hamiltonian	113
5.2.2	Band Edge Diagrams	115

6	Application to Heterostructures	118
6.1	Operator Ordered Hamiltonians	119
6.1.1	Single Group Formulation	119
6.1.2	Double Group Formulation	120
6.2	Numerical Implementation	122
6.2.1	Finite Differencing Scheme	122
6.2.2	SiGe Heterostructures	124
6.2.3	QCSE Device Operation	127
6.3	Coordinate Transformations	130
6.3.1	Hamiltonians for Arbitrary Growth Planes	130
6.3.2	Application to Arbitrary Growth Planes	132
7	Results & Conclusions	137
7.1	Group Theory & Symmetrised Basis Functions	138
7.2	Double Group Formulation of $\mathbf{k} \cdot \hat{\mathbf{p}}$ Theory	139
7.3	Extension to Strained Systems	140
7.4	Application to Heterostructures	141
7.5	The Future & Beyond	142
A	T_d Group Representation Matrices	143
A.1	Single Group Representation Matrices	143
A.2	Double Group Representation Matrices	145
B	Maple Routines	149
B.1	Clebsch-Gordan Coefficient Calculator	149
B.2	Unitary Matrix Generation	150
B.3	Linearly Independent Matrix: $A_{\mathbf{k}\cdot\hat{\pi}}^{\Gamma_8^\pm:\Gamma_6^\mp}$	151
	Bibliography	152

List of Figures

1.1	Zinc-blende (left) and Diamond (right) type FCC primitive unit cells. Figures generated using <i>CrystalMaker</i> [®] software (http://www.CrystalMaker.com)	24
1.2	Wigner-Seitz construction of the FBZ of an FCC crystal, with high symmetry axes in reciprocal space [20]	24
1.3	Empty lattice band diagram for an FCC crystal. Energies are not labelled since the lattice constant a is non-specific	26
1.4	Band edge diagram sketch showing straddling (type-I) and staggered (type-II) alignment schemes for conduction and valence band offsets. There also exists the broken (type-III) scheme as an extreme form of type-II; where E_v in material 2 overlaps with E_c in material 1.	33
1.5	Band edges and envelope functions of lowest energy sub-band states for a compressively strained 12nm Germanium well sandwiched between tensile strained $Si_{0.15}Ge_{0.85}$ barriers on a $Si_{0.1}Ge_{0.9}$ -{001} virtual substrate at 0K	34
2.1	Symmetry operations for a three pointed object, permutation group S_3 ; visualised as the equilateral triangle	39
2.2	Projections of squares and triangles for the tetrahedrally coordinated sp^3 hybridised CH_4 molecule along one of the sixfold (001) and eightfold (111) directions. Figure generated using <i>CrystalMaker</i> [®] software (http://www.CrystalMaker.com)	44
2.3	Energy level diagram displaying the lifting of degeneracy under O_h single and double group crystal fields from the $L = 2$ eigenstate of $SO(3)$	54
2.4	Illustration of the decomposition of a general deformation into symmetric strain and antisymmetric rotation components [16]	56
2.5	valence and conduction band sketch of $O_h = i \otimes T_d$ type Ge (left) and T_d type GaAs (right) showing the effect of inversion symmetry on Kramer's degeneracy	61
3.1	Demonstration of Russell-Saunders $\mathbf{L} \cdot \mathbf{S}$ Coupling of $L = 1$ with $S = 1/2$ to $J = 3/2$ and $J = 1/2$ [69]	72
4.1	Zone centre energy level schematic with symmetry classifications; with interaction parameters formulated out of the single group approach	86
4.2	Full zone 30-band $\mathbf{k} \cdot \hat{\boldsymbol{\pi}}$ double group formulation band diagram (left) and density of states (right) for bulk Silicon. The indirect conduction band minima (d) occurs at $89\% - \Delta$ with an energy of $1.17eV$. Valence band maxima (a) are chosen as the offset energy $E_v = 0$	88

4.3	Full zone 30-band $\mathbf{k} \cdot \hat{\boldsymbol{\pi}}$ double group formulation band diagram (left) and density of states (right) for bulk Germanium. The indirect conduction band minima (c) occurs at L with an energy of 0.70eV and the direct conduction band minima (b) occurs at Γ with an energy of 0.89eV	88
4.4	Indirect gap conduction band minimum variation with SiGe alloy fraction. Note the abrupt transition from Δ to L valleys at composition $x = 88\%$	89
4.5	Valence and spin-orbit band comparison between 6-band and 30-band models in bulk Silicon; up to 25% of the FBZ. The Löwdin correction matches the full zone 30-band $\mathbf{k} \cdot \hat{\boldsymbol{\pi}}$ technique well to within 5meV up to 12% to the FBZ boundary	94
4.6	Luttinger parameters and in-plane heavy & light hole effective masses as a function of SiGe alloy composition	96
4.7	Valence, spin orbit and conduction band comparison between 8-band and 30-band models in bulk Germanium; up to 25% of the FBZ	97
4.8	Euler-Rodrigues Z-X-Z rotation figure through angles θ , ϕ and ω . z is the quantisation axis of the CCS and z' is normal to the growth plane of the DCS	102
5.1	Stress cube indicating normal; σ_{xx} , σ_{yy} and σ_{zz} and shear; σ_{xy} , σ_{yz} and σ_{zx} components for respective faces	107
5.2	(a) A thin SiGe film to be grown on a Si layer with (b) compressive strain. (c) A thin Si film to be grown on an SiGe layer with (d) tensile strain [1]	109
5.3	Surface plot for general dimensionless Poisson ratio $D(\theta, \phi)$ in the domain; $0 < (\theta, \phi) < \pi/2$, using stiffness tensor values for Silicon	111
5.4	Matthews & Blakeslee [101] critical thickness versus Germanium fraction of $Si_{1-x}Ge_x$ for pseudomorphic layer on bulk Si-{001}. The metastable transition is for MBE growth at 550°C . Taken from [1]	112
5.5	Effect of hydrostatic and uniaxial strain on degenerate valence band edge. Compressive (tensile) strain moves heavy holes above (below) light holes as depicted.	114
5.6	Band discontinuities and alignments of conduction and valence bands of an unstrained interface between $Si_{0.15}Ge_{0.85}$ and Germanium using band offsets of $(\Delta E_c)68:32(\Delta E_v)$ as given by Yaguchi et al [107]	115
6.1	Valence and conduction sub-band dispersion along high symmetry axes for confined states in a compressively strained 12nm Germanium well sandwiched between tensile strained $Si_{0.15}Ge_{0.85}$ barriers on a $Si_{0.1}Ge_{0.9}$ -{001} virtual substrate at 0K. This took less than one minute in Matlab using an 8-band model	124
6.2	Joint density of states for a compressively strained 12nm Germanium well sandwiched between tensile strained $Si_{0.15}Ge_{0.85}$ barriers on a $Si_{0.1}Ge_{0.9}$ -{001} virtual substrate at 0K. This took 33 hours in Matlab	125
6.3	Absorption coefficient for a compressively strained 12nm Germanium well sandwiched between tensile strained $Si_{0.15}Ge_{0.85}$ barriers on a $Si_{0.1}Ge_{0.9}$ -{001} virtual substrate at 0K. This took 34 hours in Matlab	126

6.4	hh_1-e_1 transition absorption coefficient for a compressively strained 15nm Germanium well sandwiched between tensile strained $Si_{0.15}Ge_{0.85}$ barriers on a $Si_{0.1}Ge_{0.9}$ -{001} virtual substrate at 300K under applied electric fields of (0-50)kV/cm exhibiting the QCSE for a wavelength range (1.42-1.44) μm	127
6.5	Onset of band edge absorption excluding excitonic effects for first confined states in a Germanium well sandwiched between tensile strained $Si_{0.15}Ge_{0.85}$ barriers on a $Si_{0.1}Ge_{0.9}$ -{001} virtual substrate at 300K of variable well width. The 15nm line has been drawn for cross reference purposes with Figure 6.4	128
6.6	Onset of band edge absorption excluding excitonic effects for hh_1-e_1 transition under the influence of an externally applied electric field for 12nm and 15nm Germanium wells sandwiched between tensile strained $Si_{0.15}Ge_{0.85}$ barriers on a $Si_{0.1}Ge_{0.9}$ -{001} virtual substrate at 300K.	129
6.7	Absorption coefficient for a compressively strained 12nm Germanium well sandwiched between tensile strained $Si_{0.15}Ge_{0.85}$ barriers on a $Si_{0.1}Ge_{0.9}$ -{011} virtual substrate at 0K. Growth on the {001} plane (dotted) is included for comparison	132
6.8	Absorption coefficient for a compressively strained 12nm Germanium well sandwiched between tensile strained $Si_{0.15}Ge_{0.85}$ barriers on a $Si_{0.1}Ge_{0.9}$ -{111} virtual substrate at 0K. Growth on the {001} plane (dotted) is included for comparison	133
6.9	Transition energies of hh_1-e_1 for a a compressively strained 12nm Germanium well sandwiched between tensile strained $Si_{0.15}Ge_{0.85}$ barriers on a $Si_{0.1}Ge_{0.9}$ virtual substrate at 0K grown on arbitrary growth planes within the domain; $0 < (\theta, \phi) < \pi/2$. High index planes are indicated as the previous specific examples; {001} {011} and {111}	134

List of Tables

1.1	Crystal classifications with respective number of Bravais lattices and number of point and space groups [16]	23
2.1	Composition table for the three pointed object permutation group S_3 . Complete with inverses [55]. Elements have been demarcated into their respective conjugacy classes; identity $\{E\}$, reflections $\{3\sigma_v\}$ and 120° rotations $\{2C_3\}$	39
2.2	Summary of the crystallographic point group classes of operation	41
2.3	Character table for the permutation group, S_3 , of the equilateral triangle, complete with polar; $\{x, y, z\}$, and axial (pseudo); $\{L_x, L_y, L_z\}$, vectors	43
2.4	Character table for the T_d point group, complete with some important basis functions [2]	44
2.5	Character table for the O_h point group arranged to convey compatibility with T_d	45
2.6	Compatibility table between full rotation, $SO(3)$, and Octahedral, O_h , groups for $L = 0 \dots 6$ [54] using characters of classes $\{E\}$, $\{3C_2\}$, $\{8C_3\}$ and $\{6S_4\}$	49
2.7	Character table for double group irreps of the T_d group	51
2.8	Compatibility table between $SU(2)$ and Octahedral, O_h , double groups for $J = 1/2 \dots 9/2$ [54]. Trivial $\{3C_2\}/\{3\hat{E}C_2\}$ characters have been omitted	51
2.9	Character table for the O_h double group arranged to convey compatibility with the T_d double group	52
2.10	Direct product decomposition into symmetric and anti-symmetric direct sum parts for $\Gamma_5 \otimes \Gamma_5 = \Gamma_1 \oplus \Gamma_3 \oplus [\Gamma_4] \oplus \Gamma_5$	53
2.11	Multiplication table for single and double group irreps of the T_d group [55]. The multiplication table for O_h invokes the equivalence representation $\Gamma^{equiv} = \Gamma_1^+ + \Gamma_2^-$, and usual parity selection rules; <i>even</i> $\times$ <i>even</i> = <i>odd</i> $\times$ <i>odd</i> = <i>even</i> and <i>even</i> $\times$ <i>odd</i> = <i>odd</i> $\times$ <i>even</i> = <i>odd</i> . $[\Gamma_i]$ denotes anti-symmetric contribution, otherwise it is symmetric	55
3.1	Symmetrised Octahedral, O_h , single group irrep basis functions represented in the spherical frame [67]	67
3.2	Double group and adapted double group symmetrised normalised basis functions transforming according to O_h irreps from $J = 1/2 \dots 7/2$ [30]. Basis functions are eigenfunctions of $\hat{T}^2$, with eigenvalue -1 . Both double and adapted double group basis functions are coherent under the action of $\hat{T}$ under the Condon-Shortley phase convention	76
4.1	$Si_{1-x}Ge_x$ scaling parameters used in the double group matrix Hamiltonian. P_1 is the Kane parameter [33]	85

4.2	Double group zone centre energy eigenvalues for $Si_{1-x}Ge_x$. Subscripts denote the occurrence of an irrep given in the superscript	85
4.3	Dimensionless theoretical Luttinger parameters used in the 6-band double group matrix Hamiltonian for Silicon and Germanium	95
6.1	Transition energies between confined heavy and light holes in the valence band with electron in the conduction band. Greyed out energies denote weak optical transitions due to parity selection rules	126
6.2	Transition energies between confined heavy and light holes in the valence band with electron in the conduction band for the device grown on the {011} plane. Greyed out energies denote weak optical transitions due to parity selection rules	132
6.3	Transition energies between confined heavy and light holes in the valence band with electron in the conduction band for the device grown on the {111} plane. Greyed out energies denote weak optical transitions due to parity selection rules	133
A.1	T_d representation matrices for the identity and three 180° rotation operations for single group irreps. $\mathbf{D}(C_2(010))$ sets the choice of phase on basis through time reversal symmetry $\hat{T}$	143
A.2	T_d representation matrices for 90° improper rotations about the six equivalent (001) axes for single group irreps	144
A.3	T_d representation matrices for mirror operations about the six equivalent (001) axes for single group irreps	144
A.4	T_d representation matrices for the 120° symmetry operations about the eight equivalent (111) axes for single group irreps	145
A.5	T_d representation matrices for the identity and three 180° rotation operations for double group irreps	146
A.6	T_d representation matrices for 90° improper rotations about the six equivalent (001) axes for double group irreps	146
A.7	T_d representation matrices for mirror operations about the six equivalent (001) axes for double group irreps	147
A.8	T_d representation matrices for the 120° symmetry operations about the eight (111) axes for double group irreps	148

Abbreviations

Acronym	What (it) Stands For
QCSE	Q uantum C onfined S tark E ffect
DFT	D ensity F unctional T heory
EFA	E nvelope F unction A pproximation
BCC	B ody C entered C ubic
FCC	F ace C entered C ubic
FBZ	F irst B rillouin Z one
DKK	D resselhaus- K ip- K ittel
GOT	G reat O rthogonality T heorem
DCS	D evice C o-ordinate S ystem
CCS	C rystal C o-ordinate S ystem
DCM	D irectional C osines M atrix
MBE	M olecular B eam E pitaxy
CVD	C hemical V apour D eposition
TE	T ransverse E lectric
TM	T ransverse M agnetic

Physical Constants

Constant Name	Symbol	=	Constant Value (with units)
Speed of Light	c	=	$2.997\,925 \times 10^8 \text{ ms}^{-2}$
Electronic Charge	e	=	$1.602\,176 \times 10^{-19} \text{ C}$
Electron Rest Mass	m_0	=	$9.109\,382 \times 10^{-31} \text{ kg}$
Vacuum Permittivity	ϵ_0	=	$8.854\,188 \times 10^{-12} \text{ Fm}^{-1}$
Planck's Constant	h	=	$6.626\,068 \times 10^{-34} \text{ Js}$
Rydberg Constant	$R_\infty = \frac{m_0 e^3}{8 \epsilon_0^2 h^2}$	=	$13.605\,695 \text{ eV}$
Bohr Radius	$a = \frac{4 \pi \epsilon_0 \hbar^2}{m_0 e^2}$	=	$0.529\,177 \text{ \AA}$

Dedicated to my mother

Chapter 1

Introduction & Overview

The motives and goals for the work presented in this thesis are outlined in this introductory chapter. As the title of the thesis implies, the task in hand is to implement the double group formulation of $\mathbf{k} \cdot \hat{\mathbf{p}}$ theory for application to Silicon-Germanium (SiGe) alloy heterostructures. A considerable amount of work was done to set up a theoretical model to describe and predict the physical behaviour of a strained Germanium rich quantum well exhibiting optical modulation of the absorption edge around $1.5\mu\text{m}$ at room temperature under the quantum confined Stark effect (QCSE).

Despite Silicon constituting $\approx 97\%$ of all microelectronic chips and devices; direct band-gap semiconductors dominate optoelectronics. Consequently there is a gaping hole in the market for an all integrated system on a chip [1] employing SiGe alloy heterostructures. Construction of symmetrised valence and conduction band effective mass Hamiltonians allows for novel devices to be modelled to ever increasing degrees of accuracy. One calls for the double group formulation of $\mathbf{k} \cdot \hat{\mathbf{p}}$ theory as an enhancement to current methods without the requirement for additional input parameters to model sub-band dispersion, joint density of states and absorption coefficient.

This chapter introduces the Hamiltonian, and how it may be solved to describe the energetics of a particular system. While there is an overwhelming complexity involving systems with upwards of $10^{23}\text{atoms}/\text{cm}^3$ a simplification procedure is essential in order to solve the problem to any kind of degree of accuracy. Using a-priori knowledge about the system as an infinite cubic crystal with translational symmetry gives rise to the Floquet-Bloch principle and the concept of the wave vector $\mathbf{k}$. Using further point group symmetries; the dispersion relation, $E(\mathbf{k})$, as a band structure may be returned given appropriate semi-empirical input parameters. Bulk properties such as the indirect conduction band minima and zone centre effective masses specific to Silicon & Germanium provide excellent experimental verification of the theory.

1.1 Introduction to Electronic Structure

The ability to model materials of interest lends itself to devices tailored to needs. Classical physics was enormously successful, but relies on empirical fitting parameters determined from experiment. Modern quantum mechanical models are semi-empirical or self consistent ab-initio, which inevitably leads to solving the Schrödinger equation. The infinite square well, harmonic oscillator and spherically symmetric Hydrogen atom are analytically solved problems, but complex systems may be solved through perturbation theory.

This section introduces the concept of the many body Hamiltonian; expressible in terms of electronic and nuclear coordinates, which if solved respects the complete physics of the system. The complexity of real systems means a number of significant simplification procedures must be invoked. The adiabatic- or Born-Oppenheimer- approximations absolves the nuclear coordinate dependence and subsequently the Hartree approximation reduces the problem to a single electron Schrödinger equation under the influence of a self-consistent potential.

1.1.1 Many Body Hamiltonians

Quantum mechanics encodes everything that is knowable about a system of nuclei and electrons in the wave-function; $\Psi(\{\mathbf{R}_I\}, \{\mathbf{r}_i\}, t)$, where $\{\mathbf{R}_I\}$ and $\{\mathbf{r}_i\}$ are the positions of the I^{th} nucleus and i^{th} electron respectively. The wave-function evolves according to the time-dependent Schrödinger equation;

$$\hat{H}\Psi(\{\mathbf{R}_I\}, \{\mathbf{r}_i\}, t) = i\hbar \frac{\partial}{\partial t} \Psi(\{\mathbf{R}_I\}, \{\mathbf{r}_i\}, t) \quad (1.1)$$

The Hamiltonian operator, $\hat{H}$, has energy eigenvalue according to the time-independent Schrödinger equation;

$$\hat{H}\Psi(\{\mathbf{R}_I\}, \{\mathbf{r}_i\}, t) = E\Psi(\{\mathbf{R}_I\}, \{\mathbf{r}_i\}, t) \quad (1.2)$$

The variational principle is an alternative way of solving the above equation, based on a Legendre transformation; minimising action through the Lagrangian. The complete many body Hamiltonian for a system of interacting nuclei and electrons can be represented by sums of respective kinetic and potential energy terms¹ as;

¹factors of $\frac{1}{2}$ in both $\hat{V}_{nn}$ and $\hat{V}_{ee}$ account for double summation

$$\begin{aligned}
\hat{H} = & \underbrace{-\sum_I \frac{\hbar^2}{2M_I} \hat{\nabla}_I^2}_{\hat{T}_n: \text{Nuclear Kinetic Energy}} - \underbrace{\sum_i \frac{\hbar^2}{2m_i} \hat{\nabla}_i^2}_{\hat{T}_e: \text{Electron Kinetic Energy}} \\
& + \underbrace{\frac{e^2}{8\pi\epsilon_0} \sum_I \sum_{J \neq I} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}}_{\hat{V}_{nn}: \text{nucleus-nucleus interaction}} + \underbrace{\frac{e^2}{8\pi\epsilon_0} \sum_i \sum_{j \neq i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}}_{\hat{V}_{ee}: \text{electron-electron interaction}} \\
& - \underbrace{\frac{e^2}{4\pi\epsilon_0} \sum_I \sum_i \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_i|}}_{\hat{V}_{ne}: \text{nucleus-electron interaction}}
\end{aligned} \tag{1.3}$$

Silicon has 14 electrons per atom, so $\Psi(\{\mathbf{R}_I\}, \{\mathbf{r}_i\}, t)$ may be represented by a $3 + 3 \times 14 + 1 = 46$ dimensional representation. This is already a formidable task to solve analytically, and with upwards of 10^{23} atoms/cm³ in the solid state, clearly some sort of simplification procedure is essential before attempting to solve such a problem.

Solid state crystals form stable structures such that the Hamiltonian may be separated into electronic and nuclear contributions within reason. The many body Hamiltonian may be absolved from the nuclear coordinates, by introducing an electronic Hamiltonian; which depends parametrically on the nuclear coordinates through the nucleus-electron interaction, $\hat{V}_{ne}(\{\mathbf{R}_I\})$;

$$\begin{aligned}
\hat{H} &= \hat{H}_e(\{\mathbf{R}_I\}) + \hat{T}_n + \hat{V}_{nn} \\
\hat{H}_e(\{\mathbf{R}_I\}) &= \hat{T}_e + \hat{V}_{ee} + \hat{V}_{ne}(\{\mathbf{R}_I\})
\end{aligned} \tag{1.4}$$

Eigenvectors and eigenvalues of the electronic Hamiltonian are parameterised by the nuclear coordinates, which if used as trial solutions of $\hat{H}$ return off-diagonal elements. Clearly a recursive relation exists until eigenvectors become simultaneous solutions or eigenvalues converge. Under the adiabatic approximation nuclei are assumed to continuously deform the electronic wavefunction. Such an approximation is valid provided that the mass ratios m_i/M_I become infinitesimal. This should be compared with the alternative Born-Oppenheimer approximation, in which the lattice is assumed to be motionless, and nuclei have zero momentum from the point of view of velocity. Both approximations lead to off diagonal elements tending to zero, such that solutions simultaneously solve the electronic and many body Hamiltonians. In summary the adiabatic and Born-Oppenheimer approximations assume steady state solutions condensed into the ground state; albeit for slightly different reasons.

Atoms in devices operating at room temperature may not necessarily be assumed to be motionless, nor may the mass ratio be assumed negligible; $m_i/M_I \approx 10^{-30}/10^{-26}$.

Consequently electron-phonon interactions may be introduced through the piezoelectric effect for acoustic phonons and Fröhlich interaction [2] for optical phonons. Experimental phonon modes are typically of the order 10^{13}Hz , compared with electronic modes of the order 10^{15}Hz , in accordance with aforementioned mass ratios. Using this we may attribute effects of the order 1meV with phonons and 1eV with electronic effects in general.

For the case of long wavelength phonons, perturbations may be introduced through the treatment of static strain and deformation potentials using the techniques of Pikus & Bir [3]. Lattice matched systems, such as AlGaAs/GaAs heterostructures may be modelled in a strain free environment, however Silicon and Germanium have a 4% lattice mismatch [4] resulting in noticeable effects which must be accounted for.

1.1.2 Self-consistent Ab-initio Techniques

Under the Hartree approximation, the wave-function for N -electrons is expressed as a product of N individual one-electron wave-functions. This has the effect of reducing the many electron problem to solving a single-electron Schrödinger equation.

$$\psi(\{\mathbf{r}_i\}) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\psi_3(\mathbf{r}_3)\dots\psi_N(\mathbf{r}_N) = \prod_{i=1}^N \psi_i(\mathbf{r}_i) \quad (1.5)$$

Under the mean field approximation, the Hamiltonian reduces to the familiar electron kinetic energy and electron-nucleus interaction. The one electron is then influenced by the Hartree potential, which is a sum of attractive nuclear and repulsive electronic interactions represented as a continuous density functional, $V[\rho(\mathbf{r})]$ [5].

$$\left[-\frac{\hbar^2}{2m_i} \hat{\nabla}_i^2 + \frac{e^2}{8\pi\epsilon_0} \sum_{j \neq i} \int \frac{|\psi_j(\mathbf{r}_j)|^2}{|\mathbf{r}_j - \mathbf{r}_i|} d\mathbf{r}_j - \frac{e^2}{4\pi\epsilon_0} \sum_I \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} \right] \psi_i(\mathbf{r}_i) = E_i \psi_i(\mathbf{r}_i) \quad (1.6)$$

Several techniques are used to model the Hartree potential, all which seek out converging eigenvalues inside a recursive loop. There is a distinct flaw with such a simplified model; in that exchange and correlation terms have not been appropriately treated. Such that while bosonic systems work fine, systems involving fermions fail to accurately determine the nature of the system.

Under the Hartree approximation, correlation between electrons is always underestimated by not accounting for self energy terms. This is highlighted by the fact that current local density approximation calculations predict Germanium to be a semimetal

[2]. The GW approximation, involving Greens functions go some way to overcoming this but still underestimate potentials.

While this may be resolved through a Slater determinant [6], this significantly increases the complexity of the system; defeating the original object of simplification.

$$\begin{aligned}\psi(\{\mathbf{r}_i\}) &= \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_1(\mathbf{r}_2) & \dots & \psi_1(\mathbf{r}_N) \\ \psi_2(\mathbf{r}_1) & \psi_2(\mathbf{r}_2) & \dots & \psi_2(\mathbf{r}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(\mathbf{r}_1) & \psi_N(\mathbf{r}_2) & \dots & \psi_N(\mathbf{r}_N) \end{vmatrix} \\ &= \frac{1}{\sqrt{N!}} \sum_P (-1)^{\xi_P} \psi_{P_1}(\mathbf{r}_1) \psi_{P_2}(\mathbf{r}_2) \dots \psi_{P_N}(\mathbf{r}_N)\end{aligned}\tag{1.7}$$

The large popularity of density functional theory (DFT) may be attributed to the work of Kohn and Sham [7], whom hold the accolade of the most cited paper of all time (13,000) for their work on sets of non-interacting one electron eigenstates and their self-consistent treatment of exchange and correlation.

1.1.3 Semi-empirical Methods

As discussed in the previous section, self consistent methods may be exceptionally draining on computing resources, and do not always return results that reflect experimental data. Furthermore, much of the theory depends on electrons being condensed into the ground state, impractical for modelling of devices; since room temperature models with delocalised carriers are often sought. For this reason there is a large popularity with semi-empirical methods; which use a theoretical formalism to construct the Hamiltonian, with experimentally obtained parameters as inputs.

There are two avenues for inspection of systems where prior knowledge is assumed. One is a bottom up point of view, in that given microscopic properties of bonding states within one instance of the system, such properties may be recycled to the remainder of the system. For example, given that Zinc-blende type crystals characterise Tetrahedral (T_d) symmetry, one may apply a directed valence bonding technique to return symmetrised linear combination of atomic orbitals which coincide with the coordination of the bonds. Within this framework, atomic orbitals; a, b, c, d , may be symmetrised [8] according to the atomic site irrep $\Gamma^{a.s.} = \Gamma_1 \oplus \Gamma_5$ of the T_d group;

$$\left. \begin{aligned}\psi_1 &= \psi_a + \psi_b + \psi_c + \psi_d \\ \psi_2 &= \psi_a + \psi_b - \psi_c - \psi_d \\ \psi_3 &= \psi_a - \psi_b + \psi_c - \psi_d \\ \psi_4 &= \psi_a - \psi_b - \psi_c + \psi_d\end{aligned} \right\} \Gamma^{a.s.} = \Gamma_1 \oplus \Gamma_5\tag{1.8}$$

Considering the lowest occupied orbitals as the singly and triply degenerate s and p orbitals, it is not surprising how the term sp^3 hybridisation has stuck. However in a crystal s and p are not uniquely compatible with $\Gamma_1 \oplus \Gamma_5$, so sp^3 is somewhat of a red herring. It is perfectly valid for linear combinations of $spdf \dots$ as an expansion to represent the directed valence bonds in molecular orbitals. Indeed where parity must be considered, such as in Diamond type crystals which characterise Octahedral (O_h) symmetry; the p state is odd under inversion and therefore may not contribute to bonding orbitals per se. It therefore comes as no surprise to why semi-empirical pseudo-potential methods [9] modelling Silicon bulk band structure converge with e.g. $sp^{1.7}d^{1.3}$ rather than the pure sp^3 paradigm.

Conversely there is an alternative point of view, which is a more top-down approach. This method takes the empty infinite lattice as a starting point to expand crystal field perturbations as a Taylor series expansion of the wave-vector $\mathbf{k}$. Such a technique applies the full space group of the crystal to the Hamiltonian, leading naturally to the formulation of symmetrised matrix Hamiltonians scaled by respective semi-empirical matrix elements. Consequently the *dispersion* relation $E(\mathbf{k})$ may be returned as the eigenvalues to describe the physics of the system.

Both aforementioned techniques break one-electron eigenstates into products of two separable functions within the scope of their periodicity. The main advantage the latter holds over the former technique is the application to heterostructure modelling through a piecewise construction of Hamiltonians using Burt's envelope function approximation (EFA) [10–13]. For these reasons, the $\mathbf{k} \cdot \hat{\mathbf{p}}$ ('k-dot-p') method [14] is employed as the semi-empirical technique extensively employed in this thesis.

1.2 The $\mathbf{k} \cdot \hat{\mathbf{p}}$ Method

In this section the $\mathbf{k} \cdot \hat{\mathbf{p}}$ method is introduced as a perturbative approach to solving the one-electron Schrödinger equation in bulk crystals. To begin with; *Bloch's theorem* and Brillouin zones [15] in reciprocal space are introduced as a means of solving the unperturbed Hamiltonian within the empty lattice framework. The perturbation to the Hamiltonian is brought in through arguments based on the full space group of the lattice, which takes the form of the product of point and translation sub-groups.

Computation of the matrix Hamiltonian may be implemented through Wigner-Eckart theorem and utilisation of Clebsch-Gordan coefficients. Treatment of the relativistic spin-orbit interaction may be introduced as another perturbation as in the adapted double group formulation, or as an inclusion to the unperturbed Hamiltonian as in the double group formulation. The latter approach gives rise to the $\mathbf{k} \cdot \hat{\boldsymbol{\pi}}$ perturbation, which thanks to the properties of spherical tensor operators may be solved in an identical manner. This mathematical trick enables an increase in accuracy in modelling the

valence and conduction band structure and effective masses through the correct choice of zone centre energy eigenvalues and degeneracies.

1.2.1 Bloch's Theorem & Brillouin zones

Solids may be classified into two types; glassy (amorphous) or crystalline. Although the properties of crystalline semiconductors are prevalent in this thesis, amorphous solids are gaining a lot of interest, especially with respect to Silicon on insulator technology and MOSFET/ CMOS gate dielectrics.

A lattice is an infinite array of evenly spaced points which are similarly situated in terms of space, such that atomic arrangement appears the same when viewed from all lattice points [16]. The lattice can be considered as the points of intersection of three parallel planes which divide the crystal into elementary primitive unit cells to which translational symmetry can be applied. The French crystallographer, Bravais, studied fragments from a rhombohedral crystal and noticed that all the fragments were also rhombohedral. He subsequently classified 14 fundamental unit cells for all crystals, shown in Table 1.1.

	Bravais Lattices	Point Groups	Space Groups
Triclinic	1	2	2
Monoclinic	2	3	13
Orthorhombic	4	3	59
Tetragonal	2	7	68
Rhombohedral	1	5	25
Hexagonal	1	7	27
Cubic	3	5	36
Total	14	32	230

TABLE 1.1: Crystal classifications with respective number of Bravais lattices and number of point and space groups [16]

Cubic lattices are sub-divided into simple-, body centred- (BCC) and face centred- (FCC) cubic, to which Zinc-blende and Diamond conform to the latter with point groups T_d and O_h respectively. Hexagonal lattices have gained a lot of interest in recent years through the application of large band-gap materials; Wurtzite GaN and ZnO [17], in photonic crystal devices. There also exist magnetic point groups [18] which have the time reversal operator as an element of the group but are superfluous to this thesis.

Space groups incorporate translational symmetry, treated by invoking the Floquet-Bloch principle. Primitive lattice vectors associated with the FCC lattice are given by;

$$\mathbf{a}_1 = (a/2, a/2, 0), \quad \mathbf{a}_2 = (a/2, 0, a/2), \quad \mathbf{a}_3 = (0, a/2, a/2) \quad (1.9)$$

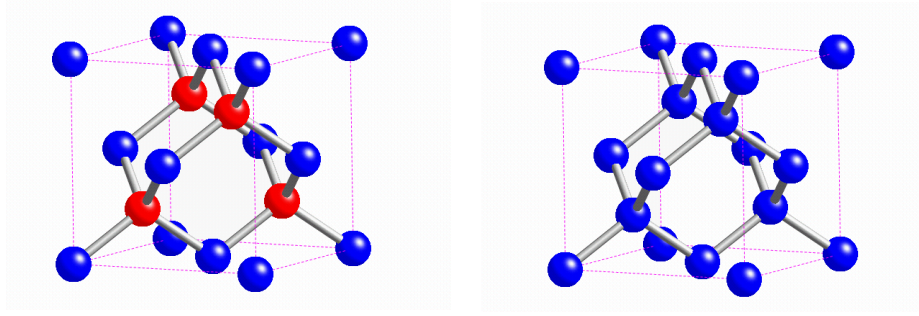


FIGURE 1.1: Zinc-blende (left) and Diamond (right) type FCC primitive unit cells. Figures generated using *CrystalMaker*[®] software (<http://www.CrystalMaker.com>)

where a is the characteristic lattice constant. This leads to the concept of the reciprocal lattice [19], with reciprocal lattice vectors² found using;

$$\mathbf{b}_i = 2\pi \frac{(\mathbf{a}_j \times \mathbf{a}_k)}{(\mathbf{a}_1 \times \mathbf{a}_2) \cdot \mathbf{a}_3} \quad (1.10)$$

The reciprocal lattice of the FCC lattice is the BCC lattice³. The first Brillouin zone (FBZ) in 3D, when represented by the Wigner-Seitz method is the smallest polyhedron confined by planes perpendicularly bisecting the reciprocal lattice vectors, shown in Figure 1.2 for an FCC crystal. Lines inside the FBZ are assigned Greek letters, and points on the surface are given Roman letters;

[001] direction $\Gamma \rightarrow \Delta \rightarrow X$

[011] direction $\Gamma \rightarrow \Sigma \rightarrow K$

[111] direction $\Gamma \rightarrow \Lambda \rightarrow L$

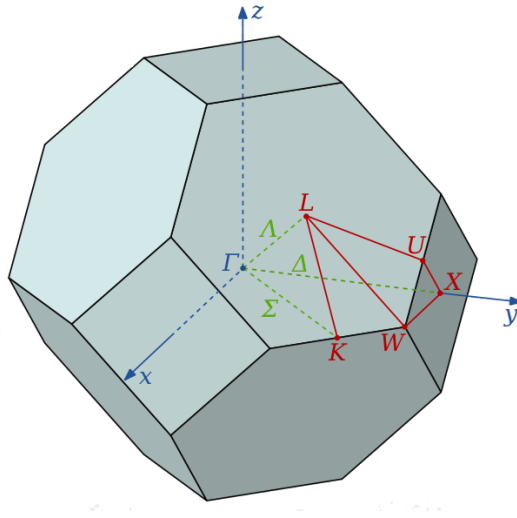


FIGURE 1.2: Wigner-Seitz construction of the FBZ of an FCC crystal, with high symmetry axes in reciprocal space [20]

Translational invariance in the real crystal and the FBZ are so intrinsically linked that every wave-vector can be brought back into the FBZ, shrinking all local crystal potentials

²real space vectors are denoted in parentheses (hkl) and reciprocal space vectors are denoted in square brackets [hkl]. This nomenclature follows Kittel [19]

³ $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$

down to a polyhedron of dimension π/a . Within such a formalism, the one electron wave function may be broken into a rapidly varying cell periodic term, $u_{n\mathbf{k}}(\mathbf{r})$ and a slowly varying envelope function, $e^{i\mathbf{k}\cdot\mathbf{r}}$, the Bloch function;

$$\psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}} \quad (1.11)$$

The wave vector, $\hbar\mathbf{k}$, may be considered as the *crystal momentum* since it is the eigenvalue of the momentum operator $\hat{\mathbf{p}}$. Note also that the Fourier transform of $\psi_{n\mathbf{k}}(\mathbf{r})$ returns the Wannier function [21] used to study point defects and/or impurities.

$$\hat{\mathbf{p}}e^{i\mathbf{k}\cdot\mathbf{r}} = -i\hbar\hat{\nabla}e^{i\mathbf{k}\cdot\mathbf{r}} = \hbar\mathbf{k}e^{i\mathbf{k}\cdot\mathbf{r}} \quad (1.12)$$

From a group theoretical perspective (Chapter 2), the group which characterises the translational symmetry sub-group is an infinite discrete group, such that $\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}\psi_{n\mathbf{k}}(\mathbf{r})$. Given that bulk crystals may contain 10^{23} atoms/cm³ the wave vector serves as a *good quantum number*, and since $\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = \psi_{n\mathbf{k}}(\mathbf{R} + \mathbf{r})$ this group is commutative, or Abelian. $\mathbf{R}$ are the elements of the group, which are Miller integer (hkl) multiples of primitive lattice vectors. Furthermore, since $e^{i\mathbf{k}\cdot\mathbf{R}}$ is merely a phase factor the measurable quantity; density, is invariant $|\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R})|^2 = |\psi_{n\mathbf{k}}(\mathbf{r})|^2$ in accordance with Noether's theorem.

The highest symmetry point occurs at the zone centre ($\mathbf{k} = 0$), or Γ -point, where the full symmetry point group of the crystal is represented. Perturbations are expanded about the Γ -point as appropriate basis functions (Chapter 3) diagonalise the unperturbed Hamiltonian with the highest implicit degeneracy. Consequently $u_{n\mathbf{k}}(\mathbf{r})$ are termed *zone centre eigenstates*. Lower symmetry points away from the Γ -point form subgroups of the full symmetry group [22] through compatibility relations, called the group of $\mathbf{k}$.

1.2.2 The Empty FCC Lattice

The single electron Schrödinger equation may be solved under the empty lattice problem, which is a neat way of introducing discussions on crystal energetics and linking it to crystal symmetry. To begin with, the Hamiltonian is solved under some stringent conditions. These are that since the lattice is empty $\hat{V}(\mathbf{r})\psi_{n\mathbf{k}}(\mathbf{r}) = 0$, the potential may be expressed as an infinite lattice of delta functions at primitive lattice points;

$$\hat{V}(\mathbf{r}) = \sum_{(hkl)=-\infty}^{\infty} \delta(\mathbf{r} + (hkl)\mathbf{a}) \quad (1.13)$$

This also sets the boundary condition $\psi_{n\mathbf{k}}(\mathbf{R}) = 0$. Alternatively zone centre eigenstates take the value of a constant normalisation factor, such that $\hat{\mathbf{p}}u_{n\mathbf{k}}(\mathbf{r}) = 0$. Both constraints return simultaneous solutions, whose energy eigenvalues take the form;

$$\hat{H}\psi_{n\mathbf{k}}(\mathbf{r}) = \left(\frac{\hat{\mathbf{p}}^2}{2m_0} + \hat{V}(\mathbf{r}) \right) \psi_{n\mathbf{k}}(\mathbf{r}) = E\psi_{n\mathbf{k}}(\mathbf{r}); \quad E = \frac{\hbar^2 (\mathbf{k} + [hkl])^2}{2m_0} \quad (1.14)$$

This simplistic model conveys the band-diagram, which are like maps one can use to study real materials, shown in Figure 1.3. Points on the bands are solutions of the Schrödinger equation and are allowed states for electrons to occupy.

The empty lattice highlights how symmetry may be used to draw flaws in models, since such a model assumes an eight-fold degeneracy at [111]. Since the largest degeneracy of the T_d and O_h single groups is three, the empty lattice conveys hidden degeneracies that have not been accounted for; which is to be expected from such a simplistic model.

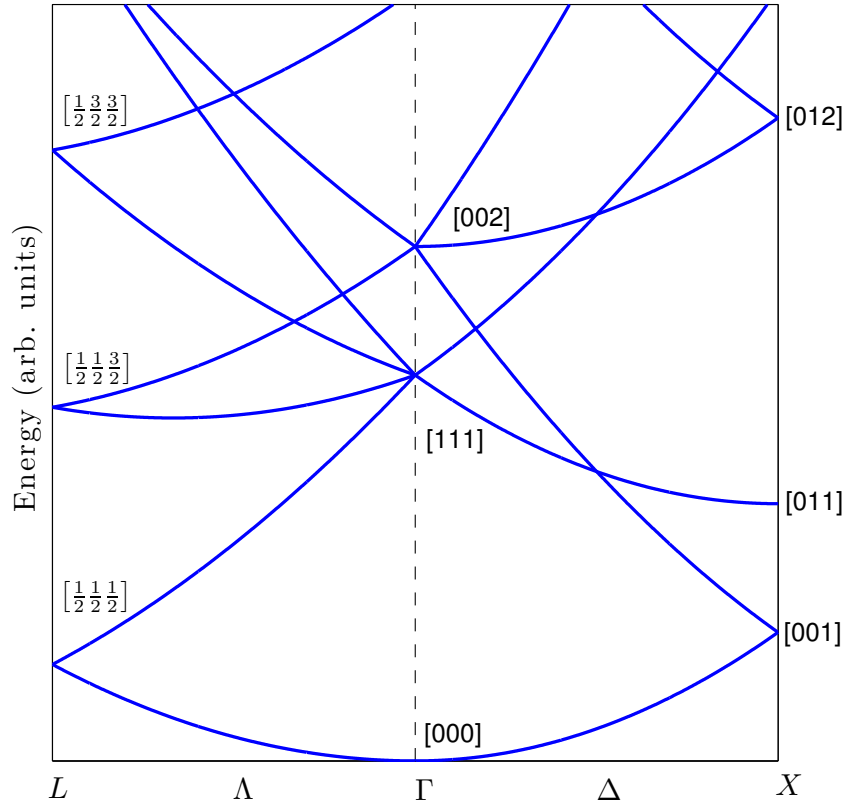


FIGURE 1.3: Empty lattice band diagram for an FCC crystal. Energies are not labelled since the lattice constant a is non-specific

One extension to this simplistic model is the Kronig-Penney model [23], which somewhat modifies the potential in Equation 1.13 to delta functions of finite strength, such that there is some degree of coupling between eigenfunctions in adjacent primitive unit cells. The resulting boundary ‘cusp’ conditions lift degeneracies at the zone centre, giving rise to the concept of the band-gap; a range of forbidden energy eigenvalues. As a

consequence of the Kronig-Penney model a plethora of materials' optical and electrical behaviour was explained in terms of insulators, semiconductors and metals.

Modern modelling techniques such as DFT, pseudopotentials and $\mathbf{k} \cdot \hat{\mathbf{p}}$ theory are better used to explain more specific intricate physical phenomena such as van Hove singularities [24] in absorption spectra, phonon-assisted transitions for indirect band gaps and anisotropic effective masses. However, the Kronig-Penney model has seen a resurgence due to interest in superlattices as sophisticated layer by layer growth techniques allow structures with far narrower barrier regions than in multiple quantum well stacks.

1.2.3 $\mathbf{k} \cdot \hat{\mathbf{p}}$ Perturbation

In the previous section, one of the constraints which led to the empty lattice model presented $\hat{\mathbf{p}}u_{n\mathbf{k}}(\mathbf{r}) = 0$, such that zone centre eigenstates are simply normalisation factors. Using prior knowledge that zone centre eigenstates are in fact symmetrised eigenstates of the full symmetry group of the crystal; in this case T_d and O_h , in general $\hat{\mathbf{p}}u_{n\mathbf{k}}(\mathbf{r}) \neq 0$. Under this formalism, the crystal momentum takes on a slightly different form;

$$\hat{\mathbf{p}}\psi_{n\mathbf{k}}(\mathbf{r}) = \hat{\mathbf{p}}u_{n\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}} = -i\hbar \left(\left(\hat{\nabla}u_{n\mathbf{k}}(\mathbf{r}) \right) e^{i\mathbf{k}\cdot\mathbf{r}} + u_{n\mathbf{k}}(\mathbf{r}) \left(\hat{\nabla}e^{i\mathbf{k}\cdot\mathbf{r}} \right) \right) = (\hat{\mathbf{p}} + \hbar\mathbf{k})\psi_{n\mathbf{k}}(\mathbf{r}) \quad (1.15)$$

Such that in the kinetic energy term we may substitute; $\hat{\mathbf{p}}^2 \rightarrow \hat{\mathbf{p}}^2 + 2\mathbf{k} \cdot \hat{\mathbf{p}} + \mathbf{k}^2$ with the constraint that $\hat{\mathbf{p}}$ now acts on the cell periodic part of the wave function only. Consequently the Hamiltonian, $\hat{H}$ may be expressed as a combination of unperturbed $\hat{H}_0$ and perturbation $\hat{H}_{\mathbf{k}\cdot\hat{\mathbf{p}}}$ terms;

$$\hat{H}_0 = \frac{\hat{\mathbf{p}}^2}{2m_0} + \hat{V}(\mathbf{r}), \quad \hat{H}_{\mathbf{k}\cdot\hat{\mathbf{p}}} = \frac{\hbar}{m_0}\mathbf{k} \cdot \hat{\mathbf{p}} \quad (1.16)$$

Eigenvalues are equivalent to $E - \frac{\hbar^2\mathbf{k}^2}{2m_0}$ to include the free electron dispersion term. The unperturbed Hamiltonian $\hat{H}_0$ is a scalar operator, which transforms according to a rank-0 spherical tensor operator, whereas $\hat{H}_{\mathbf{k}\cdot\hat{\mathbf{p}}}$ is a rank-1 spherical tensor operator. By the same token; strain is a rank-2 spherical tensor operator discussed later.

Conventionally, one expands $\mathbf{k} \cdot \hat{\mathbf{p}} = k_x\hat{p}_x + k_y\hat{p}_y + k_z\hat{p}_z$ and evaluates matrix elements as overlap integrals in a cartesian frame. However, it becomes *far* more useful to represent $\mathbf{k} \cdot \hat{\mathbf{p}}$ as projections of contragredient spherical tensor operators;

$$\mathbf{k} \cdot \hat{\mathbf{p}} = k_z \hat{p}_1^0 + \frac{1}{\sqrt{2}} (k_+ \hat{p}_1^{-1} - k_- \hat{p}_1^{+1}) \quad (1.17)$$

where subscripts and superscripts denote the rank and projection respectively. It is chosen; $k_{\pm} = k_x \pm ik_y$, such that the sign convention retains the property $k_{\pm} = (k_{\mp})^*$ to prevent confusion over the Hermitian nature of the perturbation. One may now evaluate overlap integrals with basis functions using Wigner-Eckart theorem [25], which states;

$$\langle L_1, m_{L_1} | T_{\kappa}^q | L_2, m_{L_2} \rangle = \langle L_1 | T_{\kappa} | L_2 \rangle C_{\kappa, q, L_2, m_{L_2}}^{L_1, m_{L_1}} \quad (1.18)$$

$C_{\kappa, q, L_2, m_{L_2}}^{L_1, m_{L_1}}$ are Clebsch-Gordan coefficients, and $\langle L_1 | T_{\kappa} | L_2 \rangle$ are reduced matrix elements, or scaling parameters which are projection independent. This ensures that the reduced matrix element is independent of the quantisation axis such that scaling parameters are *invariant* under canonical transformations. Note also that selection rules of Clebsch-Gordan coefficient require $q = m_{L_1} - m_{L_2}$ and $L_1 + L_2 \geq \kappa \geq |L_1 - L_2|$. T_{κ}^q is a general spherical tensor operator of rank κ and projection q , such that the commutation rules with angular momentum, as given by Merzbacher [26], satisfy;

$$\begin{aligned} [L_z, T_{\kappa}^q] &= q \hbar T_{\kappa}^q \\ [L_{\pm}, T_{\kappa}^q] &= \mp \frac{1}{\sqrt{2}} \sqrt{\kappa(\kappa+1) - q(q \pm 1)} \hbar T_{\kappa}^{q \pm 1} \end{aligned} \quad (1.19)$$

The substitution of these commutation rules into the matrix element $\langle L_1, m_{L_1} | T_{\kappa}^q | L_2, m_{L_2} \rangle$ returns a series of recursion relations and proof of Wigner-Eckart theorem is found in Modern Quantum Mechanics by J. J. Sakurai [27].

While the single group formulation proved fruitful in describing many effects in crystals such as returning full zone bulk band diagrams for Silicon and Germanium by Cardona & Pollak [28] with indirect conduction band minima at Δ and L of the FBZ respectively, it inherently neglects the appropriate treatment of the spin-orbit interaction. Consequently, the spin degenerate eigenstates $\{\uparrow, \downarrow\}$ are usually attached in a somewhat ad hoc way and the spin-orbit interaction introduced as another perturbation.

The double group formulation of the $\mathbf{k} \cdot \hat{\mathbf{p}}$ method calls for an appropriate treatment of the Hamiltonian including spin degeneracy from the outset. Within such a framework the unperturbed Hamiltonian now takes the form;

$$\hat{H}_0 = \frac{\hat{\mathbf{p}}^2}{2m_0} + \hat{V}(\mathbf{r}) + \frac{\hbar}{4m_0^2c^2} \left(\hat{\mathbf{p}} \times \nabla \hat{V}(\mathbf{r}) \right) \cdot \boldsymbol{\sigma} \quad (1.20)$$

where the final term takes into account the relativistic spin-orbit interaction, as given by G. Dresselhaus [29]. For a spherically symmetric potential the term in question reduces to $\mathbf{L} \cdot \mathbf{S}$ Russell-Saunders coupling which may be evaluated through $\frac{1}{2} (\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2)$ expectation values. There are two possible flaws of using such a method in crystals; the potential is not spherically symmetric and the pertinent basis is the adapted double group; $|L, m_L\rangle \otimes \{\uparrow, \downarrow\}$ as opposed to double group $|J, m_J\rangle$. Given the appropriate O_h double group basis by Onodera & Okazaki [30] the correct formalism may be undertaken through a $\mathbf{k} \cdot \hat{\boldsymbol{\pi}}$ perturbation akin to that above. Expanding the Bloch vector again, the perturbation takes an alternate form;

$$\hat{H}_{\mathbf{k} \cdot \hat{\boldsymbol{\pi}}} = \frac{\hbar}{m_0} \mathbf{k} \cdot \hat{\boldsymbol{\pi}} = \frac{\hbar}{m_0} \mathbf{k} \cdot \left(\hat{\mathbf{p}} + \frac{\hbar}{4m_0c^2} \boldsymbol{\sigma} \times \nabla \hat{V}(\mathbf{r}) \right) \quad (1.21)$$

Whose eigenvalues are again equivalent to $E - \frac{\hbar^2 \mathbf{k}^2}{2m_0}$. One may also express $\hat{\boldsymbol{\pi}}$ as rank-1 spherical tensor operator, such that;

$$\mathbf{k} \cdot \hat{\boldsymbol{\pi}} = k_z \hat{\pi}_1^0 + \frac{1}{\sqrt{2}} (k_+ \hat{\pi}_1^{-1} - k_- \hat{\pi}_1^{+1}) \quad (1.22)$$

One may again use Wigner-Eckart theorem to evaluate matrix elements expressible in terms of Clebsch-Gordan coefficients and reduced matrix elements, this time as $C_{\kappa, q, J_2, m_{J_2}}^{J_1, m_{J_1}}$ and $\langle J_1 || T_\kappa || J_2 \rangle$ respectively. Using SiGe scaling parameters from Rideau et al [31] one may construct a 30×30 matrix Hamiltonian and return full zone bulk band diagrams for Silicon & Germanium; this time using the double group formulation of $\mathbf{k} \cdot \hat{\mathbf{p}}$ theory and appropriate treatment of the spin-orbit interaction (Chapter 4).

Furthermore, using the Löwdin renormalisation [32] procedure and degenerate perturbation theory, *effective mass Hamiltonians* as an expansion in $\mathbf{k}$ may be returned. Effective mass Hamiltonians constructed out of the single and double group formulations of $\mathbf{k} \cdot \hat{\mathbf{p}}$ theory may subsequently be compared with those from Kane [33], Dresselhaus-Kip-Kittel (DKK) [34] and Luttinger-Kohn [35–37] using the theory of invariants; which has less stringent assumptions on the one electron potential. Expressions for heavy and light hole effective masses in terms of DKK and Luttinger parameters may be returned to greater accuracy when using the double group formulation in comparison with experimental cyclotron resonance data [38].

1.3 Introduction to Heterostructures

In this section the principle of spatial confinement of electrons and holes within a basic quantum well band edge alignment scheme is discussed. The introduction of strain through the Pikus-Bir Hamiltonian [3] as a perturbation may shift band edges and lift degeneracies in the valence band. Indeed in the SiGe system, the 4% lattice mismatch [4] ensures that strain balancing techniques are required to tailor quantum well devices which operate at chosen wavelengths within experimental constraints.

The concept of the envelope function is discussed as a more general means of solving the one-electron Schrödinger equation in heterostructures under the loss of translational symmetry [39]. Continuity of the envelope function and its derivative impose boundary conditions across an interface [40] with the physical effect of current conservation. To conclude this introductory chapter, the example of the 12nm compressively strained Germanium well sandwiched between tensile strained $Si_{0.15}Ge_{0.85}$ barriers on a $Si_{0.1}Ge_{0.9}$ -{001}⁴ virtual substrate is discussed for the application as a practical device [41].

1.3.1 Pikus-Bir Hamiltonian

Strain may be incorporated as a perturbation through the Pikus-Bir Hamiltonian [3]. Within this framework; Bravais lattice basis vectors $\mathbf{a}'$, of the strained crystal are deformations of the basis vectors $\mathbf{a}$, of the unstrained crystal. In order for the lattice of the strained crystal in its coordinate system $\mathbf{r}'$, to coincide with the *periodicity* of the unstrained crystal in its coordinate system $\mathbf{r}$, it is required that;

$$\left. \begin{aligned} \mathbf{k}' &= (\mathbb{1} + \epsilon) \mathbf{k} \\ \mathbf{r}' &= (\mathbb{1} + \epsilon)^{-1} \mathbf{r} \end{aligned} \right\} \implies \mathbf{k}' \cdot \mathbf{r}' = \mathbf{k} \cdot \mathbf{r} \quad (1.23)$$

Where ϵ is the second rank symmetric strain tensor. Expanding for small strain, one may invoke the binomial series; $(\mathbb{1} + \epsilon)^{-1} \approx (\mathbb{1} - \epsilon)$. We now intend to express some other key components in a similar manner, such as the momentum operator $\hat{\mathbf{p}} = -i\hbar\hat{\nabla}$. As $\hat{\nabla}$ is a differential with respect to $\mathbf{r}$ in the strained system, we have $\hat{\mathbf{p}}' = (\mathbb{1} + \epsilon) \hat{\mathbf{p}}$;

$$\hat{\mathbf{p}}' e^{i\mathbf{k}' \cdot \mathbf{r}'} = -i\hbar (\mathbb{1} + \epsilon) \hat{\nabla} e^{i\mathbf{k} \cdot \mathbf{r}} = \hbar (\mathbb{1} + \epsilon) \mathbf{k} e^{i\mathbf{k} \cdot \mathbf{r}} = \hbar \mathbf{k}' e^{i\mathbf{k}' \cdot \mathbf{r}'} \quad (1.24)$$

Hence we may verify that $\mathbf{k}' = (\mathbb{1} + \epsilon) \mathbf{k}$ as required.

Ultimately, the Hamiltonian is sought in the strained coordinates as this is the physical system of the potential $\hat{V}(\mathbf{r}')$. This calls for the rapidly varying cell periodic term $u_{n\mathbf{k}'}(\mathbf{r}')$

⁴braces are used for axes normal to a surface or growth plane {hkl}

as eigenstates of a sub-group of the unstrained crystal. Since one seeks the dispersion in the unstrained coordinates of the unperturbed Hamiltonian; $E(\mathbf{k})$, *strain is added as a perturbation*. In analogy with Equation 1.15 we may make the assertion;

$$\hat{\mathbf{p}}'\psi_{n\mathbf{k}'}(\mathbf{r}') = (\hat{\mathbf{p}} + \boldsymbol{\epsilon}\hat{\mathbf{p}} + \hbar\mathbf{k})\psi_{n\mathbf{k}}(\mathbf{r}) \quad (1.25)$$

$$\hat{V}(\mathbf{r}')\psi_{n\mathbf{k}'}(\mathbf{r}') = \left(\hat{V}(\mathbf{r}) + \hat{V}_{\epsilon}(\mathbf{r})\right)\psi_{n\mathbf{k}}(\mathbf{r}) \quad (1.26)$$

Consequently one sees that $\hat{\mathbf{p}}'^2 \rightarrow \hat{\mathbf{p}}^2 + 2\mathbf{k} \cdot \hat{\mathbf{p}} + \mathbf{k}^2 + 2(\mathbf{k} \cdot \boldsymbol{\epsilon}\hat{\mathbf{p}} + \hat{\mathbf{p}} \cdot \boldsymbol{\epsilon}\hat{\mathbf{p}})$ by recalling that strain is small. One may realise the first term as the unperturbed Hamiltonian, with the second and third terms the familiar $\mathbf{k} \cdot \hat{\mathbf{p}}$ perturbation and free electron dispersion respectively. Within this framework, additional terms have been generated which scale with strain;

$$\hat{H}_{\epsilon} = \frac{1}{m_0} (\hbar\mathbf{k} \cdot \boldsymbol{\epsilon}\hat{\mathbf{p}} + \hat{\mathbf{p}} \cdot \boldsymbol{\epsilon}\hat{\mathbf{p}}) + \hat{V}_{\epsilon}(\mathbf{r}) \quad (1.27)$$

Clearly one may observe that the terms in the bracket transform according to rank-1 and -0 & -2 tensor operators respectively. We shall concern ourselves with the second term in the bracket and expand it as a series of spherical tensor operators. This allows us to solve the problem by again invoking Wigner-Eckart theorem.

$$\begin{aligned} \hat{\mathbf{p}} \cdot \boldsymbol{\epsilon}\hat{\mathbf{p}} &= (\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz})\hat{p}_0^0 + \left(\sqrt{\frac{2}{3}}\epsilon_{zz} - \frac{1}{\sqrt{6}}(\epsilon_{xx} + \epsilon_{yy})\right)\hat{p}_2^0 + \dots \\ &\dots + \frac{1}{2}(\epsilon_{xx} - 2i\epsilon_{xy} - \epsilon_{yy})\hat{p}_2^2 + \frac{1}{\sqrt{2}}(\epsilon_{zx} - i\epsilon_{yz})\hat{p}_2^1 + \dots \\ &\dots + \frac{1}{2}(\epsilon_{xx} + 2i\epsilon_{xy} - \epsilon_{yy})\hat{p}_2^{-2} - \frac{1}{\sqrt{2}}(\epsilon_{zx} + i\epsilon_{yz})\hat{p}_2^{-1} \end{aligned} \quad (1.28)$$

The first term; hydrostatic strain, transforms as a scalar operator. However, one is left with a conundrum since $\hat{H}_{\epsilon}$ is a perturbation at the zone centre, the point group of the strained crystal reverts to a sub-group of the unstrained crystal lifting heavy and light hole degeneracy (Chapter 5). Indeed the application of uniaxial or biaxial stress to cubic crystals in the cyclotron resonance experiment [42] allows for greater accuracy in the measurement of effective masses.

For growth of heterostructures the constraint of biaxial stress provides experimental challenges in generating strain balanced dislocation free samples. While modern growth techniques allow for great control over layer by layer compositional variation, growth remains quite a dark art reserved to the experienced few.

1.3.2 Envelope Function Approximation

In the derivation of the $\hat{H}_{\mathbf{k}\cdot\hat{\mathbf{p}}}$ and $\hat{H}_\epsilon$ perturbations the assertion was made that the wave function was separable into a rapidly varying cell periodic term and a slowly varying envelope function; the Bloch function. Bloch functions are a special case based on translational symmetry giving rise to the good quantum numbers k_x , k_y and k_z . Using the EFA, the wave function may be expressed in the more general form as;

$$\psi_n(\mathbf{r}) = u_n(\mathbf{r})F(\mathbf{r}) \quad (1.29)$$

where the rapidly varying term still transforms according to the point group of the crystal provided the expansion is about the zone centre⁵, but the envelope function $F(\mathbf{r})$ does not necessarily represent the translational sub-group. In order for the wave function to become separable, one must neglect all non-local crystal potential terms outside the FBZ [10]. Under this formalism one may invoke;

$$\hat{\mathbf{p}}\psi_n(\mathbf{r}) = \hat{\mathbf{p}}u_n(\mathbf{r})F(\mathbf{r}) = -i\hbar \left(\left(\hat{\nabla}u_n(\mathbf{r}) \right) F(\mathbf{r}) + u_n(\mathbf{r}) \left(\hat{\nabla}F(\mathbf{r}) \right) \right) = \left(\hat{\mathbf{p}} + \hbar\hat{\mathbf{k}} \right) \psi_n(\mathbf{r}) \quad (1.30)$$

where the main result is the retention of the differential operator form of $\hat{\mathbf{k}}$, such that for example $\hat{k}_z = -i\frac{\partial}{\partial z}$ acting on the envelope function. The $\mathbf{k} \cdot \hat{\mathbf{p}}$ perturbation is restored in the event of the infinite lattice with translational symmetry as required.

This more general approach allows for the application to heterostructures [39] through a piecewise construction of semi-infinite Hamiltonians coupled between adjacent unit cells by the differential operator $\hat{\mathbf{k}}$. For the case of quantum wells, the good in-plane quantum numbers are restored, such that $F(\mathbf{r}) = e^{i(k_x x + k_y y)}F(z)$ where confinement is chosen along the conventional growth axis. Solutions to the unperturbed Hamiltonian represented by the spatial *band edge* of the system $V(z)$ at the zone centre become;

$$\left(-\frac{\hbar^2}{2m_0} \frac{\partial^2}{\partial z^2} + V(z) \right) F(z) = EF(z) \quad (1.31)$$

The position dependent band edge of valence and conduction bands may be tailored by material dependent layer by layer growth to fabricate quantum confinement. There are two distinct cases of band edge alignment; straddling (type-I) and staggered (type-II). The former is favourable for quantum well systems since the spatial overlap of confined electrons and holes is strong. Germanium rich systems are type-I; suitable for devices such as optical modulators [41], whereas Silicon rich schemes are type-II [43]; making them suitable for devices such as unipolar quantum cascade lasers [44] instead.

⁵ $u_n(\mathbf{r}) \equiv u_{n\mathbf{k}=0}(\mathbf{r})$

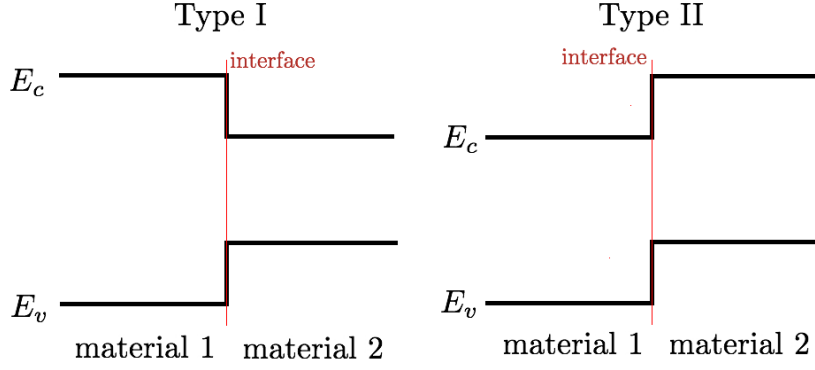


FIGURE 1.4: Band edge diagram sketch showing straddling (type-I) and staggered (type-II) alignment schemes for conduction and valence band offsets. There also exists the broken (type-III) scheme as an extreme form of type-II; where E_v in material 2 overlaps with E_c in material 1.

Boundary conditions of the envelope function and its derivative require continuity of the Hamiltonian either side of the abrupt interface. The most simple example of this is the Bastard boundary condition [45] with a position dependent effective mass $m^*(z)$.

$$\left(-\frac{\partial}{\partial z} \frac{\hbar^2}{2m^*(z)} \frac{\partial}{\partial z} + V(z) \right) F(z) = EF(z) \quad (1.32)$$

While this is suitable for the single particle in a box model, knowledge that the valence band maxima is degenerate calls for the DKK and Luttinger-Kohn effective mass Hamiltonians. Furthermore, the solutions to this problem are the specific case at the zone centre ($k_x = k_y = 0$). To obtain the in-plane dispersion relation operator ordering schemes for terms linear in $\hat{k}_z$ are required to match boundary conditions across an abrupt interface such as the ones presented by Foreman [46]. However, the method relies on the adapted double group formulation through a unitary transformation of an ordered DKK effective mass Hamiltonian. Using the double group formulation of $\mathbf{k} \cdot \hat{\mathbf{p}}$ theory prescribed in this thesis; obtaining operator ordered effective mass Hamiltonians reduces to a series of rather simple matrix multiplications (Chapter 6).

1.3.3 The Quantum Well

The motivation of this thesis to model SiGe alloy heterostructures calls for a culmination of all the arguments presented so far in this introductory chapter. We use the specific example of the compressively strained 12nm Germanium well sandwiched between tensile strained $Si_{0.15}Ge_{0.85}$ barriers on a $Si_{0.1}Ge_{0.9}$ -{001} virtual substrate [47] for the potential widespread application as a practical device. Band edges and envelope functions of the lowest energy sub-band states are shown in Figure 1.5.

Since strain lifts the degeneracy of heavy and light holes; eigenvalues of the strain Hamiltonian represent quasi-band edges in model solid theory [48]. This is a consequence of adding strain as a perturbation to the unstrained unperturbed Hamiltonian.

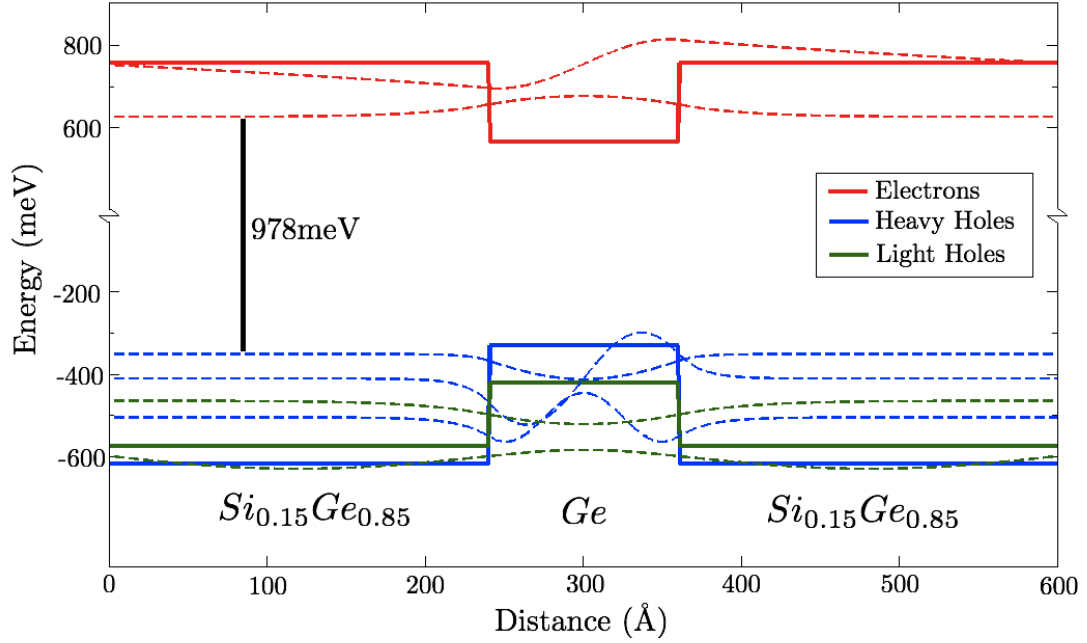


FIGURE 1.5: Band edges and envelope functions of lowest energy sub-band states for a compressively strained 12nm Germanium well sandwiched between tensile strained $Si_{0.15}Ge_{0.85}$ barriers on a $Si_{0.1}Ge_{0.9}$ -{001} virtual substrate at 0K

Such a flat band scheme assumes that there is no population of charge; frozen at 0K, nor doping otherwise a self consistent Schrödinger-Poisson solver may be called for. Sub-band dispersion may be obtained by scanning a region of reciprocal space along high symmetry axes. Joint density of states may be evaluated by taking a histogram of the dispersion for the octant region $0 \leq k_x \leq k_y$. Consequently the absorption spectra may also be found by incorporating overlap integrals of valence and conduction band envelope functions. Comparing with experimental photoluminescence spectra [49, 50] provides a validation of the theory such that theory may in turn propose devices tailored to needs (Chapter 7).

The introduction of a static electric field induces a red-shift in the absorption spectra such that the device switches between transparent and absorbing for a narrow wavelength range to encode bits of information onto an optical signal. This is in essence the principle of the optical modulator device operating under the QCSE [51]. Using Germanium rich wells [52, 53] one preys on the direct-gap energy 890meV; close to $1.5\mu\text{m}$ used in 3rd generation fibre optic communication channels for widespread technological applications.

1.4 Overview of the Thesis

Many of the arguments on the $\mathbf{k} \cdot \hat{\mathbf{p}}$ method use extensive group theoretical arguments as Diamond type cubic crystals characterise O_h point group symmetry. Symmetrised integer, $|L, m_L\rangle$ eigenstates may be used to construct a matrix Hamiltonian under the single group formulation. The inclusion of the relativistic spin-orbit interaction as a perturbation lifts the degeneracy such that eigenstates transform according to the adapted double group $|L, m_L\rangle \otimes \{\uparrow, \downarrow\}$, where half integer spin is incorporated through $\mathbf{L} \cdot \mathbf{S}$ coupling. In the double group formulation of $\mathbf{k} \cdot \hat{\mathbf{p}}$ theory; symmetrised half-integer $|J, m_J\rangle$ eigenstates are used to construct a matrix Hamiltonian where the spin-orbit interaction is included in the unperturbed Hamiltonian.

Before the task in hand may be tackled there is a lot of prior work on abstract mathematical group theory that must be undertaken in Chapter 2; *Group Theory in Cubic Crystals*. Unfortunately there is a lot of terminology and notation such as symmetry classes, irreducible representations and invariant characters to name but a few; which must be introduced for later work to make complete sense. The goals are to find such symmetrised integer and half-integer eigenstates of the point and double groups respectively, which is done in Chapter 3; *Symmetrised Basis Functions*. These symmetrised eigenstates are extensively used in Wigner-Eckart theorem for evaluating matrix elements with an operator when cast as projections of a spherical tensor operator as set out in this introductory chapter.

Group theory is of crucial importance as symmetry plays a major role in understanding how the Hamiltonian is constructed and it's transformation properties; which is why it is essential to dedicate a lot of attention to it. For example, in the theory of invariants, the only prior assumption is that the Hamiltonian transforms according to the space group of the crystal. From this the Hamiltonian may be constructed out of the product of irreducible perturbation components and linearly independent generator matrices, with an associated invariant. Such a technique relies on symmetrised tensor product decompositions which may be determined purely from multiplication tables and the character decomposition of irreps. The overlap of results of the theory of invariants with the $\mathbf{k} \cdot \hat{\mathbf{p}}$ method underpins the significant importance group theory plays in understanding electronic structure in a crystal.

In Chapter 4; *Double Group Formulation of $\mathbf{k} \cdot \hat{\mathbf{p}}$ Theory*, symmetrised eigenstates are used to construct a 30×30 $\mathbf{k} \cdot \hat{\mathbf{p}}$ matrix Hamiltonian with appropriate scaling parameters to return full zone band diagrams for bulk Silicon and Germanium. The indirect conduction band-gap is returned as a function of SiGe alloys such that a kink is returned in agreement with experimental near band-gap photoluminescence and bulk electron bulk mobilities. Using the Löwdin renormalisation procedure; 4-, 6- and 8-band Hamiltonians may be returned such that heavy hole, light hole and spin-orbit effective masses for Silicon and Germanium may be evaluated; in broad agreement with those determined

from experiment. It is shown how not only does the double group formulation serve as an improvement to the single group and adapted double group formulations, but also as a more concise and coherent mathematical treatment of the spin-orbit interaction.

As the work on bulk Silicon and Germanium evolves into work on heterostructures, the *Extension to Strained Systems* in Chapter 5 is considered. Strain provides both theoretical, through the Pikus-Bir Hamiltonian, and experimental, through the growth of dislocation free structures, constraints that must be considered for real devices. It is shown how biaxial stress in the plane of the growth surface arises when two layers with different lattice constants are pseudomorphically grown and a generalised Poisson ratio, relating in- and out-of-plane strains, for an arbitrary growth axis is generated. Band edge alignment in strained heterostructures is discussed with a view of matching conduction and valence band edges in a type-I fashion for compressively strained Germanium quantum wells.

The improvement of the accuracy of modelling techniques to reproduce experimentally observed results is not only an intellectual pursuit but also offers solutions to current practical problems. As implied in the title, this thesis is primarily concerned with ‘*Modelling of Silicon-Germanium Alloy Heterostructures using Double Group Formulation of $\mathbf{k} \cdot \hat{\mathbf{p}}$ Theory*’. In understanding SiGe alloy properties, enhancements and proposals may be made for devices such as optical detectors and modulators. This is the main point of interest in Chapter 6; *Application to Heterostructures*.

Numerical modelling of holes through a piecewise construction of 4-, 6- and 8- band block Hamiltonians under the EFA may be performed with the correct boundary conditions across an abrupt interface. Confinement energy and dispersion may be tailored through well width, depth and with the inclusion of strain; the choice of virtual substrate. Extension to model both electrons and holes through the use of an 8-band Hamiltonian is used to model a Germanium well sandwiched between $Si_{0.15}Ge_{0.85}$ barriers on an $Si_{0.1}Ge_{0.9}$ -{001} virtual substrate. Consequently the onset of absorption may be tailored such that the device exhibits the QCSE around $1.5\mu m$ at room temperature. Indeed such a device operation has been shown recently experimentally in the literature and provides results on which to compare theoretical calculations.

One of the beauties of the double group formulation of $\mathbf{k} \cdot \hat{\mathbf{p}}$ theory renders the subject of coordinate transformations a rather simple task of matrix multiplication with appropriate treatment of the transformation properties of half-integer spin. Agreement with the canonical transformation of the theory of invariants in the bulk is testament to this, with the additional advantage that the correct boundary conditions of operator ordered Hamiltonians for an arbitrary growth plane may be returned. Under such a framework, strain balanced heterostructures grown on non-trivial high index {011} and {111} surfaces may be modelled with interesting results regarding polarisation spectroscopy and changes in transition energies.

Chapter 2

Group Theory in Cubic Crystals

An object possesses symmetry if there is a general transformation which leaves the object unchanged. Symmetry operations which leave an object unchanged may be discrete, such as 90° rotations of a square, or continuous, for the case of infinitesimal rotations of a circle. Such transformations are of fundamental concern in physical laws as objects retain their form both before and after, for example; the invariance of the speed of light between rest and relativistic frames gives rise to the Lorentz transformations. The Lorentz transformations are examples of geometrical symmetries, but there also may exist internal symmetries such as spin.

Noether's Theorem links symmetry and conservation laws, such as gauge invariance in relation to total electric charge conservation. The arrangements of atoms in molecules or in crystalline solids affect many aspects of electronic and vibrational properties and also response to external thermal, mechanical and electromechanical perturbations. Bloch's treatment of wave-function invariance with respect to translational symmetry between unit cells in a crystal is one of the most poignant uses of symmetry in solid state physics as documented in numerous textbooks [2, 3, 19, 22, 54, 55].

Upon further implementation of group theory in crystals, one can construct further matrix element selection rules [56, 57] and macroscopic tensors [58] that behave in accordance with the point group. In this chapter, abstract mathematical group theory is introduced; from which the bulk of arguments in this thesis are based, and provides the mathematical toolbox from which to construct symmetrised Hamiltonians transforming according to the full space group of the crystal.

2.1 Finite Groups

Groups can be divided into two categories; discrete or continuous. The fundamental *Axioms of Group Theory* are applied to both, but there are some subtle differences in their manipulation. Continuous groups are infinite, whereas not all discrete groups are finite; in this section discrete groups will be introduced for continuous groups to be reviewed later.

Here the fundamentals of abstract mathematical group theory are laid out, with a worked example; the symmetric equilateral triangle. Application to cubic crystals with Tetrahedral (T_d) and Octahedral (O_h) point groups is discussed from the point of view of the significance of inversion.

2.1.1 Elements of Group Theory

There is a basic algebraic structure based on transformations to describe symmetry. A group, G , is a set of elements $\{e, a, b, \dots\}$ together with a composition law such as multiplication and addition. The conditions that a group must satisfy are the four fundamental axioms;

Closure The composition of any two elements is itself an element $ab = c$ in the group

Associativity For all elements a, b , and c in the group; $(ab)c = a(bc)$

Identity There exists a unique element e known as the identity¹ or unit element such that $ae = ea = a$ for all elements in the group

Inverse For every element a in the group there is a unique inverse a^{-1} , such that $aa^{-1} = a^{-1}a = e$

Closure ensures that the composition law does not generate any elements outside of the group. Associativity implies that the computation of an n -fold product of group elements does not depend on how the elements are themselves grouped together.

If a group has multiplication $ab = ba \forall a, b \in G$, it is said to be an *Abelian group*, or commutative. For example, translational invariance in an infinite crystal gives rise to the Bloch theorem, such that the group of the wave vector $\mathbf{k}$ [22] take the infinite roots of unity. Not only is the group of $\mathbf{k}$ an example of an Abelian group, but also an infinite discrete group.

The permutation group, S_3 , will now be introduced, not only as an example in abstract mathematical group theory, but also as the symmetry group of a three pointed object;

¹The German for unity is 'einheit'

an equilateral triangle. All permutations or symmetry operations of three ordered distinguishable objects give rise to a total of six unique elements, displayed in Figure 2.1. The order is the number of elements in a group; $|S_3| = 6$, and this group is not Abelian since $ab \neq ba$.

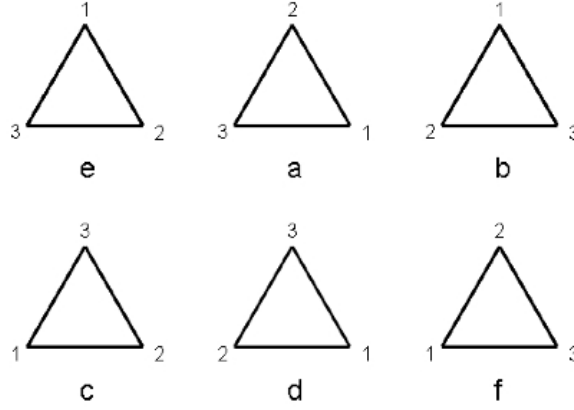


FIGURE 2.1: Symmetry operations for a three pointed object, permutation group S_3 ; visualised as the equilateral triangle

Elements a , b , and c are mirror operations, whereas d , and f are clockwise rotations by 120° and 240° respectively. The element e satisfies the identity axiom in that it trivially leaves the object unchanged, and in that respect may be thought of as a rotation by 0° or integer multiples of 360° .

A *composition table* of the operations of the permutation group, S_3 , can be constructed, and organised in such a way that elements form classes of the whole group. Clearly, Table 2.1 satisfies all of the fundamental axioms. Composition tables may seem complex at first, but when considering that Su-Doku is an example of a 9-element abstract group; such tables become no more than mathematical puzzles.

	e	a	b	c	d	f
$e (= e^{-1})$	e	a	b	c	d	f
$a (= a^{-1})$	a	e	d	f	b	c
$b (= b^{-1})$	b	f	e	d	c	a
$c (= c^{-1})$	c	d	f	e	a	b
$d (= f^{-1})$	d	c	a	b	f	e
$f (= d^{-1})$	f	b	c	a	e	d

TABLE 2.1: Composition table for the three pointed object permutation group S_3 . Complete with inverses [55]. Elements have been demarcated into their respective conjugacy classes; identity $\{E\}$, reflections $\{3\sigma_v\}$ and 120° rotations $\{2C_3\}$

2.1.2 Conjugacy Classes

Element a is conjugate to element b since it satisfies the requirement $b = aba^{-1} = bca^{-1}$. Furthermore, element b is conjugate to element c since $c = acb^{-1} = bcb^{-1}$, and also

element c is conjugate to element a . As such, elements a , b , and c form a class of operation, which is clear from the fact they are all mirror operations in a physical sense. Rotation elements d and f are conjugates of one another and as such form a class. The identity, e , always forms a trivial sub-group, and a class on its own, as do all elements in an Abelian group.

Spotting classes from the composition table is not always so easy, especially without a physical object to relate to. Table 2.1 has been arranged in such a way that makes it slightly clearer; from the way that any two subsequent rotation or mirror operations always returns the identity or rotation operations, and how a combination of rotation and mirror operations always returns a mirror operation.

There are numerous ways of labelling classes to attribute them to their physical effect, and this thesis will remain self consistent in its labelling. In Schönflies notation the identity e is denoted by the label E , and reflections are denoted by $\sigma_{h/v}$ where h/v denote horizontal/vertical reflections. Proper rotations are denoted by C_n where n is the order of rotation; such that the rotation angle is equivalent to $360^\circ/n$. For example, C_2 is a rotation by 180° , C_4 is a rotation by 90° , and so forth. The number of elements within the class precede the Schönflies label, so for example in the permutation group, S_3 , the classes of operation are $\{E\}$, $\{3\sigma_v\}$ and $\{2C_3\}$.

While there are infinite number of possible C_n in linear molecules for rotations within a crystal only C_2 , C_3 , C_4 and C_6 are permitted through the crystallographic restriction theorem [16], which states;

$$\cos(\theta) = \frac{1 - p}{2} \quad (2.1)$$

where $p = 0, \pm 1, +2, +3$; returning the aforementioned, C_n , finite rotations in a crystal plus the identity, E . While C_5 operations are not permitted in macroscopic crystals, elements may be present in icosahedral groups characterising quasi-crystals such as carbon nano-tubes.

One important class of operation is the *improper rotation*, which is a proper rotation followed by a reflection; $S_n = \sigma_{h/v}C_n$. While at this stage the difference may seem insignificant they are key to understanding parity differences between even and odd basis functions. For example, a polar vector is odd, in that its sign changes under a mirror operation, whereas this is not the case for axial vectors; while both may transform the same under a proper rotation. To understand the concept of manifolds and vector spaces, one must introduce the *irreducible representation* through invariant characters to convey their transformation properties.

The final crystallographic symmetry operation permitted is the inversion operation, i , present in centro-symmetric crystals, whose effect is to reverse the sign of polar vectors;

$i\mathbf{r} = -\mathbf{r}$. Like improper rotations, inversion is odd and gives rise to parity selection rules.

In total there are 32 unique combinations of crystal classes, summarised in Table 2.2. It is no coincidence that there are also 32 crystal point groups, each composed of a variety of classes ranging from the high-symmetry cubic; T_d and O_h groups, to the low symmetry triclinic group.

Operation	Name	
E	Identity	rotation by 0°
$\sigma_{h/v}$	Reflection	horizontal/vertical
C_n	Proper Rotation	$180^\circ/n$
S_n	Improper Rotation	$\sigma_{h/v}C_n$
i	Inversion	$i\mathbf{r} = -\mathbf{r}$

TABLE 2.2: Summary of the crystallographic point group classes of operation

2.1.3 Irreducible Representations

A representation of a group, G , under ordinary matrix multiplication, in an n -dimensional environment, is a set of $n \times n$ non-singular complex matrices. The representation is said to be ‘faithful’ or ‘unfaithful’ depending on whether the representation is *isomorphic* or *homomorphic* to the original group G . Such matrix representations, denoted $\mathbf{D}(g)$; corresponding to the element $g \in G$ satisfy the composition table of the group.

While the definition has thus far been quite vague this allows for considerable flexibility in that representations are not unique. A *similarity transformation* is one which preserves the trace of the matrix with some other significant consequences. Suppose a representation matrix of an element g can be brought into block diagonal form by a similarity transformation; $A\mathbf{D}(g)A^\dagger = \mathbf{D}'(g) \oplus \mathbf{D}''(g) \forall g \in G$, where A is an orthogonal matrix; $\mathbf{D}(g)$ is reducible, otherwise it is *irreducible* in accordance with Schur’s two lemmas [54].

For example; reducible representations of the permutation group, S_3 , which satisfy the composition table are;

$$\begin{aligned} \mathbf{D}(e) &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, & \mathbf{D}(a) &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, & \mathbf{D}(b) &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \\ \mathbf{D}(c) &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, & \mathbf{D}(d) &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, & \mathbf{D}(f) &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \end{aligned} \quad (2.2)$$

The irreducible matrix representations $\mathbf{D}'(g)$ and $\mathbf{D}''(g)$ are trivial to find, with the former being the scalar, identity, irreducible representation (irrep), and the latter being the parity irrep due to the signs of matrices of odd operations such as mirrors.

The number of irreps must equate to the number of classes; for which the permutation group, S_3 , has three. There exists an additional set of irreps which also satisfy the composition table of the group, and these are;

$$\begin{aligned} \mathbf{D}(e) &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, & \mathbf{D}(a) &= -\frac{1}{2} \begin{pmatrix} -1 & \sqrt{3} \\ \sqrt{3} & 1 \end{pmatrix}, & \mathbf{D}(b) &= \frac{1}{2} \begin{pmatrix} 1 & \sqrt{3} \\ \sqrt{3} & -1 \end{pmatrix} \\ \mathbf{D}(c) &= \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}, & \mathbf{D}(d) &= -\frac{1}{2} \begin{pmatrix} 1 & \sqrt{3} \\ -\sqrt{3} & 1 \end{pmatrix}, & \mathbf{D}(f) &= -\frac{1}{2} \begin{pmatrix} 1 & -\sqrt{3} \\ \sqrt{3} & 1 \end{pmatrix} \end{aligned} \quad (2.3)$$

Unlike the previous case; these unitary matrices are irreducible, and make up the third and final irrep. Note that the trace of the matrices under mirror operations is zero, and as such; whereas the identity and parity irreps transform like polar and axial vectors respectively, this irrep may transform like either.

One important consequence of irreps is the great orthogonality theorem (GOT), which implies that the vector spaces of inequivalent irreps, labelled Γ_i , are orthogonal for namesake;

$$\sum_{g \in G} \left(\mathbf{D}_{kl}^{(\Gamma_i)}(g) \right)^* \mathbf{D}_{k'l'}^{(\Gamma_j)}(g) = \frac{|G|}{d} \delta_{k,k'} \delta_{l,l'} \delta_{\Gamma_i, \Gamma_j} \quad (2.4)$$

The dimension, d , is found from the trace of the identity $\mathbf{D}(e)$, such that the identity and parity irreps are each 1-dimensional and the final irrep is 2-dimensional; consistent with the GOT; since $1^2 + 1^2 + 2^2 = 6$, equivalent to the order of the group, $|S_3|$. The concept of dimensionality and degeneracy of energy eigenstates are complementary, and from this help understand the nature of energy levels in real molecules and crystals.

2.1.4 Character Tables

As implied by the similarity transformation; the invariant property is the trace or *character* across elements of the same conjugacy class. Characters can be assembled in tabular form, with entries for the class and irrep. Using the axioms of group theory, one enters the characters for the identity irrep; which are 1 for all classes, and the characters for the identity class; which are the dimensionality. The GOT is then used to fill in the remaining entries.

The character table for the permutation group, S_3 , is shown in Table 2.3. Comparing the traces of the matrices given in Equations 2.2 and 2.3 all of the above criteria are satisfied.

While there is no unique set of basis functions for a given irrep, it is often useful to list some important and commonly occurring sets which have important physical properties.

	$\{E\}$	$\{3\sigma_v\}$	$\{2C_3\}$	Basis Functions
Γ_1	1	1	1	$\{L_z\}$
Γ_2	1	-1	1	$\{z\}$
Γ_3	2	0	-1	$\{L_x, L_y\}, \{x, y\}$

TABLE 2.3: Character table for the permutation group, S_3 , of the equilateral triangle, complete with polar; $\{x, y, z\}$, and axial (pseudo); $\{L_x, L_y, L_z\}$, vectors

In Table 2.3 both polar; $\{x, y, z\}$ and axial (pseudo); $\{L_x, L_y, L_z\}$ vectors have been included, which transform according to $\Gamma_2 \oplus \Gamma_3$ and $\Gamma_1 \oplus \Gamma_3$ respectively. Their differences can be attributed to the sign of the character of mirror, or more generally, odd operations.

While character tables are extremely useful it is important to note that in listing characters other useful properties of representation matrices have been lost. The projection operator technique [54] is a useful technique to obtain general basis functions which transform according to the relevant irrep using full representation matrices $\mathbf{D}(g)$.

$$\hat{P}^{(\Gamma_i)} = \frac{d}{|G|} \sum_{g \in G} \mathbf{D}^{(\Gamma_i)}(g) \hat{P}_g \quad (2.5)$$

where $\mathbf{D}^{(\Gamma_i)}(g)$ is the $d \times d$ matrix for the Γ_i irrep for $g \in G$. $\hat{P}_g$ is the element operator, g , acting on an arbitrary function. For example, consider the equilateral triangle to lie in the xy plane with the z axis normal. Under the identity and rotation operations, z is unchanged; $\hat{P}_e z = \hat{P}_d z = \hat{P}_f z = z$, whereas reflections invert the axis; $\hat{P}_a z = \hat{P}_b z = \hat{P}_c z = -z$. Invoking Equation 2.5 with the Γ_2 representation matrices the only non-zero result is $\hat{P}^{(\Gamma_2)} z = z$, and hence z is an appropriate basis function for Γ_2 . Knowing the transformation properties of x and y under symmetry operations; then any arbitrary function can be evaluated in terms of the irrep to which it transforms. The downside to this technique is normalisation is not necessarily preserved and anti-symmetric contributions may be missed, but the projection operator technique still has many very important uses.

2.1.5 T_d and O_h Single Groups

sp^3 hybridisation in Zinc-blende type crystals gives rise to tetrahedral bond coordination which characterise the point group of binary III-V crystals such as GaAs. Diamond type crystals possess an extra inversion operation such that octahedral geometry characterises the point group of group-IV crystals such as C, Si, Ge, α Sn. The molecular analogue of tetrahedral geometry is the methane molecule CH_4 ², with bonding angles of 109.5° .

²the molecular analogue of octahedral, O_h , geometry is Sulphur Hexafluoride, SF_6 [54]

Projections of the molecule along one of the six (001) directions returns a square, and along one of the eight (111) directions returns an equilateral triangle, as depicted below.

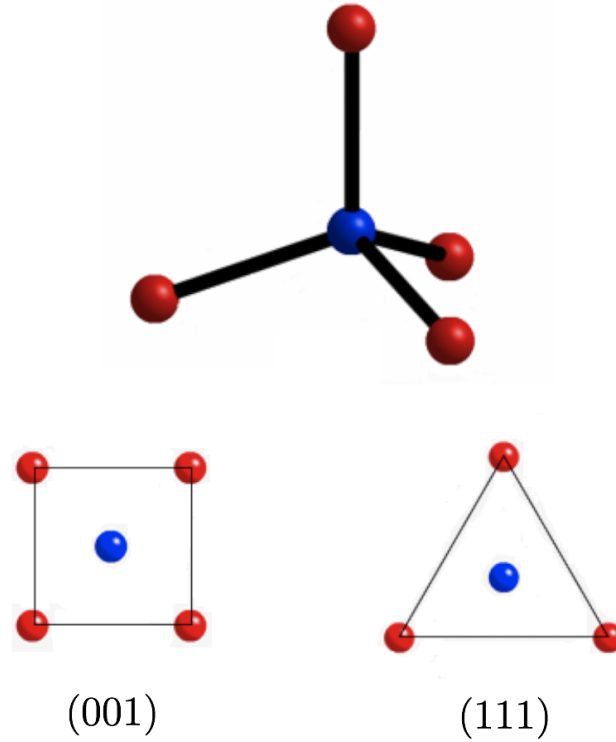


FIGURE 2.2: Projections of squares and triangles for the tetrahedrally coordinated sp^3 hybridised CH_4 molecule along one of the sixfold (001) and eightfold (111) directions. Figure generated using *CrystalMaker*[®] software (<http://www.CrystalMaker.com>)

There is a total of 24 elements in the T_d group, which can be grouped into five classes $\{E\}$, $\{3C_2\}$, $\{8C_3\}$, $\{6S_4\}$, and $\{6\sigma_v\}$, whose origination is from the relevant projection. Of the five irreps there are two 1 dimensional, one 2 dimensional and two 3 dimensional³, as indicated by the character of the identity class. Subsequent characters are found using the GOT.

	$\{E\}$	$\{3C_2\}$	$\{8C_3\}$	$\{6S_4\}$	$\{6\sigma_v\}$	Basis Functions
Γ_1	1	1	1	1	1	$\{x^2 + y^2 + z^2\}$
Γ_2	1	1	1	-1	-1	
Γ_3	2	2	-1	0	0	$\{\frac{1}{2}(x^2 - y^2), \frac{1}{\sqrt{3}}(z^2 - \frac{1}{2}(x^2 + y^2))\}$
Γ_4	3	-1	0	1	-1	$\{L_x, L_y, L_z\}$
Γ_5	3	-1	0	-1	1	$\{x, y, z\}, \{yz, zx, xy\}$

TABLE 2.4: Character table for the T_d point group, complete with some important basis functions [2]

Γ_1 and Γ_2 characterise one dimensional scalar identity and parity representations respectively. The Γ_5 irrep transforms like a cartesian polar vector, whereas Γ_4 transforms

$$\sum_i d_i^2 = 1^2 + 1^2 + 2^2 + 3^2 + 3^2 = 24 = |T_d|$$

like an axial vector in accordance with the sign of the $\{6S_4\}$ characters. While there are many mis-leading, confusing and conflicting labelling of irreps, this thesis is self consistent and as closely linked to that of Koster et al [59] as possible. All irreducible representation matrices are listed in the Appendix A for reference.

Inclusion of the inversion operation for the O_h group returns 10 classes and irreps; which now have an associated parity. O_h is isomorphic to T_d , and may be found by taking the direct product with the inversion factor group; $O_h = i \otimes T_d$. The significance of improper rotations and inversion becomes a problem in themselves; where the character table for O_h is arranged into quadrants such that the bottom right quadrant is the negative of the remaining three, which are of the form of Table 2.4.

This has the effect of interchanging Γ_1^- with Γ_2^- and Γ_4^- with Γ_5^- . This ever so subtle difference is the source of the much disputed labelling of irreps, but error propagation and mis-understanding of notation is rife.

	$\{E\}$	$\{3C_2\}$	$\{8C_3\}$	$\{6S_4\}$	$\{6\sigma_v\}$	$\{i\}$	$\{3\sigma_h\}$	$\{8S_6\}$	$\{6C_4\}$	$\{6iC_2\}$
Γ_1^+	1	1	1	1	1	1	1	1	1	1
Γ_2^+	1	1	1	-1	-1	1	1	1	-1	-1
Γ_3^+	2	2	-1	0	0	2	2	-1	0	0
Γ_4^+	3	-1	0	1	-1	3	-1	0	1	-1
Γ_5^+	3	-1	0	-1	1	3	-1	0	-1	1
Γ_2^-	1	1	1	1	1	-1	-1	-1	-1	-1
Γ_1^-	1	1	1	-1	-1	-1	-1	-1	1	1
Γ_3^-	2	2	-1	0	0	-2	-2	1	0	0
Γ_5^-	3	-1	0	1	-1	-3	1	0	-1	1
Γ_4^-	3	-1	0	-1	1	-3	1	0	1	-1

TABLE 2.5: Character table for the O_h point group arranged to convey compatibility with T_d

Since O_h has higher symmetry, the compatibility between groups descends from O_h . Polar vectors transform according to Γ_4^- in O_h since, as indicated by parity. Compare this with the vector $\{yz, zx, xy\}$; even under inversion, which transforms according to Γ_5^+ . The loss of inversion symmetry means that both $\{x, y, z\}$ and $\{yz, zx, xy\}$ transform according to Γ_5 in T_d . Parity accounts for effects such as the Raman tensor being zero in bulk Silicon, and non zero in Gallium Arsenide due to parity selection rules.

The important point to take here is that since T_d is a sub-group of O_h , irreps of T_d have an equivalent O_h irrep under the loss of inversion symmetry. Consequently we speak of the equivalence representation $\Gamma^{equiv} = \Gamma_1^+ + \Gamma_2^-$ which transforms according to the identity irrep of T_d . Compatibility will be returned to in greater detail in the next section, when considering infinite groups and chains of groups [60] as it leads to symmetrised basis functions expressible in terms of the eigenfunctions of spherical symmetry.

2.2 Infinite Groups

We may discuss symmetry operations in terms of finite elements by considering shapes such as squares or equilateral triangles, however certain objects possess continuous elements such as infinitesimal rotations of a circle. From the equation that characterises a circle the invariant property is the radius, and the perimeter traces a path whose angular dependence is expressed trigonometrically, or as a complex exponential. Conditions on the coordinate system which characterise the circle leads to a complex vector space which transforms under rotations by a phase factor. The orthogonal Lie group in 2-dimensions, is denoted $O(2)$, and for the case of spherical symmetry $O(3)$ due to the additional degree of freedom.

In this section, the special orthogonal group in 3 dimensions; $SO(3)$, and the special unitary group in 2 dimensions; $SU(2)$, are introduced and related to L and J quantum eigenstates for the Hydrogen atom without and with spin respectively. T_d and O_h double groups are introduced as a means of including spin to discrete groups such that half integer spin fermions can be treated in the appropriate manner. Group chains are discussed as a means of validating the use of symmetrised basis functions expressible in terms of the eigenfunctions of spherical symmetry

2.2.1 3D Special Orthogonal Group; $SO(3)$

A sphere is invariant under any rotation in three dimensions with the invariant property being the radius. Consider the real orthogonal bases before and after transformation to be $\{x, y, z\}$ and $\{x', y', z'\}$ respectively, with the norm-preserving constraint⁴. A suitable coordinate transformation is a rotation about the z -axis is expressible in terms of the Euler angle; θ , such that;

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos(\theta) & -\sin(\theta) & 0 \\ \sin(\theta) & \cos(\theta) & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \quad (2.6)$$

The special orthogonal rotation matrix, labelled $R_z(\theta)$ has determinant equal to positive unity, and since $R_z(\theta_1 + \theta_2) = R_z(\theta_1)R_z(\theta_2)$ the group is Abelian. A general rotation matrix, $R_i(\theta)$, may be expressed as a matrix exponential, whose exponent is the product of the angle θ and infinitesimal generator X_i , which satisfy the commutation laws of angular momentum⁵;

$$R_i(\theta) = e^{X_i\theta}; \quad [X_i, X_j] = \epsilon_{ijk}X_k \quad (2.7)$$

⁴ $x'^2 + y'^2 + z'^2 = x^2 + y^2 + z^2$

⁵ ϵ_{ijk} is the Levi-Civita symbol; +1 (-1) for even (odd) permutations of ijk and 0 otherwise

The infinitesimal generators are found from the Taylor series expansion, such that X_i form $(2L + 1)$ square matrices where $L = 0, 1, 2, \dots$. Euler rotations are the special case for orbital angular momentum, $L = 1$, with appropriate right-handed generators which are in accordance with the Euler-Rodrigues rotation formula;

$$X_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}, \quad X_y = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix}, \quad X_z = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (2.8)$$

What follows is the transition into spherical coordinates through a similarity transformation of the rotation matrix. This is done through an orthogonal matrix, A , which transforms $\{x, y, z\}$ into the complex basis $\{\frac{-1}{\sqrt{2}}(x - iy), z, \frac{+1}{\sqrt{2}}(x + iy)\}$ as given by Normand & Raynal [61].

$$\begin{pmatrix} e^{-i\theta} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{+i\theta} \end{pmatrix} = A \begin{pmatrix} \cos(\theta) & -\sin(\theta) & 0 \\ \sin(\theta) & \cos(\theta) & 0 \\ 0 & 0 & 1 \end{pmatrix} A^\dagger; \quad A = \begin{pmatrix} \frac{-1}{\sqrt{2}} & \frac{i}{\sqrt{2}} & 0 \\ 0 & 0 & 1 \\ \frac{1}{\sqrt{2}} & \frac{i}{\sqrt{2}} & 0 \end{pmatrix} \quad (2.9)$$

The rotation matrix is now diagonal, with quantised projections $m_L = 0, \pm 1$ arranged in order of the exponent of the matrix on the left hand side of Equation 2.9. The orthogonal matrix, A , assigns a quantisation direction, which in this case is the conventional z -axis and the phase is chosen such that the x -axis is real.

The trace is preserved; $\chi^{(1)}(\theta) = e^{-i\theta} + 1 + e^{i\theta} = 2\cos(\theta) + 1$, such that the proper rotations C_2 and C_3 have character; $\chi^{(1)}(180^\circ) = -1$, and; $\chi^{(1)}(120^\circ) = 0$, respectively. The improper rotations; S_4 has character; $(-1)^1 \times \chi^{(1)}(90^\circ) = -1$. Clearly the character of operations of the T_d group are compatible with those of Γ_5 , and the polar vector serves as an appropriate complete basis.

One is free to choose which space; cartesian or spherical, to work in and both have their pros and cons. For example, cartesian is popular as it is much easier to visualise conceptually, however mathematics tends to favour spherical coordinates through the use of Hermitian [62] orbital angular momentum operators since $L_i = i\hbar A X_i A^\dagger$;

$$L_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad L_y = \frac{i\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}, \quad L_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad (2.10)$$

Since L_z is diagonal it sets the conventional quantisation axis naturally, and L_i satisfy the commutation rules of angular momentum;

$$[L_i, L_j] = i\hbar\epsilon_{ijk}L_k, \quad \sum_{i=1}^3 L_i^2 = \mathbf{L}^2 \quad (2.11)$$

$\mathbf{L}^2$ is also diagonal, and as such eigenvectors expressed in the conventional Dirac-ket $|L, m_L\rangle$ notation return simultaneous eigenvalues of $\mathbf{L}^2$ and L_z . As hinted above, the use of orbital angular momentum operators lends itself to the computing of general L_i matrices through the use of ladder operators; $L_{\pm} = \frac{\mp 1}{\sqrt{2}}(L_x \pm iL_y)$.

So far the arguments concerning infinitesimal generators have been specific to $L = 1$, but a general expression for a diagonal rotation matrix in the spherical basis about the conventional quantisation axis takes the form;

$$R_z(\theta) = e^{-i\frac{L_z}{\hbar}\theta} = \begin{pmatrix} e^{-iL\theta} & 0 & \dots & 0 & 0 \\ 0 & e^{-i(L-1)\theta} & \dots & 0 & 0 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & \dots & e^{+i(L-1)\theta} & 0 \\ 0 & 0 & \dots & 0 & e^{+iL\theta} \end{pmatrix} \quad (2.12)$$

Eigenvectors span a $(2L+1)$ dimensional irreducible representation, whose vector space may be visualised as the spherical harmonics $Y_{L,m_L}(\theta, \phi)$ projected onto the cartesian space. The character for a proper rotation for a quantised eigenstate, L , is found from the trace of the matrix [54];

$$\chi^{(L)}(\theta) = e^{-iL\theta} + e^{-i(L-1)\theta} + \dots + e^{+i(L-1)\theta} + e^{+iL\theta} = \frac{\sin[(L + \frac{1}{2})\theta]}{\sin(\frac{1}{2}\theta)} \quad (2.13)$$

Using characters of proper and improper rotations one can evaluate the compatible irreps in T_d with $\text{SO}(3)$. Trivially $L = 0$ is compatible with Γ_1 and previously it was shown that $L = 1$ was compatible with Γ_5 . For the case of $L = 2$, the proper rotations C_2 and C_3 have character; $\chi^{(2)}(180^\circ) = 1$, and; $\chi^{(2)}(120^\circ) = -1$, respectively, and the improper rotation S_4 has character; $(-1)^2 \times (\chi^{(2)}(90^\circ)) = -1$. Consequently $\Gamma_3 \oplus \Gamma_5$ are compatible with $L = 2$, and appropriate second order basis functions were included in Table 2.4. In this case the degeneracy of $L = 2$ is lifted by the action of the T_d -ligand, or -crystal field due to the loss of spherical symmetry as depicted in Figure 2.3.

A compatibility table for orbital angular momentum up to and including $L = 6$ is shown below between the full rotation $\text{SO}(3)$ and Octahedral, O_h , groups, in accordance with Altmann et al [63]. Only the proper and improper rotations of the T_d group have been included since the associated parity on irreps depends only on whether L is even or odd. One important consequence of Table 2.6 is that sub-groups are not backwards compatible so L and m_L do not serve as good quantum numbers in T_d and O_h . $\Gamma_i^\pm$

irreps may constitute a linear combination of angular momentum eigenstates, hence the pure sp^3 paradigm fails in pseudopotential models of Silicon.

	L	$\{E\}$	$\{3C_2\}$	$\{8C_3\}$	$\{6S_4\}$	
S	0	1	1	1	1	Γ_1^+
P	1	3	-1	0	-1	Γ_4^-
D	2	5	1	-1	-1	$\Gamma_3^+ \oplus \Gamma_5^+$
F	3	7	-1	1	1	$\Gamma_2^- \oplus \Gamma_4^- \oplus \Gamma_5^-$
G	4	9	1	0	1	$\Gamma_1^+ \oplus \Gamma_3^+ \oplus \Gamma_4^+ \oplus \Gamma_5^+$
H	5	11	-1	-1	-1	$\Gamma_3^- \oplus 2\Gamma_4^- \oplus \Gamma_5^-$
I	6	13	1	1	-1	$\Gamma_1^+ \oplus \Gamma_2^+ \oplus \Gamma_3^+ \oplus \Gamma_4^+ \oplus 2\Gamma_5^+$

TABLE 2.6: Compatibility table between full rotation, $SO(3)$, and Octahedral, O_h , groups for $L = 0 \dots 6$ [54] using characters of classes $\{E\}$, $\{3C_2\}$, $\{8C_3\}$ and $\{6S_4\}$

Using appropriate angular momentum generator matrices and symmetrised basis functions; rotation matrices are block diagonalised under point group operations such that matrix representations of the O_h group are returned. With these the projection operator technique may be employed to obtain all higher order basis functions thereafter.

2.2.2 2D Special Unitary Group; $SU(2)$

While the irreps of the $SO(3)$ Lie group are appropriate to describe systems which possess rotational symmetries in 3 dimensions, it does not pertain to systems with internal degrees of freedom such as spin. The Pauli spin matrices satisfy the criteria for $1/2$ integer spin fermionic particles such as electrons;

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (2.14)$$

Defining $J_i = \frac{1}{2}\hbar\sigma_i$ then J_i satisfy the familiar commutation rules for angular momentum; $[J_i, J_j] = i\hbar\epsilon_{ijk}J_k$. Note that whenever integer and half-integer spin particles are manipulated the convention is to use L_i and J_i respectively to distinguish generators in both cases.

Special unitary rotation matrices, now labelled $U_i(\theta)$, are evaluated in a similar manner as the case for $SO(3)$, such that;

$$U_z(\theta) = e^{-i\frac{J_z}{\hbar}\theta} = \begin{pmatrix} e^{-\frac{1}{2}i\theta} & 0 \\ 0 & e^{+\frac{1}{2}i\theta} \end{pmatrix} \quad (2.15)$$

with the significant consequence being $U_z(360^\circ) = -U_z(0^\circ)$ due to the half integer in the exponent.

Where $\text{SO}(3)$ possesses the integer orbital angular momentum quantum number L , $\text{SU}(2)$ possesses the half integer total angular momentum quantum number; $J = 1/2, 3/2, 5/2, \dots$. One should also note the analogy between Equation 2.12 such that a general J may be employed in an equivalent fashion, and the formula for the character of a proper rotation, $\chi^{(J)}(\theta)$, in Equation 2.13 remains valid. We also now speak of $|J, m_J\rangle$ basis functions which characterise eigenvalues of $\mathbf{J}^2$ and J_z respectively.

The example using Pauli spin matrices is the special case $J = S = 1/2$, and we speak of spin-up and -down eigenstates $\{\uparrow, \downarrow\}$ as basis functions in accordance with their projections $m_S = \pm 1/2$. Through $\mathbf{L} \cdot \mathbf{S}$ Russell-Saunders coupling, basis functions expressible in terms of $|L, m_L\rangle \otimes \{\uparrow, \downarrow\}$ may be obtained for two cases; $J = L \pm S$, as given by Onodera & Okazaki [30];

$$|J, m_J\rangle = \begin{cases} +\sqrt{\frac{L+m_J+1/2}{2L+1}} |L, m_J - 1/2\rangle \uparrow + \sqrt{\frac{L-m_J+1/2}{2L+1}} |L, m_J + 1/2\rangle \downarrow; & J = L + S \\ -\sqrt{\frac{L-m_J+1/2}{2L+1}} |L, m_J - 1/2\rangle \uparrow + \sqrt{\frac{L+m_J+1/2}{2L+1}} |L, m_J + 1/2\rangle \downarrow; & J = L - S \end{cases} \quad (2.16)$$

where expressions preceding the $|L, m_J \pm 1/2\rangle$ are Clebsh-Gordan coefficients for this very specific case of $S = 1/2$. For example, consider the $L = 1$ state, which instead of becoming $2 \times 3 = 6$ fold degenerate under the inclusion of spin, becomes $2 \times 3 = 4 + 2$ fold degenerate;

$$\begin{aligned} J = 3/2 & \begin{cases} |3/2, +3/2\rangle = |1, +1\rangle \uparrow \\ |3/2, +1/2\rangle = \sqrt{\frac{2}{3}} |1, 0\rangle \uparrow + \sqrt{\frac{1}{3}} |1, +1\rangle \downarrow \\ |3/2, -1/2\rangle = \sqrt{\frac{1}{3}} |1, -1\rangle \uparrow + \sqrt{\frac{2}{3}} |1, 0\rangle \downarrow \\ |3/2, -3/2\rangle = |1, -1\rangle \downarrow \end{cases} \\ J = 1/2 & \begin{cases} |1/2, +1/2\rangle = -\sqrt{\frac{1}{3}} |1, 0\rangle \uparrow + \sqrt{\frac{2}{3}} |1, +1\rangle \downarrow \\ |1/2, -1/2\rangle = -\sqrt{\frac{2}{3}} |1, -1\rangle \uparrow + \sqrt{\frac{1}{3}} |1, 0\rangle \downarrow \end{cases} \end{aligned} \quad (2.17)$$

Expressing basis functions as $|L, m_L\rangle \otimes \{\uparrow, \downarrow\}$ or $|J, m_J\rangle$ has its advantages and disadvantages. The former is formulated out of the 2×3 degeneracy pertaining to that of the T_d and O_h single groups rather than the aforementioned $4 + 2$. However in the example above it is also possible to have $J = 1/2$ and $J = 3/2$ originating from $L = 0$ and $L = 2$ respectively, so one must be careful when considering spatial parity which may become ‘lost in translation’.

2.2.3 T_d and O_h Double Groups

Inclusion of spin to the T_d and O_h single groups introduces a new operation, which acts like the identity operation, E for integer spin particles, but differently for half integer spin particles. Where one may consider the identity operation to be a rotation by 0° , we now introduce the $\hat{E}$ operation [2], which is a rotation by 360° such that when considering half-integer fermionic particles $E = -\hat{E}$, in accordance with the $SU(2)$ group.

The number of symmetry operations in the group is now doubled, such that there are $24 \times 2 = 48$ in the T_d double group. In general, the number of classes is also doubled except for classes of operation involving rotations by 180° and/or mirror planes. Consequently there are 8, not 10 classes in the T_d double group. Accordingly there are 3 additional irreps, which form a character table shown in Table 2.7 in accordance with Dresselhaus [29] which has been condensed for brevity.

	$\{E\}$	$\{3C_2\}/\{3\hat{E}C_2\}$	$\{8C_3\}$	$\{6S_4\}$	$\{6\sigma_v\}/\{6\hat{E}\sigma_v\}$	$\{\hat{E}\}$	$\{8\hat{E}C_3\}$	$\{6\hat{E}S_4\}$
Γ_6	2	0	1	$\sqrt{2}$	0	-2	-1	$-\sqrt{2}$
Γ_7	2	0	1	$-\sqrt{2}$	0	-2	-1	$\sqrt{2}$
Γ_8	4	0	-1	0	0	-4	1	0

TABLE 2.7: Character table for double group irreps of the T_d group

For the O_h group, like previously the additional inversion operation leads to a doubling of the number of classes and irreps. A full double group character table for the O_h Group is shown in Table 2.9, arranged into quadrants where once again, the ordering on Γ_7^- and Γ_6^- is reversed.

One may now construct a double group compatibility table based on half-integer quantum numbers and double group irreps, where in this case the $\hat{E}$ operation adds 360° to the angle. So for example, where an C_3 operation invokes an angle $\theta = 120^\circ$, an $\hat{E}C_3$ operation uses an angle $\theta = 480^\circ$. In general $\chi^{(J)}(\theta) = -\chi^{(J)}(\theta + 2\pi)$.

As implied at the end of the previous section one must take care for improper rotations, since duplicate J may originate from even and odd orbital angular momentum, such that the factor $(-1)^L$ may be ± 1 for the same J .

J	$\{E\}$	$\{8C_3\}$	$\{6S_4\}$	$\{\hat{E}\}$	$\{8\hat{E}C_3\}$	$\{6\hat{E}S_4\}$	
$1/2$	2	1	$\pm\sqrt{2}$	-2	-1	$\mp\sqrt{2}$	$\Gamma_6^\pm$
$3/2$	4	-1	0	-4	1	0	$\Gamma_8^\pm$
$5/2$	6	0	$\mp\sqrt{2}$	-6	0	$\pm\sqrt{2}$	$\Gamma_7^\pm \oplus \Gamma_8^\pm$
$7/2$	8	1	0	-8	-1	0	$\Gamma_6^\pm \oplus \Gamma_7^\pm \oplus \Gamma_8^\pm$
$9/2$	10	-1	$\pm\sqrt{2}$	-10	1	$\mp\sqrt{2}$	$\Gamma_6^\pm \oplus 2\Gamma_8^\pm$

TABLE 2.8: Compatibility table between $SU(2)$ and Octahedral, O_h , double groups for $J = 1/2 \dots 9/2$ [54]. Trivial $\{3C_2\}/\{3\hat{E}C_2\}$ characters have been omitted

	$\{E\}$	$\{3C_2\}/\{3\hat{E}C_2\}$	$\{8C_3\}$	$\{6S_4\}$	$\{6\sigma_v\}/\{6\hat{E}\sigma_v\}$	$\{\hat{E}\}$	$\{8\hat{E}C_3\}$	$\{6\hat{E}S_4\}$	$\{i\}$	$\{3\sigma_h\}/\{3\hat{E}\sigma_h\}$	$\{8S_3\}$	$\{6C_4\}$	$\{6iC_2\}/\{6\hat{E}iC_2\}$	$\{\hat{E}i\}$	$\{8\hat{E}S_3\}$	$\{6\hat{E}C_4\}$
Γ_1^+	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Γ_2^+	1	1	1	-1	-1	1	1	-1	1	1	1	-1	-1	1	1	-1
Γ_3^+	2	2	-1	0	0	2	-1	0	2	2	-1	0	0	2	-1	0
Γ_4^+	3	-1	0	1	-1	3	0	1	3	-1	0	1	-1	3	0	1
Γ_5^+	3	-1	0	-1	1	3	0	-1	3	-1	0	-1	1	3	0	-1
Γ_6^+	2	0	1	$\sqrt{2}$	0	-2	-1	$-\sqrt{2}$	2	0	1	$\sqrt{2}$	0	-2	-1	$-\sqrt{2}$
Γ_7^+	2	0	1	$-\sqrt{2}$	0	-2	-1	$\sqrt{2}$	2	0	1	$-\sqrt{2}$	0	-2	-1	$\sqrt{2}$
Γ_8^+	4	0	-1	0	0	-4	1	0	4	0	-1	0	0	-4	1	0
Γ_2^-	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1
Γ_1^-	1	1	1	-1	-1	1	1	-1	-1	-1	-1	1	1	-1	-1	1
Γ_3^-	2	2	-1	0	0	2	-1	0	-2	-2	1	0	0	-2	1	0
Γ_5^-	3	-1	0	1	-1	3	0	1	-3	1	0	-1	1	-3	0	-1
Γ_4^-	3	-1	0	-1	1	3	0	-1	-3	1	0	1	-1	-3	0	1
Γ_7^-	2	0	1	$\sqrt{2}$	0	-2	-1	$-\sqrt{2}$	-2	0	-1	$-\sqrt{2}$	0	2	1	$\sqrt{2}$
Γ_6^-	2	0	1	$-\sqrt{2}$	0	-2	-1	$\sqrt{2}$	-2	0	-1	$\sqrt{2}$	0	2	1	$-\sqrt{2}$
Γ_8^-	4	0	-1	0	0	-4	1	0	-4	0	1	0	0	-4	-1	0

TABLE 2.9: Character table for the O_h double group arranged to convey compatibility with the T_d double group

The important consequence of the double group compatibility table is that the special case $J = S = 1/2$ is compatible with Γ_6^+ , such that spin-up and -down basis functions $\{\uparrow, \downarrow\}$ transform according to this irrep. Double group irrep $|J, m_J\rangle$ basis constructed from $|L, m_L\rangle \otimes \{\uparrow, \downarrow\}$ must then transform according to the direct product of single group irreps with Γ_6^+ . For example, since $L = 1$ is compatible with Γ_4^- , consider the character product decomposition; $\Gamma_4^- \otimes \Gamma_6^+ = \Gamma_6^- \oplus \Gamma_8^-$ such that basis functions in Equation 2.17 are in agreement with Table 2.8 as required.

2.3 Reducible Tensor Operators

Tensor operators including the Hamiltonian are invariant with respect to symmetry operations of the group [58]. Scalars and vectors are tensors in the zeroth and first rank respectively such as the unperturbed Hamiltonian and $\mathbf{k} \cdot \hat{\mathbf{p}}$ perturbation respectively. Higher ranked tensor operators such as strain are second and the electromechanical tensor attributed with the piezoelectric effect is third rank.

Multiplication tables for the T_d and O_h groups may be obtained through character product decomposition. The use extends to the matrix element theorem and the theory of invariants where the occurrence of the identity indicates a non zero scaling parameter. The most notable example concerns parity selection rules concerning even and odd order tensor operators in T_d and O_h . Indeed symmetry forbids the piezoelectric effect in Diamond but not in Zinc-blende.

2.3.1 Multiplication Tables

Multiplication tables are the essential tool to facilitate symmetrisation procedures. The *Direct Product*, labelled by the symbol ‘ $\otimes$ ’ is the Kronecker or tensor product of the irreps between Γ_i and Γ_j . Generally $\Gamma_i \otimes \Gamma_j$ is reducible such that it may be block diagonalised under a similarity transformation. Since the character is invariant, rather than compute Kronecker products and then apply a similarity transformation one may consider direct sums of irreps with equivalent character.

Evaluating the similarity transformation does reveal further information on the direct product, as one may identify specific symmetric and anti-symmetric components. Anti-symmetric components [55] are listed in square brackets $[\Gamma_i]$, otherwise the component is symmetric. For example; consider the $\Gamma_5 \otimes \Gamma_5$ direct product;

	$\{E\}$	$\{3C_2\}$	$\{8C_3\}$	$\{6S_4\}$	$\{6\sigma_v\}$	
$\Gamma_5 \otimes \Gamma_5$	9	1	0	1	1	$\Gamma_1 \oplus \Gamma_3 \oplus [\Gamma_4] \oplus \Gamma_5$

TABLE 2.10: Direct product decomposition into symmetric and anti-symmetric direct sum parts for $\Gamma_5 \otimes \Gamma_5 = \Gamma_1 \oplus \Gamma_3 \oplus [\Gamma_4] \oplus \Gamma_5$

The number occurrence of the scalar identity irrep, Γ_1 , in the tensor decomposition is equivalent to the number of invariants in the cross space, and generally $\Gamma_i \otimes \Gamma_i = \Gamma_1 \oplus \dots, \forall i$ [55]. Since a similarity transformation preserves character the invariant property is the trace.

Working through all the irreps of the T_d double group a multiplication table given in Table 2.11 may be assembled. To say O_h multiplication tables are large is an understatement, so for this reason we consult the T_d group multiplication table and apply the equivalence representation, noting that where parity is concerned the familiar rules; $even \times even = odd \times odd = even$ and $even \times odd = odd \times even = odd$ apply.

In the example of Equation 2.17 consider $\Gamma_5 \otimes \Gamma_6 = \Gamma_7 \oplus \Gamma_8$, and invoke the equivalence representation, such that $\Gamma_4^- \otimes \Gamma_6^+ = \Gamma_6^- \oplus \Gamma_8^-$. Furthermore, since $L = 2$ is compatible with $\Gamma_3^+ \oplus \Gamma_5^+$, upon consulting the multiplication table, one sees that $(\Gamma_3^+ \oplus \Gamma_5^+) \otimes \Gamma_6^+ = \Gamma_7^+ \oplus 2\Gamma_8^+$. Which is in accordance with the compatibility for $J = 3/2$ and $J = 5/2$ states given in Table 2.8. In this second example, the crystal field lifts the degeneracy of $L = 2$, however when the spin-orbit interaction is included Γ_3^+ and Γ_5^+ mix in their contribution to $2\Gamma_8^+$. The degree of mixing is dependent upon the crystal field strength and spin orbit interaction leading to two limiting cases.

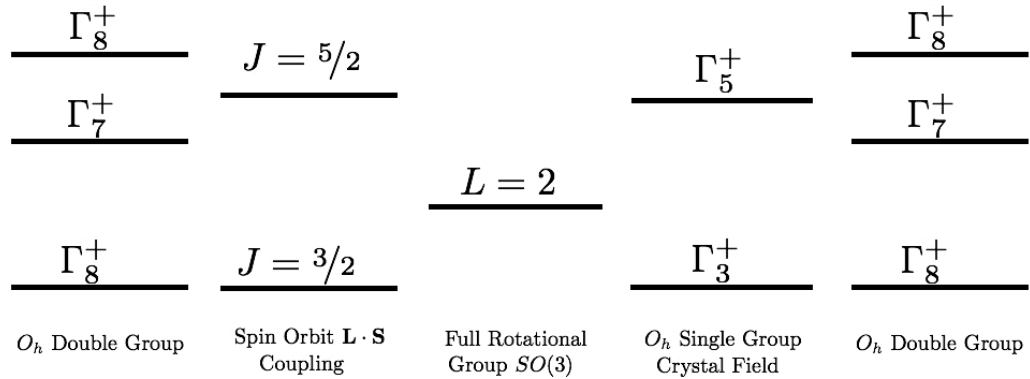


FIGURE 2.3: Energy level diagram displaying the lifting of degeneracy under O_h single and double group crystal fields from the $L = 2$ eigenstate of $SO(3)$

2.3.2 Symmetrisation Procedures

Any general dimensionless transformation e_{ij} where $i, j = \{x, y, z\}$; forms a second rank Cartesian tensor such that e_{ij} is the differential of deformation, u_i , with respect to the natural coordinate r_j . Such a transformation may be decomposed into symmetric strain; ϵ_{ij} , and an anti-symmetric counterpart characterising rotations ω_{ij} shown in Figure 2.4.

$$e_{ij} = \frac{\partial u_i}{\partial r_j} = \underbrace{\frac{1}{2} \left(\frac{\partial u_i}{\partial r_j} + \frac{\partial u_j}{\partial r_i} \right)}_{\epsilon_{ij}} + \underbrace{\frac{1}{2} \left(\frac{\partial u_i}{\partial r_j} - \frac{\partial u_j}{\partial r_i} \right)}_{\omega_{ij}} \quad (2.18)$$

Γ_1	Γ_2	Γ_3	Γ_4	Γ_5	Γ_6	Γ_7	Γ_8	
Γ_1	Γ_2	Γ_3	Γ_4	Γ_5	Γ_6	Γ_7	Γ_8	Γ_1
Γ_1	Γ_2	Γ_3	Γ_4	Γ_5	Γ_6	Γ_7	Γ_8	Γ_2
	Γ_1	Γ_3	Γ_5	Γ_4	Γ_7	Γ_6	Γ_8	Γ_3
		$\Gamma_1 \oplus [\Gamma_2] \oplus \Gamma_3$	$\Gamma_4 \oplus \Gamma_5$	$\Gamma_4 \oplus \Gamma_5$	Γ_8	Γ_8	$\Gamma_6 \oplus \Gamma_7 \oplus \Gamma_8$	Γ_4
			$\Gamma_1 \oplus \Gamma_3 \oplus [\Gamma_4] \oplus \Gamma_5$	$\Gamma_2 \oplus \Gamma_3 \oplus \Gamma_4 \oplus \Gamma_5$	$\Gamma_6 \oplus \Gamma_8$	$\Gamma_7 \oplus \Gamma_8$	$\Gamma_6 \oplus \Gamma_7 \oplus 2\Gamma_8$	Γ_5
				$\Gamma_1 \oplus \Gamma_3 \oplus [\Gamma_4] \oplus \Gamma_5$	$\Gamma_7 \oplus \Gamma_8$	$\Gamma_6 \oplus \Gamma_8$	$\Gamma_6 \oplus \Gamma_7 \oplus 2\Gamma_8$	Γ_6
					$\Gamma_1 \oplus [\Gamma_4]$	$\Gamma_2 \oplus \Gamma_5$	$\Gamma_3 \oplus \Gamma_4 \oplus \Gamma_5$	Γ_7
						$\Gamma_1 \oplus [\Gamma_4]$	$\Gamma_3 \oplus \Gamma_4 \oplus \Gamma_5$	Γ_8
							$\Gamma_1 \oplus \Gamma_3 \oplus \Gamma_5 \oplus [\Gamma_2 \oplus 2\Gamma_4 \oplus \Gamma_5]$	

TABLE 2.11: Multiplication table for single and double group irreps of the T_d group [55]. The multiplication table for O_h invokes the equivalence representation $\Gamma^{equiv} = \Gamma_1^+ + \Gamma_2^-$, and usual parity selection rules; *even* $\times$ *even* = *odd* $\times$ *odd* = *even* and *even* $\times$ *odd* = *odd* $\times$ *even* = *odd*. $[\Gamma_i]$ denotes anti-symmetric contribution, otherwise it is symmetric

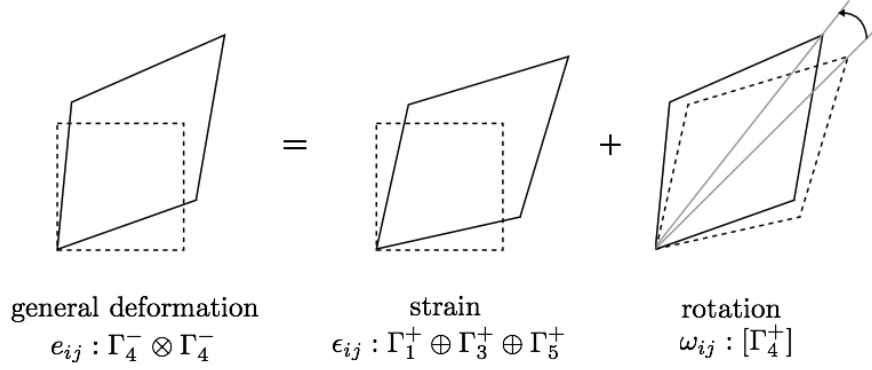


FIGURE 2.4: Illustration of the decomposition of a general deformation into symmetric strain and antisymmetric rotation components [16]

Since the polar vector transforms according to Γ_5 in T_d , we consult the relevant $\Gamma_5 \otimes \Gamma_5$ entry in the multiplication table.

Infinitesimal generators of the rotation matrix, $\{L_x, L_y, L_z\}$, satisfy the commutation rules of angular momentum, and are appropriate basis functions to the $[\Gamma_4]$ irrep of the T_d group, given in Table 2.4. Invoking the equivalence representation; $(\Gamma_4^- \otimes \Gamma_4^-)_{anti-sym}$ transforms according to $[\Gamma_4^+]$ in O_h .

As suggested in the previous section, the invariant property associated with the trace of the symmetric strain tensor is hydrostatic strain, or dilation, which transforms according to the identity irrep, Γ_1^+ . Strain may also be decomposed into the traceless uniaxial and shear transforming according to Γ_3^+ and Γ_5^+ respectively as given by Yu & Cardona [2];

$$\epsilon(\Gamma_1^+) = \frac{1}{3} \begin{pmatrix} \epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz} & 0 & 0 \\ 0 & \epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz} & 0 \\ 0 & 0 & \epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz} \end{pmatrix} \quad (2.19)$$

$$\epsilon(\Gamma_3^+) = \frac{1}{3} \begin{pmatrix} 2\epsilon_{xx} - (\epsilon_{yy} + \epsilon_{zz}) & 0 & 0 \\ 0 & 2\epsilon_{yy} - (\epsilon_{zz} + \epsilon_{xx}) & 0 \\ 0 & 0 & 2\epsilon_{zz} - (\epsilon_{xx} + \epsilon_{yy}) \end{pmatrix} \quad (2.20)$$

$$\epsilon(\Gamma_5^+) = \begin{pmatrix} 0 & \epsilon_{xy} & \epsilon_{xz} \\ \epsilon_{xy} & 0 & \epsilon_{yz} \\ \epsilon_{xz} & \epsilon_{yz} & 0 \end{pmatrix} \quad (2.21)$$

For each symmetrised matrix there is a corresponding deformation potential; l , m and n , as an associated invariant. This symmetrisation procedure leads to the concept of the theory of invariants; an extremely useful tool in developing symmetrised tensor operators as a polynomial function of irreducible perturbation components.

While this choice example of strain is very neat, there are some exceptions which add complexity to the theory of invariants. For example, when considering $(\Gamma_5 \otimes \Gamma_8) \otimes \Gamma_8$

and $\Gamma_5 \otimes (\Gamma_8 \otimes \Gamma_8)$ in the multiplication table, there are subtle differences between the number of scaling parameters and invariants due to antisymmetric components. Consequently multiple occurrences require linear independence in the symmetrisation procedure [56]. This highlights another disparity between the adapted double group and double group formulations as $\Gamma_6 \otimes (\Gamma_5 \otimes \Gamma_5) \otimes \Gamma_6$ is not necessarily equivalent to $(\Gamma_6 \otimes \Gamma_5) \otimes (\Gamma_5 \otimes \Gamma_6) = (\Gamma_7 \oplus \Gamma_8) \otimes (\Gamma_7 \oplus \Gamma_8)$ from the point of view of adding spin-orbit as a perturbation or to the unperturbed Hamiltonian respectively.

Comparison of T_d with the O_h group introduces significant parity considerations in relation to odd-order effects. The third rank electromechanical tensor; attributed with the piezoelectric effect is the coupling of strain to an applied or induced polar electric field. Consequently, the electromechanical tensor transforms according to $(\Gamma_5 \otimes \Gamma_5)_{sym} \otimes \Gamma_5 = \Gamma_1 \oplus \dots$ in T_d . The occurrence of the identity indicates a non-zero, scalar, invariant and as such Zinc-blende type crystals may exhibit the piezoelectric effect. In O_h parity requires; $(\Gamma_4^- \otimes \Gamma_4^-)_{sym} \otimes \Gamma_4^- = \Gamma_2^- \oplus \dots$, and the occurrence of Γ_2^- rather than the identity irrep, Γ_1^+ indicates no non-zero invariants. Diamond-type crystals do not exhibit the piezoelectric effect and similarly any other odd-rank tensors such as the Raman tensor.

2.4 Anti-Unitary Operators

While the work thus far has taught invaluable information about the transformation properties of specific groups, one important symmetry has been overlooked; the time reversal operator $\hat{T}$. While the concept of time reversal may seem more grand than it actually is, it simply reverses the sign of vectors which may have time varying derivatives. This has significant consequences in the description of magnetic (Zeeman) and electric (Stark) effects, which are odd and even under time inversion respectively.

Conservation of energy and time-evolution of the Hamiltonian operator introduces Herring's rules [64], for the cases with and without spin. While all cubic crystals are anti-ferromagnetic one may use Herring's rules to gain additional information and identify further properties of representation matrices. Magnetic point groups include the time reversal operation as an actual element of the group, but are considered superfluous to this thesis.

2.4.1 Time Reversal Symmetry

The time reversal operator, $\hat{T}$, acting on vectors reverses the sign on time-odd vectors such as linear momentum; $\hat{T}\mathbf{p} = -\mathbf{p}$, whilst leaving time-even vectors such as position; $\hat{T}\mathbf{r} = \mathbf{r}$ unchanged [55]. Angular momentum is time-odd, since $\mathbf{L} = \mathbf{r} \times \mathbf{p}$. One should compare this with the spatial parity operator $\hat{P}$ ⁶, for which angular momentum

⁶introduced as inversion $\{i\}$ in Section 2.1.2

is spatially-even since both linear momentum $\hat{P}\mathbf{p} = -\mathbf{p}$ and position $\hat{P}\mathbf{r} = -\mathbf{r}$ are both spatially-odd. Both kinetic $\frac{\mathbf{p}^2}{2m}$ and potential energy $V(\mathbf{r})$ are even under time reversal in accordance with the time-independent Schrödinger equation.

Time reversal is an anti-unitary operator, such that $\hat{T} = U\hat{K}$, where U is a unitary operator, and $\hat{K}$ is the anti-linear, conjugation operator; $\hat{K}i = -i$. Considering the time dependent Schrödinger equation this also ensures the Hamiltonian is time-even. For the case of a spin-less particle such as SO(3), U is the unit operator, whereas for spin-degenerate particles such as the irreps of SU(2) with $S = 1/2$, then $U = e^{-\frac{1}{2}i\pi\sigma_y} = -i\sigma_y$.

Operating on the complex spin-less basis $\left\{ \frac{-1}{\sqrt{2}}(x - iy), z, \frac{+1}{\sqrt{2}}(x + iy) \right\}$ with the time reversal operator returns $\left\{ \frac{-1}{\sqrt{2}}(x + iy), z, \frac{+1}{\sqrt{2}}(x - iy) \right\}$. Such a basis still diagonalises the rotation matrix;

$$\begin{pmatrix} e^{+i\theta} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{-i\theta} \end{pmatrix} = A \begin{pmatrix} \cos(\theta) & -\sin(\theta) & 0 \\ \sin(\theta) & \cos(\theta) & 0 \\ 0 & 0 & 1 \end{pmatrix} A^\dagger; \quad A = \begin{pmatrix} \frac{-1}{\sqrt{2}} & \frac{-i}{\sqrt{2}} & 0 \\ 0 & 0 & 1 \\ \frac{1}{\sqrt{2}} & \frac{-i}{\sqrt{2}} & 0 \end{pmatrix} \quad (2.22)$$

Accordingly; the difference is that the orthogonal matrix A in Equation 2.22 is the complex conjugate of the orthogonal matrix in Equation 2.9. The two complex basis functions are linked through the relation;

$$\begin{pmatrix} \frac{-1}{\sqrt{2}}(x + iy) \\ z \\ \frac{+1}{\sqrt{2}}(x - iy) \end{pmatrix} = \begin{pmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{pmatrix} \begin{pmatrix} \frac{-1}{\sqrt{2}}(x - iy) \\ z \\ \frac{+1}{\sqrt{2}}(x + iy) \end{pmatrix} \quad (2.23)$$

The above 3×3 matrix is equivalent to the $C_2(y)$ representation matrix for Γ_4^- , and $(x \pm iy)$ form a time-reversed conjugate pair. Using the Condon-Shortley [65] phase convention, one returns the general relation;

$$\hat{T} |L, m_L\rangle = (-1)^{m_L} |L, -m_L\rangle \quad (2.24)$$

This leads to the definition that the cartesian basis; $\left\{ \frac{-1}{\sqrt{2}}(x + iy), z, \frac{+1}{\sqrt{2}}(x - iy) \right\}$ corresponds to the spherical basis; $\{|1, +1\rangle, |1, 0\rangle, |1, -1\rangle\}$ which sets the phase for the right-handed coordinate system. While $|L, m_L\rangle$ are not necessarily eigenvectors of $\hat{T}$, linear combinations may satisfy the eigenvalue equation, such as; $\frac{-1}{\sqrt{2}}(|1, +1\rangle - |1, -1\rangle)$ with eigenvalue $+1$.

Recall the angular momentum matrices for $L = 1$, given in Equation 2.10. Time reversal implies that $\hat{T}L_i\hat{T}^{-1} = -L_i^\dagger$ in accordance with angular momentum being time-odd. The time-reversed angular momentum matrices may be expressed as;

$$\begin{aligned}\hat{T}L_x\hat{T}^{-1} &= \frac{-\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, & \hat{T}L_y\hat{T}^{-1} &= \frac{-i\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix} \\ \hat{T}L_z\hat{T}^{-1} &= -\hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}\end{aligned}\quad (2.25)$$

which still satisfy the commutation rules of angular momentum. Note that these are equivalent to the matrices one would have obtained through computing $L_i = i\hbar AX_i A^\dagger$ using A , this time, given in Equation 2.22.

Equation 2.24 is also applicable to half-integer spin, where the exponent is replaced by $J - m_J - L$ [66] under the Condon-Shortley phase convention;

$$\hat{T}|J, m_J\rangle = (-1)^{J-m_J-L} |J, -m_J\rangle \quad (2.26)$$

For spin-up and -down particles this reduces to $S - m_S$ in accordance with the previous assertion that $\hat{T} = -i\sigma_y \hat{K}$;

$$\hat{T}\uparrow = \downarrow, \quad \hat{T}\downarrow = -\uparrow \quad (2.27)$$

Despite Equations 2.24 and 2.26 not being eigenvalue problems, relations involving $\hat{T}^2$ are, with eigenvalues $+1$ and -1 for integer and half integer spin respectively. This leaves the choice of phase on U completely arbitrary, such that $\hat{T} = +i\sigma_y \hat{K}$ is also valid. Conventionally U is chosen as the $C_2(y)$ representation matrix of the group.

2.4.2 Herring Rules without Spin

Conservation of energy implies that the Hamiltonian commutes with the time reversal operator; $[H, \hat{T}] = 0$, so eigenstates of the Hamiltonian, ψ , must also be eigenstates of $\hat{T}$. Consequently, the operation of $\hat{T}$ on eigenstates return the complex conjugate; $\hat{T}\psi = \psi^*$. The implication on representation matrices $\mathbf{D}(g)$ is that, where ψ transforms according to $\mathbf{D}(g)$, then ψ^* transforms according to $\mathbf{D}(g)^*$. There are three possibilities which emerge to formulate Herring's rules [64];

- (a) All of the representation matrices are real; $\mathbf{D}(g) = \mathbf{D}(g)^*, \forall g \in G$
- (b) No unitary transformation may bring equivalence $\mathbf{D}(g) \neq U\mathbf{D}(g)^*U^{-1}, \forall g \in G$
- (c) Unitary transformation may bring equivalence $\mathbf{D}(g) = U\mathbf{D}(g)^*U^{-1}, \forall g \in G$, but representation matrices are complex

Case (a) is the simplest case as far as the degeneracy is concerned, since the time reversal operator leaves $\mathbf{D}(g)$ and ψ unchanged; there is no additional degeneracy. Case (b) is slightly more involved since the representations $\mathbf{D}(g)$ and $\mathbf{D}(g)^*$ constitute a time reversal pair so ψ and ψ^* become degenerate. Recall that $|1, +1\rangle$ and $|1, -1\rangle$ form a time-reversed conjugate pair; so satisfy this, however since they fall into the same irrep of T_d they are already degenerate and satisfy case (a). To observe the time-reversal properties of case (b) for this example, one must consider sub-groups of T_d which have the symmetry of a perturbation, such as the $\mathbf{k} \cdot \hat{\mathbf{p}}$ Hamiltonian for $\mathbf{k} \neq 0$. The final case (c), like case (b) leads to a doubling of the degeneracy across irreps with the same arguments.

One may identify to which case irreps fall into through the Herring space group test, where one evaluates the sum of the characters for squared operations in the group, $g^2 \in G$. Consider the composition table for the group, such that in T_d ; $(C_2)^2 = E$, and $(S_4)^2 = C_2$, etc. The sum of the squared characters of the pertinent operations either returns zero or $\pm|G|$, where $|G|$ is the order of the group. Alternatively should all representation matrices be known, one may use the more manageable formula;

$$\sum_{g \in G} \text{Tr} [\mathbf{D}(g)^2] = \begin{cases} +|G| & \text{case (a)} \\ 0 & \text{case (b)} \\ -|G| & \text{case (c)} \end{cases} \quad (2.28)$$

For the case of the T_d single group, all irreps fall into case (a) and there is no additional degeneracy. Similarly this is the case for O_h . Accordingly one expects all representation matrices $\mathbf{D}(g)$, to be real.

2.4.3 Herring Rules with Spin

When spin is included to the point group, double group irreps were introduced to account for the behaviour of half integer spin particles such as electrons. Consequently the degeneracy of all double group irreps is even for T_d and O_h . As previously stated the time reversal operator including spin is $\hat{T} = -i\sigma_y \hat{K}$, such that the operation of $\hat{T}$ on degenerate eigenstates of the spinor returns; $\hat{T}\psi_{\uparrow} = \psi_{\downarrow}^*$.

Herring's rules now apply with differing consequences. Case (a) for the spin-less case implied no extra degeneracy, however the action of $\hat{T}$ now requires a duplication of $\mathbf{D}(g)$

such that irreps are degenerate under time reversal symmetry. Case (b) for the spin-less case implied a doubling of degeneracy, and this remains for the case including spin. The final case (c), unlike case (b), leads to no extra degeneracy since the action of $\hat{T}$ now says that $\mathbf{D}(g)$ already accounts for spin degeneracy.

One may apply Herring's test in Equation 2.28 again for the T_d and O_h groups, such that all double group irreps now fall into case (c); however yet once again there is no extra degeneracy to consider. This also implies that double group representation matrices are complex unlike for the single group.

The use of time reversal symmetry with Bloch's theorem is of pivotal importance in understanding band diagrams of crystals with and without inversion symmetry. Kramer's degeneracy including spin leads to the requirement that $E_{\uparrow}(\mathbf{k}) = E_{\downarrow}(-\mathbf{k})$. In O_h , the inversion element in the group takes $i\mathbf{k} = -\mathbf{k}$ and all levels are doubly degenerate in the Brillouin zone. For the case of the T_d group, linear $\mathbf{k}$ and any other odd order terms enter the Hamiltonian lift the two fold Kramers degeneracy by the Dresselhaus spin orbit term [29].

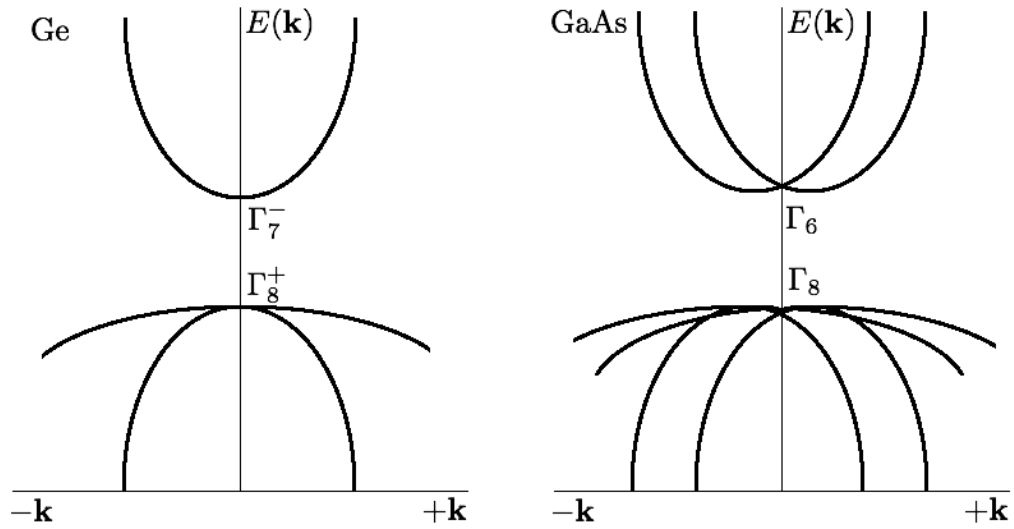


FIGURE 2.5: valence and conduction band sketch of $O_h = i \otimes T_d$ type Ge (left) and T_d type GaAs (right) showing the effect of inversion symmetry on Kramer's degeneracy

Time odd and even applied magnetic (Zeeman) and electric (Stark) perturbations may also lift Kramers degeneracy leading to the splitting of energy levels giving rise to many interesting and useful effects.

Summary

The study of symmetry through group theory must be one of the most beautiful examples of the physical world behaving in accordance with abstract mathematics. From the four axioms at the top of this chapter, a whole plethora of tools emerge to aid our understanding of material properties based purely on symmetry alone. The T_d and O_h groups are characteristic of those of many common semiconducting crystals and consequently single and double character and multiplication tables may be formulated. Compatibility with the full rotation $SO(3)$ and $SU(2)$ groups may also be assigned through pertinent symmetry operations of sub-group chains. Finally, the time reversal operator was discussed in relation to the properties of representation matrices and Kramer's degeneracy through Herring's space group test.

Using the mathematical tools devised, a framework from which the thesis is largely based is presented. In the next chapter, these tools are used in a more specific sense to obtain *Symmetrised Basis Functions* for both T_d and O_h single and double groups expressible in terms of $|L, m_L\rangle$ and $|J, m_J\rangle$ eigenstates. Most interestingly further assertions on the adapted double group basis $|L, m_L\rangle \otimes \{\uparrow, \downarrow\}$ are made to further justify the use of the double group formulation of $\mathbf{k} \cdot \hat{\mathbf{p}}$ theory for application to Silicon-Germanium alloy heterostructures from the point of view of degeneracy.

Chapter 3

Symmetrised Basis Functions

The previous chapter laid the foundations for abstract mathematical group theory applied to single and double point groups, common to tetrahedrally oriented cubic crystals. This constructed a framework from which a whole arsenal of tools emerged to aid the understanding of physical effects. In this chapter, specific single [67] and double group [30] symmetrised basis functions will be obtained, which transform according to the invariant subspaces of T_d and O_h point group irreps. These may be utilised to obtain linearly independent matrices which also transform according to the point group under the action of a tensor operator such as the Hamiltonian, or more specifically the $\mathbf{k} \cdot \hat{\mathbf{p}}$ perturbation.

Discussions centre around obtaining general orbital and total angular momentum matrices for use in both single and double groups respectively and then evaluating the rotation matrix for point group operations of T_d . Application of the appropriate similarity transformation brings all rotation matrices into block diagonal form with T_d character in accordance with the compatibility with $SO(3)$ and $SU(2)$ for single and double group irreps respectively. Extension to O_h is discussed through the parity transformation such that irrep matrices are compliant with inversion symmetry thereafter.

Techniques such as the projection operator and the use of Clebsch-Gordan coefficients to link single and double group basis functions are performed to convey the self-consistency of group theoretical methods. Possibly the most significant results of this chapter is the procedure to evaluate numerical Clebsch-Gordan coefficients for computation of matrix elements using Wigner-Eckart theorem. With this; linearly independent matrices which form the building blocks of the matrix Hamiltonian [68] may be constructed using the symmetrised basis functions presented.

Maple source code complementary to this chapter was uploaded to the Mapleprimes (26/08/2011) user forum: <http://www.mapleprimes.com/posts/125172-Td-Group>

3.1 Single Group Basis Functions

Basis functions are central to representing symmetry sub-spaces onto a tangible reference frame. Significant examples include polar and axial (pseudo) vectors. Compatibility of the full rotational group $SO(3)$ with T_d and O_h single group irreps implies that basis functions may be formulated out of symmetrised $|L, m_L\rangle$ eigenstates.

General rules for obtaining orbital angular momentum generator matrices are discussed from quantum mechanical operators. A worked example using the $L = 2$ state is performed, compatible with $\Gamma_3^+ \oplus \Gamma_5^+$. Irreducible representation matrices may be found by a similarity transformation of the rotation matrix under point group operations. These may then be used in tandem with the projection operator technique to return real space symmetrised basis functions for any given irrep.

3.1.1 Angular Momentum Operators

Orbital angular momentum matrices for $L = 1$ are appropriate infinitesimal generators of the Euler-Rodrigues rotation formula when evaluated as a matrix exponential. It should come as no surprise that the diagonal infinitesimal generators, L_z and $\mathbf{L}^2$, are related to Hermitian quantum mechanical angular momentum operators through the eigenvalue equations, as given by Merzbacher [26];

$$L_z |L, m_L\rangle = m_L \hbar |L, m_L\rangle, \quad \mathbf{L}^2 |L, m_L\rangle = L(L+1) \hbar^2 |L, m_L\rangle \quad (3.1)$$

L_x and L_y may also be found from ladder operators using; $L_{\pm} = \frac{\mp 1}{\sqrt{2}}(L_x \pm iL_y)$;

$$L_{\pm} |L, m_L\rangle = \mp \frac{1}{\sqrt{2}} \sqrt{L(L+1) - m_L(m_L \pm 1)} \hbar |L, m_L \pm 1\rangle \quad (3.2)$$

Commutation rules may be extended to include; $[L_z, L_{\pm}] = \pm \hbar L_{\pm}$ and $[L_+, L_-] = -\hbar L_z$. In addition we have; $[\mathbf{L}^2, L_z] = [\mathbf{L}^2, L_{\pm}] = 0$ since $\mathbf{L}^2$ is a scalar operator. One may also compute $\mathbf{L}^2$ using the alternate $L_z^2 - (L_+ L_- + L_- L_+)$ symmetrically ordered form.

Trivially for $L = 0$, one returns $L_x = L_y = L_z = \mathbf{L}^2 = (0)$, but a more involved example is $L = 2$. Using the eigenvalue equations, expressions for L_z and $\mathbf{L}^2$ become;

$$L_z = \hbar \begin{pmatrix} 2 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & -2 \end{pmatrix}, \quad \mathbf{L}^2 = \hbar^2 \begin{pmatrix} 6 & 0 & 0 & 0 & 0 \\ 0 & 6 & 0 & 0 & 0 \\ 0 & 0 & 6 & 0 & 0 \\ 0 & 0 & 0 & 6 & 0 \\ 0 & 0 & 0 & 0 & 6 \end{pmatrix} \quad (3.3)$$

and using the ladder operators, expressions for L_x and L_y are obtained;

$$L_x = \frac{\hbar}{2} \begin{pmatrix} 0 & \sqrt{4} & 0 & 0 & 0 \\ \sqrt{4} & 0 & \sqrt{6} & 0 & 0 \\ 0 & \sqrt{6} & 0 & \sqrt{6} & 0 \\ 0 & 0 & \sqrt{6} & 0 & \sqrt{4} \\ 0 & 0 & 0 & \sqrt{4} & 0 \end{pmatrix}, \quad L_y = \frac{i\hbar}{2} \begin{pmatrix} 0 & -\sqrt{4} & 0 & 0 & 0 \\ \sqrt{4} & 0 & -\sqrt{6} & 0 & 0 \\ 0 & \sqrt{6} & 0 & -\sqrt{6} & 0 \\ 0 & 0 & \sqrt{6} & 0 & -\sqrt{4} \\ 0 & 0 & 0 & \sqrt{4} & 0 \end{pmatrix} \quad (3.4)$$

Which indeed satisfy all aforementioned commutation rules. Where $L = 1$ is completely compatible with Γ_4^- , $L = 2$ becomes reducible into $\Gamma_3^+ \oplus \Gamma_5^+$ irreps of O_h . In the next section, it will be shown how the rotation matrix may be brought into block diagonal form under point group operations by a similarity transformation.

3.1.2 Representation Matrices I

General rotations by an angle θ about an axis by given by the unit vector $\mathbf{n}$ may be expressed in terms of the Euler-Rodrigues formula using angular momentum generators;

$$R_{\mathbf{n}}(\theta) = e^{-i\frac{\mathbf{n} \cdot \mathbf{L}}{\hbar}\theta} \quad (3.5)$$

Previous examples of this general formula have been used to explain the importance of the quantisation axis, such that $R_z(\theta)$ is diagonal. From the projections of the methane molecule (Figure 2.2); point group operations of the T_d group may be employed.

For the three C_2 operations, one may take $\mathbf{n} = (100)$, (010) , (001) with $\theta = 180^\circ$, where Miller index notation has been used. The eight C_3 operations employ $\mathbf{n} = (111)$, $(\bar{1}\bar{1}1)$, $(1\bar{1}\bar{1})$, $(11\bar{1})$, $(\bar{1}\bar{1}\bar{1})$, $(\bar{1}1\bar{1})$, $(1\bar{1}\bar{1})$, $(\bar{1}\bar{1}\bar{1})$, with $\theta = 120^\circ$. Improper rotations are slightly more involved, since a pre-factor of $(-1)^L$ is required. Mirror operations maybe treated as improper C_2 rotations, so for the six σ_v operations; $\mathbf{n} = (110)$, $(\bar{1}10)$, (101) , $(\bar{1}01)$, (011) , $(0\bar{1}1)$ with $\theta = 180^\circ$.

A similarity transformation block diagonalises the matrix exponential into irreducible representation matrices, using an orthogonal matrix;

$$A^\dagger e^{-i\frac{\mathbf{n} \cdot \mathbf{L}}{\hbar}\theta} A = \mathbf{D}^{(\Gamma_i^\pm)}(g) \oplus \mathbf{D}^{(\Gamma_j^\pm)}(g) \oplus \dots \forall g \in G \quad (3.6)$$

Trivially all representation matrices for Γ_1 are (1) and the $L = 1$ state is completely compatible with Γ_4^- . Representation matrices are also diagonal for the identity, $\mathbf{D}(E)$, and 180° rotations, $\mathbf{D}(C_2(100))$, $\mathbf{D}(C_2(010))$ and $\mathbf{D}(C_2(001))$. For these reasons consider

the $S_4(100)$ improper rotation for $L = 2$, compatible with $\Gamma_3^+ \oplus \Gamma_5^+$ irreps. Using L_x given in Equation 3.4, and an angle $\theta = \pi/2$, with the orthogonal matrix $A^\dagger$ given below;

$$A^\dagger = \begin{pmatrix} \frac{1}{\sqrt{2}} & 0 & 0 & 0 & \frac{1}{\sqrt{2}} \\ 0 & 0 & 1 & 0 & 0 \\ 0 & \frac{i}{\sqrt{2}} & 0 & \frac{i}{\sqrt{2}} & 0 \\ 0 & \frac{-1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} & 0 \\ \frac{-i}{\sqrt{2}} & 0 & 0 & 0 & \frac{i}{\sqrt{2}} \end{pmatrix} \quad (3.7)$$

leads to the the block diagonal form of $\mathbf{D}^{(\Gamma_3^+ \oplus \Gamma_5^+)}(S_4(100))$;

$$\mathbf{D}^{(\Gamma_3^+ \oplus \Gamma_5^+)}(S_4(100)) = (-1)^2 A^\dagger e^{-i \frac{L_x}{\hbar} \pi/2} A = \begin{pmatrix} \frac{1}{2} & \frac{-\sqrt{3}}{2} & 0 & 0 & 0 \\ \frac{-\sqrt{3}}{2} & \frac{-1}{2} & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 1 & 0 \end{pmatrix} \quad (3.8)$$

These representation matrices are equivalent to those tabulated in the Appendix A for Γ_3 and Γ_5 irreps under the improper rotation $S_4(100)$ operation in Table A.2. For completeness; Tables A.1 ... A.4 list all $5 \times 24 = 120$ representation matrices for each symmetry operation and irrep of the T_d single group. Traces for representation matrices are in accordance with the character table and all matrices are real in accordance with case (a) of Herring's space group test.

Extension to the O_h group invokes the inversion factor group and the equivalence representation. Consequently the sign of all matrices for odd irreps in the additional inversion classes is reversed such that representation matrices retain their associated parity. For example, the representation matrix for Γ_5^+ satisfies; $\mathbf{D}^{(\Gamma_5^+)}(C_4(100)) = +\mathbf{D}^{(\Gamma_5)}(S_4(100))$, whereas for Γ_4^- one has $\mathbf{D}^{(\Gamma_4^-)}(C_4(100)) = -\mathbf{D}^{(\Gamma_5)}(S_4(100))$.

The further significance of the orthogonal matrix $A^\dagger$, is that it returns symmetrised basis functions expressed in the spherical frame. By inspection one may identify; $\left\{ \frac{1}{\sqrt{2}}(|2, +2\rangle + |2, -2\rangle), |2, 0\rangle \right\}$ as basis functions for Γ_3^+ and also $\left\{ \frac{i}{\sqrt{2}}(|2, +1\rangle + |2, -1\rangle), \frac{-1}{\sqrt{2}}(|2, +1\rangle - |2, -1\rangle), \frac{-i}{\sqrt{2}}(|2, +2\rangle - |2, -2\rangle) \right\}$ for Γ_5^+ . Further single group basis functions for $L = 0 \dots 4$ are given in Table 3.1 for the O_h group [67]. Note that all basis functions are eigenvectors of the time reversal operator $\hat{T}$, with eigenvalue +1.

At this point one should discuss the choice of frame in which to represent basis functions. The use of basis functions in the spherical frame lends itself to the realm of quantum

L	$\Gamma_i^\pm$	$ L, m_L\rangle$
0	Γ_1^+	$ 0, 0\rangle$
1	Γ_4^-	$\frac{-1}{\sqrt{2}}(1, +1\rangle - 1, -1\rangle)$ $\frac{i}{\sqrt{2}}(1, +1\rangle + 1, -1\rangle)$ $ 1, 0\rangle$
2	Γ_3^+	$\frac{1}{\sqrt{2}}(2, +2\rangle + 2, -2\rangle)$ $ 2, 0\rangle$
	Γ_5^+	$\frac{i}{\sqrt{2}}(2, +1\rangle + 2, -1\rangle)$ $\frac{-1}{\sqrt{2}}(2, +1\rangle - 2, -1\rangle)$ $\frac{-i}{\sqrt{2}}(2, +2\rangle - 2, -2\rangle)$
3	Γ_2^-	$\frac{i}{\sqrt{2}}(3, +2\rangle - 3, -2\rangle)$
	Γ_4^-	$\frac{1}{\sqrt{16}}(\sqrt{3}(3, +1\rangle - 3, -1\rangle) - \sqrt{5}(3, +3\rangle - 3, -3\rangle))$ $\frac{-i}{\sqrt{16}}(\sqrt{3}(3, +1\rangle + 3, -1\rangle) + \sqrt{5}(3, +3\rangle + 3, -3\rangle))$ $ 3, 0\rangle$
	Γ_5^-	$\frac{-1}{\sqrt{16}}(\sqrt{3}(3, +1\rangle - 3, -1\rangle) + \sqrt{5}(3, +3\rangle - 3, -3\rangle))$ $\frac{-i}{\sqrt{16}}(\sqrt{3}(3, +1\rangle + 3, -1\rangle) - \sqrt{5}(3, +3\rangle + 3, -3\rangle))$ $\frac{1}{\sqrt{2}}(3, +2\rangle + 3, -2\rangle)$
4	Γ_1^+	$\frac{1}{\sqrt{24}}(\sqrt{14} 4, 0\rangle + \sqrt{5}(4, +4\rangle + 4, -4\rangle))$
	Γ_3^+	$\frac{1}{\sqrt{2}}(4, +2\rangle + 4, -2\rangle)$ $\frac{-1}{\sqrt{24}}(\sqrt{10} 4, 0\rangle - \sqrt{7}(4, +4\rangle + 4, -4\rangle))$
	Γ_4^+	$\frac{1}{\sqrt{16}}((4, +3\rangle + 4, -3\rangle) + \sqrt{7}(4, +1\rangle + 4, -1\rangle))$ $\frac{i}{\sqrt{16}}((4, +3\rangle - 4, -3\rangle) - \sqrt{7}(4, +1\rangle - 4, -1\rangle))$ $\frac{1}{\sqrt{2}}(4, +4\rangle - 4, -4\rangle)$
	Γ_5^+	$\frac{i}{\sqrt{16}}(\sqrt{7}(4, +3\rangle + 4, -3\rangle) - (4, +1\rangle + 4, -1\rangle))$ $\frac{1}{\sqrt{16}}(\sqrt{7}(4, +3\rangle - 4, -3\rangle) + (4, +1\rangle - 4, -1\rangle))$ $\frac{-i}{\sqrt{2}}(4, +2\rangle - 4, -2\rangle)$

TABLE 3.1: Symmetrised Octahedral, O_h , single group irrep basis functions represented in the spherical frame [67]

mechanics leading to the far simpler computation of matrix elements through Wigner-Eckart theorem and Clebsch-Gordan coefficients. However, this detracts from the physical intuition associated with cartesian operators and vectors, which is favourable when visualising tangible objects such as bulk cubic crystals.

The projection operator technique may be introduced as an application of the representation matrices in the Appendix A along with symmetry operations to generate symmetrised cartesian basis functions in terms of real space harmonics.

3.1.3 Projection Operator Technique

The projection operator technique is a very useful tool to generate cartesian basis functions which transform according to irreps of the group. The formula given in the previous

chapter in Equation 2.5 along with the representation matrices, $\mathbf{D}(g)$ and symmetry operations $\hat{P}_g$ given in Tables A.1 ... A.4 in the Appendix A are used.

As a worked example consider the Γ_5 irrep and the general function $f(x, y, z) = x$. One may compute the product of 3×3 representation matrices $\mathbf{D}^{(\Gamma_5)}(g)$ along with symmetry operations acting on $\hat{P}_g f(x, y, z)$. Rather than computing all elements in the summation the task will be condensed by grouping into classes;

$$\begin{aligned} \hat{P}^{(\Gamma_5)} x = \frac{3}{24} & \left(\begin{pmatrix} x & 0 & 0 \\ 0 & x & 0 \\ 0 & 0 & x \end{pmatrix} + \begin{pmatrix} 3x & 0 & 0 \\ 0 & -x & 0 \\ 0 & 0 & -x \end{pmatrix} + \begin{pmatrix} 2x & 2y & 2z \\ -2y & 0 & 0 \\ -2z & 0 & 0 \end{pmatrix} + \dots \right. \\ & \left. \dots + \begin{pmatrix} 2x & 2y & 2z \\ 2y & 0 & 0 \\ 2z & 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 4y & 4z \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \right) = \begin{pmatrix} x & y & z \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \end{aligned}$$

Hence the operator $\hat{P}^{(\Gamma_5)}$ has projected out the partners; y and z . From this one identifies symmetrised basis functions $\{x, y, z\}$ which transform according to the Γ_5 . The projection operator returns an empty matrix for any other irrep in accordance with the great orthogonality theorem. Projecting out the function $f(x, y, z) = x + 2y + 3z$ conveys linear independence;

$$\hat{P}^{(\Gamma_5)}(x + 2y + 3z) = \begin{pmatrix} x & y & z \\ 2x & 2y & 2z \\ 3x & 3y & 3z \end{pmatrix} \quad (3.9)$$

where this example highlights the fact that the projection operator technique does not always return normalised basis sets. Comparing basis functions in spherical and cartesian frames, one is at liberty to use whichever frame is appropriate specific to the task at hand. Application of the equivalence representation with O_h using the inversion factor group projects these basis to Γ_4^- ;

$$\Gamma_4^- \begin{cases} \frac{-1}{\sqrt{2}}(|1, +1\rangle - |1, -1\rangle) & = x \\ \frac{i}{\sqrt{2}}(|1, +1\rangle + |1, -1\rangle) & = y \\ |1, 0\rangle & = z \end{cases} \quad (3.10)$$

We may also show that $\{yz, zx, xy\}$ transform according to Γ_5 with a little extra effort. Using the second order polynomial $f(x, y, z) = yz$, one evaluates associative operations; $\hat{P}_g(yz) = \hat{P}_g y \times \hat{P}_g z$ in accordance with the axioms of group theory. For example,

one returns $\hat{P}_E(yz) = yz$ for the identity and $\hat{P}_{C_2(100)}(yz) = -yz$. Further examples from other classes are $\hat{P}_{S_4(100)}(yz) = -zy$, $\hat{P}_{\sigma_v(011)}(yz) = zy$, and $\hat{P}_{C_3(111)}(yz) = xy$. Condensing all remaining symmetry operations into classes returns the projection;

$$\begin{aligned} \hat{P}^{(\Gamma_5)}yz = \frac{3}{24} & \left(\begin{pmatrix} yz & 0 & 0 \\ 0 & yz & 0 \\ 0 & 0 & yz \end{pmatrix} + \begin{pmatrix} 3yz & 0 & 0 \\ 0 & -yz & 0 \\ 0 & 0 & -yz \end{pmatrix} + \begin{pmatrix} 2yz & 2zx & 2xy \\ -2zx & 0 & 0 \\ -2xy & 0 & 0 \end{pmatrix} + \dots \right. \\ & \left. \dots + \begin{pmatrix} 2yz & 2zx & 2xy \\ 2zx & 0 & 0 \\ 2xy & 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 4zx & 4xy \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \right) = \begin{pmatrix} yz & zx & xy \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \end{aligned}$$

which is familiar to the previous example with $\{x, y, z\}$, but expected since $\{yz, zx, xy\}$ also transforms according to Γ_5 . One should bear in mind that under inversion $\hat{P}_i\{x, y, z\} = \{\bar{x}, \bar{y}, \bar{z}\}$ and $\hat{P}_i\{yz, zx, xy\} = \{yz, zx, xy\}$ in agreement with compatibility to O_h group irreps Γ_4^- and Γ_5^+ respectively.

There exists two more second order polynomials which transform according to Γ_3 . We proceed to project out the function; $f(x, y, z) = \frac{1}{2}(x^2 - y^2)$;

$$\begin{aligned} \hat{P}^{(\Gamma_3)}\left(\frac{1}{2}(x^2 - y^2)\right) &= \frac{2}{24} \left(\begin{pmatrix} \frac{1}{2}(x^2 - y^2) & 0 \\ 0 & \frac{1}{2}(x^2 - y^2) \end{pmatrix} + \begin{pmatrix} \frac{3}{2}(x^2 - y^2) & 0 \\ 0 & \frac{3}{2}(x^2 - y^2) \end{pmatrix} + \dots \right. \\ &\quad \dots + \begin{pmatrix} \frac{3}{2}(y^2 - x^2) & \sqrt{3}(z^2 - \frac{1}{2}(x^2 + y^2)) \\ \sqrt{3}(z^2 - \frac{1}{2}(x^2 + y^2)) & \frac{3}{2}(x^2 - y^2) \end{pmatrix} + \dots \\ &\quad \dots + \begin{pmatrix} \frac{3}{2}(y^2 - x^2) & \sqrt{3}(z^2 - \frac{1}{2}(x^2 + y^2)) \\ \sqrt{3}(z^2 - \frac{1}{2}(x^2 + y^2)) & \frac{3}{2}(x^2 - y^2) \end{pmatrix} + \dots \\ &\quad \left. \dots + \begin{pmatrix} x^2 - y^2 & -\sqrt{3}(2z^2 - (x^2 + y^2)) \\ \sqrt{3}(2z^2 - (x^2 + y^2)) & x^2 - y^2 \end{pmatrix} \right) \\ &= \begin{pmatrix} 0 & 0 \\ \frac{1}{\sqrt{3}}(z^2 - \frac{1}{2}(x^2 + y^2)) & \frac{1}{2}(x^2 - y^2) \end{pmatrix} \end{aligned}$$

Clearly the projection operator has returned the orthogonal partner of $\frac{1}{2}(x^2 - y^2)$ as $\frac{1}{\sqrt{3}}(z^2 - \frac{1}{2}(x^2 + y^2))$. We may compare and contrast the spherical basis functions in Table 3.1, with those obtained through the projection operator technique¹ for both Γ_3^+ and Γ_5^+ irreps through equating;

¹ $|0, 0\rangle = x^2 + y^2 + z^2 = 1$ transforms according to Γ_1^+

$$\begin{aligned}
\Gamma_3^+ \begin{cases} \frac{1}{\sqrt{2}}(|2, +2\rangle + |2, -2\rangle) & = \frac{1}{2}(x^2 - y^2) \\ |2, 0\rangle & = \frac{1}{\sqrt{3}}(z^2 - \frac{1}{2}(x^2 + y^2)) \end{cases} \\
\Gamma_5^+ \begin{cases} \frac{i}{\sqrt{2}}(|2, +1\rangle + |2, -1\rangle) & = yz \\ \frac{-1}{\sqrt{2}}(|2, +1\rangle - |2, -1\rangle) & = zx \\ \frac{-i}{\sqrt{2}}(|2, +2\rangle - |2, -2\rangle) & = xy \end{cases}
\end{aligned} \tag{3.11}$$

One may recognise these functions as real harmonics associated with Legendre polynomials used to visualise the spherical harmonics $Y_{L,m_L}(\theta, \phi)$. As one might have expected from the real harmonics under the Condon-Shortley [65] phase convention; all bases are eigenvectors of the time reversal operator, with eigenvalue $+1$.

The projection operator technique is useful not only for checking basis functions, but primarily to identify to which irrep any order polynomial; $f(x, y, z) = x^l y^m z^n$ transforms. This is far easier than block diagonalising a large rotation matrix exponential according to symmetrised orbital angular momentum eigenstates under point group operations.

3.2 Double Group Basis Functions

Linear combinations of integer $|L, m_L\rangle$ eigenstates are ideal for expressing symmetrised basis functions of T_d and O_h single group irreps. The inclusion of half integer spin fermions call for the use of linear combinations of $|J, m_J\rangle$ eigenstates transforming according to T_d and O_h double group irreps. Double group basis functions [30] have significance in accounting for spin induced effects and are of pivotal importance in understanding the behaviour of real crystals within a quantum mechanical framework.

This doesn't mean that the work on the single group is redundant, since one may account for spin orbit through $\mathbf{L} \cdot \mathbf{S}$ coupling using the adapted double group $|L, m_L\rangle \otimes \{\uparrow, \downarrow\}$. One advantage of the adapted double group is the retention of parity. This section makes the distinction between double group and adapted double group basis functions through a unitary matrix with discussions on the implications of both cases.

3.2.1 Clebsch-Gordan Coefficients

Clebsch-Gordan coefficients were introduced in the previous chapter, as a means of coupling single group basis functions to spin eigenfunctions $\{\uparrow, \downarrow\}$ through diagonalising $\mathbf{L} \cdot \mathbf{S}$. In this section, the general procedure is introduced from the point of view of orbital and total angular momentum operators. The Kronecker product of integer orbital angular momentum with $S = 1/2$ Hilbert spaces a couples to a $2 \times (2L + 1)$ dimensional

half integer vector space. Using L_i with the Pauli spin matrices; $S_i = \frac{1}{2}\sigma_i$ returns generator matrices for total angular momentum $J = (L + S) \oplus (L - S)$ through;

$$J_i = \mathbb{1}_{2 \times 2} \otimes L_i + S_i \otimes \mathbb{1}_{L \times L} \quad (3.12)$$

However; expressions for J_i evaluated this crude way do not conform to the eigenvalue equations or ladder operators given in Section 3.1.1. Clebsch-Gordan coefficients diagonalise $\mathbf{J}^2$ into a vector space with $|J, m_J\rangle$ eigenfunctions such that J_i behave in accordance with ladder operators. We now proceed to use the example of $L = 1$ coupled to the $S = 1/2$ Hilbert space to return $J = 3/2 \oplus 1/2$ blocks also encountered in Section 2.2.2, with the eventual goal of obtaining a general formula for evaluating Clebsch-Gordan coefficients. Employing the above formula with L_x and $S_x = \frac{1}{2}\sigma_x$; one obtains;

$$J_x = \frac{\hbar}{2} \begin{pmatrix} 0 & \sqrt{2} & 0 & 1 & 0 & 0 \\ \sqrt{2} & 0 & \sqrt{2} & 0 & 1 & 0 \\ 0 & \sqrt{2} & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & \sqrt{2} & 0 \\ 0 & 1 & 0 & \sqrt{2} & 0 & \sqrt{2} \\ 0 & 0 & 1 & 0 & \sqrt{2} & 0 \end{pmatrix} \quad (3.13)$$

Transformation of J_x by a 6×6 matrix returns J_x into a form which satisfies the ladder operator equations with the appropriate normalisation;

$$C_{L, m_L, S, m_S}^{J, m_J} J_x \left(C_{L, m_L, S, m_S}^{J, m_J} \right)^\dagger = \frac{\hbar}{2} \begin{pmatrix} 0 & \sqrt{3} & 0 & 0 & 0 & 0 \\ \sqrt{3} & 0 & \sqrt{4} & 0 & 0 & 0 \\ 0 & \sqrt{4} & 0 & \sqrt{3} & 0 & 0 \\ 0 & 0 & \sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix} \quad (3.14)$$

where the expression for $C_{L, m_L, S, m_S}^{J, m_J}$ satisfy;

$$\begin{pmatrix} |3/2, +3/2\rangle \\ |3/2, +1/2\rangle \\ |3/2, -1/2\rangle \\ |3/2, -3/2\rangle \\ |1/2, +1/2\rangle \\ |1/2, -1/2\rangle \end{pmatrix} = \underbrace{\begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & \sqrt{\frac{2}{3}} & 0 & \frac{1}{\sqrt{3}} & 0 & 0 \\ 0 & 0 & \frac{1}{\sqrt{3}} & 0 & \sqrt{\frac{2}{3}} & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & \frac{-1}{\sqrt{3}} & 0 & \sqrt{\frac{2}{3}} & 0 & 0 \\ 0 & 0 & -\sqrt{\frac{2}{3}} & 0 & \frac{1}{\sqrt{3}} & 0 \end{pmatrix}}_{C_{L, m_L, S, m_S}^{J, m_J}} \begin{pmatrix} |1, +1\rangle \uparrow \\ |1, 0\rangle \uparrow \\ |1, -1\rangle \uparrow \\ |1, +1\rangle \downarrow \\ |1, 0\rangle \downarrow \\ |1, -1\rangle \downarrow \end{pmatrix} \quad (3.15)$$

Using a similar approach for J_y leads to a coherent set of matrices satisfying the ladder operator arithmetic given at the start of this chapter expressed as direct sums of $J = 3/2$ and $J = 1/2$ half integer particles. Furthermore, J_z is diagonal and ordered in ascending order of m_J eigenvalues for the relevant block. Evaluation of $\mathbf{J}^2$ also returns a diagonal matrix whose eigenvalues are in blocks satisfying $J = 3/2 \oplus 1/2$.

$$\mathbf{J}^2 = \frac{\hbar^2}{4} \begin{pmatrix} 15 & 0 & 0 & 0 & 0 & 0 \\ 0 & 15 & 0 & 0 & 0 & 0 \\ 0 & 0 & 15 & 0 & 0 & 0 \\ 0 & 0 & 0 & 15 & 0 & 0 \\ 0 & 0 & 0 & 0 & 3 & 0 \\ 0 & 0 & 0 & 0 & 0 & 3 \end{pmatrix} \quad (3.16)$$

This is a demonstration of the Russell-Saunders $\mathbf{L} \cdot \mathbf{S}$ coupling shown below;

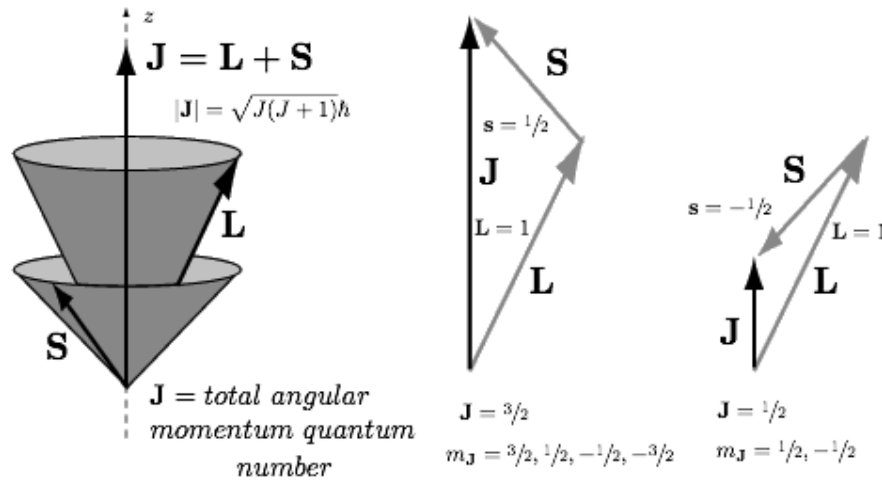


FIGURE 3.1: Demonstration of Russell-Saunders $\mathbf{L} \cdot \mathbf{S}$ Coupling of $L = 1$ with $S = 1/2$ to $J = 3/2$ and $J = 1/2$ [69]

C_{L,m_L,S,m_S}^{J,m_J} may be identified as the normalised coefficients occurring in Equation 2.17. Performing the same procedure for $L = 2$ would obtain a 10×10 matrices for $J = 5/2 \oplus 3/2$.

The next step is to account for the general case when $S \neq 1/2$ and find Clebsch-Gordan coefficients; $C_{J_1,m_{J_1},J_2,m_{J_2}}^{J_3,m_{J_3}}$, where the state $|J_1, m_{J_1}\rangle$ is coupled to $|J_2, m_{J_2}\rangle$ to return the vector $|J_3, m_{J_3}\rangle$. A numerical formula for obtaining $C_{J_1,m_{J_1},J_2,m_{J_2}}^{J_3,m_{J_3}}$ is rather convoluted so for this reason they are often sourced through lookup tables. There are also several notations such as a Wigner $3j^2$ - or Racah V - symbols [25], normalisations and phase conventions which make lookup tables error prone. Using modern computers; numerical algorithms for finding Clebsch-Gordan coefficients are possible, so for this reason a Maple

$${}^2 \begin{pmatrix} J_1 & J_2 & J_3 \\ m_{J_1} & m_{J_2} & m_{J_3} \end{pmatrix}$$

routine [70] is given in Appendix B. The routine evaluates the formula below, where the triangle coefficient, $\Delta(J_1, J_2, J_3)$, and function, $f(J_i, m_{J_i})$, are used to simplify the expression;

$$\Delta(J_1, J_2, J_3) = \frac{(J_1 + J_2 - J_3)! \times (J_3 + J_1 - J_2)! \times (J_2 + J_3 - J_1)!}{(J_1 + J_2 + J_3 + 1)!} \quad (3.17)$$

$$f(J_i, m_{J_i}) = (J_i + m_{J_i})! \times (J_i - m_{J_i})! \quad (3.18)$$

Naturally $f(J_i, m_{J_i})$ is zero for $m_{J_i} > J_i$, and one should consider the requirement $0! = 1$ for $J_i = \pm m_{J_i}$. The general formula for $C_{J_1, m_{J_1}, J_2, m_{J_2}}^{J_3, m_{J_3}}$ is then given as;

$$\begin{aligned} C_{J_1, m_{J_1}, J_2, m_{J_2}}^{J_3, m_{J_3}} = & \sqrt{(2J_3 + 1)! \times \Delta(J_1, J_2, J_3) \times f(J_1, m_{J_1}) \times f(J_2, m_{J_2}) \times f(J_3, m_{J_3})} \times \dots \\ & \dots \times \sum_{z=z_{\min}}^{z_{\max}} \frac{(-1)^z}{z! \times (c_1 - z)! \times (c_2 - z)! \times (c_3 - z)! \times (z - c_4)! \times (z - c_5)!} \end{aligned} \quad (3.19)$$

where $c_1 = J_1 + J_2 - J_3$, $c_2 = J_1 - m_{J_1}$, $c_3 = J_2 + m_{J_2}$, $c_4 = J_2 - J_3 - m_{J_1}$, and $c_5 = J_1 - J_3 + m_{J_2}$, and $z_{\max} = \min(c_1, c_2, c_3)$, $z_{\min} = \max(0, c_4, c_5)$.

In accordance with conservation of angular momentum; $m_{J_3} = m_{J_1} + m_{J_2}$ and $J_1 + J_2 \geq J_3 \geq |J_1 - J_2|$. One further property of Clebsch-Gordan coefficients is the inversion of m_{J_i} numbers [60]. In addition to this, consider particle exchange. This has significant implications on the phase associated with time reversal symmetry.

$$C_{J_1, m_{J_1}, J_2, m_{J_2}}^{J_3, m_{J_3}} = (-1)^{J_3 - J_1 - J_2} C_{J_1, -m_{J_1}, J_2, -m_{J_2}}^{J_3, -m_{J_3}} = (-1)^{J_3 - J_1 - J_2} C_{J_2, m_{J_2}, J_1, m_{J_1}}^{J_3, m_{J_3}} \quad (3.20)$$

From this one identifies $|L, m_L\rangle |S, m_S\rangle = \pm |S, m_S\rangle |L, m_L\rangle$ under exchange for $J = L \pm S$. Time reversal symmetry under the Condon-Shortley phase convention requires; $\hat{T} |J, m_J\rangle = (-1)^{J - m_J - L} |J, -m_J\rangle$, yet this is at odds with $\hat{T} |L, m_L\rangle |S, m_S\rangle = (-1)^{-m_L} |L, -m_L\rangle (-1)^{S - m_S} |S, -m_S\rangle$ for $J = L - S$. Consequently $\hat{T}$ also exchanges particles;

$$\hat{T} |L, m_L\rangle |S, m_S\rangle = (-1)^{-m_L + S - m_S} |S, -m_S\rangle |L, -m_L\rangle = (-1)^{J - m_J - L} |J, -m_J\rangle \quad (3.21)$$

The phase convention of Clebsch-Gordan coefficients must be in accordance with the time reversal operator $\hat{T}$. Using the Condon Shortley phase convention leads to purely real

single group eigenfunctions. The alternative is to use the Fano-Racah phase convention, where a factor i^L is included to single group basis functions, such that $\hat{T}|L, m_L\rangle = (-1)^{L-m_L}|L, -m_L\rangle$ and similarly for $L \rightarrow J$. One is at liberty which phase convention to use; after all they are just definitions, but it is chosen to use Condon-Shortley such that all single group basis are real.

The most poignant use of Clebsch-Gordan coefficients is through Wigner-Eckart theorem, where matrix elements between states $|J_1, m_{J_1}\rangle$ and $|J_2, m_{J_2}\rangle$ under the action of a spherical tensor operator T_κ^q may be evaluated numerically as $C_{\kappa, q, J_2, m_{J_2}}^{J_1, m_{J_1}}$. Since the unperturbed Hamiltonian and $\mathbf{k} \cdot \hat{\mathbf{p}}$ perturbations are zeroth- (scalar) and first- (vector) rank tensor operators respectively; Clebsch-Gordan coefficients are the single most important tool at our disposal within the context of this thesis. Further application to second- and third- tensors associated with strain and the electromechanical force attributed with the piezoelectric effect present further application. Using symmetrised single group and double group basis functions given in this chapter; linearly independent matrices may be enumerated, underpinning the application of group theory to describe physical behaviour of the crystal.

3.2.2 Representation Matrices II

Evaluation of double group representation matrices follows roughly the same procedure as that of the single group, in that the matrix exponential is evaluated for all point group operations of the T_d group, and brought into block diagonal form by a similarity transformation using an orthogonal matrix. The main difference is that the operations $\theta + 360^\circ$, account for the additional double group elements. Rather than evaluate all $2 \times 24 = 48$ representation matrices, the additional element $\hat{E}$ reverses the sign of counterpart single group elements, so $\mathbf{D}(\hat{E}g) = -\mathbf{D}(g) \forall g \in T_d$ for double group irreps. Since J contains no information on spatial parity a factor of $(-1)^L$ for improper rotations inherits from the parity of the O_h irrep. Akin to Section 3.1.2 the computation of $\mathbf{D}^{(\Gamma_8^\pm \oplus \Gamma_6^\pm)}(S_4(100))$ are performed. Using J_x in Equation 3.14, computing the matrix exponential with $\theta = \pi/2$ returns a block diagonal matrix;

$$\mathbf{D}^{(\Gamma_8^\pm \oplus \Gamma_6^\pm)}(S_4(100)) = \pm e^{-i \frac{J_x}{\hbar} \pi/2} = \frac{\mp 1}{2\sqrt{2}} \begin{pmatrix} -1 & i\sqrt{3} & \sqrt{3} & -i & 0 & 0 \\ i\sqrt{3} & 1 & i & \sqrt{3} & 0 & 0 \\ \sqrt{3} & i & 1 & i\sqrt{3} & 0 & 0 \\ -i & \sqrt{3} & i\sqrt{3} & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -2 & 2i \\ 0 & 0 & 0 & 0 & 2i & -2 \end{pmatrix} \quad (3.22)$$

T_d double group irreducible representation matrices are given in Tables A.5 ... A.8 in the Appendix A, and are in agreement with those given by Onodera & Okazaki [30]. In

accordance with case (c) of Herring's space group test [64], representation matrices are complex, but since this is the case with spin, there is no extra degeneracy.

Since $J = 5/2$ is compatible with $\Gamma_7^\pm \oplus \Gamma_8^\pm$, a similarity transformation block diagonalises the matrix exponential. The orthogonal matrix, returns symmetrised basis functions also tabulated by Onodera & Okazaki [30]. Both adapted double group and double group basis functions are given in Table 3.2. While basis functions are *not* eigenvectors of the time reversal operator, $\hat{T}$, they are eigenvectors of $\hat{T}^2$, with eigenvalue -1 .

3.2.3 Adapted Double Group Basis

The coupling of $L = 1$ with $S = 1/2$ to return $J = 3/2 \oplus 1/2$ in Section 3.2.1 was a choice pick, since C_{L,m_L,S,m_S}^{J,m_J} may also be used to formulate a general method for projecting out partner functions into the double group. Transforming $|L, m_L\rangle \otimes \{\uparrow, \downarrow\}$ into $\{x, y, z\} \otimes \{\downarrow, \uparrow\}$, then a matrix is returned that will transform representation matrices of $\Gamma_4^- \otimes \Gamma_6^+$ into $\Gamma_8^- \oplus \Gamma_6^-$ (given in the Appendix B.2). This method is prescribed by Cracknell & Joshua [71] used to return the adapted double group basis functions;

$$\begin{pmatrix} |3/2, +3/2\rangle \\ |3/2, +1/2\rangle \\ |3/2, -1/2\rangle \\ |3/2, -3/2\rangle \\ |1/2, +1/2\rangle \\ |1/2, -1/2\rangle \end{pmatrix} = \begin{pmatrix} \frac{-1}{\sqrt{2}} & \frac{-i}{\sqrt{2}} & 0 & 0 & 0 & 0 \\ 0 & 0 & \sqrt{\frac{2}{3}} & \frac{-1}{\sqrt{6}} & \frac{-i}{\sqrt{6}} & 0 \\ \frac{1}{\sqrt{6}} & \frac{-i}{\sqrt{6}} & 0 & 0 & 0 & \sqrt{\frac{2}{3}} \\ 0 & 0 & 0 & \frac{1}{\sqrt{2}} & \frac{-i}{\sqrt{2}} & 0 \\ 0 & 0 & \frac{-1}{\sqrt{3}} & \frac{-1}{\sqrt{3}} & \frac{-i}{\sqrt{3}} & 0 \\ \frac{-1}{\sqrt{3}} & \frac{i}{\sqrt{3}} & 0 & 0 & 0 & \frac{1}{\sqrt{3}} \end{pmatrix} \begin{pmatrix} x \uparrow \\ y \uparrow \\ z \uparrow \\ x \downarrow \\ y \downarrow \\ z \downarrow \end{pmatrix} \quad (3.23)$$

We may then use $L = 3$ compatible Γ_4^- basis functions to return an $J = 7/2 \oplus 5/2$ adapted double group basis also transforming according to $\Gamma_6^- \oplus \Gamma_8^-$. Representation matrices $\mathbf{D}^{(\Gamma_4^-)}(g) \otimes \mathbf{D}^{(\Gamma_6^+)}(g) \rightarrow \mathbf{D}^{(\Gamma_6^-)}(g) \oplus \mathbf{D}^{(\Gamma_8^-)}(g)$ may also be obtained by computing the Kronecker product and applying a similarity transformation using the matrix above.

From the multiplication Table 2.11 and compatibility relations for Γ_8^+ , a similar procedure for $\Gamma_5^+ \otimes \Gamma_6^+ = \Gamma_7^+ \oplus \Gamma_8^+$ may be applied. However, the matrix used must undergo a subsequent parity transformation. One may be forgiven for substituting $\{yz, zx, xy\}$ as cartesian basis functions for Γ_5^+ in replace of $\{x, y, z\}$, however this does not respect improper rotations. Consequently the matrix must be premultiplied by a 6×6 complex matrix presented in a publication by the author [72];

J	$ J, m_J\rangle$	Γ_i^+	$ L, m_L\rangle \otimes \{\uparrow, \downarrow\}$	Γ_i^-	$ L, m_L\rangle \otimes \{\uparrow, \downarrow\}$
$1/2$	$ 1/2, +1/2\rangle$	Γ_6^+	$ 0, 0\rangle \uparrow$	Γ_6^-	$\frac{-1}{\sqrt{3}} 1, 0\rangle \uparrow + \sqrt{\frac{2}{3}} 1, +1\rangle \downarrow$
	$ 1/2, -1/2\rangle$		$ 0, 0\rangle \downarrow$		$-\sqrt{\frac{2}{3}} 1, -1\rangle \uparrow + \frac{1}{\sqrt{3}} 1, 0\rangle \downarrow$
$3/2$	$ 3/2, +3/2\rangle$	Γ_8^+	$\frac{-2}{\sqrt{6}} 2, +1\rangle \uparrow + \frac{2}{\sqrt{5}} 2, +2\rangle \downarrow$	Γ_8^-	$ 1, +1\rangle \uparrow$
	$ 3/2, +1/2\rangle$		$-\sqrt{\frac{2}{5}} 2, 0\rangle \uparrow + \sqrt{\frac{3}{5}} 2, +1\rangle \downarrow$		$\sqrt{\frac{2}{3}} 1, 0\rangle \uparrow + \frac{1}{\sqrt{3}} 1, +1\rangle \downarrow$
$5/2$	$ 3/2, -1/2\rangle$		$-\sqrt{\frac{3}{5}} 2, -1\rangle \uparrow + \sqrt{\frac{2}{5}} 2, 0\rangle \downarrow$		$\frac{1}{\sqrt{3}} 1, -1\rangle \uparrow + \sqrt{\frac{2}{3}} 1, 0\rangle \downarrow$
	$ 3/2, -3/2\rangle$		$\frac{-2}{\sqrt{6}} 2, -2\rangle \uparrow + \frac{1}{\sqrt{5}} 2, -1\rangle \downarrow$		$ 1, -1\rangle \downarrow$
$5/2$	$\sqrt{\frac{5}{6}} 5/2, -3/2\rangle - \frac{1}{\sqrt{6}} 5/2, +5/2\rangle$	Γ_7^+	$\frac{1}{\sqrt{6}} 2, -2\rangle \uparrow + \frac{2}{\sqrt{6}} 2, -1\rangle \downarrow - \frac{1}{\sqrt{6}} 2, +2\rangle \uparrow$	Γ_7^-	$\frac{-5}{\sqrt{42}} 3, -2\rangle \uparrow + \sqrt{\frac{5}{21}} 3, -1\rangle \downarrow + \sqrt{\frac{1}{42}} 3, +2\rangle \uparrow - \frac{1}{\sqrt{7}} 3, +3\rangle \downarrow$
	$\sqrt{\frac{5}{6}} 5/2, +3/2\rangle - \frac{1}{\sqrt{6}} 5/2, -5/2\rangle$		$\frac{1}{\sqrt{6}} 2, +2\rangle \downarrow + \frac{2}{\sqrt{6}} 2, +1\rangle \uparrow - \frac{1}{\sqrt{6}} 2, -2\rangle \downarrow$		$\frac{5}{\sqrt{42}} 3, +2\rangle \downarrow - \sqrt{\frac{5}{21}} 3, +1\rangle \uparrow - \frac{1}{\sqrt{42}} 3, -2\rangle \downarrow + \frac{1}{\sqrt{7}} 3, -3\rangle \uparrow$
$5/2$	$\frac{-1}{\sqrt{6}} 5/2, +3/2\rangle - \sqrt{\frac{5}{6}} 5/2, -5/2\rangle$	Γ_8^+	$\frac{-2}{\sqrt{30}} 2, +1\rangle \uparrow - \frac{1}{\sqrt{30}} 2, +2\rangle \downarrow - \frac{5}{\sqrt{30}} 2, -2\rangle \downarrow$	Γ_8^-	$\frac{1}{\sqrt{21}} 3, +1\rangle \uparrow - \sqrt{\frac{5}{42}} 3, +2\rangle \uparrow + \sqrt{\frac{5}{7}} 3, -3\rangle \uparrow - \sqrt{\frac{5}{42}} 3, -2\rangle \downarrow$
	$ 5/2, +1/2\rangle$		$\sqrt{\frac{2}{5}} 2, +1\rangle \downarrow + \sqrt{\frac{3}{5}} 2, 0\rangle \uparrow$		$-\sqrt{\frac{2}{7}} 3, 0\rangle \uparrow + \frac{2}{\sqrt{7}} 3, +1\rangle \downarrow$
$5/2$	$ 5/2, -1/2\rangle$		$-\sqrt{\frac{3}{5}} 2, 0\rangle \downarrow - \sqrt{\frac{2}{5}} 2, -1\rangle \uparrow$		$-\sqrt{\frac{3}{7}} 3, 0\rangle \downarrow + \frac{2}{\sqrt{7}} 3, -1\rangle \uparrow$
	$\frac{1}{\sqrt{6}} 5/2, -3/2\rangle + \sqrt{\frac{5}{6}} 5/2, +5/2\rangle$		$\frac{2}{\sqrt{30}} 2, -1\rangle \downarrow + \frac{1}{\sqrt{30}} 2, -2\rangle \uparrow + \frac{5}{\sqrt{30}} 2, +2\rangle \uparrow$		$\frac{1}{\sqrt{21}} 3, -1\rangle \downarrow - \sqrt{\frac{5}{42}} 3, -2\rangle \downarrow + \sqrt{\frac{5}{7}} 3, +3\rangle \downarrow - \sqrt{\frac{5}{42}} 3, +2\rangle \uparrow$
$7/2$	$\sqrt{\frac{7}{12}} 7/2, +1/2\rangle + \sqrt{\frac{5}{12}} 7/2, -7/2\rangle$	Γ_6^+	$-\sqrt{\frac{7}{27}} 4, 0\rangle \uparrow + \sqrt{\frac{35}{108}} 4, +1\rangle \downarrow - \sqrt{\frac{10}{27}} 4, -4\rangle \uparrow + \sqrt{\frac{5}{108}} 4, -3\rangle \downarrow$	Γ_6^-	$\frac{1}{\sqrt{3}} 3, 0\rangle \uparrow + \frac{1}{2} 3, +1\rangle \downarrow + \sqrt{\frac{5}{12}} 3, -3\rangle \downarrow$
	$-\sqrt{\frac{7}{12}} 7/2, -1/2\rangle - \sqrt{\frac{5}{12}} 7/2, +7/2\rangle$		$-\sqrt{\frac{7}{27}} 4, 0\rangle \downarrow + \sqrt{\frac{35}{108}} 4, -1\rangle \uparrow - \sqrt{\frac{10}{27}} 4, +4\rangle \downarrow + \sqrt{\frac{5}{108}} 4, +3\rangle \uparrow$		$-\frac{1}{\sqrt{3}} 3, 0\rangle \downarrow - \frac{1}{2} 3, -1\rangle \uparrow - \sqrt{\frac{5}{12}} 3, +3\rangle \uparrow$
$7/2$	$-\frac{\sqrt{3}}{2} 7/2, +5/2\rangle + \frac{1}{2} 7/2, -3/2\rangle$	Γ_7^+	$\frac{1}{\sqrt{6}} 4, +2\rangle \uparrow - \sqrt{\frac{7}{12}} 4, +3\rangle \downarrow - \frac{1}{\sqrt{6}} 4, -2\rangle \uparrow + \sqrt{\frac{1}{12}} 4, -1\rangle \downarrow$	Γ_7^-	$-\sqrt{\frac{9}{14}} 3, +2\rangle \uparrow - \sqrt{\frac{3}{28}} 3, +3\rangle \downarrow + \frac{1}{\sqrt{14}} 3, -2\rangle \uparrow + \sqrt{\frac{5}{28}} 3, -1\rangle \downarrow$
	$\frac{\sqrt{3}}{2} 7/2, -5/2\rangle - \frac{1}{2} 7/2, +3/2\rangle$		$\frac{1}{\sqrt{6}} 4, -2\rangle \downarrow - \sqrt{\frac{7}{12}} 4, -3\rangle \uparrow - \frac{1}{\sqrt{6}} 4, +2\rangle \downarrow + \sqrt{\frac{1}{12}} 4, +1\rangle \uparrow$		$\sqrt{\frac{9}{14}} 3, -2\rangle \downarrow + \sqrt{\frac{3}{28}} 3, -3\rangle \uparrow - \frac{1}{\sqrt{14}} 3, +2\rangle \downarrow - \sqrt{\frac{5}{28}} 3, +1\rangle \uparrow$
$7/2$	$\frac{\sqrt{3}}{2} 7/2, +3/2\rangle + \frac{1}{2} 7/2, -5/2\rangle$	Γ_8^+	$-\frac{1}{2} 4, +1\rangle \uparrow + \frac{1}{\sqrt{2}} 4, +2\rangle \downarrow - \sqrt{\frac{7}{36}} 4, -3\rangle \uparrow + \frac{1}{\sqrt{18}} 4, -2\rangle \downarrow$	Γ_8^-	$\sqrt{\frac{15}{28}} 3, +1\rangle \uparrow + \sqrt{\frac{3}{14}} 3, +2\rangle \downarrow + \frac{1}{\sqrt{28}} 3, -3\rangle \uparrow + \sqrt{\frac{3}{14}} 3, -2\rangle \downarrow$
	$-\sqrt{\frac{5}{12}} 7/2, +1/2\rangle + \sqrt{\frac{7}{12}} 7/2, -7/2\rangle$		$\sqrt{\frac{5}{27}} 4, 0\rangle \uparrow - \sqrt{\frac{5}{108}} 4, +1\rangle \downarrow - \sqrt{\frac{14}{27}} 4, -4\rangle \uparrow + \sqrt{\frac{7}{108}} 4, -3\rangle \downarrow$		$-\sqrt{\frac{21}{5}} 3, 0\rangle \uparrow - \sqrt{\frac{15}{84}} 3, +1\rangle \downarrow + \sqrt{\frac{49}{84}} 3, -3\rangle \downarrow$
$7/2$	$-\sqrt{\frac{5}{12}} 7/2, -1/2\rangle + \sqrt{\frac{7}{12}} 7/2, +7/2\rangle$		$-\sqrt{\frac{5}{27}} 4, 0\rangle \downarrow + \sqrt{\frac{5}{108}} 4, -1\rangle \uparrow + \sqrt{\frac{14}{27}} 4, +4\rangle \downarrow - \sqrt{\frac{7}{108}} 4, +3\rangle \uparrow$		$-\sqrt{\frac{5}{21}} 3, 0\rangle \downarrow - \sqrt{\frac{15}{84}} 3, -1\rangle \uparrow + \sqrt{\frac{49}{84}} 3, +3\rangle \uparrow$
	$\frac{\sqrt{3}}{2} 7/2, -3/2\rangle + \frac{1}{2} 7/2, +5/2\rangle$		$\frac{1}{2} 4, -1\rangle \downarrow - \frac{1}{\sqrt{2}} 4, -2\rangle \uparrow + \sqrt{\frac{7}{36}} 4, +3\rangle \downarrow - \sqrt{\frac{1}{18}} 4, +2\rangle \uparrow$		$\sqrt{\frac{15}{28}} 3, -1\rangle \downarrow + \sqrt{\frac{3}{14}} 3, -2\rangle \uparrow + \frac{1}{\sqrt{28}} 3, +3\rangle \downarrow + \sqrt{\frac{3}{14}} 3, +2\rangle \uparrow$

TABLE 3.2: Double group and adapted double group symmetrised normalised basis functions transforming according to O_h irreps from $J = 1/2 \dots 7/2$ [30]. Basis functions are eigenfunctions of $\hat{T}^2$, with eigenvalue -1 . Both double and adapted double group basis functions are coherent under the action of $\hat{T}$ under the Condon-Shortley phase convention

$$\underline{\mathbf{T}} = \begin{pmatrix} 0 & 0 & i & 0 & 0 & 0 \\ 0 & 0 & 0 & -i & 0 & 0 \\ -i & 0 & 0 & 0 & 0 & 0 \\ 0 & i & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & i & 0 \\ 0 & 0 & 0 & 0 & 0 & i \end{pmatrix} \quad (3.24)$$

to return the unitary matrix for Γ_5^+ ;

$$\begin{pmatrix} \frac{i}{\sqrt{6}} & \frac{1}{\sqrt{6}} & 0 & 0 & 0 & i\sqrt{\frac{2}{3}} \\ 0 & 0 & 0 & \frac{-i}{\sqrt{2}} & \frac{-1}{\sqrt{2}} & 0 \\ \frac{i}{\sqrt{2}} & \frac{-1}{\sqrt{2}} & 0 & 0 & 0 & 0 \\ 0 & 0 & i\sqrt{\frac{2}{3}} & \frac{-i}{\sqrt{6}} & \frac{1}{\sqrt{6}} & 0 \\ 0 & 0 & \frac{-i}{\sqrt{3}} & \frac{-i}{\sqrt{3}} & \frac{1}{\sqrt{3}} & 0 \\ \frac{-i}{\sqrt{3}} & \frac{-1}{\sqrt{3}} & 0 & 0 & 0 & \frac{i}{\sqrt{3}} \end{pmatrix} \begin{pmatrix} yz \uparrow \\ zx \uparrow \\ xy \uparrow \\ yz \downarrow \\ zx \downarrow \\ xy \downarrow \end{pmatrix} \quad (3.25)$$

One must note that this does not necessarily return equivalent $|J, m_J\rangle$ basis functions; because there an additional $\Gamma_3^+ \otimes \Gamma_6^+ = \Gamma_8^+$ component has been overlooked. Since $L = 2$ gives rise to two independent Γ_8^+ contributions under transformation into the double group from $J = L - S = 3/2$ and $J = L + S = 5/2$ as depicted in Figure 2.3. The contribution to Γ_7^+ from $J = 5/2$ is purely from Γ_5^+ , and consequently the bottom two rows in Equation 3.25 return the appropriate basis functions.

Transformation of $\Gamma_3^+ \otimes \Gamma_6^+$ into Γ_8^+ is done via the 4×4 matrix;

$$\begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \frac{1}{2}(x^2 - y^2) \uparrow \\ \frac{1}{\sqrt{3}}(z^2 - \frac{1}{2}(x^2 + y^2)) \uparrow \\ \frac{1}{2}(x^2 - y^2) \downarrow \\ \frac{1}{\sqrt{3}}(z^2 - \frac{1}{2}(x^2 + y^2)) \downarrow \end{pmatrix} \quad (3.26)$$

Consequently, a weighting of $-\sqrt{\frac{2}{5}}$ and $\sqrt{\frac{3}{5}}$ is ascribed for Γ_3^+ and Γ_5^+ contributions respectively to $J = 3/2$, and $\sqrt{\frac{3}{5}}$ and $\sqrt{\frac{2}{5}}$ for respective contributions to $J = 5/2$. One may indeed check that substitution into spherical harmonics given in Equation 3.11 indeed returns the correct functions in Table 3.2.

This mixing of contributions highlights a fundamental flaw in the adapted double group when the spin orbit interaction dominates over the crystal field strength. Since spin

orbit is generally proportional to the proton number of the core nucleus, the single group framework may suffice in Silicon, but may begin to break down in Germanium. The beauty of the double group formulation is by accounting for this in the appropriate manner using Wigner-Eckart theorem.

3.2.4 Zinc-blende Basis Functions

The loss of inversion symmetry lifts well defined parity such that irreps become equivalent; $\Gamma_5 \otimes \Gamma^{equiv} = \Gamma_5^+ + \Gamma_4^-$. basis functions of T_d become linear combinations of their equivalent O_h ones, measured by the difference in electronegativity [73] from bulk inversion anisotropy. Elemental group IV crystals are special cases of zero difference in electronegativity as neighbouring atoms are equivalent and form a covalent bond. Conversely; inequivalent atoms in III-V binary crystals form a polar bond due to the difference in electronegativity, and this difference is exacerbated in II-VIs and so forth.

T_d group basis functions may be composed of constituent O_h basis functions;

$$|J, m_J\rangle = c_1 |J, m_J\rangle^+ + c_2 \underline{\underline{\mathbf{T}}} |J, m_J\rangle^- \quad (3.27)$$

where superscripts have been used to indicate spatial parity and c_1 and c_2 are normalised coefficients and $\underline{\underline{\mathbf{T}}}$ is given in Equation 3.24.

The physical consequence of this is that where odd tensor operators are zero on parity grounds in O_h , there is a non-zero weighting of $c_1^*c_2 + c_1c_2^*$ in T_d . Similarly even tensor operators which are permitted in O_h have a weighting of $|c_1|^2 + |c_2|^2$ in T_d . The existence of odd tensor matrix elements is further evidence for the non-zero electromechanical tensor attributed with the piezoelectric effect in T_d .

Summary

This chapter has made use of much of the abstract mathematical group theory introduced in Chapter 2 to generate symmetrised single and double group basis functions for the O_h and T_d groups. In addition the methodology for computing representation matrices was discussed such that all matrices for elements and irreps in the T_d group are tabulated in Appendix A. The projection operator technique was used as a means of converting single group basis functions from their spherical $|L, m_L\rangle$ to cartesian $\{x, y, z\}$ notations under the respective Condon-Shortley phase convention.

The link between double group $|J, m_J\rangle$ basis functions with the adapted double group basis $|L, m_L\rangle \otimes \{\uparrow, \downarrow\}$ was discussed through the use of normalised Clebsch-Gordan coefficients, whose property under time reversal now includes exchange of particle. Clebsch-Gordan coefficients were also generalised to include arbitrary indices $C_{J_2, m_{J_2}, J_3, m_{J_3}}^{J_1, m_{J_1}}$ for use later as a means of coupling states to a spherical tensor operator.

A unitary matrix was also introduced as a general means of obtaining adapted double group basis and highlighted a significant flaw in using single group basis functions for crystals with comparatively high spin-orbit interactions with respect to crystal field. Finally basis functions in Zinc-blende type crystals were introduced to convey the way odd order tensor operators have non-zero matrix elements in accordance with the discussion originating in Section 2.3.2.

Overall Chapters 2 and 3 have defined the mathematical framework to which the rest of this thesis abides by. The use of tensor operators between symmetrised basis functions allows for the generation of linearly independent matrices for use in modelling the band structures of bulk cubic crystals and heterostructures such as quantum wells.

Chapter 4

Double Group Formulation of $\mathbf{k} \cdot \hat{\mathbf{p}}$ Theory

The $\mathbf{k} \cdot \hat{\mathbf{p}}$ method has been one of the most successful modelling techniques for well over half a century because of its innate ability to return the dispersion $E(\mathbf{k})$ as a band diagram with relative ease. Yet it is constantly being refreshed and revamped to keep up with the demands of increasing experimental accuracies. Because it is inherently a semi-empirical technique the temptation to adjust parameters rather than look at the basic formulation often proves too great despite the limitations being well known. The double group formulation of the $\mathbf{k} \cdot \hat{\mathbf{p}}$ method takes the spin-orbit interaction into the unperturbed Hamiltonian to return the $\mathbf{k} \cdot \hat{\boldsymbol{\pi}}$ perturbation. Eigenvectors are then symmetrised $|J, m_J\rangle$ basis given in the previous chapter.

Parameters taken from the single and adapted double groups return full zone bulk band dispersion for Silicon-Germanium (SiGe) under the double group formulation. Using the Löwdin renormalisation procedure [32] one may identify improvements that the double group provides. These include numerical values for Luttinger parameters and heavy and light hole effective masses for comparison with experimental cyclotron resonance [38] results.

The theory of invariants [37] provides an alternate way to generate 4-, 6- and 8-band Hamiltonians with less stringent assumptions on the self consistent one electron potential. Comparison of the two methods provides not just verification of results but an altogether different way of solving the same problem using group multiplication tables. Furthermore, using canonical transformations one may transform the quantisation axis for use in heterostructures grown on arbitrary crystallographic faces with relative ease.

Matlab source code complementary to this chapter was uploaded to the Mathworks file exchange server: <http://www.mathworks.com/matlabcentral/fileexchange/32595>

4.1 The $\mathbf{k} \cdot \hat{\mathbf{p}}$ Hamiltonian

The $\mathbf{k} \cdot \hat{\mathbf{p}}$ Hamiltonian may be evaluated for single and double group formulations in an identical manner since both $\hat{\mathbf{p}}$ and $\hat{\pi}$ transform according to a rank-1 tensor operator. Matrix elements may be evaluated using Wigner-Eckart theorem such that linearly independent matrices between sets of irreps may be returned using Clebsch-Gordan coefficients and symmetrised basis functions from the previous chapter.

Constructing a 30×30 concatenated block matrix Hamiltonian, full zone bulk band diagrams for Silicon and Germanium may be returned [28] given appropriate scaling parameters. The indirect conduction band minima in Silicon and Germanium may be realised with an abrupt transition from Δ to L valleys at $Si_{0.12}Ge_{0.88}$ in agreement with the kink in experimental near band-gap photoluminescence [74].

4.1.1 Single Group Formulation

Using Wigner-Eckart theorem the interaction matrix between Γ_1^+ and Γ_4^- states returns just one linearly independent matrix;

$$\left. \begin{aligned} \langle 1, \pm 1 | \mathbf{k} \cdot \hat{\mathbf{p}} | 0, 0 \rangle &= \frac{\pm 1}{\sqrt{6}} k_{\pm} \\ \langle 1, 0 | \mathbf{k} \cdot \hat{\mathbf{p}} | 0, 0 \rangle &= \frac{-1}{\sqrt{3}} k_z \end{aligned} \right\} \implies A_{\mathbf{k} \cdot \hat{\mathbf{p}}}^{\Gamma_4^-: \Gamma_1^+} = \begin{pmatrix} k_x & x \\ k_y & y \\ k_z & z \end{pmatrix} \quad (4.1)$$

where the matrix is cast into cartesian form to coincide with the literature. This is also equivalent to $A_{\mathbf{k} \cdot \hat{\mathbf{p}}}^{\Gamma_5^+: \Gamma_2^-}$ when using Γ_5^+ and Γ_2^- states. $A_{\mathbf{k} \cdot \hat{\mathbf{p}}}^{\Gamma_4^-: \Gamma_1^+}$ is commonly used to model inter-band transition rates when scaled by P_1 ; the Kane parameter [33], and/or to incorporate conduction band non-parabolicity in 8-band models [75].

We now proceed to calculate two matrices for interactions between Γ_4^- and $\Gamma_5^+ \oplus \Gamma_3^+$;

$$\left. \begin{aligned} \langle 1, \pm 1 | \mathbf{k} \cdot \hat{\mathbf{p}} | 2, \pm 2 \rangle &= \frac{\mp 1}{\sqrt{2}} k_{\mp} \\ \langle 1, \pm 1 | \mathbf{k} \cdot \hat{\mathbf{p}} | 2, \pm 1 \rangle &= \frac{1}{\sqrt{2}} k_z \\ \langle 1, 0 | \mathbf{k} \cdot \hat{\mathbf{p}} | 2, \pm 1 \rangle &= \frac{\mp 1}{2} k_{\mp} \\ \langle 1, \pm 1 | \mathbf{k} \cdot \hat{\mathbf{p}} | 2, 0 \rangle &= \frac{\pm 1}{2\sqrt{3}} k_{\pm} \\ \langle 1, 0 | \mathbf{k} \cdot \hat{\mathbf{p}} | 2, 0 \rangle &= \sqrt{\frac{2}{3}} k_z \end{aligned} \right\} \implies \begin{aligned} A_{\mathbf{k} \cdot \hat{\mathbf{p}}}^{\Gamma_4^-: \Gamma_3^+} &= \begin{pmatrix} -\sqrt{3}k_x & k_x \\ \sqrt{3}k_y & k_y \\ 0 & -2k_z \end{pmatrix} \\ A_{\mathbf{k} \cdot \hat{\mathbf{p}}}^{\Gamma_4^-: \Gamma_5^+} &= \begin{pmatrix} 0 & k_z & k_y \\ k_z & 0 & k_x \\ k_y & k_x & 0 \end{pmatrix} \end{aligned} \quad (4.2)$$

These three matrices are self-adjoint and constitute the widely used single group linearly independent matrices in accordance with the symmetric decomposition; $(\Gamma_4^- \otimes \Gamma_4^-)_{sym} = \Gamma_1^+ \oplus \Gamma_3^+ \oplus \Gamma_5^+$. The first point to mention is that irreps are not basis specific, so one

could just equally have used Γ_4^- states of $L = 3$ to return linearly dependent matrices. Indeed if one had done; $A_{\mathbf{k} \cdot \hat{\mathbf{p}}}^{\Gamma_4^-: \Gamma_4^+}$ emerges anti-symmetric [76]. Furthermore while $A_{\mathbf{k} \cdot \hat{\mathbf{p}}}^{\Gamma_5^+: \Gamma_4^-}$ is equivalent to $A_{\mathbf{k} \cdot \hat{\mathbf{p}}}^{\Gamma_4^-: \Gamma_5^+}$ the same may not be said for $A_{\mathbf{k} \cdot \hat{\mathbf{p}}}^{\Gamma_5^+: \Gamma_3^-}$ and $A_{\mathbf{k} \cdot \hat{\mathbf{p}}}^{\Gamma_4^-: \Gamma_3^+}$. Using symmetrised eigenstates of Γ_5^+ and Γ_3^- instead returns;

$$A_{\mathbf{k} \cdot \hat{\mathbf{p}}}^{\Gamma_5^+: \Gamma_3^-} = \begin{pmatrix} k_x & \sqrt{3}k_x \\ k_y & -\sqrt{3}k_y \\ -2k_z & 0 \end{pmatrix} \begin{matrix} yz \\ zx \\ xy \end{matrix} \quad (4.3)$$

A 15×15 concatenated block matrix Hamiltonian with appropriate scaling parameters is enough to return full zone band diagrams. Indeed the indirect gaps of Silicon at Δ and Germanium at L were first realised by Cardona & Pollak [28], and the absorption spectra explained in terms of optical transitions within the FBZ. Furthermore, the DKK Hamiltonian [34] may be returned by evaluating $A_{\mathbf{k} \cdot \hat{\mathbf{p}}}^{\Gamma_4^-: \Gamma_j^+} \times \left(A_{\mathbf{k} \cdot \hat{\mathbf{p}}}^{\Gamma_4^-: \Gamma_j^+} \right)^\dagger$ and scaling by effective mass parameters, although this is explored in more detail later.

While the single group was very successful at reproducing experimental results the formulation neglects the spin-orbit interaction. Efforts to incorporate spin into a 30×30 concatenated block matrix Hamiltonian [31, 77] generally use the adapted double group $|L, m_L\rangle \otimes \{\uparrow, \downarrow\}$. The following section attempts to incorporate spin through the $\mathbf{k} \cdot \hat{\boldsymbol{\pi}}$ Hamiltonian and symmetrised $|J, m_J\rangle$ basis functions such that spin-orbit is included in the unperturbed Hamiltonian with appropriate double group degeneracy at the zone centre.

4.1.2 Double Group Formulation

Using the half integer basis functions $J = 1/2$ and $J = 3/2$ we may evaluate the linearly independent matrix $A_{\mathbf{k} \cdot \hat{\boldsymbol{\pi}}}^{\Gamma_8^\pm: \Gamma_6^\mp}$. This is the example given in the Appendix B.3.

$$\left. \begin{aligned} \langle 3/2, \pm 3/2 | \mathbf{k} \cdot \hat{\boldsymbol{\pi}} | 1/2, \pm 1/2 \rangle &= \frac{\pm 1}{2} k_\pm \\ \langle 3/2, \pm 1/2 | \mathbf{k} \cdot \hat{\boldsymbol{\pi}} | 1/2, \pm 1/2 \rangle &= \frac{\mp 1}{\sqrt{3}} k_z \\ \langle 3/2, \mp 1/2 | \mathbf{k} \cdot \hat{\boldsymbol{\pi}} | 1/2, \pm 1/2 \rangle &= \frac{\pm 1}{2\sqrt{3}} k_\mp \end{aligned} \right\} \implies A_{\mathbf{k} \cdot \hat{\boldsymbol{\pi}}}^{\Gamma_8^\pm: \Gamma_6^\mp} = \frac{-1}{\sqrt{2}} \begin{pmatrix} -\sqrt{3}k_+ & 0 \\ 2k_z & -k_+ \\ k_- & 2k_z \\ 0 & \sqrt{3}k_- \end{pmatrix} \quad (4.4)$$

In Section 3.2.3, a unitary matrix was introduced as a means of transforming $\{x, y, z\} \otimes \{\uparrow, \downarrow\}$ into the $J = 3/2 \oplus 1/2$ adapted double group basis. We may also generate $A_{\mathbf{k} \cdot \hat{\boldsymbol{\pi}}}^{\Gamma_8^\pm: \Gamma_6^\mp}$ by evaluating a unitary transformation of; $A_{\mathbf{k} \cdot \hat{\mathbf{p}}}^{\Gamma_4^-: \Gamma_1^+} \otimes \{\uparrow, \downarrow\}$;

$$A_{\mathbf{k}\cdot\hat{\mathbf{p}}}^{\Gamma_4^-:\Gamma_1^+} \otimes \{\uparrow, \downarrow\} = \begin{pmatrix} k_x & 0 \\ k_y & 0 \\ k_z & 0 \\ 0 & k_x \\ 0 & k_y \\ 0 & k_z \end{pmatrix} \begin{matrix} x \uparrow \\ y \uparrow \\ z \uparrow \\ x \downarrow \\ y \downarrow \\ z \downarrow \end{matrix} \Rightarrow \begin{pmatrix} -\sqrt{3}k_+ & 0 \\ 2k_z & -k_+ \\ k_- & 2k_z \\ 0 & \sqrt{3}k_- \end{pmatrix} \begin{matrix} |3/2, +3/2\rangle \\ |3/2, +1/2\rangle \\ |3/2, -1/2\rangle \\ |3/2, -3/2\rangle \end{matrix} \quad (4.5)$$

Both matrices returned are linearly dependent, such that both double and adapted double group methods return coherent solutions albeit within a normalisation factor. While this factor may be absorbed into the reduced matrix element, it is essential that scalings are consistent between both methods.

At this point, one may ask what is the difference between the adapted double and double group formulations since these results are in agreement. As discussed at the end of Section 2.3.2, there are *two* linearly independent matrices when computing $A_{\mathbf{k}\cdot\hat{\boldsymbol{\pi}}}^{\Gamma_8^\pm:\Gamma_8^\mp}$. Recall that $\Gamma_3^+ \otimes \Gamma_6^+ = \Gamma_8^+$ and $\Gamma_5^+ \otimes \Gamma_6^+ = \Gamma_7^+ \oplus \Gamma_8^+$. Casting $A_{\mathbf{k}\cdot\hat{\mathbf{p}}}^{\Gamma_4^-:\Gamma_5^+}$ and $A_{\mathbf{k}\cdot\hat{\mathbf{p}}}^{\Gamma_4^-:\Gamma_3^+}$ onto the adapted double group basis returns the linearly independent matrices;

$$A_{\mathbf{k}\cdot\hat{\boldsymbol{\pi}},1}^{\Gamma_8^\pm:\Gamma_8^\mp} = \begin{pmatrix} k_z & 0 & 0 & k_- \\ 0 & -k_z & k_+ & 0 \\ 0 & k_- & k_z & 0 \\ k_+ & 0 & 0 & -k_z \end{pmatrix} \quad (4.6)$$

$$A_{\mathbf{k}\cdot\hat{\boldsymbol{\pi}},2}^{\Gamma_8^-:\Gamma_8^+} = \frac{1}{\sqrt{6}} \begin{pmatrix} 0 & -\sqrt{3}k_+ & 0 & 3k_- \\ -\sqrt{3}k_- & -4k_z & k_+ & 0 \\ 0 & k_- & 4k_z & -\sqrt{3}k_+ \\ 3k_+ & 0 & -\sqrt{3}k_- & 0 \end{pmatrix}$$

In Section 3.2.3, weightings of $\sqrt{\frac{3}{5}}$ and $-\sqrt{\frac{2}{5}}$ for the contributions from Γ_5^+ and Γ_3^+ respectively to $J = 3/2$, and weightings of $\sqrt{\frac{2}{5}}$ and $\sqrt{\frac{3}{5}}$ for the respective contributions to $J = 5/2$ were ascribed. Taking weighted linear combinations of $A_{\mathbf{k}\cdot\hat{\boldsymbol{\pi}},1}^{\Gamma_8^\pm:\Gamma_8^\mp}$ and $A_{\mathbf{k}\cdot\hat{\boldsymbol{\pi}},2}^{\Gamma_8^-:\Gamma_8^+}$ above the resulting matrices are now in accordance with the double group formulation presented in a co-authored publication [72];

$$\sqrt{\frac{3}{5}} A_{\mathbf{k}\cdot\hat{\boldsymbol{\pi}},1}^{\Gamma_8^\pm:\Gamma_8^\mp} - \sqrt{\frac{2}{5}} A_{\mathbf{k}\cdot\hat{\boldsymbol{\pi}},2}^{\Gamma_8^-:\Gamma_8^+} = \frac{1}{\sqrt{15}} \begin{pmatrix} 3k_z & \sqrt{3}k_+ & 0 & 0 \\ \sqrt{3}k_- & k_z & 2k_+ & 0 \\ 0 & 2k_- & -k_z & \sqrt{3}k_+ \\ 0 & 0 & \sqrt{3}k_- & -3k_z \end{pmatrix} \quad (4.7)$$

$$\sqrt{\frac{2}{5}}A_{\mathbf{k}\cdot\hat{\boldsymbol{\pi}},1}^{\Gamma_8^\pm:\Gamma_8^\mp} + \sqrt{\frac{3}{5}}A_{\mathbf{k}\cdot\hat{\boldsymbol{\pi}},2}^{\Gamma_8^\pm:\Gamma_8^\mp} = \frac{-1}{\sqrt{10}} \begin{pmatrix} -2k_z & \sqrt{3}k_+ & 0 & -5k_- \\ \sqrt{3}k_- & 6k_z & -3k_+ & 0 \\ 0 & -3k_- & -6k_z & \sqrt{3}k_+ \\ -5k_+ & 0 & \sqrt{3}k_- & 2k_z \end{pmatrix} \quad (4.8)$$

Casting $A_{\mathbf{k}\cdot\hat{\mathbf{p}}}^{\Gamma_5^+:\Gamma_4^-}$ onto the adapted double group basis returns $A_{\mathbf{k}\cdot\hat{\boldsymbol{\pi}},1}^{\Gamma_8^+:\Gamma_8^-} \equiv A_{\mathbf{k}\cdot\hat{\boldsymbol{\pi}},1}^{\Gamma_8^-:\Gamma_8^+}$ as implied, however applying the same logic to $A_{\mathbf{k}\cdot\hat{\mathbf{p}}}^{\Gamma_5^+:\Gamma_3^-}$ does not return $A_{\mathbf{k}\cdot\hat{\boldsymbol{\pi}},2}^{\Gamma_8^-:\Gamma_8^+}$, rather;

$$A_{\mathbf{k}\cdot\hat{\boldsymbol{\pi}},2}^{\Gamma_8^+:\Gamma_8^-} = \frac{1}{\sqrt{6}} \begin{pmatrix} 4k_z & \sqrt{3}k_+ & 0 & k_- \\ \sqrt{3}k_- & 0 & 3k_+ & 0 \\ 0 & 3k_- & 0 & \sqrt{3}k_+ \\ k_+ & 0 & \sqrt{3}k_- & -4k_z \end{pmatrix} \quad (4.9)$$

Bearing in mind that using $\underline{\mathbf{T}}$ given in Equation 3.24, one may transform $\Gamma_8^\pm$ into $\Gamma_8^\mp$. Therefore; $\underline{\mathbf{T}}A_{\mathbf{k}\cdot\hat{\boldsymbol{\pi}},2}^{\Gamma_8^+:\Gamma_8^+}\underline{\mathbf{T}}^\dagger = A_{\mathbf{k}\cdot\hat{\boldsymbol{\pi}},2}^{\Gamma_8^+:\Gamma_8^-}$. This essentially just permutes the entries in the matrix, leaving eigenvalues completely unchanged. However the effect on *eigenvectors* plays an important role in interpreting the ordering of heavy and light hole effective masses in 4-band models. One may also consider the anti-hermitian Rössler matrix [78]; $\underline{\mathbf{T}}A_{\mathbf{k}\cdot\hat{\boldsymbol{\pi}},1}^{\Gamma_8^\pm:\Gamma_8^\mp}$ attributed with linear- $\mathbf{k}$ terms in Zinc-blende type crystals.

One may evaluate $A_{\mathbf{k}\cdot\hat{\boldsymbol{\pi}}}^{\Gamma_6^\pm:\Gamma_6^\mp}$ using two $J = 1/2$ states. Applying the equivalence representation $\Gamma_{6,7} \otimes \Gamma^{equiv} = \Gamma_{6,7}^+ + \Gamma_{7,6}^-$. Since the multiplication table predicts just one linearly independent matrices for $\Gamma_6 \otimes \Gamma_7$ in the T_d group, then $A_{\mathbf{k}\cdot\hat{\boldsymbol{\pi}}}^{\Gamma_6^\pm:\Gamma_6^\mp} \equiv A_{\mathbf{k}\cdot\hat{\boldsymbol{\pi}}}^{\Gamma_7^\mp:\Gamma_7^\pm}$.

$$\left. \begin{aligned} \langle 1/2, \pm 1/2 | \mathbf{k} \cdot \hat{\boldsymbol{\pi}} | 1/2, \pm 1/2 \rangle &= \frac{\pm 1}{\sqrt{3}}k_z \\ \langle 1/2, \pm 1/2 | \mathbf{k} \cdot \hat{\boldsymbol{\pi}} | 1/2, \mp 1/2 \rangle &= \frac{1}{\sqrt{3}}k_\pm \end{aligned} \right\} \longrightarrow A_{\mathbf{k}\cdot\hat{\boldsymbol{\pi}}}^{\Gamma_6^\pm:\Gamma_6^\mp} = A_{\mathbf{k}\cdot\hat{\boldsymbol{\pi}}}^{\Gamma_7^\mp:\Gamma_7^\pm} = \begin{pmatrix} k_z & k_+ \\ k_- & -k_z \end{pmatrix} \quad (4.10)$$

There remains one final matrix required to be evaluated, and this is $A_{\mathbf{k}\cdot\hat{\boldsymbol{\pi}}}^{\Gamma_8^\pm:\Gamma_7^\mp}$. Using Clebsch-Gordan coefficients between $J = 3/2$ and applying the appropriate symmetrisation procedure to return $\Gamma_7^\pm$ basis for $J = 5/2$, one returns;

$$A_{\mathbf{k}\cdot\hat{\boldsymbol{\pi}}}^{\Gamma_8^\pm:\Gamma_7^\mp} = \frac{1}{\sqrt{2}} \begin{pmatrix} k_- & 2k_z \\ 0 & -\sqrt{3}k_- \\ \sqrt{3}k_+ & 0 \\ 2k_z & -k_+ \end{pmatrix} \quad (4.11)$$

The same matrix is returned when casting $A_{\mathbf{k}\hat{\mathbf{p}}}^{\Gamma_5^+:\Gamma_2^-}$ onto the relevant adapted double group basis in accordance with group multiplication tables.

All linearly independent matrices for the double group formulation of $\mathbf{k} \cdot \hat{\mathbf{p}}$ theory using spherical tensor operator projections of $\hat{\pi}$ and double group basis functions have now been generated. These are the building blocks for the 30×30 concatenated block matrix Hamiltonian. In the next section, it is shown how using semi-empirical input parameters full zone bulk band diagrams for Silicon, Germanium and respective SiGe alloys may be returned.

4.1.3 Full Zone Bulk Band Diagrams

The $\mathbf{k} \cdot \hat{\mathbf{p}}$ method is a semi-empirical technique and relies on input parameters obtained experimentally or otherwise to scale the Hamiltonian. Using the work of Rideau et al [31], input parameters are given within a 30-band adapted double group model using $A_{\mathbf{k}\hat{\mathbf{p}}}^{\Gamma_i^-:\Gamma_j^+}$ for Silicon and Germanium with respective alloy parameters following Vegard's Law [79]. However, to be completely faithful to the double group formulation, one calls for $A_{\mathbf{k}\hat{\pi}}^{\Gamma_i^\pm:\Gamma_j^\mp}$ and double group degeneracies for reasons discussed.

Scaling parameters and zone centre energy eigenvalues are given in Tables 4.1 and 4.2.

Parameter	Value (eV)	Parameter	Value (eV)
P_1	$+9.584 - 0.267x$	Q_1	$-8.389 - 0.054x$
P_2	$-0.063 + 0.613x - 0.393x^2$	Q_2	$+5.149 + 0.826x$
P_3	$+1.226 - 0.064x$	R_1	$-4.263 - 0.694x$
P_4	$+11.194 - 0.207x$	R_2	$-6.553 + 0.099x$
T_1	$-9.159 + 0.194x + 0.314x^2$	-	-
T_2	$-2.278 - 0.063x$	-	-

TABLE 4.1: $Si_{1-x}Ge_x$ scaling parameters used in the double group matrix Hamiltonian. P_1 is the Kane parameter [33]

Bonding	Energy (eV)	Anti-Bonding	Energy(eV)
$E_1^{\Gamma_6^+}$	$-12.7 - 0.18x$	$E_1^{\Gamma_7^-}$	$E_c = 4.15 - 3.26x$
$E_1^{\Gamma_7^+}$	$\Delta = -0.044 - 0.2x - 0.052x^2$	$E_1^{\Gamma_6^-}$	$3.302 - 0.379x$
$E_1^{\Gamma_8^+}$	$E_v = 0$	$E_1^{\Gamma_8^-}$	$3.335 - 0.222x$
$E_2^{\Gamma_6^+}$	$8.4 - 1.6x$	$E_2^{\Gamma_7^-}$	$15.8 - 1.8x$
$E_2^{\Gamma_7^+}$	$11.6988 - 0.37x$	-	-
$E_2^{\Gamma_8^+}$	$11.7 - 0.34x$	$E_2^{\Gamma_8^-}$	$8.54 + 1.76x$

TABLE 4.2: Double group zone centre energy eigenvalues for $Si_{1-x}Ge_x$. Subscripts denote the occurrence of an irrep given in the superscript

Double group zone centre energy eigenvalues set the four-fold degenerate valence band maximum of symmetry type Γ_8^+ as the band offset reference $E_v = 0$. Additionally, the spin-orbit split off band of symmetry type Γ_7^+ is an energy Δ beneath the valence band maximum. The zone centre conduction band minimum is Γ_6^- in Silicon, and Γ_7^- in Germanium; switching at $x = 29\%$. This is depicted in Figure 4.1; inspired by similar figures in Richard et al [77], el Kurdi et al [43] and Fraj et al [80].

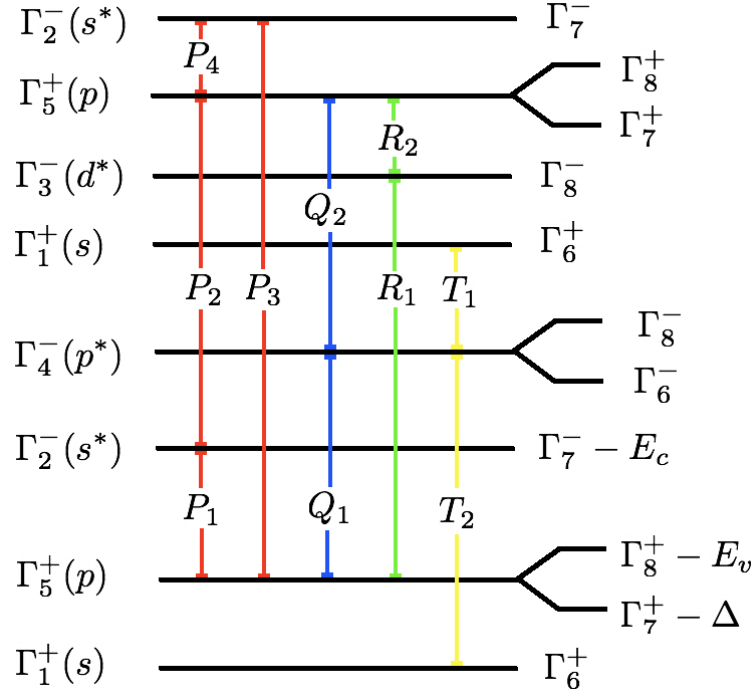


FIGURE 4.1: Zone centre energy level schematic with symmetry classifications; with interaction parameters formulated out of the single group approach

One of the headaches associated with the literature¹ has been to ascribe the valence bands as Γ_4^- and conduction band as Γ_1^+ . This stems from the sp^3 hybridisation paradigm and atomic site representation; $\Gamma^{a.s.} = \Gamma_1 \oplus \Gamma_5$ in T_d . Application of the equivalence representation $\Gamma^{equiv} = \Gamma_1^+ \oplus \Gamma_2^-$ into O_h comes with a severe warning. At first glance the difference appears insignificant, however as discussed in the previous section, $\underline{\mathbf{T}}$ transforms $\Gamma_8^\pm$ into $\Gamma_8^\mp$ and $\Gamma_{6,7}^\pm$ into $\Gamma_{7,6}^\mp$. Applying $\underline{\mathbf{T}}$ leaves eigenvalues unchanged and permutes eigenvectors. This subtle difference may cause problems!

It is chosen to stick with the convention in the literature, but one should heed the caution. For example consider the somewhat misleading arrangement of $H_{\mathbf{k} \cdot \hat{\boldsymbol{\pi}}}^{30 \times 30}$ overleaf. To be comfortable with the form presented, one should revert back to T_d and apply compatibility to discover the potential source of error.

¹unpublished work by F. Herman referred to in [34]

$$H_{\mathbf{k}, \hat{\pi}}^{30 \times 30} = \begin{pmatrix} 0 & 0 & 0 & 0 & T_2 A_{\mathbf{k}, \hat{\pi}}^{\Gamma_7^\mp: \Gamma_7^\pm} & T_2 \left(A_{\mathbf{k}, \hat{\pi}}^{\Gamma_8^\pm: \Gamma_7^\mp} \right)^\dagger & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -P_1 A_{\mathbf{k}, \hat{\pi}}^{\Gamma_6^\pm: \Gamma_6^\mp} & 0 & 0 & -Q_1 \left(A_{\mathbf{k}, \hat{\pi}}^{\Gamma_8^\pm: \Gamma_6^\mp} \right)^\dagger & 0 & \sqrt{2} R_1 \left(A_{\mathbf{k}, \hat{\pi}}^{\Gamma_8^\pm: \Gamma_6^\mp} \right)^\dagger & 0 & 0 & 0 \\ 0 & 0 & P_1 A_{\mathbf{k}, \hat{\pi}}^{\Gamma_8^\pm: \Gamma_6^\mp} & Q_1 A_{\mathbf{k}, \hat{\pi}, 1}^{\Gamma_8^\pm: \Gamma_8^\mp} & 0 & Q_1 A_{\mathbf{k}, \hat{\pi}, 1}^{\Gamma_8^\pm: \Gamma_8^\mp} & 0 & \sqrt{3} R_1 A_{\mathbf{k}, \hat{\pi}, 2}^{\Gamma_8^\pm: \Gamma_8^\mp} & 0 & -P_2 A_{\mathbf{k}, \hat{\pi}}^{\Gamma_6^\pm: \Gamma_6^\mp} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_2 \left(A_{\mathbf{k}, \hat{\pi}}^{\Gamma_8^\pm: \Gamma_6^\mp} \right)^\dagger & 0 \\ 0 & 0 & 0 & 0 & T_1 A_{\mathbf{k}, \hat{\pi}}^{\Gamma_7^\mp: \Gamma_7^\pm} & 0 & T_1 A_{\mathbf{k}, \hat{\pi}}^{\Gamma_7^\mp: \Gamma_7^\pm} & 0 & 0 & Q_2 \left(A_{\mathbf{k}, \hat{\pi}}^{\Gamma_8^\pm: \Gamma_7^\mp} \right)^\dagger & 0 \\ 0 & 0 & 0 & 0 & T_1 A_{\mathbf{k}, \hat{\pi}}^{\Gamma_8^\pm: \Gamma_7^\mp} & 0 & T_1 A_{\mathbf{k}, \hat{\pi}}^{\Gamma_8^\pm: \Gamma_7^\mp} & 0 & -Q_2 A_{\mathbf{k}, \hat{\pi}}^{\Gamma_8^\pm: \Gamma_6^\mp} & Q_2 A_{\mathbf{k}, \hat{\pi}, 1}^{\Gamma_8^\pm: \Gamma_8^\mp} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{2} R_2 A_{\mathbf{k}, \hat{\pi}}^{\Gamma_8^\pm: \Gamma_6^\mp} & \sqrt{3} R_2 A_{\mathbf{k}, \hat{\pi}, 2}^{\Gamma_8^\pm: \Gamma_8^\mp} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -P_4 A_{\mathbf{k}, \hat{\pi}}^{\Gamma_6^\pm: \Gamma_6^\mp} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_4 A_{\mathbf{k}, \hat{\pi}}^{\Gamma_8^\pm: \Gamma_6^\mp} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \begin{array}{c} \Gamma_6^+ \\ \hline \Gamma_7^+ \\ \Gamma_8^+ \\ \Gamma_7^- \\ \hline \Gamma_6^- \\ \Gamma_8^- \\ \Gamma_6^+ \\ \Gamma_8^- \\ \Gamma_7^+ \\ \Gamma_8^+ \\ \Gamma_7^- \end{array}$$

Full zone 30-band $\mathbf{k} \cdot \hat{\mathbf{p}}$ double group band diagram for bulk Silicon and Germanium are shown below. Both figures realise the indirect band-gap nature of both Silicon and Germanium with their respective conduction band energy minima and location on the first Brillouin zone (FBZ). Due to the locations of the indirect band-gaps; the $[011]$ direction $\Gamma \rightarrow \Sigma \rightarrow K$ is omitted for brevity. Density of states, $D(E)$, is calculated from a histogram of the dispersion relation, by counting the number of states with energy E .

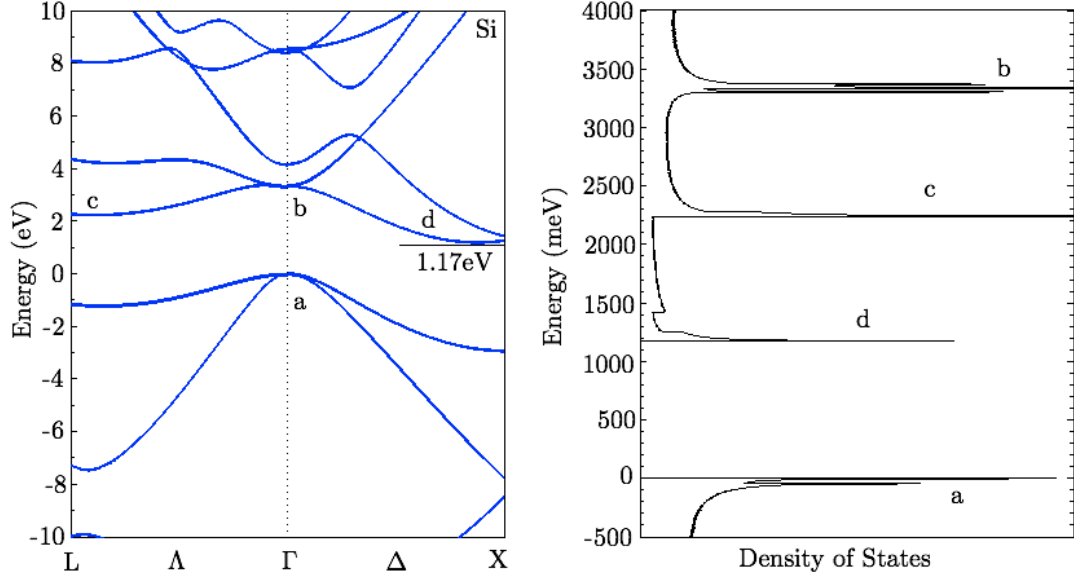


FIGURE 4.2: Full zone 30-band $\mathbf{k} \cdot \hat{\mathbf{p}}$ double group formulation band diagram (left) and density of states (right) for bulk Silicon. The indirect conduction band minima (d) occurs at $89\% - \Delta$ with an energy of 1.17eV . Valence band maxima (a) are chosen as the offset energy $E_v = 0$

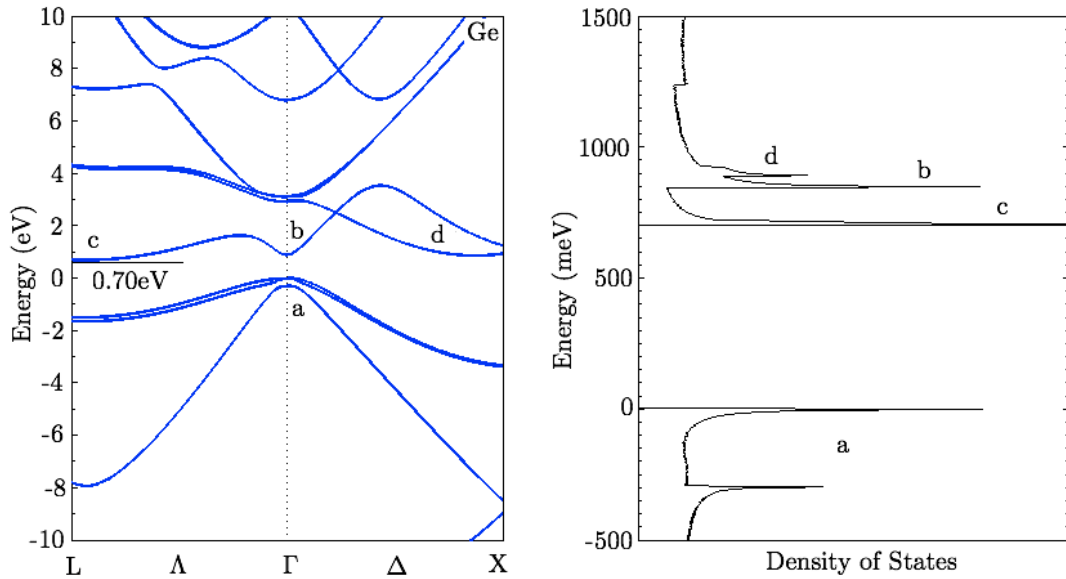


FIGURE 4.3: Full zone 30-band $\mathbf{k} \cdot \hat{\mathbf{p}}$ double group formulation band diagram (left) and density of states (right) for bulk Germanium. The indirect conduction band minima (c) occurs at L with an energy of 0.70eV and the direct conduction band minima (b) occurs at Γ with an energy of 0.89eV

By the indirect band-gap, electrons are in a lower energy state when they have non zero momentum than when stationary. This means that an additional particle, a phonon, is required to conserve momentum for the lowest energy transition between conduction electrons and holes. Since recombination rates are much lower for indirect transitions, Silicon and Germanium are poor photon emitters. Conversely they are ideal for absorption processes, where generated carriers have a relatively long lifetime, for use in devices such as photodetectors.

One further point to mention regarding the indirect band-gap is that the indirect conduction band changes abruptly between Δ to L valleys at $x = 88\%$. This leads to a kink in the near band-gap photoluminescence (Figure 9 of Weber & Alonso [74]) and electron bulk mobility [81] as a function of composition x that follows the behaviour of the electron effective masses. Using the 30-band $\mathbf{k} \cdot \hat{\pi}$ double group, a plot of conduction band minimum energy versus SiGe alloy fraction is shown below.

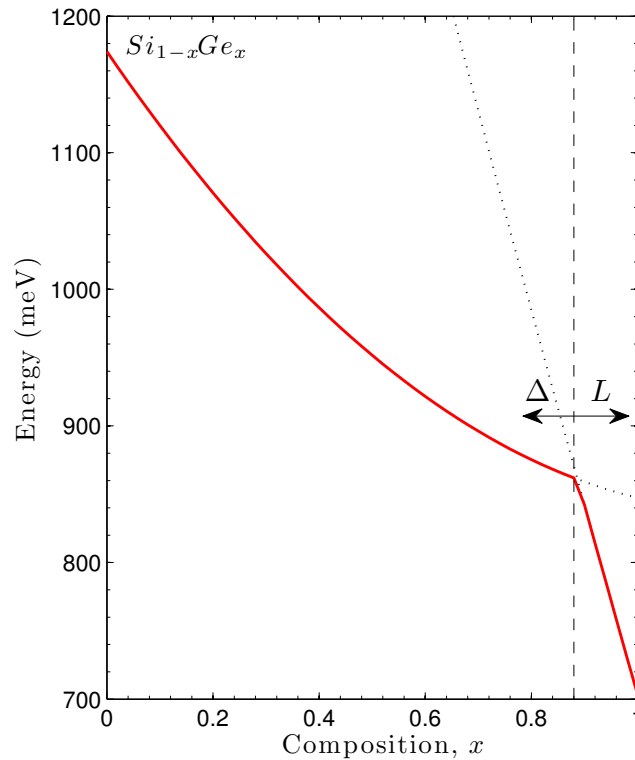


FIGURE 4.4: Indirect gap conduction band minimum variation with SiGe alloy fraction. Note the abrupt transition from Δ to L valleys at composition $x = 88\%$

In the next section it will be shown how the 30-band $\mathbf{k} \cdot \hat{\pi}$ double group Hamiltonian may be brought into a more compact form through the Löwdin renormalisation procedure [32]. Through this 4-, 6-, and 8-band models may be generated using 2^{nd} order degenerate perturbation theory [35, 36]. Input parameters, known as the Luttinger parameters [37] may be generated, which may be compared with experimental effective mass data from cyclotron resonance [38] and Shubnikov-de Haas oscillations.

4.2 Löwdin Renormalisation

While the full zone 30-band $\mathbf{k} \cdot \hat{\mathbf{p}}$ double group calculations return results that agree well with experimental observations, the quest for results has been at the expense of some physical intuition. Considering the work function of Silicon to be $\approx 4.5\text{eV}$; high energy levels lose their physicality. The major points of interest are where delocalised carriers lie for charge transport and optical transitions; the valence and conduction bands.

Using degenerate perturbation theory the 30-band $\mathbf{k} \cdot \hat{\mathbf{p}}$ Hamiltonian may be condensed into more manageable 4-, 6- and 8-band effective mass Hamiltonians [35] constructed out of the double group formulation. Invariants expressible in terms of function of scaling parameters return theoretical zone centre effective masses for heavy and light holes and compared with cyclotron resonance experiment results.

4.2.1 2^{nd} Order Perturbation Theory

As aforementioned specific regions of interest are where delocalised carriers lie; the valence, spin-orbit and conduction bands. By demarcating the near set $\{|\Gamma_\alpha\rangle, |\Gamma_\beta\rangle\}$ from remote set $|\Gamma_j\rangle$ eigenstates; one may evaluate mediated interactions using 2^{nd} order degenerate perturbation theory. This enables the construction of 4-, 6- and 8-band models pending the solutions sought.

Using the notation of the $\mathbf{k} \cdot \hat{\mathbf{p}}$ perturbation, the 2^{nd} order approximation to the Hamiltonian is found using;

$$H^{\Gamma_\alpha:\Gamma_\beta} = \langle \Gamma_\alpha | \hat{H}_0 + \hat{H}_{\mathbf{k}\cdot\hat{\mathbf{p}}} | \Gamma_\beta \rangle + \sum_{\Gamma_\alpha, \Gamma_\beta \neq \Gamma_j} \frac{\langle \Gamma_\alpha | \hat{H}_{\mathbf{k}\cdot\hat{\mathbf{p}}} | \Gamma_j \rangle \langle \Gamma_j | \hat{H}_{\mathbf{k}\cdot\hat{\mathbf{p}}} | \Gamma_\beta \rangle}{\sqrt{(E^{\Gamma_j} - E^{\Gamma_\alpha})(E^{\Gamma_j} - E^{\Gamma_\beta})}} \quad (4.12)$$

Where the former corresponds to the 1^{st} order formalism currently developed, with the latter the 2^{nd} order correction; the Löwdin term [32]. The remote set must not be degenerate with the near set either otherwise the Löwdin term diverges. Additionally, $|\Gamma_j\rangle \langle \Gamma_j|$ may be thought of as a projection operator independent of the frame of reference.

Given that the linearly independent matrices have just been computed, one is left with the rather simple evaluation of $A_{\mathbf{k}\cdot\hat{\mathbf{p}}}^{\Gamma_\alpha:\Gamma_j} \times \left(A_{\mathbf{k}\cdot\hat{\mathbf{p}}}^{\Gamma_\beta:\Gamma_j}\right)^\dagger$. The form of the Hamiltonian also lends itself favourably to the concept of operator ordering and boundary conditions across an abrupt interface for non-commuting differential operators under the envelope function approximation [10–13].

4.2.2 DKK Effective Mass Hamiltonian

The DKK effective mass Hamiltonian [34] is probably one of the most recognisable Hamiltonians in the literature. Valence bands are treated as bonding p -type orbitals transforming according to Γ_4^- , compatible with $L = 1$ eigenstates of $\text{SO}(3)$. Consequently the DKK effective mass Hamiltonian may be obtained using the single group interaction matrices; $A_{\mathbf{k} \cdot \hat{\mathbf{p}}}^{\Gamma_4^- : \Gamma_j^+} \times \left(A_{\mathbf{k} \cdot \hat{\mathbf{p}}}^{\Gamma_4^- : \Gamma_j^+} \right)^\dagger$ and scaling by the Foreman parameters σ , π and δ [46]. For example;

$$A_{\mathbf{k} \cdot \hat{\mathbf{p}}}^{\Gamma_4^- : \Gamma_1^+} \times \left(A_{\mathbf{k} \cdot \hat{\mathbf{p}}}^{\Gamma_4^- : \Gamma_1^+} \right)^\dagger = \begin{pmatrix} k_x^2 & k_x k_y & k_x k_z \\ k_y k_x & k_y^2 & k_y k_z \\ k_z k_x & k_z k_y & k_z^2 \end{pmatrix} \quad (4.13)$$

While Foreman attributes his parameters to remote states; s^* , p^* , and d^* his presumption were matrix elements with a specific basis. This is contrary to the formalism presented here since $A_{\mathbf{k} \cdot \hat{\mathbf{p}}}^{\Gamma_i^- : \Gamma_j^+}$ emerge as basis independent. Regardless of this the DKK parameters, L , M , and N and Foreman parameters may be linked by the matrix;

$$\begin{pmatrix} L \\ M \\ N \end{pmatrix} = \begin{pmatrix} 1 & -6 & 0 & -12 \\ 1 & 0 & -6 & 0 \\ 0 & -6 & -6 & 6 \end{pmatrix} \begin{pmatrix} 1 \\ \sigma \\ \pi \\ \delta \end{pmatrix} \quad (4.14)$$

Where the free electron mass term has been included. The overall DKK effective mass Hamiltonian [34] takes the form;

$$H_{DKK} = \begin{pmatrix} Lk_x^2 + M(k_y^2 + k_z^2) & Nk_x k_y & Nk_x k_z \\ Nk_y k_x & Lk_y^2 + M(k_z^2 + k_x^2) & Nk_y k_z \\ Nk_z k_x & Nk_z k_y & Lk_z^2 + M(k_x^2 + k_y^2) \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \quad (4.15)$$

Where H_{DKK} is expressed with respect to bases of $\{x, y, z\}$ as illustrated. A common procedure in the literature is to apply the adapted double group to $\{x, y, z\} \otimes \{\uparrow, \downarrow\}$ into $J = 3/2 \oplus 1/2$ to generate a 6-band Hamiltonian. Since valence bands are Γ_5^+ in the single group, an alternate form to apply $\{yz, zx, xy\} \otimes \{\uparrow, \downarrow\}$ into the adapted double group must be done. The resulting difference stems from arguments on $\underline{\mathbf{T}}$ previously discussed.

In addition the adapted double group assumes that parameters are equivalent for valence and spin-orbit band blocks. For this reason a concatenated Hamiltonian must be constructed out of blocks with necessarily unique sets of scaling parameters. This will be addressed in the next section where double group scaling parameters $\zeta_{\alpha;\beta}^j$ emerge, equivalent to Foreman parameters [46] if and only if the spin-orbit interaction is zero.

4.2.3 Silicon 6-Band Model

One intrinsic flaw of the adapted group applied to H_{DKK} is the presumption that valence bands are 3×2 fold degenerate when entering the denominator of the Löwdin term. However, as known from the double group; the valence and spin-orbit bands are in fact $4 + 2$ fold degenerate at the zone centre. Casting the valence and spin-orbit bands into the near-set returns Löwdin terms, such that the block Hamiltonian may be constructed out of intra- $H_{VB:VB}$ and $H_{SO:SO}$ and inter-band $H_{VB:SO}$ matrices;

$$\begin{pmatrix} H_{VB:VB} & H_{VB:SO} \\ H_{VB:SO}^\dagger & H_{SO:SO} \end{pmatrix} \quad (4.16)$$

where $H_{VB:VB}$ on it's own comprises the 4-band Luttinger-Kohn [35] effective mass Hamiltonian. The degree of coupling between spin-orbit and valence bands scales with spin-orbit interaction strength, and in Silicon 6-band models are imperative and less so in Germanium.

$$\begin{aligned} H_{VB:VB} &= \begin{pmatrix} P+Q & S & R & 0 \\ S^\dagger & P-Q & 0 & R \\ R^\dagger & 0 & P-Q & -S \\ 0 & R^\dagger & -S^\dagger & P+Q \end{pmatrix} \begin{matrix} hh \\ lh \\ lh \\ hh \end{matrix} \\ H_{VB:SO} &= \sqrt{2} \begin{pmatrix} \frac{1}{2}S' & R' \\ -Q' & -\frac{\sqrt{3}}{2}S' \\ -\frac{\sqrt{3}}{2}(S')^* & Q' \\ -(R')^* & \frac{1}{2}(S')^* \end{pmatrix}, \quad H_{SO:SO} = \begin{pmatrix} P' & 0 \\ 0 & P' \end{pmatrix} \end{aligned} \quad (4.17)$$

Where individual terms for the trivial (001) quantisation axis are;

$$\left. \begin{aligned} P &= \gamma_1 (k_+ k_- + k_z^2) \\ Q &= \gamma_2 (k_+ k_- - 2k_z^2) \\ R &= \sqrt{3} (\mu k_-^2 - \bar{\gamma} k_+^2) \\ S &= -2\sqrt{3} \gamma_3 k_z k_+ \end{aligned} \right\} (001) \quad (4.18)$$

γ_1 , γ_2 , and γ_3 are the Luttinger parameters [37]. $\mu = \frac{1}{2}(\gamma_3 - \gamma_2)$ is the ‘warping’ term [82], which presents a deviation from the spherical approximation under the crystal field [83] and $\bar{\gamma} = \frac{1}{2}(\gamma_3 + \gamma_2)$. Within the single group framework, Luttinger parameters are expressible in terms of the DKK parameters through;

$$\begin{pmatrix} \gamma_1 \\ \gamma_2 \\ \gamma_3 \end{pmatrix} = \frac{-1}{6} \begin{pmatrix} 2 & 4 & 0 \\ 1 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} L \\ M \\ N \end{pmatrix} \quad (4.19)$$

Using the double group framework presented Luttinger parameters are also expressible in terms of double group scaling parameters $\zeta_{\alpha;\beta}^j$;

$$\left. \begin{aligned} \gamma_1 + R_\infty &= 2\zeta_{\Gamma_8^+:\Gamma_8^+}^{\Gamma_7^-} + 2\zeta_{\Gamma_8^+:\Gamma_8^+}^{\Gamma_6^-} + 2\zeta_{\Gamma_8^+:\Gamma_8^+,1}^{\Gamma_8^-} + 4\zeta_{\Gamma_8^+:\Gamma_8^+,2}^{\Gamma_8^-} \\ \gamma_2 &= \zeta_{\Gamma_8^+:\Gamma_8^+}^{\Gamma_7^-} - \zeta_{\Gamma_8^+:\Gamma_8^+}^{\Gamma_6^-} + 2\zeta_{\Gamma_8^+:\Gamma_8^+,2}^{\Gamma_8^-} \\ \gamma_3 &= \zeta_{\Gamma_8^+:\Gamma_8^+}^{\Gamma_7^-} + \zeta_{\Gamma_8^+:\Gamma_8^+}^{\Gamma_6^-} - \zeta_{\Gamma_8^+:\Gamma_8^+,2}^{\Gamma_8^-} \end{aligned} \right\} \quad (4.20)$$

where R_∞ is the Rydberg constant such that γ_1 incorporates the scalar free electron mass term $\frac{\hbar^2 \mathbf{k}^2}{2m_0}$. Individual $\zeta_{\alpha;\beta}^j$ parameters may be found using;

$$\left. \begin{aligned} 2\zeta_{\Gamma_8^+:\Gamma_8^+}^{\Gamma_7^-} &= \frac{P_1^2}{(E_c - E_v)} + \frac{P_3^2}{(E_2^{\Gamma_7^-} - E_v)} & 2\zeta_{\Gamma_8^+:\Gamma_8^+}^{\Gamma_6^-} &= \frac{Q_1^2}{(E_1^{\Gamma_6^-} - E_v)} \\ 2\zeta_{\Gamma_8^+:\Gamma_8^+,1}^{\Gamma_8^-} &= \frac{Q_1^2}{(E_1^{\Gamma_8^-} - E_v)} & \zeta_{\Gamma_8^+:\Gamma_8^+,2}^{\Gamma_8^-} &= \frac{R_1^2}{(E_2^{\Gamma_8^-} - E_v)} \end{aligned} \right\} \quad (4.21)$$

Comparing these with Foreman parameters [46] returns $\sigma = \zeta_{\Gamma_8^+:\Gamma_8^+}^{\Gamma_7^-}$ and $\delta = \zeta_{\Gamma_8^+:\Gamma_8^+,2}^{\Gamma_8^-}$. However, the single group approach implies $\pi = \zeta_{\Gamma_8^+:\Gamma_8^+}^{\Gamma_6^-} = \zeta_{\Gamma_8^+:\Gamma_8^+,1}^{\Gamma_8^-}$ returned if and only if the spin-orbit interaction is zero. One should also consider should the $\zeta_{\Gamma_8^+:\Gamma_8^+}^{\Gamma_6^-}$ term dominate, γ_2 may become negative; as is the case for Diamond [84].

Primes on $H_{VB:SO}$ and $H_{SO:SO}$ require inequivalent parameters due to the non degeneracy of valence and spin-orbit bands.

$$\left. \begin{aligned} \gamma'_1 + R_\infty &= 2\zeta_{\Gamma_7^+:\Gamma_7^+}^{\Gamma_7^-} + 4\zeta_{\Gamma_7^+:\Gamma_7^+,1}^{\Gamma_8^-} + 4\zeta_{\Gamma_7^+:\Gamma_7^+,2}^{\Gamma_8^-} \\ \gamma'_2 &= \zeta_{\Gamma_7^+:\Gamma_7^+}^{\Gamma_7^-} - \zeta_{\Gamma_7^+:\Gamma_7^+,1}^{\Gamma_8^-} + 2\zeta_{\Gamma_7^+:\Gamma_7^+,2}^{\Gamma_8^-} \\ \gamma'_3 &= \zeta_{\Gamma_7^+:\Gamma_7^+}^{\Gamma_7^-} + \zeta_{\Gamma_7^+:\Gamma_7^+,1}^{\Gamma_8^-} - \zeta_{\Gamma_7^+:\Gamma_7^+,2}^{\Gamma_8^-} \end{aligned} \right\} \quad (4.22)$$

$$\begin{aligned}
2\zeta_{\Gamma_7^+:\Gamma_7^+}^{\Gamma_7^-} &= \frac{P_1^2}{(E_c - \Delta)} + \frac{P_3^2}{(E_2^{\Gamma_7^-} - \Delta)} \\
2\zeta_{\Gamma_7^+:\Gamma_7^+,1}^{\Gamma_8^-} &= \frac{Q_1^2}{(E_1^{\Gamma_8^-} - \Delta)} \quad \zeta_{\Gamma_7^+:\Gamma_7^+,2}^{\Gamma_8^-} = \frac{R_1^2}{(E_2^{\Gamma_8^-} - \Delta)}
\end{aligned} \tag{4.23}$$

$$\begin{aligned}
2\zeta_{\Gamma_7^+:\Gamma_8^+}^{\Gamma_7^-} &= \frac{P_1^2}{\sqrt{(E_c - \Delta)(E_c - E_v)}} + \frac{P_3^2}{\sqrt{(E_2^{\Gamma_7^-} - \Delta)(E_2^{\Gamma_7^-} - E_v)}} \\
2\zeta_{\Gamma_7^+:\Gamma_8^+,1}^{\Gamma_8^-} &= \frac{Q_1^2}{\sqrt{(E_1^{\Gamma_8^-} - \Delta)(E_1^{\Gamma_8^-} - E_v)}} \quad \zeta_{\Gamma_7^+:\Gamma_8^+,2}^{\Gamma_8^-} = \frac{R_1^2}{\sqrt{(E_2^{\Gamma_8^-} - \Delta)(E_2^{\Gamma_8^-} - E_v)}}
\end{aligned} \tag{4.24}$$

Where again if and only if the spin-orbit interaction is zero one recovers the single and adapted double group formulations.

Using parameters given in Tables 4.1 and 4.2 dispersion for the 6-band model may be computed for Silicon. The Löwdin correction matches the full zone 30-band $\mathbf{k} \cdot \hat{\boldsymbol{\pi}}$ technique well to within 5meV up to 12% to the FBZ boundary as shown in Figure 4.5. This sets a limit to the validity of the 2^{nd} order correction as a Taylor series expansion.

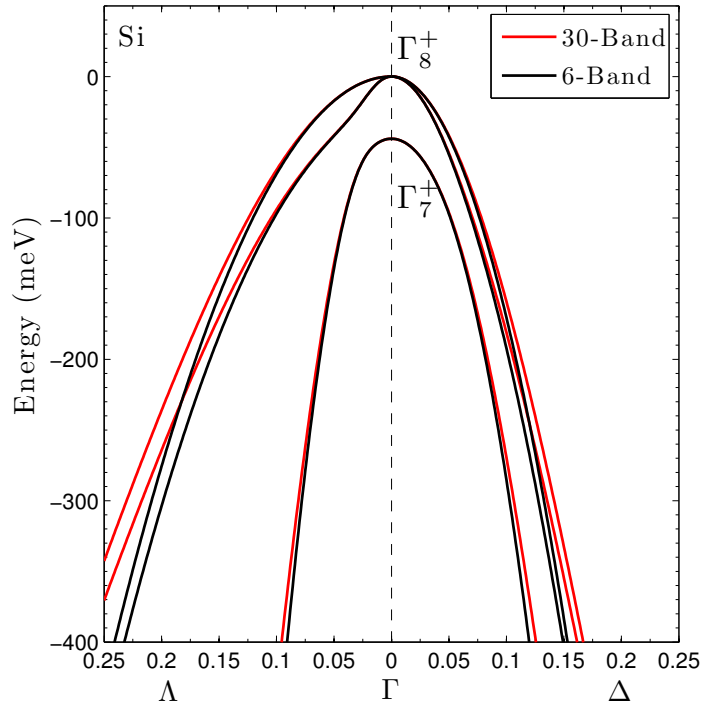


FIGURE 4.5: Valence and spin-orbit band comparison between 6-band and 30-band models in bulk Silicon; up to 25% of the FBZ. The Löwdin correction matches the full zone 30-band $\mathbf{k} \cdot \hat{\boldsymbol{\pi}}$ technique well to within 5meV up to 12% to the FBZ boundary

Luttinger parameters for both Silicon and Germanium may also be evaluated for comparison with heavy and light hole zone centre effective masses found from experiment. Dexter et al [38] quote experimental effective masses in Germanium of $m_{hh}^* = 0.284 \pm 0.001$,

$m_{lh}^* = 0.0438 \pm 0.003$ and in Silicon of $m_{hh}^* = 0.46 \pm 0.01$, $m_{lh}^* = 0.171 \pm 0.006$. These are in alignment with the more recent ones quoted by Friedrich Schäffler [81] of $m_{hh}^* = 0.28$ and $m_{lh}^* = 0.04$ for Germanium and $m_{hh}^* = 0.53$, $m_{lh}^* = 0.15$ for Silicon. Schäffler also quotes experimental values of $m_{so}^* = 0.09$ for Germanium and $m_{so}^* = 0.23$ for Silicon all in units of the free electron mass m_0 .

Zone centre in-plane effective masses are calculated using;

$$m_{hh}^* = \frac{1}{\gamma_1 - 2\gamma_2}, \quad m_{lh}^* = \frac{1}{\gamma_1 + 2\gamma_2}, \quad m_{so}^* = \frac{1}{\gamma_1'}, \quad (4.25)$$

Parameter	Silicon	Germanium	Parameter	Silicon	Germanium
γ_1	4.38	10.36	γ_1'	4.30	8.14
γ_2	0.35	3.04	γ_2'	0.35	2.65
γ_3	1.44	4.31	γ_3'	1.43	3.74
m_{hh}^*	$0.27m_0$	$0.23m_0$	m_{so}^*	$0.23m_0$	$0.12m_0$
m_{lh}^*	$0.20m_0$	$0.06m_0$			

TABLE 4.3: Dimensionless theoretical Luttinger parameters used in the 6-band double group matrix Hamiltonian for Silicon and Germanium

The greater difference between $\gamma_{1,2,3}$ and $\gamma'_{1,2,3}$ for Germanium than Silicon clearly shows how the double group formulation is a spin-orbit interaction induced correction. Indeed for the same reasons 4-band models are inadequate to accurately describe the valence bands in Silicon due to the contribution from $H_{VB:SO}$. Clearly experimental and theoretical effective masses are in quite close agreement with those in Germanium but are at odds with respect to those of Silicon. The main reasons for the discrepancy in Silicon stems from experiment; since there is a much stronger warping of valence bands and the direct gap minima is a point of inflexion. Consequently cyclotron resonance frequencies become harder to resolve and often the density of states effective mass is quoted instead; averaged over all crystallographic directions.

Figure 4.6 shows the monotonic variation of the Luttinger parameters and heavy & light hole in-plane effective masses as a function of SiGe alloy composition, found using the expressions in Equation 4.20 directly. Clearly it is not justifiable to use a Vegard's law [79] relation for Luttinger parameters; e.g. $\gamma_1 = 4.38 + 5.98x$, which is why explicit expressions for $\zeta_{\alpha;\beta}^j$ are so invaluable. R. Braunstein [85] gives experimental effective mass ratios up to $63\% < x < 100\%$, which appear to follow the curvature of Figure 4.6, however without data for $0\% < x < 63\%$ one cannot be definite. The curvature at relatively large Germanium compositions also stresses the need for operator ordered Hamiltonians when setting boundary conditions for material dependent parameters in the application to heterostructures.

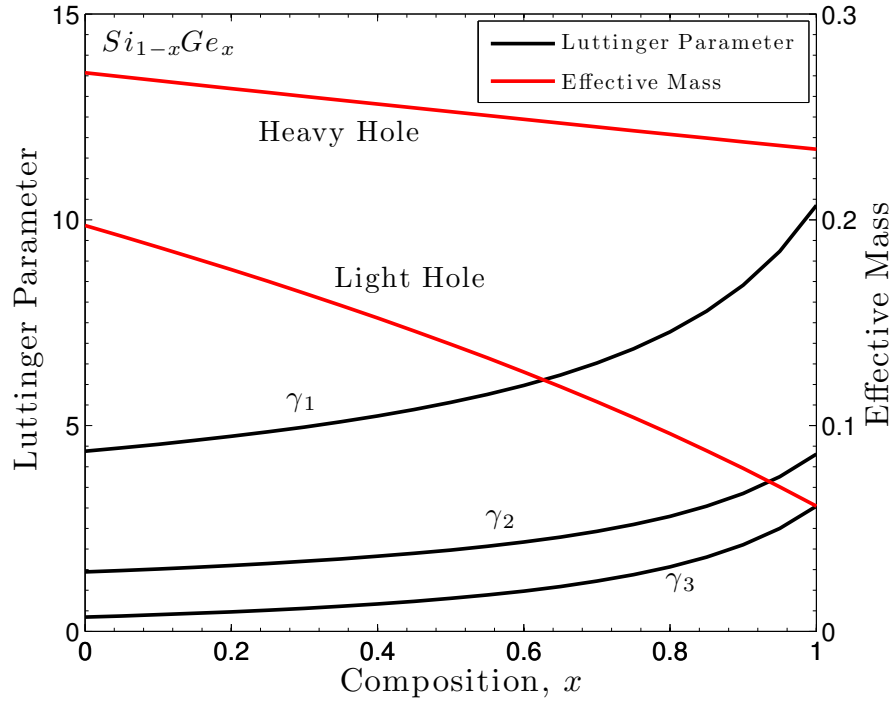


FIGURE 4.6: Luttinger parameters and in-plane heavy & light hole effective masses as a function of SiGe alloy composition

4.2.4 Germanium 8-Band Model

Since the Germanium direct gap is $E_c - E_v = 890\text{meV}$; close to $1.5\mu\text{m}$ used in 3rd generation optical communications [41]; an effective mass Hamiltonian including the conduction band is required. Consequently, the conduction band is incorporated into the near set returning an 8-band Hamiltonian as given by T. B. Bahder [75].

$$\begin{pmatrix} H_{CB:CB} & H_{CB:VB} & H_{CB:SO} \\ H_{CB:VB}^\dagger & H_{VB:VB} & H_{VB:SO} \\ H_{CB:SO}^\dagger & H_{VB:SO}^\dagger & H_{SO:SO} \end{pmatrix} \quad (4.26)$$

The 6×6 valence and spin orbit blocks takes on the same form as before with the exception that since the conduction band has been brought into the near set, $\zeta_{\Gamma_8^+:\Gamma_8^+}^{\Gamma_7^-}$, $\zeta_{\Gamma_7^+:\Gamma_7^+}^{\Gamma_7^-}$ and $\zeta_{\Gamma_7^+:\Gamma_8^+}^{\Gamma_7^-}$ exclude the corresponding mediated interaction scaled by the Kane parameter P_1 [33]. Inter-band $H_{CB:VB}^\dagger$ and $H_{CB:SO}^\dagger$ blocks take on the linear- $\mathbf{k}$ interaction matrices given in the 30-band $\mathbf{k} \cdot \hat{\boldsymbol{\pi}}$ double group matrix Hamiltonian as $P_1 A_{\mathbf{k} \cdot \hat{\boldsymbol{\pi}}}^{\Gamma_8^+:\Gamma_6^+}$ and $-P_1 A_{\mathbf{k} \cdot \hat{\boldsymbol{\pi}}}^{\Gamma_6^+:\Gamma_6^+}$ respectively to account for conduction band non-parabolicity. The intra-band $H_{CB:CB}$ takes on a form akin to $H_{SO:SO}$ with the exception that the scaling parameter is the zone-centre electron effective mass m_e^* ;

$$H_{CB:CB} = \begin{pmatrix} A & 0 \\ 0 & A \end{pmatrix}, \quad A = \frac{1}{m_e^*} (k_+ k_- + k_z^2) \quad (4.27)$$

An effective zone-centre electron effective mass may be employed as;

$$\frac{1}{m_e^*} + R_\infty = P_2^2 \left(\frac{1}{E_2^{\Gamma_7^+} - E_c} + \frac{2}{E_2^{\Gamma_8^+} - E_c} \right) \quad (4.28)$$

Although this is not quite the zone centre electron effective mass since there is no Kane parameter P_1 for the valence band mediated interaction. Using the relevant scaling parameters, a Germanium 8-band model may be computed, as shown in Figure 4.7. The perturbation technique is again valid to within 5meV up to 12% to the FBZ boundary for valence bands but only 5.5% for the conduction band.

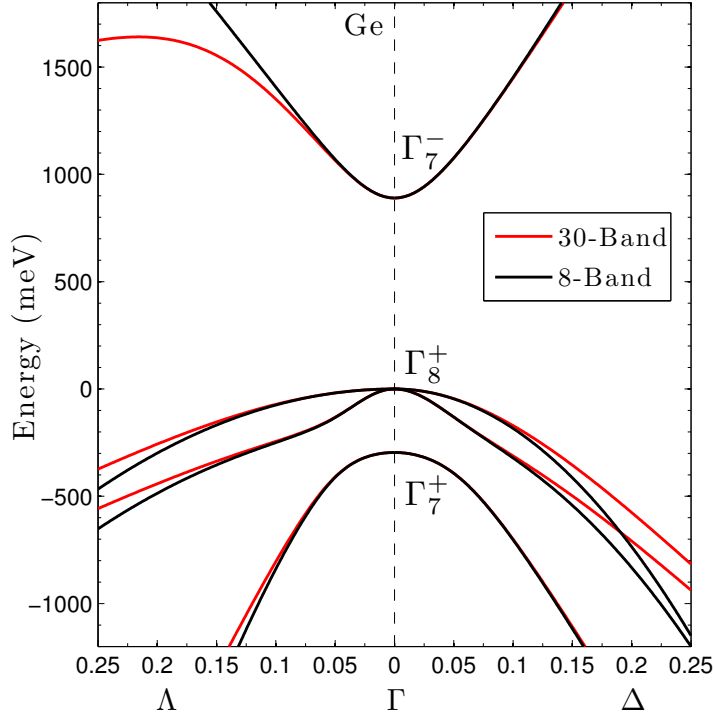


FIGURE 4.7: Valence, spin orbit and conduction band comparison between 8-band and 30-band models in bulk Germanium; up to 25% of the FBZ

The deviation in curvature along the Λ direction in the conduction band is symptomatic of the indirect band-gap minima at the L point due to non-parabolicity. While this is cause for concern, there are two reasons to allay such fears; the first is that uniaxial strain may bring the direct gap minima lower than that of the indirect gap [86] and the second is that Germanium heterostructures have a straddling (type-I) band edge alignment. Consequently the spatial overlap element of inter band optical matrix elements are strong for direct and weak for indirect, phonon assisted, transitions.

4.3 The Theory of Invariants

The $\mathbf{k} \cdot \hat{\boldsymbol{\pi}}$ Hamiltonian was obtained using matrix elements of the tensor operator, $\hat{\boldsymbol{\pi}}$ and symmetrised eigenstates to determine linearly independent matrices. The theory of invariant formulation presented [37] here has less stringent assumptions on the self consistent one electron potential, and is rather general; with the only constraint being that the Hamiltonian transforms according to the entire space group of the crystal.

The Hamiltonian, may be expressed as an invariant polynomial functional whose arguments are linearly independent generator matrices and irreducible perturbation components. 4- 6- and 8-band effective mass Hamiltonians may be generated using this method and compared to those in the previous sections. Further to this, a canonical transformation may be applied to the situation where the quantisation and crystallographic axes no longer coincide [87, 88]. The original motivation was for the application of an arbitrarily oriented applied magnetic field, but within the context of this thesis is for modelling heterostructures grown on arbitrary crystallographic faces.

4.3.1 Irreducible Perturbation Components & Generator Matrices

Components of the Bloch vector transform according to Γ_4^- , compatible with the $L = 1$ eigenstate of the full rotational $\text{SO}(3)$ group. Quadratic irreducible components may be decomposed into symmetrised contributions [27] transforming according to $\Gamma_1^+ \oplus \Gamma_3^+ \oplus [\Gamma_4^+] \oplus \Gamma_5^+$ compatible with $L = 0, 1, 2$.

$$k_i k_j = \underbrace{\frac{\mathbf{k} \cdot \mathbf{k}}{3} \delta_{ij}}_{L=0: \Gamma_1^+} + \underbrace{\frac{[k_i, k_j]}{2}}_{L=1: [\Gamma_4^+]} + \underbrace{\frac{\{k_i, k_j\}}{2} - \frac{\mathbf{k} \cdot \mathbf{k}}{3} \delta_{ij}}_{L=2: \Gamma_3^+ \oplus \Gamma_5^+} \quad (4.29)$$

Where anti-commutator $\{a, b\} = ab + ba$, and commutator $[a, b] = ab - ba$ algebraic notation has been invoked. The antisymmetric component $[\Gamma_4^+]$ clearly vanishes in the bulk and does not contribute other than by interfacial symmetry breaking and/or an externally applied magnetic field, $\mathbf{H}$; where $[k_i, k_j] = -i\epsilon_{ijk}H_k$.

One may also compare this with the results of the projection operator technique in Section 3.1.3. Substituting in the irreducible perturbation component $\mathbf{k}$ into Equation 3.11 as a polar vector returns;

$$\Gamma_1^+ : \mathbf{k}^2 = k_x^2 + k_y^2 + k_z^2 \quad \Gamma_3^+ : \begin{cases} \frac{1}{\sqrt{3}} (k_z^2 - \frac{1}{2}(k_x^2 + k_y^2)) \\ \frac{1}{2} (k_x^2 - k_y^2) \end{cases} \quad \Gamma_5^+ : \begin{cases} k_y k_z \\ k_z k_x \\ k_x k_y \end{cases} \quad (4.30)$$

Hence symmetric quadratic components of the Bloch vector may be symmetrised into irreps of the O_h group as above. It may also be shown how a second rank symmetric tensor such as strain; ϵ_{ij} , transforms according to $\Gamma_1^+ \oplus \Gamma_3^+ \oplus \Gamma_5^+$, with the anti-symmetric contribution transforming according to $[\Gamma_4^+]$ ascribed to the physical effect of a rotation; ω_{ij} (Section 2.3.2). This is directly analogous to the components of the quadratic Bloch vector, and unsurprisingly arguments above about $k_i k_j$ may also be applied to the general transformation $e_{ij} = \epsilon_{ij} + \omega_{ij}$.

Linearly independent generator matrices form the building blocks of the effective mass Hamiltonian. In the DKK model, valence bands were treated as bonding p -type orbitals transforming according to Γ_4^- compatible with $L = 1$ eigenstates of $\text{SO}(3)$. Conveniently the symmetry of irreducible perturbation component and generator matrices coincide. Generators matrices for $L = 1$ such as; $\{X_x, X_y, X_z\}$ used in the Euler-Rodrigues rotation formula may be employed;

$$[\Gamma_4^+] : X_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}, \quad X_y = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix}, \quad X_z = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (4.31)$$

since the dimension of the tensor decomposition of $\Gamma_4^- \otimes \Gamma_4^-$ is 9, with six symmetric and three antisymmetric, it follows logically that the number of 3×3 linearly independent matrices is also 9. Given that the generators above satisfy the commutation relations $[X_i, X_j] = \epsilon_{ijk} X_k$, they comprise the three antisymmetric $[\Gamma_4^+]$ components. We may also evaluate the symmetric contributions as;

$$\begin{aligned} \Gamma_1^+ : \quad \mathbf{X}^2 &= X_x^2 + X_y^2 + X_z^2 = \begin{pmatrix} -2 & 0 & 0 \\ 0 & -2 & 0 \\ 0 & 0 & -2 \end{pmatrix} = -2\mathbf{1}_{3 \times 3} \\ \Gamma_3^+ : \quad \frac{1}{\sqrt{3}} (X_z^2 - \frac{1}{2} (X_x^2 + X_y^2)) &= \frac{1}{2\sqrt{3}} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix}, \quad \frac{1}{2} (X_x^2 - X_y^2) = \frac{1}{2} \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \\ \Gamma_5^+ : \quad \{X_y, X_z\} &= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad \{X_z, X_x\} = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \quad \{X_x, X_y\} = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \end{aligned} \quad (4.32)$$

Taking coincidental symmetrised irreducible perturbation components $k_i k_j$ with generator matrices, there are three associated invariants; the DKK valence band parameters. A simplified form of the long-hand explicit field-free Hamiltonian reduces to;

$$H_{DKK} = L\mathbf{k}^2 \mathbf{1}_{3 \times 3} + (L - M) (k_x^2 X_x^2 + k_y^2 X_y^2 + k_z^2 X_z^2) + \dots \quad (4.33)$$

$$\dots + N (k_y k_z \{X_y, X_z\} + k_z k_x \{X_z, X_x\} + k_x k_y \{X_x, X_y\})$$

Using X_i rather than angular momentum generators; $L_i = i\hbar A X_i A^{-1}$ returns the matrix expressed with respect to bases of $\{x, y, z\}$ as in Equation 4.15. What has been shown here is that the theory of invariants and perturbation theory approach; despite having polar opposite presumptions, return exactly the same form of Hamiltonian. Substituting in components of strain with associated deformation potentials l , m , and n returns the Pikus-Bir Hamiltonian [3] although is discussed in greater detail in the following chapter.

4.3.2 Luttinger-Kohn Valence Band Hamiltonian

Fortunately the theory of invariants may also be applied to the realm of half integer domains for the double group formulation consideration [37]. This incorporates the Luttinger parameters γ_1 , γ_2 and γ_3 , which were introduced in the previously in a somewhat ad hoc way. In this section; they are introduced in a more rigorous manner from the point of view of invariance.

Using $J = 3/2$ angular momentum matrices as generators; there exists $4 \times 4 = 16$ linearly independent matrix generators; transforming according to $\Gamma_8^\pm \otimes \Gamma_8^\pm = \Gamma_1^+ \oplus \Gamma_3^+ \oplus \Gamma_5^+ \oplus [\Gamma_2^+ \oplus 2\Gamma_4^+ \oplus \Gamma_5^+]$. As encountered in the previous section we have; $\Gamma_1^+ : \mathbf{1}_{4 \times 4}$ and also $\Gamma_3^+ : \left\{ \frac{1}{\sqrt{3}} (J_z^2 - \frac{1}{2} (J_x^2 + J_y^2)), \frac{1}{2} (J_z^2 - J_y^2) \right\}$ with the anti-commutators $\Gamma_5^+ : \{\{J_y, J_z\}, \{J_z, J_x\}, \{J_x, J_y\}\}$. Similarly, the commutators are antisymmetric; $[\Gamma_4^+] : \{[J_y, J_z], [J_z, J_x], [J_x, J_y]\}$

But now, there also exists $[\Gamma_2^+] : \{J_x J_y J_z + J_z J_y J_x\}$ and also $[\Gamma_4^+] : \{J_x^3, J_y^3, J_z^3\}$ and finally $[\Gamma_5^+] : \{V_x, V_y, V_z\}$ where $V_i = (J_j - J_k) J_i$ to complete the set. However, since the irreducible perturbation components do not include $[\Gamma_2^+]$ nor $[\Gamma_5^+]$ there is no invariant parameter as there is no coincidence of irreps with the generators. Substituting J_i for X_i in Equation 4.33, and introducing the Luttinger parameters, the field-free Luttinger-Kohn [35] valence band Hamiltonian $H_{VB:VB}$ may also be returned using;

$$H_{VB:VB} = \left(\gamma_1 + \frac{5\gamma_2}{2} \right) \mathbf{k}^2 \mathbf{1}_{4 \times 4} - 2\gamma_2 (k_x^2 J_x^2 + k_y^2 J_y^2 + k_z^2 J_z^2) - \dots \quad (4.34)$$

$$\dots - 2\gamma_3 (k_y k_z \{J_y, J_z\} + k_z k_x \{J_z, J_x\} + k_x k_y \{J_x, J_y\})$$

The theory of invariants has also been formulated for 6- and 8-band models by Hensel² & Suzuki [89, 90] and by Trebin et al [91]. The procedure uses the methodology set out in this section for individual blocks and concatenating them in the same manner as Equation 4.26.

In the next section, the irreducible perturbation components and generator matrices are generalised in the event that the quantisation and crystallographic axes no longer coincide. The original motivation was born out of a general alignment of magnetic field $\mathbf{H}$ when interpreting cyclotron resonance data for warped constant energy surfaces, however the motivation in this thesis is modelling heterostructures grown on a general crystallographic face.

4.3.3 Coordinate Transformations

One rather large assumption has been made that has so far been overlooked. This is that the quantisation axis (001) coincides with the crystallographic axis of the system. Here, it is discussed how to transform between the device coordinate system (DCS) and the crystal coordinate system (CCS). This is an obvious necessary transformation if say the crystal is cut along a general surface with a heterostructure grown normal to this face.

We define a DCS and CCS; related by a transformation, where $\{J_x, J_y, J_z\}$ are the previously encountered angular momentum matrices, and z' is normal to the growth plane of the DCS. For quantum mechanical commutation relations or classical Poisson bracket to be conserved, the transformation must be *canonical*; such that the Hamiltonian is invariant and energy conserved by the principle of least action;

$$\begin{pmatrix} J_{x'} \\ J_{y'} \\ J_{z'} \end{pmatrix} = \begin{pmatrix} a_1 & a_2 & a_3 \\ b_1 & b_2 & b_3 \\ c_1 & c_2 & c_3 \end{pmatrix} \begin{pmatrix} J_x \\ J_y \\ J_z \end{pmatrix} \quad (4.35)$$

To conserve commutation relations, the determinant of the 3×3 matrix must be $+1$. This is the original criteria of the norm-preserving $SO(3)$ group. An appropriate matrix is the directional cosines matrix (DCM); evaluated using the Euler-Rodrigues formula as a matrix exponential. Given that rotation matrices do not commute [26], the order of rotation is significant;

$$R(\theta, \phi, \omega) = e^{X_z \theta} e^{X_x \phi} e^{X_z \omega} \quad (4.36)$$

Such a transformation is termed Z-X-Z, yet it is also possible to perform Z-Y-Z through the relevant $X_x \rightarrow X_y$ substitution.

²J. C. Hensel wrote the foreword to the English translated Pikus & Bir [3]

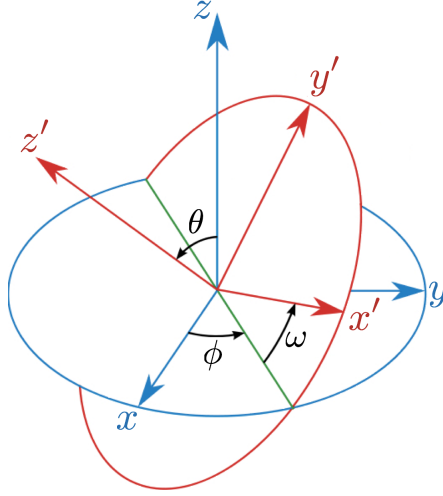


FIGURE 4.8: Euler-Rodrigues Z-X-Z rotation figure through angles θ , ϕ and ω . z is the quantisation axis of the CCS and z' is normal to the growth plane of the DCS

Given that C_2 and S_4 symmetry operations are elements of cubic T_d and O_h groups, the phase of a Z-Y-Z doesn't affect the energy eigenvalues of the Hamiltonian. Additionally; since the physical object of interest in heterostructures is a plane, the final rotation by ω is merely a phase factor. For these reasons; within the context of this thesis, $R(\theta, \phi) = R(\theta, \phi, 0)$ is quoted [92];

$$R(\theta, \phi) = \begin{pmatrix} \cos(\theta) & -\sin(\theta) \cos(\phi) & \sin(\theta) \sin(\phi) \\ \sin(\theta) & \cos(\theta) \cos(\phi) & -\cos(\theta) \sin(\phi) \\ 0 & \sin(\phi) & \cos(\phi) \end{pmatrix} \begin{matrix} x \\ y \\ z \end{matrix} \quad (4.37)$$

One may also note that $R(\theta, \phi, \omega)^{-1} = e^{-X_z \omega} e^{-X_x \phi} e^{-X_z \theta}$, and both have determinant +1. The choice to use X_i matrices returns $R(\theta, \phi)$ expressed with respect to bases of $\{x, y, z\}$, however since $\hat{\mathbf{p}}$ is cast into projections of rank-1 spherical tensor operators one may substitute the angular momentum generators; L_i instead. Both scenarios retain the determinant and commutation relations so X_i and L_i are interchangeable as and when necessary.

To transform the coordinate system to the (011) quantisation axis, rotation angles $\theta = 0$, $\phi = \pi/4$ are used. Under these angles, $J_x = J_{x'}$, $J_y = \frac{1}{\sqrt{2}} (J_{y'} - J_{z'})$ and $J_z = \frac{1}{\sqrt{2}} (J_{y'} + J_{z'})$ [93]. Note that $J_x^2 + J_y^2 + J_z^2 = J_{x'}^2 + J_{y'}^2 + J_{z'}^2$ since $\mathbf{J}^2$ transforms like a scalar. Similarly, transformations of the irreducible perturbation components yield; $k_x = k_{x'}$, $k_y = \frac{1}{\sqrt{2}} (k_{y'} - k_{z'})$ and $k_z = \frac{1}{\sqrt{2}} (k_{y'} + k_{z'})$.

In an identical manner, to transform the coordinate system to the (111) quantisation axis, the rotation angles $\theta = \pi/4$, $\phi = \arctan(\sqrt{2})$ are used. Under these rotation angles, $J_x = \frac{1}{\sqrt{6}} (\sqrt{3}J_{x'} - J_{y'} + \sqrt{2}J_{z'})$, $J_y = \frac{1}{\sqrt{6}} (\sqrt{3}J_{x'} + J_{y'} - \sqrt{2}J_{z'})$ and

$J_z = \frac{1}{\sqrt{3}} (\sqrt{2}J_{y'} + J_{z'})$, and similarly the perturbation components k_x , k_y , and k_z follow the same pattern.

Such coordinate transformations may be visualised in Figure 4.9.

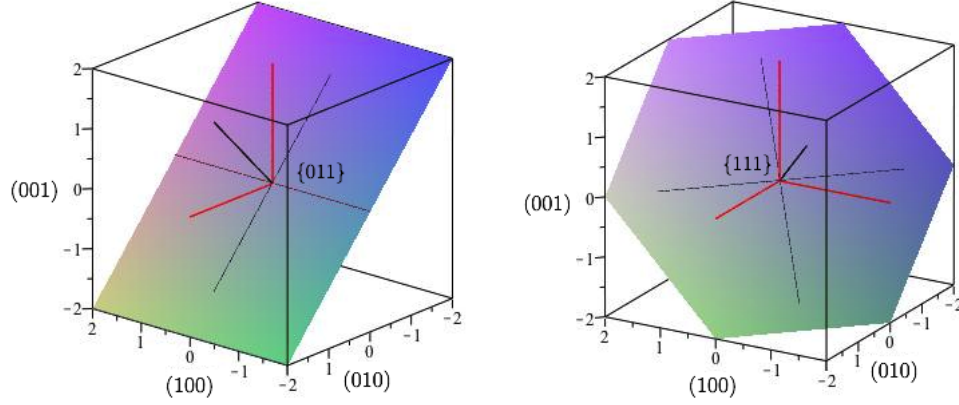


FIGURE 4.9: Coordinate transformation to the $\{011\}$ growth plane (left) and $\{111\}$ growth plane (right). Red axes indicate CCS whereas black axes indicate DCS. The z' -axis is normal to the plane

Substituting expressions for $\{J_x, J_y, J_z\}$ and $\{k_x, k_y, k_z\}$ into the Luttinger-Kohn valence band Hamiltonian and dropping the primes for brevity returns the coefficients;

$$\left. \begin{aligned} P &= \gamma_1 (k_+ k_- + k_z^2) \\ Q &= \gamma_2 k_y^2 - \frac{1}{2} (\gamma_2 - 3\gamma_3) k_x^2 - \frac{1}{2} (\gamma_2 + 3\gamma_3) k_z^2 \\ R &= -\sqrt{3} (\gamma_2 k_y^2 - \bar{\gamma} k_x^2 + 2i\gamma_3 k_x k_y + \mu k_z^2) \\ S &= -2\sqrt{3} (\gamma_2 k_x + i\gamma_3 k_y) k_z \end{aligned} \right\} (011) \quad (4.38)$$

where one may recall the warping term; $\mu = \frac{1}{2} (\gamma_3 - \gamma_2)$, $\bar{\gamma} = \frac{1}{2} (\gamma_3 + \gamma_2)$, and $k_{\pm} = k_x \pm ik_y$. The terms are in agreement with the work of Xia [87] and of Ikonik et al [88]. Clearly, the P term is unchanged, which is as expected since $\mathbf{J}^2$ transforms like a scalar independent of frame of reference. since the R term now includes a k_z^2 term, interpreting effective masses is somewhat more difficult since bases no longer translate to pure heavy and light hole states rather an admixture.

In addition, one may return the (111) quantised terms as entered into the Luttinger-Kohn valence band Hamiltonian as;

$$\left. \begin{aligned} P &= \gamma_1 (k_+ k_- + k_z^2) \\ Q &= \gamma_3 (k_+ k_- - 2k_z^2) \\ R &= \frac{2}{\sqrt{3}} \left(\left(\frac{1}{2}\gamma_2 + \gamma_3 \right) k_-^2 + 2\sqrt{2}i\mu k_- k_z \right) \\ S &= \frac{-2}{\sqrt{3}} \left((2\gamma_2 + \gamma_3) k_+ k_z - \sqrt{2}i\mu k_-^2 \right) \end{aligned} \right\} (111) \quad (4.39)$$

One may test that the dispersion along the [111] direction in reciprocal space for the (001) quantisation in real space is equivalent to the dispersion along the [001] direction for the (111) quantisation. In other words $\mathbf{k}' \cdot \mathbf{r}' = \mathbf{k} \cdot \mathbf{r}$ is conserved, as they transform contragrediently to one another, and the Hamiltonian becomes equivalent for the two cases. This is a good check to show not only that expressions for P , Q , R and S are correct, but also highlights the fact that the dispersion is independent of the choice of quantisation direction in accordance with the canonical property of the transformation.

At this point, one may ask the question; what is the point of a coordinate transformation since the Hamiltonian is shown to be invariant? Much of the original work on coordinate transformations was to interpret cyclotron resonance data for a magnetic field oriented along a general axis of the crystal. Within the context of this thesis however we desire k_z as normal to the growth plane of the DCS rather than along the quantisation axis of the CCS. The motivation is two fold;

1. Under the loss of translational symmetry; $k_z \rightarrow \hat{k}_z = -i\frac{\partial}{\partial z}$ becomes a differential operator, such that the Hamiltonian is not diagonal at $k_x = k_y = 0$. Consequently heavy and light holes interact, such that confinement energies become a function of θ and ϕ . This also means that the optical polarisation properties may be tailored through the choice of growth plane.
2. Under the piecewise construction of the Hamiltonian, material dependent parameters take the form of rectangular step functions across an interface. This leads to the principle of operator ordering schemes in $\hat{k}_z$ which impose boundary conditions [45] and connection rules of envelope functions across an interface.

Summary

In this chapter much progress has been made to implement the mathematical tools of previous chapters to generate results which agree with experiment through the semi-empirical $\mathbf{k} \cdot \hat{\mathbf{p}}$ double group formulation. The linearly independent matrices $A_{\mathbf{k} \cdot \hat{\mathbf{p}}}^{\Gamma_i^{\pm} : \Gamma_j^{\mp}}$ and $A_{\mathbf{k} \cdot \hat{\mathbf{p}}}^{\Gamma_i^{\pm} : \Gamma_j^{\mp}}$ were generated using Wigner-Eckart theorem and symmetrised basis of Chapter 3. Such matrices are characteristic of the T_d and O_h point groups and are of fundamental importance in understanding the material properties.

A set of zone centre energy eigenvalues and scaling parameters were used to generate full zone band diagrams for both Silicon and Germanium using a 30 Band $\mathbf{k} \cdot \hat{\mathbf{p}}$ double group matrix Hamiltonian. From these diagrams the indirect band-gap nature was identified with the transition from Δ to L conduction band minimum valleys at SiGe alloy composition $x = 88\%$ and related to experimental near band-gap photoluminescence and bulk electron bulk mobilities.

Using degenerate perturbation theory to 2^{nd} order, the DKK and Silicon 6-band effective mass Hamiltonians were discussed in relation to the experimental validation of results with cyclotron resonance experiments and zone centre effective masses; m_{hh}^* and m_{lh}^* . However, the main stalwart of the $\mathbf{k} \cdot \hat{\mathbf{p}}$ method was the Germanium 8-band model, for application to modelling devices designed for use in optical communications technology.

To conclude this chapter, the theory of invariants was discussed as a means of returning effective mass Hamiltonians with less stringent assumptions on the self-consistent one electron potential. It was shown how the DKK and Luttinger-Kohn valence band Hamiltonians may be returned by expressing the Hamiltonian as a polynomial with arguments as linearly independent generator matrices and irreducible perturbation components. Finally, canonical transformations were implemented to return effective mass Hamiltonians for when the quantisation and crystallographic axes no longer coincide.

Chapter 5

Extension to Strained Systems

The work in the preceding chapter concerned unstrained bulk Silicon and Germanium. In this chapter, strain is discussed to account for systems where there is a lattice mismatch between adjacent layers. Strain also presents significant experimental limitations in constructing defect free heterostructures as it places an upper limit on layer thicknesses if not strain balanced accordingly. Band offsets are discussed from the point of view of conduction and valence band edge alignment in quantum well heterostructures and strain is incorporated into the Hamiltonian through the treatment of Pikus & Bir [3].

In the Born-Oppenheimer approximation; nuclei were said to be motionless such that electronic eigenstates are simultaneous eigenstates of the many body Hamiltonian. Consequently electron-phonon interactions may be introduced as a perturbation, and for the case of long wavelength phonons, this is done through static strain and deformation potentials. The 4% lattice mismatch between Silicon and Germanium [4] calls for the appropriate treatment of strain in heterostructures discussed in this chapter.

The overwhelming effect of strain is to shift valence and conduction band edges, such that devices may be engineered to operate at chosen frequencies by controlling the direct band-gap. One further advantage is the lifting of heavy and light hole degeneracies under uniaxial and shear strain; allowing accurate determination of deformation potentials under the cyclotron resonance experiment [42]. While strain does add further complexity, much of the work of the preceding chapter may be recycled through properties concerning the nature of spherical tensor operators.

5.1 Stress & Strain

In this section, the principles of stress & strain are discussed and related via a form of Hooke's law involving the fourth rank stiffness tensor. It is shown how the conservation of matter principle gives rise to the Poisson ratio, relating in- and out-of plane strain to one another, and may be generalised for an arbitrary growth axis under the constraint of biaxial stress.

The experimental implications of stress & strain are also discussed which imposes a critical layer thickness when growing pseudomorphic thin films without introducing misfit dislocations into the device. Indeed the challenges of the SiGe heterostructure overwhelmingly reside at the principles of growth [94] in sophisticated Molecular Beam Epitaxy (MBE) and Chemical Vapour Deposition (CVD) techniques.

5.1.1 Principles of Strain

A body is in a state of stress when acted on by external forces. Where body forces (e.g. gravity) are proportional in magnitude to volume, forces on the surface are proportional to area. Force per unit area is termed stress, and σ_{ij} is the i^{th} component of a force vector per unit area acting on a plane whose outward normal is parallel to the positive j direction. Components of stress σ_{ij} form a second rank tensor composed of normal ($i = j$) and shear ($i \neq j$) components; symmetric when considering moments, such that contrary torques are equal, about the centre of the cube.

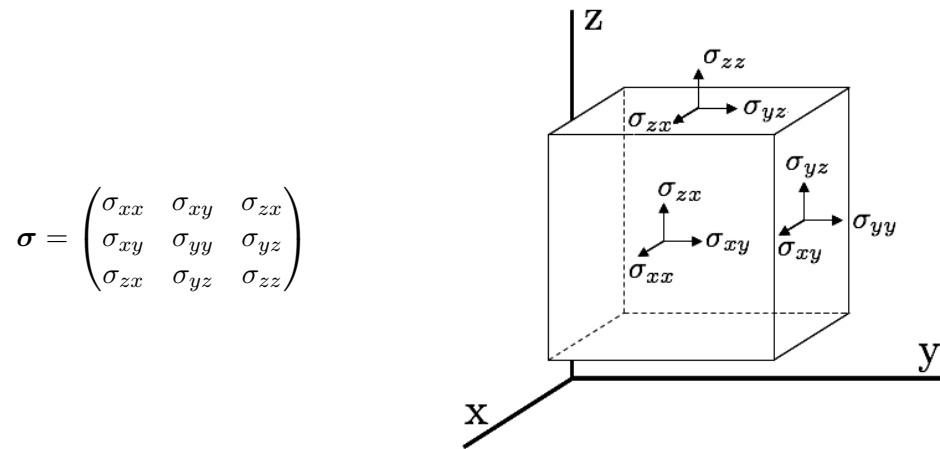


FIGURE 5.1: Stress cube indicating normal; σ_{xx} , σ_{yy} and σ_{zz} and shear; σ_{xy} , σ_{yz} and σ_{zx} components for respective faces

As shown in Figure 5.1, σ_{xy} is the force exerted in the y -direction on the face normal to the x -axis. σ_{xx} , σ_{yy} and σ_{zz} are normal and σ_{xy} , σ_{yz} and σ_{zx} are shear components. The trace is the scalar bulk modulus; $\rho = -\frac{1}{3}Tr[\sigma] = -\frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$. There are some important special cases of the stress tensor, corresponding to biaxial stress

and hydrostatic pressure with the former the condition for thin films growth on a plane normal the z -axis of the DCS.

$$\boldsymbol{\sigma} = \begin{pmatrix} \sigma_1 & 0 & 0 \\ 0 & \sigma_2 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \boldsymbol{\sigma} = \begin{pmatrix} -P & 0 & 0 \\ 0 & -P & 0 \\ 0 & 0 & -P \end{pmatrix} \quad (5.1)$$

The final special case is uniaxial stress, which may be decomposed into biaxial stress and hydrostatic pressure, so is considered superfluous.

Stress and strain are linked by a very general form of Hooke's law involving the fourth rank cartesian stiffness, C_{ijkl} and compliance, S_{ijkl} tensors¹;

$$\sigma_{ij} = \sum_{kl} C_{ijkl} \epsilon_{kl}, \quad \epsilon_{ij} = \sum_{kl} S_{ijkl} \sigma_{kl}, \quad (5.2)$$

where stiffness and compliance are each other's inverse. Using principles of the theory of invariants, the coincidence of identity representations in the decomposition of tensor products indicates the number of independent variables. In cubic crystals, fourth rank cartesian tensors such as stiffness have three independent variables [95, 96] since $(\Gamma_4^- \otimes \Gamma_4^-)_{sym} \otimes (\Gamma_4^- \otimes \Gamma_4^-)_{sym} = 3\Gamma_1^+ \oplus \dots$

Representing stress and strain tensors in Voigt notation [16], the stiffness tensor reduces to a 6×6 matrix, symmetrised according to the cubic T_d and O_h groups;

$$\begin{pmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{yz} \\ \sigma_{xz} \\ \sigma_{xy} \end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{pmatrix} \begin{pmatrix} \epsilon_{xx} \\ \epsilon_{yy} \\ \epsilon_{zz} \\ 2\epsilon_{yz} \\ 2\epsilon_{xz} \\ 2\epsilon_{xy} \end{pmatrix} \quad (5.3)$$

Components of compliance may be related to those of stiffness through;

$$C_{11} - C_{12} = \frac{1}{S_{11} - S_{12}}, \quad C_{11} + 2C_{12} = \frac{1}{S_{11} + 2S_{12}}, \quad C_{44} = \frac{1}{S_{44}} \quad (5.4)$$

For $Si_{1-x}Ge_x$, experimental values following a Vegard's law correlation, in units of $\times 10^{11}$ dyn/cm² = 0.01GPa of the stiffness tensor are [97];

¹why they are labelled this way I will never know

$$\left. \begin{aligned} C_{11} &= 1.675 - 0.360x \\ C_{12} &= 0.650 - 0.156x \\ C_{44} &= 0.801 - 0.117x \end{aligned} \right\} \quad (5.5)$$

Biaxial stress, applicable to thin film growth on the trivial $\{001\}$ plane returns a diagonal strain tensor, with in- ($\epsilon_{\parallel}$) and out of-plane ($\epsilon_{\perp}$) strains related through the dimensionless Poisson ratio, D .

$$\epsilon_{\parallel} = \frac{a}{a_0} - 1, \quad \epsilon_{\perp} = -D\epsilon_{\parallel} \quad (5.6)$$

where a_0 and a are the characteristic lattice constants of the substrate and thin film respectively and positive (negative) values for $\epsilon_{\parallel}$ represent tensile (compressive) strain. For SiGe there is a 4% lattice mismatch, where the lattice parameter follows a quadratic relation [4] as a function of composition, x ;

$$a_{Si_{1-x}Ge_x} = 5.387 + 0.1428x + 0.0532x^2 \quad (5.7)$$

where $a_{Si_{1-x}Ge_x}$ is in Angstroms $\text{\AA}$. Growing a thin $Si_{1-x}Ge_x$ layer on unstrained $Si_{1-y}Ge_y$ yields either a *compressive* ($x > y$) or *tensile* ($x < y$) strained layer, in accordance with the conservation of matter, provided Poisson's ratio is positive.

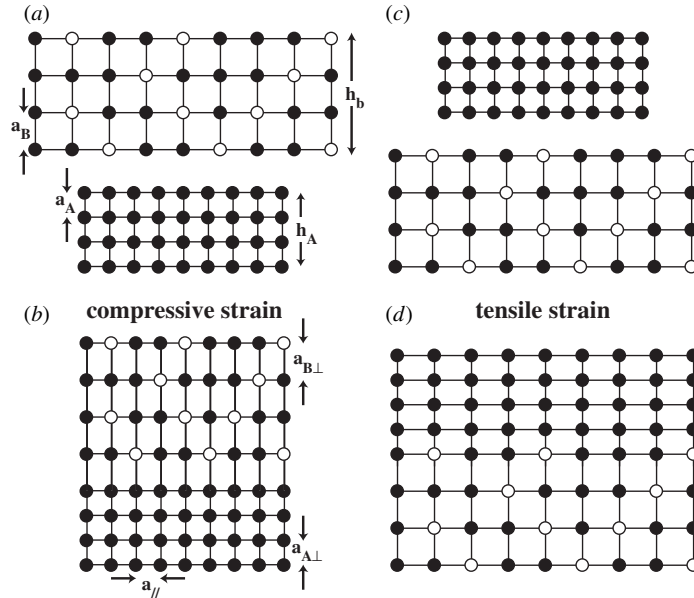


FIGURE 5.2: (a) A thin SiGe film to be grown on a Si layer with (b) compressive strain. (c) A thin Si film to be grown on an SiGe layer with (d) tensile strain [1]

While Poisson's ratio is generally positive, auxetic materials exhibit a negative Poisson ratio; to which a lot of research is devoted in the field of blast protection.

$$D_{\{001\}} = \frac{2C_{12}}{C_{11}}, \quad \begin{cases} \epsilon_{xx} = \epsilon_{yy} = \epsilon_{\parallel} \\ \epsilon_{zz} = \epsilon_{\perp} \\ \epsilon_{xy} = \epsilon_{yz} = \epsilon_{xz} = 0 \end{cases} \quad (5.8)$$

5.1.2 Generalised Poisson Ratio

Equation 5.8 is the special case when the CCS and DCS coincide. However, we may generate a general Poisson ratio $D(\theta, \phi)$ and expressions for ϵ_{ij} to ensure biaxial stress normal to the growth plane of the DCS.

Transforming the components of strain in Equation 5.8, using $\epsilon = R(\theta, \phi)\epsilon R^\dagger(\theta, \phi)$, components in the CCS become [92];

$$\begin{cases} \epsilon_{xx} &= -\epsilon_{\parallel} ((1 + D(\theta, \phi)) \sin^2(\theta) \sin^2(\phi) - 1) \\ \epsilon_{yy} &= -\epsilon_{\parallel} ((1 + D(\theta, \phi)) \cos^2(\theta) \sin^2(\phi) - 1) \\ \epsilon_{zz} &= -\epsilon_{\parallel} (D(\theta, \phi) \cos^2(\phi) - \sin^2(\phi)) \\ \epsilon_{yz} &= +\epsilon_{\parallel} (1 + D(\theta, \phi)) \cos(\theta) \cos(\phi) \sin(\phi) \\ \epsilon_{zx} &= -\epsilon_{\parallel} (1 + D(\theta, \phi)) \sin(\theta) \cos(\phi) \sin(\phi) \\ \epsilon_{xy} &= +\epsilon_{\parallel} (1 + D(\theta, \phi)) \cos(\theta) \sin(\theta) \sin^2(\phi) \end{cases} \quad (5.9)$$

Putting these into Equation 5.3 an expression for stress in the CCS is returned. Transforming this back to the DCS coordinate system $\sigma = R^\dagger(\theta, \phi)\sigma R(\theta, \phi)$, and invoking the requirement for biaxial stress; $\sigma_{zz} = 0$, a general Poisson ratio may be returned.

$$D(\theta, \phi) = \frac{g(\theta, \phi) (C_{11} - 2C_{44}) + 2C_{12} (\sin^2(\phi) (1 - \cos^2(\theta) \sin^2(\theta) \sin^2(\phi)) + \cos^4(\phi))}{g(\theta, \phi) (C_{12} + 2C_{44}) + C_{11} (\sin^4(\phi) (\cos^4(\theta) + \sin^4(\theta)) + \cos^4(\phi))} \quad (5.10)$$

where $g(\theta, \phi) = 2 \sin^2(\phi) (\cos^2(\theta) \sin^2(\theta) \sin^2(\phi) + \cos^2(\phi))$. Using trivial angles the aforementioned case $D_{\{001\}}$ is returned. Furthermore, using angles $\theta = 0$, $\phi = \pi/4$, and $\theta = \pi/4$, $\phi = \arctan(\sqrt{2})$, some previously encountered cases are returned [98];

$$D_{\{011\}} = \frac{C_{11} + 3C_{12} - 2C_{44}}{C_{11} + C_{12} + 2C_{44}}, \quad D_{\{111\}} = \frac{2(C_{11} + 2C_{12} - 2C_{44})}{C_{11} + 2C_{12} + 4C_{44}} \quad (5.11)$$

A surface plot for the values of the dimensionless Poisson ratio $D(\theta, \phi)$ using stiffness tensor values for Silicon is shown in Figure 5.3. Clearly for Silicon; Poisson's ratio is positive for all angles; $D(\theta, \phi) > 0 \forall (\theta, \phi)$, as is also the case for Germanium.

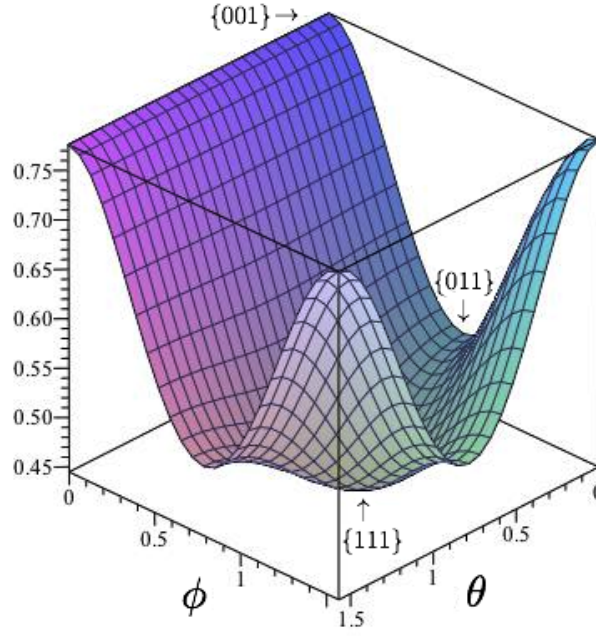


FIGURE 5.3: Surface plot for general dimensionless Poisson ratio $D(\theta, \phi)$ in the domain; $0 < (\theta, \phi) < \pi/2$, using stiffness tensor values for Silicon

5.1.3 Experimental Implications

The lattice mismatch between Silicon & Germanium results in compressively (tensile) strained layer formation when SiGe alloys are grown pseudomorphically onto a Silicon (Germanium) substrate as depicted in Figure 5.2. Because Germanium rich quantum well devices are the main motivation for this thesis, in an ideal world; one would use Germanium substrates, however a more economical solution is to use a virtual substrate out of strain balanced SiGe layers with a Germanium rich cap several micrometers thick [99].

The basic principles for growth is that for a small enough lattice mismatch between substrate and epilayer; the layer will adopt the lattice parameter of substrate and grow pseudomorphically until the thickness exceeds some critical thickness. Should this thickness be exceeded, it may become energetically favourable to overcome the kinetic barrier and release some of the stored energy through the formation of a defect such as a misfit dislocation². The introduction of such defects renders any grown device defunct and should be avoided at all costs.

Several models have been proposed to estimate such critical thicknesses in the literature, from van der Merwe [100] and Matthews & Blakeslee [101] based on the principles of energy minimisation and balancing of forces respectively. But while the subject of growth is not an exact science, in general; the rule of thumb rule is that the device is generally stable if $|\epsilon_{||}|L \lesssim 200\%$ [102], where $|\epsilon_{||}|$ is the absolute in-plane strain and

²the analogy being stretching a rubber band so much that it snaps

L is the layer thickness in Angstroms $\text{\AA}$. For example; consider a 12nm compressively strained Germanium quantum well grown on a $\text{Si}_{0.1}\text{Ge}_{0.9}$ -{001} virtual substrate, where $|\epsilon_{\parallel}|L \approx 50\%$, which should remain stable.

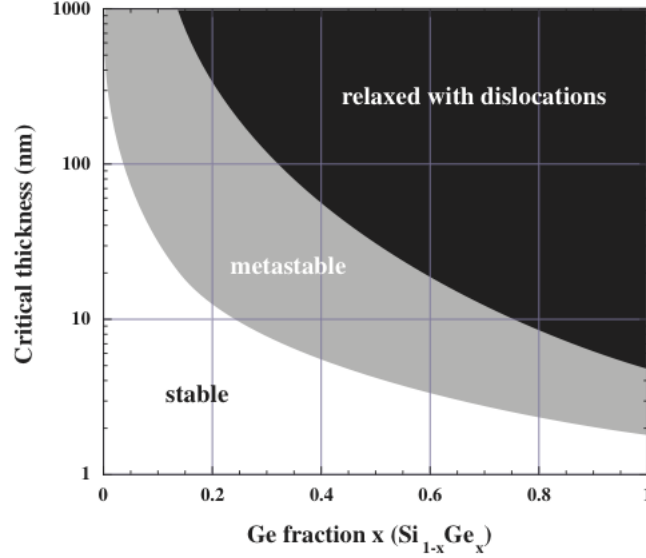


FIGURE 5.4: Matthews & Blakeslee [101] critical thickness versus Germanium fraction of $\text{Si}_{1-x}\text{Ge}_x$ for pseudomorphic layer on bulk Si-{001}. The metastable transition is for MBE growth at 550°C . Taken from [1]

The devices proposed in this thesis are not expected to suffer from such defect formation, however it should be stressed that the greatest challenge experimentally is in the Germanium rich virtual substrate grown on a Silicon wafer [103]; as many layers have to be stacked with sequential stress balancing and composition overshoots. The gradual increase in Germanium composition means that growth is protracted out over a longer distance and there is wide scope for the introduction of defects. Advances in technology such as low-energy plasma-enhanced CVD [49, 50] and gas source MBE [99] have allowed for such high quality virtual substrates to be grown such that the devices modelled in this thesis have a tangible experimental reference.

5.2 Band Edges in Heterostructures

In this section, the effect of strain is introduced into the Hamiltonian through the formulation of Pikus & Bir [3]. Akin to the work in the previous chapter, the problem may be tackled from both the perturbation theory and theory of invariants approaches through the direct analogy of irreducible perturbation components of the Bloch vector $k_i k_j$ with strain components ϵ_{ij} . Although theory of invariants approach is discussed here only since the subject of canonical coordinate transformations was considered in the previous chapter.

The impact of strain on the Hamiltonian is discussed in terms of lifting heavy and light hole degeneracies in terms of the band edge. Additionally, band offsets are discussed in relation to the fabrication of devices. To conclude this section, the band edge diagram typical to strained quantum well heterostructures is discussed.

5.2.1 Pikus-Bir Hamiltonian

The Pikus-Bir Hamiltonian [3] was introduced in Section 1.3.1. Using the methods of the previous chapter one may use Wigner-Eckart theorem or the theory of invariants by substituting ϵ_{ij} in place of $k_i k_j$ as irreducible perturbation components. Direct substitution with the associated invariants gives rise to [2, 75];

$$H_{DKK}^{\epsilon} = \begin{pmatrix} l\epsilon_{xx} + m(\epsilon_{yy} + \epsilon_{zz}) & n\epsilon_{xy} & n\epsilon_{zx} \\ n\epsilon_{xy} & l\epsilon_{yy} + m(\epsilon_{zz} + \epsilon_{xx}) & n\epsilon_{yz} \\ n\epsilon_{zx} & n\epsilon_{yz} & l\epsilon_{zz} + m(\epsilon_{xx} + \epsilon_{yy}) \end{pmatrix} \quad (5.12)$$

It is often customary to use hydrostatic-, uniaxial- and shear-strain deformation potentials a_v , b , and d analogous to the Luttinger parameters instead of the l , m and n here. Without wanting to repeat the process in too much detail of Luttinger's valence band Hamiltonian in Section 4.3.2, for brevity we simply substitute in the deformation potentials in place of the Luttinger parameters and strain components ϵ_{ij} in place of Bloch vectors $k_i k_j$. Terms in the Pikus-Bir Hamiltonian for the valence band $H_{VB:VB}$ become [104];

$$\left. \begin{aligned} P_{\epsilon} &= a_v (\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}) \\ Q_{\epsilon} &= b (\epsilon_{xx} + \epsilon_{yy} - 2\epsilon_{zz}) \\ R_{\epsilon} &= \sqrt{3} (b (\epsilon_{yy} - \epsilon_{xx}) - 2id\epsilon_{xy}) \\ S_{\epsilon} &= -2\sqrt{3}d (\epsilon_{zx} + i\epsilon_{yz}) \end{aligned} \right\} (001) \quad (5.13)$$

a_v is the valence band hydrostatic deformation potential and $Tr[\epsilon] = (\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz})$ the dilation or fractional volume change; $\Delta\Omega/\Omega$, such that under hydrostatic pressure, the valence band edges shift with no lifting of degeneracy. Experimentally what is frequently measured is the rate of change in band gap with respect to pressure; and from this it is possible to extract a deformation potential for the energy gap. In terms of individual bands this is expressed as $a_c - a_v$, and often resolving the two is not easy. Application of biaxial stress lifts the heavy and light hole degeneracy allowing for a more accurate determination of deformation potentials under the cyclotron resonance experiment [42]. Deformation potentials for $Si_{1-x}Ge_x$ are given below in units of eV [47].

$$\left. \begin{aligned} a_c - a_v &= 12.19 + 0.58x \\ b &= 2.10 + 0.76x \\ d &= 4.85 + 0.43x \end{aligned} \right\} \quad (5.14)$$

For application to coordinate transformations one may then use canonical transformations in the theory of invariants and enter these terms into the Hamiltonian as P_ϵ , Q_ϵ , R_ϵ and S_ϵ in an identical manner as before. General expressions for ϵ_{ij} with the constraint for growth as biaxial stress in the DCS returning the generalised Poisson ratio were also given in Section 5.1.2, so consequently the strain Hamiltonian for any growth plane may be obtained as a function of θ and ϕ rotation angles.

The band-gap is also affected by temperature, a scalar quantity, inducing a dilation through thermal expansion. Scaling is through the Varshni [105] parameters α and β for $Si_{1-x}Ge_x$, such that the direct gap is scaled by temperature through;

$$E_g(T) = E_g(T = 0K) - \frac{\alpha T^2}{T + \beta}; \quad \left\{ \begin{aligned} \alpha &= 0.5367 + 0.1475x \quad \text{meV/K} \\ \beta &= 745.8 - 347.8x \quad \text{K} \end{aligned} \right. \quad (5.15)$$

It is important to note that as temperature rises, the band gap decreases, so measurements at say room temperature will in general be in the longer wavelength range than when the sample is cooled.

Extension into strained systems lifts the degeneracy of heavy and light holes through uniaxial strain, such that compressive (tensile) strain shifts the heavy hole band edge above (below) the light hole band edge [1, 81] as depicted below;

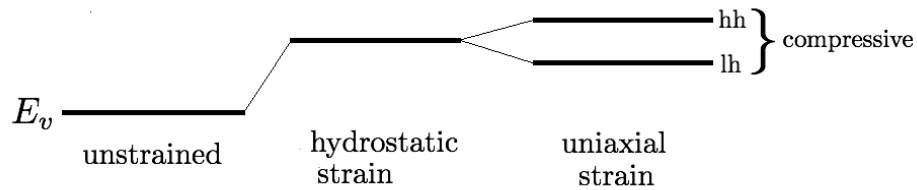


FIGURE 5.5: Effect of hydrostatic and uniaxial strain on degenerate valence band edge. Compressive (tensile) strain moves heavy holes above (below) light holes as depicted.

The degree of splitting between heavy and light holes for the case of biaxial strain grown on the $\{001\}$ plane of a substrate comes from the Q_ϵ term [106], and any shear terms grown on an arbitrary plane from the R_ϵ and S_ϵ terms where ϵ_{xy} , ϵ_{yz} , and ϵ_{zx} are non zero. Unfortunately, in the latter instance, the strain Hamiltonian is no longer diagonal and where the band edge actually lies becomes mixed along with heavy and light hole eigenvectors.

Band edge diagrams may be drawn for devices grown on the $\{001\}$ plane when considering diagonal terms alone, although one should bear in mind that the Q_ϵ term couples light holes with the spin-orbit band in $H_{VB:SO}$. Alternatively eigenvalues of the strain Hamiltonian may be found as quasi-band edges in model solid theory [48], but eigenvectors are no longer compatible with those of the effective mass Hamiltonian.

In the next section, band edge diagrams are discussed from the point of view of depicting the strained quantum well heterostructure; similar to the set up in the Germanium rich device in Figure 1.5.

5.2.2 Band Edge Diagrams

Compositionally varying heterostructures may be grown to confine electrons and holes in potential wells from which much device physics is derived. At an abrupt interface, the most notable material dependent parameter; the band gap is discontinuous, and this discontinuity is scaled by the band offsets ΔE_c and ΔE_v . In Germanium rich SiGe the direct band gap is a minima and favours the straddling (type-I) band edge alignment scheme with a band offset ratio of $(E_c)68:32(E_v)$ as given by Yaguchi et al [107].

Consider the interface between $Si_{0.15}Ge_{0.85}$ and Germanium as depicted in Figure 5.6 for the unstrained case. Here the band offsets are $\Delta E_c = 303\text{meV}$ and $\Delta E_v = 186\text{meV}$ in accordance with values for $E_c - E_v$ given in Table 4.2. The spin orbit band follows the valence band offsets, however in Germanium the spin orbit interaction is 296meV so is large enough to be omitted for illustration purposes; it actually forms a staggered (type-II) and broken (type-III) band edge alignment with E_v in Germanium and Silicon rich devices respectively.

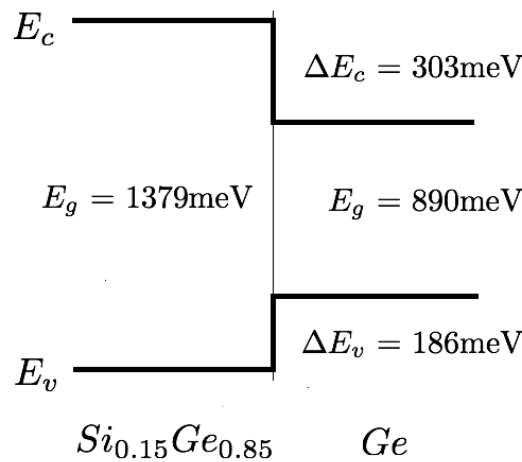


FIGURE 5.6: Band discontinuities and alignments of conduction and valence bands of an unstrained interface between $Si_{0.15}Ge_{0.85}$ and Germanium using band offsets of $(\Delta E_c)68:32(\Delta E_v)$ as given by Yaguchi et al [107]

It was previously stated in the introductory chapter that Silicon rich systems are type-II yet the band offsets quoted here do not take this into account. The reasons for this may be due to the fact that at the direct conduction band minima changes character abruptly from s -antibonding ($\Gamma_2^- \otimes \Gamma_6^+ = \Gamma_7^-$) at $x = 29\%$ to p -antibonding ($\Gamma_4^- \otimes \Gamma_6^+ = \Gamma_6^- \oplus \Gamma_8^-$). Since the compositions quoted in this thesis are for Germanium rich devices this issue never arises but should be considered as a potential problem nevertheless.

Clearly, by sandwiching Germanium either side of $Si_{0.15}Ge_{0.85}$ barriers generates the familiar band edge alignment of typical quantum well devices such as laser diodes, photodetectors and optical modulators. When grown on a $Si_{0.1}Ge_{0.9}$ virtual substrate, such a device may become strain balanced; in that the compressive strain in the well balances tensile strain in the barriers such that multiple quantum well stacks may be grown. Confinement energies, and therefore inter-band transition energies, may be tailored by choice of well thickness and well/barrier composition for the device to operate at chosen wavelengths such as those around $1.5\mu\text{m}$ for use in 3^{rd} generation fibre optic communication channels [41].

All the tools are now at our disposal to investigate such heterostructures in the next chapter and it is shown how to model sub-band dispersion, joint density of states and absorption coefficient and their effect under the application of an externally applied electric field through the quantum confined Stark effect [51].

Summary

Some of the original work on heterostructures was on lattice matched AlGaAs/GaAs systems and strain was not considered. As work progressed into InGaAs/GaAs devices many studies on strain were performed; and within the context of this thesis many of this work may be recycled into SiGe heterostructures. In this chapter some of the more basic principles of strain were introduced and it was shown how biaxial stress is the constraint for 2-dimensional structures. The Poisson ratio, which relates in- ($\epsilon_{\parallel}$) and out of-plane ($\epsilon_{\perp}$) strains was generalised for an arbitrary growth plane and expressions for the $\{011\}$ and $\{111\}$ plane were obtained in accordance with those in the literature.

While strain may be treated from a theoretical perspective, it has far reaching consequences in the growth and fabrication of devices. A critical thickness, or upper limit was placed on device dimension, $|\epsilon_{\parallel}|L \lesssim 200\%$, which should not be exceeded for the device to remain dislocation free. Indeed the greatest challenge in the SiGe system is in growing a defect free Germanium rich virtual substrate on a Silicon wafer for economic reasons.

To conclude the chapter, strain was discussed in terms of where it enters the Hamiltonian through the work of Pikus & Bir. It was shown how hydrostatic, biaxial and shear strain terms may be accounted for through their respective deformation potentials, and how heavy & light hole degeneracy may be lifted through biaxial strain. Band offsets across an interface were discussed, and it was shown how for compressive strain the heavy hole band moves above the light hole band and vice versa for tensile strain.

Indeed the compressively strained 12nm Germanium well sandwiched between tensile strained $Si_{0.15}Ge_{0.85}$ barriers on a $Si_{0.1}Ge_{0.9}$ - $\{001\}$ virtual substrate discussed in the introductory chapter underpins the arguments presented this chapter.

Chapter 6

Application to Heterostructures

Heterostructure devices enter modern life in so many ways; as envisaged by Moore [108] and L. Esaki & R. Tsu [39]. In this chapter, the effective mass and strain Hamiltonians discussed previously are applied within numerical schemes to model sub-band dispersion, joint density of states and the absorption coefficient for quantum well devices. Using the relevant input parameters the compressively strained Germanium well sandwiched between tensile strained $Si_{0.15}Ge_{0.85}$ barriers on a $Si_{0.1}Ge_{0.9}$ -{001} virtual substrate is modelled for the widespread application as a practical device.

Indeed, a Silicon-Germanium (SiGe) based optical modulator working under the quantum confined Stark effect (QCSE) [51] around $1.5\mu m$ at room temperature for use in 3^{rd} generation fibre optic communication channels is one of the main motivations for the work presented in this thesis. By using such a low-power device that may be grown directly onto Silicon, the functionality of the all integrated system on a chip [1] employing SiGe alloy properties may be enhanced to the realm of optoelectronics with widespread application.

Using effective mass Hamiltonians a piecewise construction into a finite element mesh with compositionally varying input parameters and boundary conditions may be employed to model the quantum well heterostructure. Sub-band dispersion and joint density of states may reveal information about such a device's behaviour and by incorporating transition probabilities the absorption spectra may be modelled and compared with experimental photoluminescence spectra [49, 50]. To conclude this chapter the modelling of novel devices on arbitrary growth planes is performed with the specific examples of the {011} and {111} growth plane investigating both polarisation spectroscopy and transition energies.

6.1 Operator Ordered Hamiltonians

The effective mass Hamiltonians in Chapter 4 were derived for infinite bulk like crystals. Translational symmetry in three dimensions gives rise to the good quantum numbers k_x , k_y , and k_z born out of the Floquet-Bloch principle. In a quantum well heterostructure; layer by layer compositional variation breaks translational symmetry along the device coordinate system (DCS) growth axis.

In this section operator ordered effective mass Hamiltonians used to model heterostructures are generated in accordance with the envelope function approximation (EFA) [10–13]. The single group and adapted double group formulations return boundary conditions across an abrupt interface for degenerate valence bands. Using the double group formulation operator ordered Hamiltonians may be returned with consummate ease.

6.1.1 Single Group Formulation

In the derivation of the $\mathbf{k} \cdot \hat{\mathbf{p}}$ perturbation; the one electron wave function was decomposed into a rapidly varying cell periodic term, $u_{n\mathbf{k}}(\mathbf{r})$ modulated by a slowly varying Bloch function; $e^{i\mathbf{k} \cdot \mathbf{r}}$. Consequently the wave function in an infinite crystal has the symmetry properties of the entire space group as the product of the point and translational subgroups. Under the EFA, the Bloch function is a special case of a more general function $F(\mathbf{r})$. Making the substitution $e^{i\mathbf{k} \cdot \mathbf{r}} \rightarrow F(\mathbf{r})$, one may retain the differential form of the operators; for example, $k_z \rightarrow \hat{k}_z = -i \frac{\partial}{\partial z}$ as discussed in Section 1.3.2.

An operator ordered form of the DKK Hamiltonian in Equation 4.15 is given by Stavrinou & van-Dalen [109, 110];

$$\begin{pmatrix} \hat{k}_x L \hat{k}_x + \hat{k}_y M \hat{k}_y + \hat{k}_z M \hat{k}_z & \hat{k}_x N_1 \hat{k}_y + \hat{k}_y N_2 \hat{k}_x & \hat{k}_x N_1 \hat{k}_z + \hat{k}_z N_2 \hat{k}_x \\ \hat{k}_y N_1 \hat{k}_x + \hat{k}_x N_2 \hat{k}_y & \hat{k}_y L \hat{k}_y + \hat{k}_z M \hat{k}_z + \hat{k}_x M \hat{k}_x & \hat{k}_y N_1 \hat{k}_z + \hat{k}_z N_2 \hat{k}_y \\ \hat{k}_z N_1 \hat{k}_x + \hat{k}_x N_2 \hat{k}_z & \hat{k}_z N_1 \hat{k}_y + \hat{k}_y N_2 \hat{k}_z & \hat{k}_z L \hat{k}_z + \hat{k}_x M \hat{k}_x + \hat{k}_y M \hat{k}_y \end{pmatrix} \quad (6.1)$$

Where L and M have their usual meanings, and $N_1 + N_2 = N$. The advantage of the Foreman parameters [46] is that they lend themselves to operator ordering schemes favourably, as $N_1 = -6\sigma + 6\delta$ and $N_2 = -6\pi$.

The general slowly varying envelope function is retained for quantum dots [111], however for quantum wires one axis of translational symmetry is restored. In this scheme the good quantum number k_z emerges and $F(\mathbf{r}) = F(x, y)e^{ik_z z}$ [112]. The complexity of the problem remains large, however transformation into cylindrical polar coordinates may lead to some simplification in for example carbon nano-tubes. Within the context of this thesis, quantum wells restore the good in-plane quantum numbers such that

$F(\mathbf{r}) = e^{i(k_x x + k_y y)} F(z)$ where the z -axis is chosen as the conventional growth axis normal to the plane of the well in the DCS.

Casting the DKK Hamiltonian onto the adapted double group for a quantum well returns an ordered form of the 4-band Luttinger-Kohn [35] effective mass Hamiltonian;

$$H_{VB:VB} = \begin{pmatrix} P+Q & S & R & 0 \\ S^\dagger & P-Q & C & R \\ R^\dagger & C^\dagger & P-Q & -(S^*)^\dagger \\ 0 & R^\dagger & -S^* & P+Q \end{pmatrix} \begin{matrix} hh \\ lh \\ lh \\ hh \end{matrix} \quad (6.2)$$

Operator ordering gives rise to an interfacial C term which vanishes in the bulk. Retaining ordering on the S term for the trivial (001) quantisation axis gives [46];

$$C = 2k_+ \left(\hat{k}_z (\sigma - \pi - \delta) - (\sigma - \pi - \delta) \hat{k}_z \right) \quad (6.3)$$

$$S = -2\sqrt{3}k_+ \left((\sigma - \delta) \hat{k}_z + \hat{k}_z \pi \right) \quad (6.4)$$

As the P and Q terms for the (001) case involve only $k_\pm k_\mp$ and $\hat{k}_z^2$, ordering is redundant and symmetric in accordance with Bastard [45] respectively. Furthermore as the R term has only $k_\pm k_\pm$ terms ordering is also redundant. However for arbitrary growth directions this is no longer the case. A set of general rules for constructing the correct operator ordered Hamiltonian for quantum well heterostructures grown on arbitrary growth directions may be returned by transforming the ordered DKK Hamiltonian as set out in [110].

Using this approach the transformation properties of spin $\{\uparrow, \downarrow\}$ are not fully accounted for when cast onto the adapted double group. The double group formulation on the other hand takes into account the transformation properties of half integer eigenstates $|J, m_J\rangle$ through the full $J = 1/2$ and $J = 3/2$ rotation matrices. Yet since spin is an internal symmetry, the physics of both formulations should be identical to within a phase factor on the $|J, m_J\rangle$ basis, also discussed in [110].

6.1.2 Double Group Formulation

To obtain the operator ordering schemes under the double group formulation, one uses the linearly independent matrices given in the previous chapter. By imposing the property that the differential operator does not commute with material dependent parameters across an interface $[\zeta_{\alpha;\beta}^j(z), \hat{k}_z] \neq 0$, one may generate the ordered Löwdin term out of $A_{\mathbf{k}\cdot\hat{\pi}}^{\Gamma_\alpha:\Gamma_j} \times \left(A_{\mathbf{k}\cdot\hat{\pi}}^{\Gamma_\beta:\Gamma_j} \right)^\dagger$. An example of this is given in the Appendix B.3.

$$H_{VB:VB} = \begin{pmatrix} P+Q & S & R & Z \\ S^\dagger & P-Q & C & R \\ R^\dagger & C^\dagger & P-Q & -(S^*)^\dagger \\ Z^\dagger & R^\dagger & -S^* & P+Q \end{pmatrix} \begin{matrix} hh \\ lh \\ lh \\ hh \end{matrix} \quad (6.5)$$

Where this time operator ordering gives rise to the previously omitted interfacial Z term presented in a paper by the author [72]. Ordering on the S term for the (001) quantisation axis for the double group, in terms of the $\zeta_{\alpha;\beta}^j$ parameters returns;

$$C = 2k_+ \left(\hat{k}_z \left(\zeta_{\Gamma_8^+:\Gamma_8^+}^{\Gamma_7^-} - \zeta_{\Gamma_8^+:\Gamma_8^+,1}^{\Gamma_8^-} - \zeta_{\Gamma_8^+:\Gamma_8^+,2}^{\Gamma_8^-} \right) - \left(\zeta_{\Gamma_8^+:\Gamma_8^+}^{\Gamma_7^-} - \zeta_{\Gamma_8^+:\Gamma_8^+,1}^{\Gamma_8^-} - \zeta_{\Gamma_8^+:\Gamma_8^+,2}^{\Gamma_8^-} \right) \hat{k}_z \right) \quad (6.6)$$

$$Z = 2k_- \left(\left(\zeta_{\Gamma_8^+:\Gamma_8^+}^{\Gamma_6^-} - \zeta_{\Gamma_8^+:\Gamma_8^+,1}^{\Gamma_8^-} \right) \hat{k}_z - \hat{k}_z \left(\zeta_{\Gamma_8^+:\Gamma_8^+}^{\Gamma_6^-} - \zeta_{\Gamma_8^+:\Gamma_8^+,1}^{\Gamma_8^-} \right) \right) \quad (6.7)$$

$$S = -2\sqrt{3}k_+ \left(\left(\zeta_{\Gamma_8^+:\Gamma_8^+}^{\Gamma_7^-} - \zeta_{\Gamma_8^+:\Gamma_8^+,1}^{\Gamma_8^-} \right) \hat{k}_z + \hat{k}_z \zeta_{\Gamma_8^+:\Gamma_8^+}^{\Gamma_6^-} \right) \quad (6.8)$$

The new Z term is missed through the single group formulation because of the treatment of the spin-orbit interaction as a perturbation rather than included into the unperturbed Hamiltonian. Under the absence of the spin-orbit interaction in the unperturbed Hamiltonian, the single group formalism is recovered with identical operator ordering on the S and C terms as required. Using values for Germanium, this interfacial coupling through Z may be calculated as; $\zeta_{\Gamma_8^+:\Gamma_8^+}^{\Gamma_6^-} - \zeta_{\Gamma_8^+:\Gamma_8^+,1}^{\Gamma_8^-} = 0.055$ in dimensionless units.

This may be compared with values for the C term; $\zeta_{\Gamma_8^+:\Gamma_8^+}^{\Gamma_7^-} - \zeta_{\Gamma_8^+:\Gamma_8^+,1}^{\Gamma_8^-} - \zeta_{\Gamma_8^+:\Gamma_8^+,2}^{\Gamma_8^-} = 1.151$ and with those of the Luttinger parameters in Table 4.3. It was expected for the Z term to be small [46] since $\pi = \zeta_{\Gamma_8^+:\Gamma_8^+}^{\Gamma_6^-} = \zeta_{\Gamma_8^+:\Gamma_8^+,1}^{\Gamma_8^-}$ in the single group formulation but not necessarily zero as shown here.

The methodology for obtaining an operator ordered form of the Luttinger-Kohn [35] valence band Hamiltonian, $H_{VB:VB}$ may also be applied to $H_{VB:SO}$ and $H_{SO:SO}$. Retaining the non-commutative form of $\hat{k}_z$ and using the appropriate matrix multiplication returns the Löwdin terms;

$$H_{VB:SO} = \sqrt{2} \begin{pmatrix} \frac{1}{2}S' & R' \\ -Q' & -\frac{\sqrt{3}}{2}\Sigma' \\ -\frac{\sqrt{3}}{2}(\Sigma')^* & Q' \\ -(R')^* & \frac{1}{2}(S')^* \end{pmatrix}, \quad H_{SO:SO} = \begin{pmatrix} P' & C' \\ (C')^\dagger & P' \end{pmatrix} \quad (6.9)$$

where the ordered terms are;

$$C' = 2k_+ \left(\hat{k}_z \left(\zeta_{\Gamma_7^+:\Gamma_7^+}^{\Gamma_7^-} - \zeta_{\Gamma_7^+:\Gamma_7^+,1}^{\Gamma_8^-} - \zeta_{\Gamma_7^+:\Gamma_7^+,2}^{\Gamma_8^-} \right) - \left(\zeta_{\Gamma_7^+:\Gamma_7^+}^{\Gamma_7^-} - \zeta_{\Gamma_7^+:\Gamma_7^+,1}^{\Gamma_8^-} - \zeta_{\Gamma_7^+:\Gamma_7^+,2}^{\Gamma_8^-} \right) \hat{k}_z \right) \quad (6.10)$$

$$S' = -2\sqrt{3}k_+ \left(\left(\zeta_{\Gamma_7^+:\Gamma_8^+}^{\Gamma_7^-} - \zeta_{\Gamma_7^+:\Gamma_8^+,2}^{\Gamma_8^-} \right) \hat{k}_z + \hat{k}_z \zeta_{\Gamma_7^+:\Gamma_8^+,1}^{\Gamma_8^-} \right) \quad (6.11)$$

$$\Sigma' = -2\sqrt{3}k_+ \left(\left(\frac{2}{3} \left(\zeta_{\Gamma_7^+:\Gamma_8^+}^{\Gamma_7^-} - \zeta_{\Gamma_7^+:\Gamma_8^+,2}^{\Gamma_8^-} \right) + \frac{1}{3} \zeta_{\Gamma_7^+:\Gamma_8^+,1}^{\Gamma_8^-} \right) \hat{k}_z + \hat{k}_z \left(\frac{1}{3} \left(\zeta_{\Gamma_7^+:\Gamma_8^+}^{\Gamma_7^-} - \zeta_{\Gamma_7^+:\Gamma_8^+,2}^{\Gamma_8^-} \right) + \frac{2}{3} \zeta_{\Gamma_7^+:\Gamma_8^+,1}^{\Gamma_8^-} \right) \right) \quad (6.12)$$

Clearly the ordering on S' and Σ' differ, which implies that the operator ordering schemes across an abrupt interface are not trivial to say the least.

The process of obtaining the correct operator ordering is cumbersome and error prone only to be exacerbated when considering arbitrary growth planes. Later on this chapter a general method is prescribed to return operator ordered Hamiltonians using a process of rather simple matrix multiplications involving the rotation matrix. Next the numerical implementation of ordered Hamiltonians applied to the SiGe quantum well heterostructure is discussed in order to model sub-band dispersion, joint density of states and absorption coefficient.

6.2 Numerical Implementation

By discretising a region of interest into a finite element mesh, adjacent elements become coupled through differential operators and matching conditions. The construction of a block tridiagonal matrix allows for numerical evaluation of eigenvalues (energy levels) and eigenvectors (envelope functions) for confined states in a potential well using numerical schemes presented here.

Iteration over the in-plane quantum numbers k_x and k_y returns the dispersion and may reveal information about joint density of states by taking a histogram of $E(\mathbf{k})$. The absorption coefficient may be subsequently evaluated by incorporating the spatial overlap integrals of envelope functions and investigated under the action of the QCSE for an externally applied electric field.

6.2.1 Finite Differencing Scheme

The first derivative in a finite element mesh may be constructed using forwards, centred or backwards differencing schemes via;

$$\left. \frac{\partial F(z)}{\partial z} \right|_i = \begin{cases} \frac{1}{h} (F_{i+1}(z) - F_i(z)) & \text{Forward} \\ \frac{1}{2h} (F_{i+1}(z) - F_{i-1}(z)) & \text{Centred} \\ \frac{1}{h} (F_i(z) - F_{i-1}(z)) & \text{Backward} \end{cases} \quad (6.13)$$

where h is the distance between adjacent mesh-points. The second derivative at the i^{th} mesh-point is twice this using both backward and forward differencing methods in a centred differencing scheme;

$$\left. \frac{\partial^2 F(z)}{\partial z^2} \right|_i = \frac{1}{2h} \left(\left. \frac{\partial F(z)}{\partial z} \right|_{i+1} - \left. \frac{\partial F(z)}{\partial z} \right|_{i-1} \right) = \frac{1}{2h^2} (F_{i+1}(z) - 2F_i(z) + F_{i-1}(z)) \quad (6.14)$$

The Jacobi-Davidson procedure [113] provides by far the most appropriate method for the task in hand as the tridiagonal matrices concerned in this context are sparse. Fortunately there are open source NAG routines and libraries available such that a simple ‘eigs’ command in Matlab has been pre-programmed already for convenience.

For material dependent effective masses; operator ordering for second derivatives are symmetric under the Bastard [45] boundary condition;

$$\left. \frac{\partial}{\partial z} \frac{1}{m^*(z)} \frac{\partial F(z)}{\partial z} \right|_i = \frac{1}{2h^2} \left(\frac{F_{i+1}(z) - F_i(z)}{m_{i-1}^*(z)} - \frac{F_i(z) - F_{i-1}(z)}{m_{i+1}^*(z)} \right) \quad (6.15)$$

For degenerate effective mass Hamiltonians one calls for block tridiagonal matrices such that m^* takes on the form of 4×4 , 6×6 , and 8×8 matrices. However, this does not come without significantly draining computing resources; for example a 500 point mesh may become up to a 4000×4000 block tridiagonal matrix requiring 128Mb of RAM!

In the expansion states method [114], envelope functions are found at the zone centre using the diagonal approximation. Overlap integrals of P , Q , R , and S are evaluated, and a block matrix Hamiltonian is constructed and iterated over k_x and k_y to return the dispersion. This method was developed primarily due to limited computing resources but also for application to Schrödinger-Poisson solvers for incorporating charge and doping profiles [115] such as in modelling high electron mobility transistors. It is chosen not to use the expansion states method; mainly because of the advancement in computing power, but also because we are interested in intrinsic, undoped, profiles so there is no significant advantage to employing a Schrödinger-Poisson solver.

For these reasons, we shall attempt to use the somewhat colloquially named brute force technique which, as the name implies, uses block tridiagonal matrices in their raw form with very little in the way of a simplification procedure. This does mean that the first derivatives must be incorporated with the correct boundary conditions as stipulated in the EFA [10–13];

$$\frac{1}{m^*(z)} \frac{\partial F(z)}{\partial z} \Big|_i = \frac{1}{2h} \left(\frac{F_{i+1}(z)}{m_{i-1}^*(z)} - \frac{F_{i-1}(z)}{m_{i+1}^*(z)} \right) \quad (6.16)$$

$$\frac{\partial F(z)}{\partial z} \Big|_i \frac{1}{m^*(z)} = \frac{1}{2h} \left(\frac{F_{i+1}(z) - F_{i-1}(z)}{m_i^*(z)} \right) \quad (6.17)$$

So for example, ordered terms on S may be entered into the block tridiagonal matrix, as can the interfacial C and Z terms in the correct manner. In fact this technique affords greater flexibility since the effective mass Hamiltonian may be entered as terms independent of-, terms linear in- and terms quadratic in- $\hat{k}_z$ with correct boundary conditions as a function of growth plane directly.

6.2.2 SiGe Heterostructures

In Section 1.3.3, the specific example of the compressively strained 12nm Germanium well sandwiched between tensile strained $Si_{0.15}Ge_{0.85}$ barriers on a $Si_{0.1}Ge_{0.9}$ -{001} virtual substrate was introduced for the widespread application as a practical device. Band edges and envelope functions of lowest energy sub-band states were shown in Figure 1.5 for zone centre eigenstates and the first strong transition hh_1 - e_1 occurs at an energy of 978meV. Using numerical schemes just discussed we may employ the double group operator ordered 8-band effective mass Hamiltonians to return the in-plane sub-band dispersion, shown below.

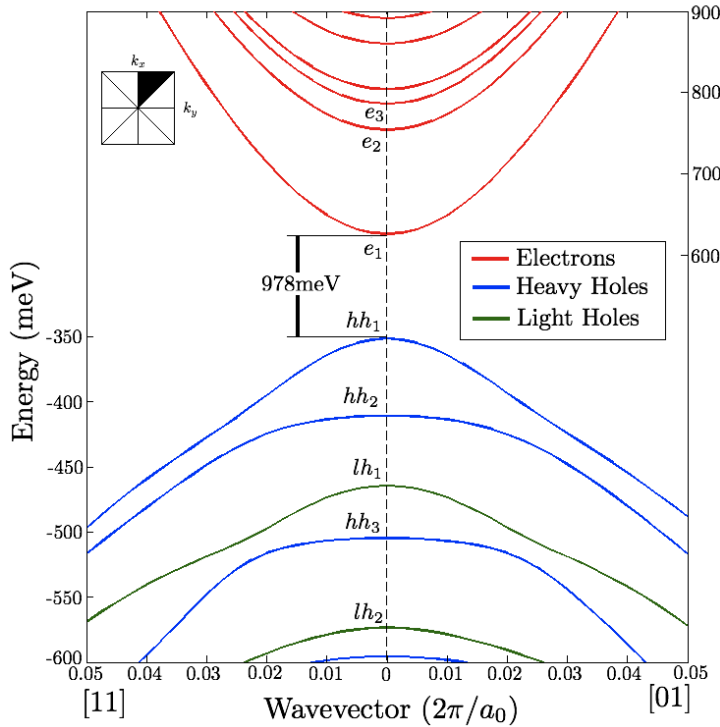


FIGURE 6.1: Valence and conduction sub-band dispersion along high symmetry axes for confined states in a compressively strained 12nm Germanium well sandwiched between tensile strained $Si_{0.15}Ge_{0.85}$ barriers on a $Si_{0.1}Ge_{0.9}$ -{001} virtual substrate at 0K. This took less than one minute in Matlab using an 8-band model

Figure 6.1 is in good agreement with Figure 2 of D. J. Paul [47] who used the single group formulation in commercially available NEXTNANO¹ software. Clearly from the in-plane dispersion heavy and light hole confined states interact away from the zone centre through off diagonal S and R terms of the effective mass Hamiltonian. Indeed lh_1 and hh_3 exhibit level anti-crossing characteristic of fermions 2% from the zone centre. The extent of mixing between heavy and light holes away from the zone centre may be observed in the polarisation spectra of the absorption coefficient.

While the sub-band dispersion relation is very useful, one seeks data which may be directly compared with experimental photoluminescence spectra of real devices. This requires a far greater section of reciprocal space to determine the density of states by computing a histogram of $E_c(\mathbf{k})$ and $E_v(\mathbf{k})$ or the joint density of states using $E_c(\mathbf{k}) - E_v(\mathbf{k})$. Since the in-plane translational subgroup incorporates symmetry operations within the reciprocal lattice and the Hamiltonian is hermitian, only half a quadrant $0 \leq k_x \leq k_y$ is required, as depicted below, thus reducing the overall compute time by a factor of 8.

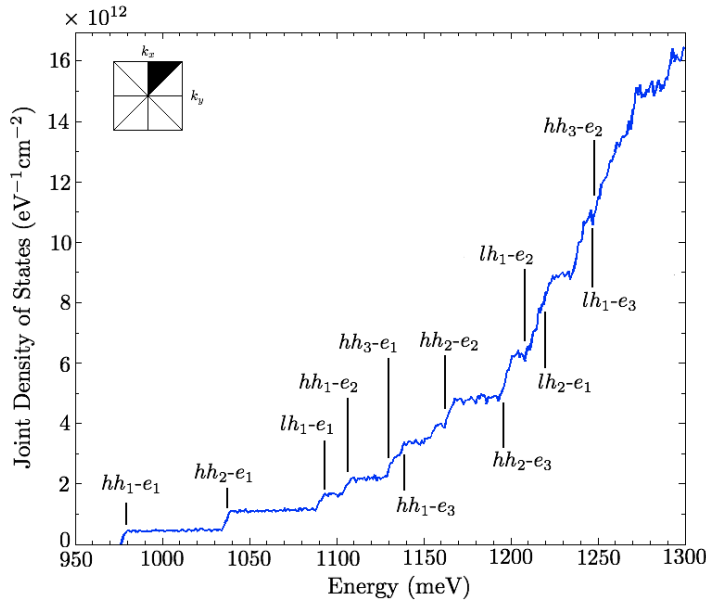


FIGURE 6.2: Joint density of states for a compressively strained 12nm Germanium well sandwiched between tensile strained $Si_{0.15}Ge_{0.85}$ barriers on a $Si_{0.1}Ge_{0.9}$ -{001} virtual substrate at 0K. This took 33 hours in Matlab

Figure 6.2 is characteristic of a quantum well heterostructure such that the density of states forms a series of unit step functions; a so called ‘staricase’, prior to the onset of the continuum. To obtain the absorption coefficient one must subsequently include transition probabilities through Fermi’s Golden rule using the spatial overlap between envelope functions. For example; the onset of absorption occurs with the strong transition hh_1-e_1 , at an energy of 978meV however due to parity selection rules overlap hh_2-e_1 is weak (greyed out in Table 6.1) and the second observed strong transition is lh_1-e_1 at an energy 1091meV.

¹<http://www.nextnano.de>

	e_1	e_2	e_3
hh_1	978meV	1104meV	1141meV
hh_2	1037meV	1164meV	1200meV
hh_3	1131meV	1258meV	-
lh_1	1091meV	1217meV	1254meV
lh_2	1225meV	-	-

TABLE 6.1: Transition energies between confined heavy and light holes in the valence band with electron in the conduction band. Greyed out energies denote weak optical transitions due to parity selection rules

Furthermore, the point group symmetry leads to a polarisation dependence named transverse electric (TE) and transverse magnetic (TM) through the introduction of $\mathbf{A} \cdot \hat{\pi}$ into the Hamiltonian², where $\mathbf{A}$ is the coulomb gauge vector potential [116]. One may recognise this as analogous to the $\mathbf{k} \cdot \hat{\pi}$ perturbation, and may be treated in an identical manner. The inter-band matrix may again be evaluated through Clebsch-Gordan coefficients and takes the form;

$$A_{\mathbf{A} \cdot \hat{\pi}}^{\Gamma_8^{\pm}, \Gamma_6^{\mp}} \Rightarrow \begin{pmatrix} -\sqrt{3}A_+ & 0 \\ 2A_z & -A_+ \\ A_- & 2A_z \\ 0 & \sqrt{3}A_- \end{pmatrix} \begin{matrix} hh \\ lh \\ lh \\ hh \end{matrix} \quad (6.18)$$

Where oscillator strengths are scaled by the Kane parameter P_1 [33] in the well region giving transition rates. So for incident light with electric field vector perpendicular (parallel) to the confinement axis, we find TE $\rightarrow$ 1 (TM $\rightarrow$ 0) for hh - e transitions, and TE $\rightarrow$ $\frac{1}{3}$ (TM $\rightarrow$ $\frac{4}{3}$) for lh - e transitions [102, 117].

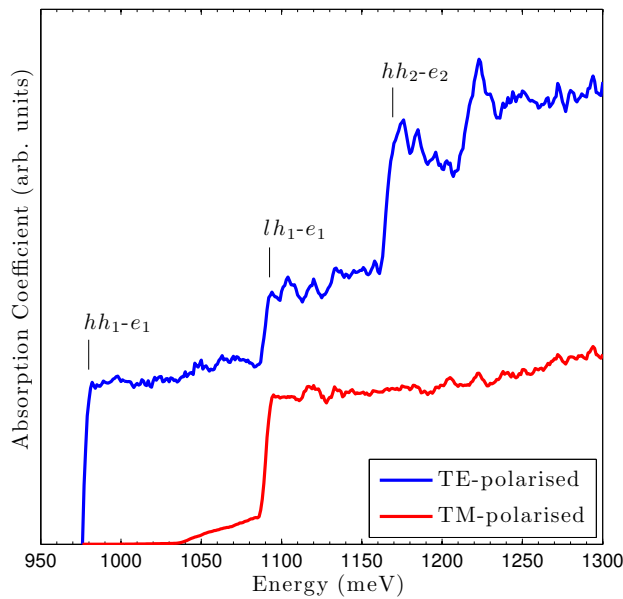


FIGURE 6.3: Absorption coefficient for a compressively strained 12nm Germanium well sandwiched between tensile strained $Si_{0.15}Ge_{0.85}$ barriers on a $Si_{0.1}Ge_{0.9}$ -{001} virtual substrate at 0K. This took 34 hours in Matlab

²there also exists an $\mathbf{A}^2$ term responsible for two photon processes

The unfortunate noisy features in Figure 6.3 is due to numerical fluctuations in computing degenerate eigenvectors as orthonormal entities. While a smoothing procedure would improve aesthetics it was chosen not to perform this to highlight this problem associated with the numerical schemes employed. The gradual onset of absorption for the TM-polarisation prior to 1091meV is due to the fact that away from the zone centre light hole character is introduced into the eigenvectors by off diagonal R and S terms in the effective mass Hamiltonian.

6.2.3 QCSE Device Operation

Bonfanti et al [49, 50] have shown experimentally that by using a well region 15nm thick the onset of absorption at room temperature, 300K occurs at 870meV. As discussed the main motivation in this thesis is to have an optical modulator under the action of the QCSE [51] around to $1.5\mu\text{m}$ at room temperature for use in 3^{rd} generation fibre optic communication channels. Generally, the electric field is applied in the same direction as the growth axis ($\hat{H}_{Stark} = e\mathbf{E} \cdot \mathbf{r} = eEz$) as this is where electrical contacts are made; consequently the TE mode is more prevalent in the use of switching devices where optical confinement is also a concern. This provides further justification for using a compressively strained well region as hh_1-e_1 is the first observed transition.

Using a well width of 15nm with the same aforementioned profile otherwise, optical modulation effects for wavelengths $(1.42-1.44)\mu\text{m}$ for an applied electric field of $(0-50)\text{kV/cm}$ is shown below;

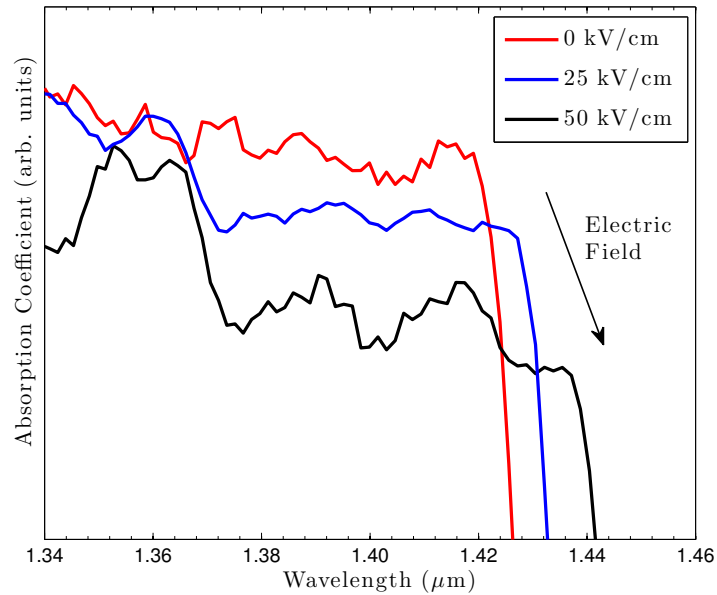


FIGURE 6.4: hh_1-e_1 transition absorption coefficient for a compressively strained 15nm Germanium well sandwiched between tensile strained $Si_{0.15}Ge_{0.85}$ barriers on a $Si_{0.1}Ge_{0.9}$ -{001} virtual substrate at 300K under applied electric fields of $(0-50)\text{kV/cm}$ exhibiting the QCSE for a wavelength range $(1.42-1.44)\mu\text{m}$

Clearly the results indicate a red shift in the absorption spectra for wavelength bands used in modern fibre optic communication channels at room temperature. One should also note that under the QCSE, the skew in envelope functions for electrons and holes is towards opposite sides of the well, decreasing the overlap integral; as indicated by the direction of the arrow in Figure 6.4. The skew also renders transitions otherwise forbidden by parity to be allowed, such as hh_2-e_1 , for which the onset of absorption occurs at $1.36\mu m$.

One problem with the modelling technique presented here is that excitonic effects have not been included. Electron-hole exciton binding energies may further reduce the transition energy in accordance with the Elliott formula [118] to bring the aforementioned device in alignment with optical modulation at $1.55\mu m$ as shown recently by Lever et al [53]. However, due to the indirect gap in Silicon and Germanium carriers are rapidly scattered away from the zone centre and exciton lifetimes are exceptionally short.

Useful investigations into structures leads to the question of how the absorption wavelength is affected by the width of the well, as shown in Figure 6.5. Here the Germanium well width is varied with all other things being equal and the example above is indicated for a well width of 15nm. The change of lh_1-e_1 with hh_2-e_2 as the second observed transition indicates how the hole confinement energy scales with effective mass, such that heavy holes are more sensitive to changes in well width. Also, as the well width increases the transition energies converge asymptotically to bulk strained Germanium values as expected and required.

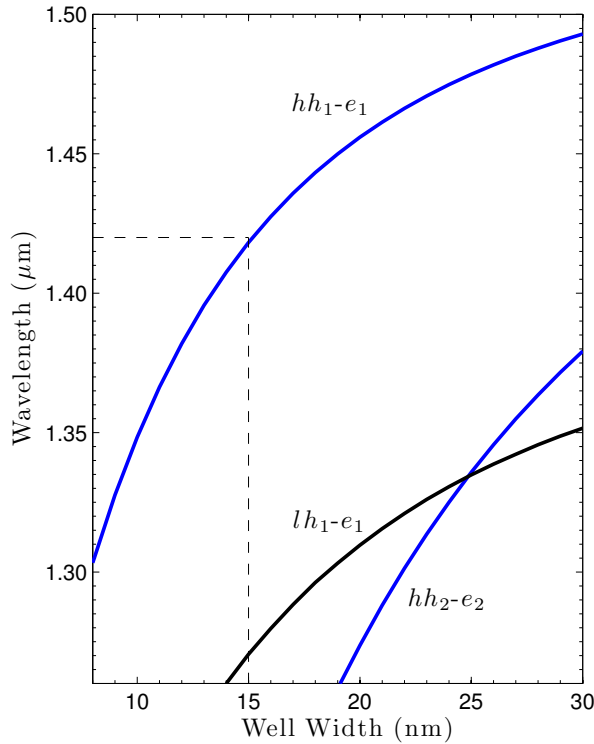


FIGURE 6.5: Onset of band edge absorption excluding excitonic effects for first confined states in a Germanium well sandwiched between tensile strained $Si_{0.15}Ge_{0.85}$ barriers on a $Si_{0.1}Ge_{0.9}$ -{001} virtual substrate at 300K of variable well width. The 15nm line has been drawn for cross reference purposes with Figure 6.4

Additionally; widening the well width strengthens the QCSE. The two well widths used as examples in this chapter; 12nm and 15nm are again used in Figure 6.6 to convey how the onset of band edge absorption of the hh_1-e_1 transition is affected by an applied electric field.

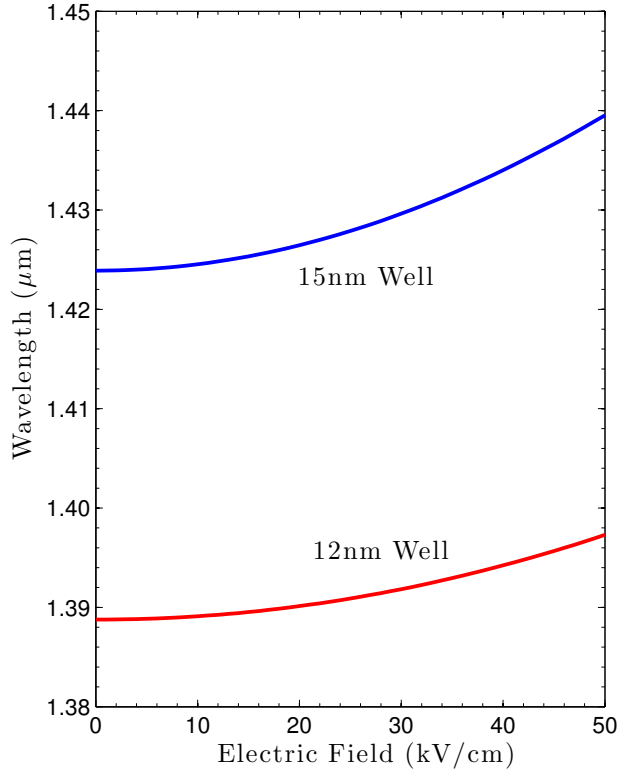


FIGURE 6.6: Onset of band edge absorption excluding excitonic effects for hh_1-e_1 transition under the influence of an externally applied electric field for 12nm and 15nm Germanium wells sandwiched between tensile strained $Si_{0.15}Ge_{0.85}$ barriers on a $Si_{0.1}Ge_{0.9}$ -{001} virtual substrate at 300K.

What Figures 6.5 and 6.6 provide is a framework to go into the lab and grow and characterise devices such that the samples may be tailored to operate at given wavelengths. So for example, if someone wants a device working, at for example $1.41\mu\text{m}$, one can advise a well width of 14nm. Similarly, if one wants a device with a stronger QCSE, one can advise a wider well and adjust the barrier or substrate composition to bring the device into operation at $1.41\mu\text{m}$.

Overall, SiGe devices offer the most viable opportunity to integrate optoelectronic devices with electronics for widespread commercial application. Germanium rich devices exhibiting the QCSE may be exploited as optical modulators in low power fast bit rate data transmission systems [41] at wavelength bands currently used in optical communication channels. Indeed the SiGe system on a chip [1] proposes the use of such optical modulators as demonstrated in this chapter to improve the functionality of the classic Silicon chip.

6.3 Coordinate Transformations

In this final section of the thesis, the topic of coordinate transformations is returned from the point of view of the double group formulation of $\mathbf{k} \cdot \hat{\mathbf{p}}$ theory. It was discussed how to transform the Luttinger-Kohn [35] valence band effective mass Hamiltonian for the situation when the DCS and CCS do not coincide within the theory of invariants framework. It was also shown how to return strain components within the constraint of biaxial stress applied to the Pikus-Bir Hamiltonian [3].

All these principles are used when entered into the finite differencing scheme, but in this section operator ordered Hamiltonians applied to any growth plane are shown how to be generated. Absorption spectra for some special cases; the $\{011\}$ and $\{111\}$ growth planes are returned, and a dependence on $hh_1\text{-}e_1$ transition energy as a function of growth plane is obtained.

6.3.1 Hamiltonians for Arbitrary Growth Planes

One major advantage of the double group formulation is that the coordinate transformations procedure reduces to a series of simple matrix multiplications. In the evaluation of the matrix elements $\langle L_1, m_{L_1} | \mathbf{k} \cdot \hat{\mathbf{p}} | L_2, m_{L_2} \rangle$ and $\langle J_1, m_{J_1} | \mathbf{k} \cdot \hat{\boldsymbol{\pi}} | J_2, m_{J_2} \rangle$ it was assumed that the quantisation axis or the crystal coordinate system (CCS) coincided with the growth axis of the heterostructure, the DCS. Under the matrix element theorem, invariance requires [26];

$$\langle L_1, m_{L_1} | \mathbf{k} \cdot \hat{\mathbf{p}} | L_2, m_{L_2} \rangle = \mathbf{k}' \cdot (|L_1, m_{L_1}\rangle')^\dagger \hat{\mathbf{p}} |L_2, m_{L_2}\rangle' \quad (6.19)$$

$$\langle J_1, m_{J_1} | \mathbf{k} \cdot \hat{\boldsymbol{\pi}} | J_2, m_{J_2} \rangle = \mathbf{k}' \cdot (|J_1, m_{J_1}\rangle')^\dagger \hat{\boldsymbol{\pi}} |J_2, m_{J_2}\rangle' \quad (6.20)$$

Where since $\hat{\mathbf{p}}$ and $\hat{\boldsymbol{\pi}}$ transform like a polar vector, their transformation properties may be picked up by the contragredient Bloch vector; $\mathbf{k}' = R(\theta, \phi)\mathbf{k}$ as discussed by Eppenga & Schurman [119]. For transformation of basis states, one uses $|L, m_L\rangle' = R_L(\theta, \phi) |L, m_L\rangle$ and $|J, m_J\rangle' = R_J(\theta, \phi) |J, m_J\rangle$ for integer and half integer spin respectively. $R_L(\theta, \phi)$ may be evaluated through $e^{-iL_z\theta}e^{-iL_x\phi}$, where L_z and L_x are the angular momentum generator matrices. For example, we will consult the single group linearly independent matrix $A_{\mathbf{k}\cdot\hat{\mathbf{p}}}^{\Gamma_4^-:\Gamma_1^+}$;

$$R_{L=1}^\dagger(\theta, \phi) A_{\mathbf{k}'\cdot\hat{\mathbf{p}}}^{\Gamma_4^-:\Gamma_1^+} R_{L=0}(\theta, \phi) = \begin{pmatrix} k_x \\ k_y \\ k_z \end{pmatrix} \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} \quad (6.21)$$

Interestingly, $A_{\mathbf{k}\cdot\hat{\mathbf{p}}}^{\Gamma_4^-:\Gamma_1^+}$ is completely independent of quantisation axis. The reasons are quite simply because $L = 1$ and $L = 0$ are *complete* eigenstates of Γ_4^- and Γ_1^+ respectively, and there is no mixing of invariant subspaces through a canonical transformation. Also since $L = 0$ is spherically symmetric one might have expected this from the outset. The Löwdin term is also quantisation axis independent due to the projection operator nature of the remote set;

$$R_{L=1}^\dagger(\theta, \phi) A_{\mathbf{k}\cdot\hat{\mathbf{p}}}^{\Gamma_4^-:\Gamma_1^+} \times \left(A_{\mathbf{k}'\cdot\hat{\mathbf{p}}}^{\Gamma_4^-:\Gamma_1^+} \right)^\dagger R_{L=1}(\theta, \phi) = \begin{pmatrix} k_x^2 & k_x k_y & k_x k_z \\ k_y k_x & k_y^2 & k_y k_z \\ k_z k_x & k_z k_y & k_z^2 \end{pmatrix} \quad (6.22)$$

For the remote states $\Gamma_3^+ \oplus \Gamma_5^+$, the $L = 2$ degeneracy in $\text{SO}(3)$ is lifted through the crystal field. Consequently invariant subspaces mix for non point group operations and the boundary conditions become a function of θ and ϕ . A general set of operator ordering rules for constructing the valence band Hamiltonian for arbitrary growth directions [110] was generated by transforming the DKK effective mass Hamiltonian and casting into the adapted double group. Using the double group formulation, the appropriate transformation of spin $\{\uparrow, \downarrow\}$ may be employed through the use of $R_J(\theta, \phi)$ for half integer particles, for example;

$$R_{J=3/2}^\dagger(\theta, \phi) A_{\mathbf{k}'\cdot\hat{\boldsymbol{\pi}}}^{\Gamma_8^\pm:\Gamma_6^\mp} R_{J=1/2}(\theta, \phi) = \frac{-1}{\sqrt{2}} \begin{pmatrix} -\sqrt{3}k_+ & 0 \\ 2k_z & -k_+ \\ k_- & 2k_z \\ 0 & \sqrt{3}k_- \end{pmatrix} \begin{matrix} |3/2, +3/2'\rangle \\ |3/2, +1/2'\rangle \\ |3/2, -1/2'\rangle \\ |3/2, -3/2'\rangle \end{matrix} \quad (6.23)$$

Like before because $J = 3/2$ and $J = 1/2$ are complete eigenstates of $\Gamma_8^\pm$ and $\Gamma_6^\mp$ respectively there is no mixing of invariant subspaces through a canonical transformation. One may also expect the Löwdin term as quantisation axis independent. Furthermore, the analogous operator $\mathbf{A} \cdot \hat{\boldsymbol{\pi}}$ for considering polarisation spectra also returns an interaction matrix that is rotationally invariant.

However for $J = 5/2$ the crystal field lifts the degeneracy into $\Gamma_8^\mp$ and $\Gamma_7^\mp$ double group irreps. As the projection operator is quantisation axis independent, a general Luttinger-Kohn [35] valence band effective mass Hamiltonian may be obtained for arbitrary growth directions by the evaluation of;

$$H_{VB:VB} = R_{J=3/2}^\dagger(\theta, \phi) A_{\mathbf{k}'\cdot\hat{\mathbf{p}}}^{\Gamma_8^\pm:\Gamma_j} \times \left(A_{\mathbf{k}'\cdot\hat{\mathbf{p}}}^{\Gamma_8^\pm:\Gamma_j} \right)^\dagger R_{J=3/2}(\theta, \phi) \quad (6.24)$$

There is an alternative approach which omit the $R_{J=3/2}(\theta, \phi)$ since it is simply a unitary transformation leaving eigenvalues unchanged. However, this quantises Bloch vector components in the DCS and eigenvectors in the CCS such that they do not coincide. This makes physical interpretation of states rather convoluted which is why it is not widely adopted in the literature, nor in this thesis.

6.3.2 Application to Arbitrary Growth Planes

The numerical modelling schemes presented in this thesis has also been cast for the case of non trivial growth planes as just discussed. For example, using rotation angles of $\theta = 0, \phi = \pi/4$ the compressively strained 12nm Germanium well sandwiched between tensile strained $Si_{0.15}Ge_{0.85}$ barriers on a $Si_{0.1}Ge_{0.9}$ -{011} virtual substrate may be modelled. Transition energies are tabulated below with an absorption spectra to match.

	e_1	e_2	e_3
hh_1	965meV	1092meV	1127meV
hh_2	1011meV	1137meV	1172meV
hh_3	1080meV	1206meV	1241meV
lh_1	1096meV	1221meV	1255meV
lh_2	1176meV	-	-

TABLE 6.2: Transition energies between confined heavy and light holes in the valence band with electron in the conduction band for the device grown on the {011} plane. Greyed out energies denote weak optical transitions due to parity selection rules

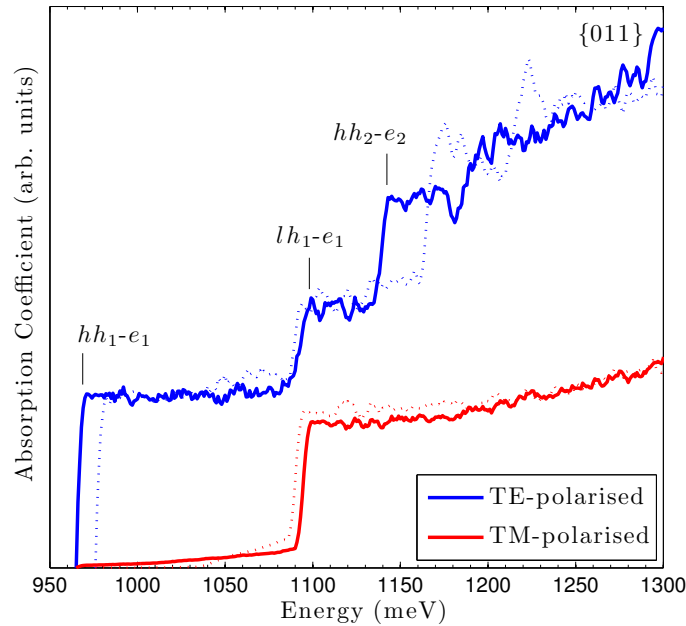


FIGURE 6.7: Absorption coefficient for a compressively strained 12nm Germanium well sandwiched between tensile strained $Si_{0.15}Ge_{0.85}$ barriers on a $Si_{0.1}Ge_{0.9}$ -{011} virtual substrate at 0K. Growth on the {001} plane (dotted) is included for comparison

Since the only feature of the device which have changed is the growth plane, there are not major differences. However, it is important to note that the strain conditions have reduced heavy hole transition energies (hh_1-e_1 : -13meV) whilst increasing light hole transition energies (lh_1-e_1 : +5meV) corresponding to wavelength changes of +17nm and -5nm respectively. This is due to the introduction of shear and more pronounced biaxial strain components, but also due to a reduction in the Poisson ratio; $D(0,0) > D(0,\pi/4)$. All these contribute to an increase in the Q_ϵ term such that changes in heavy and light hole sub-band energies move in opposite ways.

Additionally using the compressively strained 12nm Germanium well sandwiched between tensile strained $Si_{0.15}Ge_{0.85}$ barriers on a $Si_{0.1}Ge_{0.9}$ -{111} virtual substrate may be modelled by using rotation angles of $\theta = \pi/4$, $\phi = \arctan(\sqrt{2})$. Similarly, transition energies are tabulated below with a modelled absorption spectra shown in Figure 6.8.

	e_1	e_2	e_3
hh_1	966meV	1092meV	1125meV
hh_2	1016meV	1141meV	1174meV
hh_3	1096meV	1221meV	1253meV
lh_1	1093meV	1220meV	1251meV
lh_2	1171meV	1296meV	-

TABLE 6.3: Transition energies between confined heavy and light holes in the valence band with electron in the conduction band for the device grown on the {111} plane.

Greyed out energies denote weak optical transitions due to parity selection rules

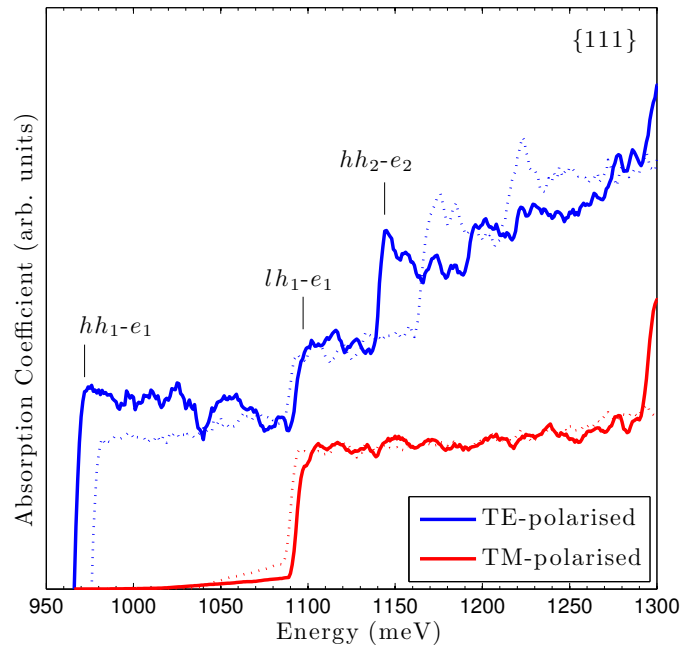


FIGURE 6.8: Absorption coefficient for a compressively strained 12nm Germanium well sandwiched between tensile strained $Si_{0.15}Ge_{0.85}$ barriers on a $Si_{0.1}Ge_{0.9}$ -{111} virtual substrate at 0K. Growth on the {001} plane (dotted) is included for comparison

The differences between the devices grown on the $\{011\}$ and $\{111\}$ plane are much less significant in terms of the change in transition energies. This comes down to the fact that what may be considered as warping within the strain context; $\mu_\epsilon = \frac{1}{2}(d-b)$ is small in Germanium. Therefore uniaxial components are not expected to have a dominating effect over biaxial components as far as strain is concerned. One should note that since Germanium is diamond type, piezoelectric fields need not be considered, whereas this is not the case for heterostructures grown on $\{111\}$ for Zinc-blende type material.

There was expected to be a more significant change in polarisation profiles due to the change in growth plane which has not materialised in the results. Since the conduction band is s -type ($L = 0$) and spherically symmetric this must now be revised. Reconsidering the effective mass Hamiltonian as diagonally dominant for $\{011\}$ and $\{111\}$; light hole character is not introduced into the eigenvectors by as much as first thought. Experimental verification of these assertions should help to prove or disprove this.

The final investigation was to map out the hh_1-e_1 transition energies as a function of (θ, ϕ) to highlight the curvature and angular dependence. The figure below clearly matches the profile of the Poisson ratio (Figure 5.3) - indeed one might ponder if the generalised Poisson ratio is the dominant parameter of the strain perturbation. The path for $\{001\} \rightarrow \{011\} \rightarrow \{111\}$ also follows on from arguments on warping within the strain context.

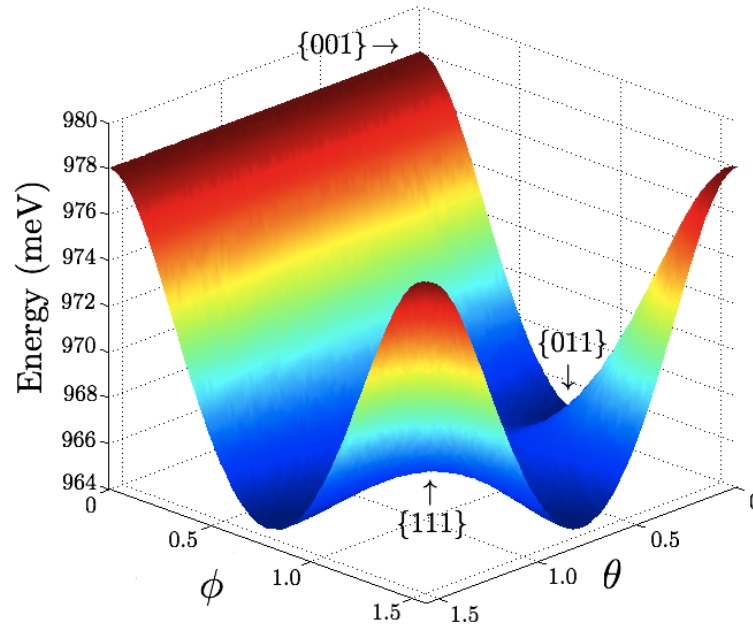


FIGURE 6.9: Transition energies of hh_1-e_1 for a a compressively strained 12nm Germanium well sandwiched between tensile strained $Si_{0.15}Ge_{0.85}$ barriers on a $Si_{0.1}Ge_{0.9}$ virtual substrate at 0K grown on arbitrary growth planes within the domain; $0 < (\theta, \phi) < \pi/2$. High index planes are indicated as the previous specific examples; $\{001\}$ $\{011\}$ and $\{111\}$

In fact the most challenging aspect of the SiGe system is the growth of a stable Germanium rich virtual substrate, not least on non trivial growth planes. Indeed, growth on the 7×7 -Takayanagi reconstruction [120] for the Silicon- $\{111\}$ surface is near impossible due to surface adatoms significantly lowering the surface energy [121]. Consequently growth favours the Stranski-Krastanov growth mode [122] leading to conditions unsuitable for device fabrication. This challenge places significant restrictions on the SiGe system as a malleable material to work with and to study despite its economic and industrial advantages for the semiconductor industry.

Summary

In this chapter the development of the double group formulation of $\mathbf{k} \cdot \hat{\mathbf{p}}$ theory applied to SiGe heterostructures has been used to model devices with widespread applications. The culmination of the work was the exhibition of optical modulation under the QCSE for a wavelength range (1.42-1.44) μm under applied electric fields of (0-50)kV/cm using a compressively strained 15nm Germanium well sandwiched between tensile strained $\text{Si}_{0.15}\text{Ge}_{0.85}$ barriers on a $\text{Si}_{0.1}\text{Ge}_{0.9}$ -{001} virtual substrate at 300K. Although the model does not include excitonic effects; it is expected for the device to operate at 1.55 μm as shown recently in the literature.

The chapter began by discussing boundary conditions across an interface in both single and double group formulations, and it was shown how the double group formulation returns an interfacial Z term. The Z term is otherwise missed by the presumption that $\pi = \zeta_{\Gamma_8^+:\Gamma_8^+}^{\Gamma_6^-} = \zeta_{\Gamma_8^+:\Gamma_8^+,1}^{\Gamma_8^-}$ from the point of view of single group degeneracy as presented by Foreman. And the chapter ended by returning to the concept of operator ordering applied to arbitrary growth planes through transformation of Bloch vector components and a unitary transformation of the basis to bring the CCS and DCS into alignment as a function of the rotation matrix $R(\theta, \phi)$.

Indeed using the numerical schemes presented, absorption spectra for compressively strained 12nm Germanium well sandwiched between tensile strained $\text{Si}_{0.15}\text{Ge}_{0.85}$ barriers on a $\text{Si}_{0.1}\text{Ge}_{0.9}$ virtual substrate at 0K was returned for {001}, {011} and {111} growth planes. Interestingly, the biggest change is in the hh_1 - e_1 transition energy, which follows the same angular dependence as the generalised Poisson ratio, indicating that the generalised Poisson ratio may actually be the dominant parameter in the strain perturbation.

Chapter 7

Results & Conclusions

This final chapter serves as a recap of some of the results and conclusions of the thesis as a whole and makes suggestions and proposals for future research. From the outset the challenge was to develop a semi-empirical method to solve the many body Hamiltonian to within a good degree of accuracy with experimental observations. The $\mathbf{k} \cdot \hat{\mathbf{p}}$ method was chosen for it's innate ability to return the dispersion relation $E(\mathbf{k})$ as eigenvalues about a point of expansion in terms of the perturbation component, $\mathbf{k}$.

Despite enjoying lasting success for the last 60 years; by reproducing experimental observations such as the kink in the near band-gap photoluminescence for bulk Silicon-Germanium (SiGe), the $\mathbf{k} \cdot \hat{\mathbf{p}}$ method still called for development within a rigorous mathematical framework to incorporate the spin-orbit interaction in the unperturbed Hamiltonian without the need to adjust parameters. Of course the pursuit in this thesis has not just been a validation of experimental results to increasing accuracy but also served as a mathematical exercise of beauty by applying extensive group theoretical arguments to already existing solutions with a new twist.

The development of the double group formulation of $\mathbf{k} \cdot \hat{\mathbf{p}}$ theory using appropriate double group basis functions allowed for a more intuitive way of developing effective mass Hamiltonians based on spin degenerate zone centre eigenstates and input parameters from the literature. Subsequently the application to heterostructures showed how the new formulation returns operator ordered interfacial terms such as the Z term and takes into account the appropriate transformation properties of spin when applied to arbitrary growth directions. The strained Germanium rich quantum well exhibiting the quantum confined Stark effect (QCSE) around $1.5\mu\text{m}$ at room temperature really served as the icing on the cake to the development to illustrate the success of the double group formulation of the $\mathbf{k} \cdot \hat{\mathbf{p}}$ method as a modelling technique for practical devices.

7.1 Group Theory & Symmetrised Basis Functions

Using the principles of group theory applied to cubic crystals significant assertions were made about transformation properties of basis functions and tensor operators in terms of symmetry operations and irreps. Recalling the nomenclature of the O_h group, it was shown how single and double group irreps were compatible with eigenstates of the full rotational groups $SO(3)$ and $SU(2)$ respectively. The most notable one being Γ_4^- compatible with $L = 1$ eigenstates; and ultimately polar vectors such as the rank-1 tensor operator $\hat{\mathbf{p}}$.

Originating from the sp^3 hybridisation paradigm it was shown how $\mathbf{L} \cdot \mathbf{S}$ coupling gives rise to the half integer $J = L \pm S = 3/2 \oplus 1/2$ basis for the valence band maxima compatible with $\Gamma_4^- \otimes \Gamma_6^+ = \Gamma_8^- \oplus \Gamma_6^-$. Consequently the significant spin-orbit diagonalisation matrix based on Clebsch-Gordan coefficients $\{x, y, z\} \otimes \{\uparrow, \downarrow\} \rightarrow |J, m_J\rangle$ was obtained in accordance with extensive work in the literature.

However, the problem of associating bonding orbitals with odd parity irreps calls for an adapted double group basis based on Γ_5^+ in accordance with the equivalence representation; $\{yz, zx, xy\} \otimes \{\uparrow, \downarrow\} \rightarrow |J, m_J\rangle$. Indeed the difference for $\Gamma_5^+ \otimes \Gamma_6^+ = \Gamma_8^+ \oplus \Gamma_7^+$ gave rise to the significant permutation matrix labelled $\underline{\mathbf{T}}$. This was noted in a publication by the author [72] and maple source code written by the author is available for download at <http://www.mapleprimes.com/posts/125172-Td-Group>.

The compatibility of $L = 2$ eigenstates of $SO(3)$ with $\Gamma_3^+ \oplus \Gamma_5^+$ irreps is applicable to rank-2 irreducible perturbation components such as uniaxial and shear strain terms respectively, and appropriate irreducible perturbation components for Γ_3^+ were obtained through the projection operator technique. Originating from $L = 2$ eigenstates; $\mathbf{L} \cdot \mathbf{S}$ coupling gives rise to $J = L \pm S = 5/2 \oplus 3/2$ eigenstates of $SU(2)$ which in turn are compatible with $2\Gamma_8^+ \oplus \Gamma_7^+$. The occurrence of the factor of two gives rise to linear independence such that weightings of $\sqrt{\frac{3}{5}}$ and $\sqrt{\frac{2}{5}}$ were ascribed to the Γ_5^+ and Γ_3^+ adapted double group basis.

In conclusion to Chapters 2 and 3 much effort went into developing a coherent, accurate and succinct mathematical framework to develop the double group formulation of $\mathbf{k} \cdot \hat{\mathbf{p}}$ theory. This is despite extensive libraries on group theory applied to cubic crystals which all have their own definitions, nomenclature and phase conventions to make an already complicated subject that little bit harder.

7.2 Double Group Formulation of $\mathbf{k} \cdot \hat{\mathbf{p}}$ Theory

By expressing the single group; $\mathbf{k} \cdot \hat{\mathbf{p}}$ and double group; $\mathbf{k} \cdot \hat{\boldsymbol{\pi}}$ perturbations as a series of projections of a rank-1 spherical tensor operator, Wigner-Eckart theorem was invoked to evaluate matrix elements using the symmetrised integer and half integer basis functions developed in Chapter 3. The single group formulation returned linearly independent matrices $A_{\mathbf{k} \cdot \hat{\mathbf{p}}}^{\Gamma_i^{\pm} : \Gamma_j^{\mp}}$ and using the adapted double group basis the double group linearly independent matrices $A_{\mathbf{k} \cdot \hat{\boldsymbol{\pi}}}^{\Gamma_i^{\pm} : \Gamma_j^{\mp}}$ were returned through a unitary transformation of $A_{\mathbf{k} \cdot \hat{\mathbf{p}}}^{\Gamma_i^{\pm} : \Gamma_j^{\mp}} \otimes \{\uparrow, \downarrow\}$. The main result was the two linearly independent matrices $A_{\mathbf{k} \cdot \hat{\boldsymbol{\pi}}, 1}^{\Gamma_8^{\pm} : \Gamma_8^{\mp}}$ and $A_{\mathbf{k} \cdot \hat{\boldsymbol{\pi}}, 2}^{\Gamma_8^{\pm} : \Gamma_8^{\mp}}$ for the interaction originating from Γ_5^+ and Γ_3^+ respectively.

Using parameters in the literature, full zone bulk band diagrams using a 30-band $\mathbf{k} \cdot \hat{\boldsymbol{\pi}}$ Hamiltonian for Silicon and Germanium were returned showing the indirect gap minima. Indeed for $Si_{1-x}Ge_x$ alloys it was shown how there is an abrupt change in the conduction band minima from Δ to L valleys at a composition $x = 88\%$ in agreement with the kink in experimental near band-gap photoluminescence and electron bulk mobility. Matlab source code written by the author was uploaded to the mathworks user forum <http://www.mathworks.com/matlabcentral/fileexchange/32595>.

Effective mass Hamiltonians were obtained using the Löwdin renormalisation procedure, and it was shown how the DKK Hamiltonian is returned when using the single group interaction matrices $A_{\mathbf{k} \cdot \hat{\mathbf{p}}}^{\Gamma_4^- : \Gamma_j^+} \times \left(A_{\mathbf{k} \cdot \hat{\mathbf{p}}}^{\Gamma_4^- : \Gamma_j^+} \right)^\dagger$ with associated scaling parameters. However using the appropriate zone centre degeneracies the double group interaction matrices were used to evaluate the valence band and spin-orbit effective mass Hamiltonians $A_{\mathbf{k} \cdot \hat{\boldsymbol{\pi}}}^{\Gamma_\alpha : \Gamma_j} \times \left(A_{\mathbf{k} \cdot \hat{\boldsymbol{\pi}}}^{\Gamma_\beta : \Gamma_j} \right)^\dagger$ with associated scaling parameters $\zeta_{\alpha:\beta}^j$. Luttinger parameters are expressible in terms of the $\zeta_{\alpha:\beta}^j$ and were subsequently compared with experimental data from the cyclotron resonance experiment.

The final part of the chapter culminated in developing the theory of invariants, which has less stringent assumptions on the self consistent one electron potential. Indeed the Luttinger-Kohn valence band Hamiltonian is expressible as a polynomial function in terms of coincidental irreducible perturbation components and generator matrices with an associated invariant. The main advantage of the theory of invariants is the application to arbitrary growth directions through a canonical transformation with the original work dedicated to the application of an arbitrary oriented magnetic field in the cyclotron resonance experiment.

In conclusion to Chapter 4 considerable progress was made to develop the double group formulation of $\mathbf{k} \cdot \hat{\mathbf{p}}$ theory applied to bulk Silicon and Germanium using semi-empirical input parameters. The effective mass Hamiltonians and material dependent parameters become important tools for a piecewise construction of adjacent unit cells to model heterostructures using the envelope function approximation (EFA).

7.3 Extension to Strained Systems

Lattice mismatch in SiGe calls for an additional perturbation involving strain through the Pikus-Bir Hamiltonian. Both Wigner-Eckart theorem and the theory of invariants return identical solutions analogous to the effective mass Hamiltonian by virtue of the rank-2 property of strain ϵ_{ij} and quadratic Bloch vector components $k_i k_j$. Indeed the application of biaxial stress, the constraint for thin film growth, lifts heavy and light hole degeneracy in the valence band.

It was shown how for growth of a pseudomorphic thin film, there exists biaxial stress which gave rise to the Poisson ratio; as a relation to in- and out of-plane strain. Application to arbitrary growth planes called for a canonical transformation such that strain components and the Poisson ratio become a function of the rotation angle $D(\theta, \phi)$. Indeed the prevalent challenge of experimental strain balancing techniques is to generate a dislocation free Germanium rich virtual substrate on a Silicon wafer through management of biaxial stress normal to the growth plane. Strain balancing techniques by using compositional overshoots may ensure that the critical thickness is never exceeded over a large enough distance such that dislocation free structures may be grown.

In conclusion to Chapter 5 the band edge alignment was discussed from the point of view of forming a Germanium rich heterostructure with a type-I alignment for conduction and valence bands. Such an arrangement ensures strong spatial overlap for confined states ideal for optoelectronic device application such as photodetectors and optical modulators.

7.4 Application to Heterostructures

The effective mass Hamiltonians obtained in Chapter 4 were employed in the EFA with the caveat that the differential operator aligned normal to the growth axis of the heterostructure does not commute with material dependent parameters across an interface; $[\zeta_{\alpha;\beta}^j(z), \hat{k}_z] \neq 0$. Consequently operator ordering schemes were devised which retain the Hermitian property of the Hamiltonian with appropriate boundary conditions to conserve continuity of current. It was shown how the interfacial C term was returned in both single and double group approaches however using the new double group formulation the Z term was returned. This was noted in a publication by the author [72].

Numerical implementation for modelling of a compressively strained 12nm Germanium well sandwiched between tensile strained $Si_{0.15}Ge_{0.85}$ barriers on a linearly graded relaxed $Si_{0.1}Ge_{0.9}$ -{001} virtual substrate was performed and the dispersion, joint density of states and absorption coefficient was returned at 0K and shown to be in agreement with experimental data in recent publications. Using a 15nm Germanium well optical modulation for wavelengths $(1.42-1.44)\mu\text{m}$ for an applied electric field of $(0-50)\text{kV/cm}$ at room temperature was shown to be suitable for fibre optic communication channels. Although the model does not include excitonic effects; it is expected for this device to operate at $1.55\mu\text{m}$ as shown recently in the literature.

One of the biggest advantages in the double group formulation of $\mathbf{k} \cdot \hat{\mathbf{p}}$ applied to heterostructures is that the methodology of obtaining a general operator ordered Hamiltonian under a canonical transformation in terms of the rotation angles (θ, ϕ) was outlined and reduced down to a series of rather trivial matrix multiplications. By using rotation matrices for half-integer particles, the transformation properties of spin are inherently included in the formulation retaining the phase relationship between degenerate states. Modelling of the absorption spectra for devices grown on the {011} and {111} planes showed how transition energies change under the introduction of shear strain. The surface plot of hh_1-e_1 as a function of growth angles (θ, ϕ) was returned, and followed the same angular dependence as the generalised Poisson ratio, indicating that the generalised Poisson ratio may actually be the dominant parameter in the strain perturbation.

In conclusion to Chapter 6 the practical consequences of the work presented in the thesis using the double group formulation of $\mathbf{k} \cdot \hat{\mathbf{p}}$ theory applied to SiGe heterostructures using material dependent semi-empirical input parameters was performed and shown to be in good agreement with recent experimental results in the literature.

7.5 The Future & Beyond

As long as Silicon continues to dominate microelectronic chips and devices research and development will continue; further affirming it's dominance. SiGe alloys offer the clearest platform to integrate optoelectronic devices directly onto Silicon with the realisation of the all integrated system on a chip a not too distant possibility. When this is achieved on an industrial level the challenges of main stream computing and data processing will take a new emphasis from more Moore's law to offering high speed optical data transmission directly from chip to chip across integrated networks.

The work presented in this thesis merely serves as a theoretical justification of the possibilities that exist. While the work does not answer all questions, there exists future research topics that serve as inspiration for further study;

- The single and double group formulations of $\mathbf{k} \cdot \hat{\mathbf{p}}$ theory clearly differ to the extent of the spin-orbit split off energy, which is 44meV in Silicon and 300meV in Germanium. A lot of current work is devoted to large spin-orbit crystals such as Cadmium Telluride and Zinc Telluride, which have large spin-orbit split off energies ($\approx 900\text{meV}$) of the order of the direct gap energy. It would be interesting to see the difference for effective mass parameters between single and double group formulations for such materials.
- Silicon and Germanium are Diamond type crystals with inversion symmetry, which formed the basis of the $\mathbf{k} \cdot \hat{\mathbf{p}}$ Hamiltonians presented. It would be interesting to see how the linear- $\mathbf{k}$ terms enter the Hamiltonian in Zinc-blende type crystals or in SiGe alloys using the double group formulation. Clearly inversion and time-reversal symmetry play a pivotal role in the Stark and Zeeman effects, so one could use the double group formulation to investigate spin-splitting under magnetic fields.
- In the modelling of heterostructures one can include a self consistent Schrödinger-Poisson solver to investigate the effects of charge and doping in pn-junctions and/or high electron mobility transistors. Furthermore, the modelling has excluded excitonic effects, which play a significant role in narrow well with devices where the binding energy of electron-hole pairs is strong, so it would be interesting to include these effects. Especially when applied to arbitrary growth planes as the warping in hole effective masses may affect the binding energy.

Appendix A

T_d Group Representation Matrices

A.1 Single Group Representation Matrices

Tables A.1 . . . A.4 list all representation matrices for each symmetry operation and irrep of the T_d single group. To obtain O_h representation matrices ($O_h = i \otimes T_d$), one applies compatibility relations, such that for odd parity irreps (Γ_i^-) inversion class representation matrices are the negative of their respective T_d group counterpart, whereas for even parity irreps (Γ_i^+) the sign is retained.

The final column indicates the transformation of the cartesian basis under the action of the symmetry operation, $\hat{P}_g\{x, y, z\}$, for use in the projection operator technique. over-lines denote opposite signum, so $\bar{x} = -x$.

$\mathbf{D}(g)$	Γ_1	Γ_2	Γ_3	Γ_4	Γ_5	$\hat{P}_g\{x, y, z\}$
$\mathbf{D}(E)$	(1)	(1)	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\{x, y, z\}$
$\mathbf{D}(C_2(100))$	(1)	(1)	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$	$\{x, \bar{y}, \bar{z}\}$
$\mathbf{D}(C_2(010))$	(1)	(1)	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$	$\{\bar{x}, y, \bar{z}\}$
$\mathbf{D}(C_2(001))$	(1)	(1)	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\{\bar{x}, \bar{y}, z\}$

TABLE A.1: T_d representation matrices for the identity and three 180° rotation operations for single group irreps. $\mathbf{D}(C_2(010))$ sets the choice of phase on basis through time reversal symmetry $\hat{T}$

$\mathbf{D}(E)$, $\mathbf{D}(C_2(100))$, $\mathbf{D}(C_2(010))$, and $\mathbf{D}(C_2(001))$ are diagonal for all irreps, so any direct sums are also diagonal. For this reason these operations are not suitable in explaining the block diagonalisation procedure by a similarity transformation in Section 3.1.2.

$\mathbf{D}(g)$	Γ_1	Γ_2	Γ_3	Γ_4	Γ_5	$\hat{P}_g\{x, y, z\}$
$\mathbf{D}(S_4(100))$	(1)	(-1)	$-\frac{1}{2} \begin{pmatrix} -1 & \sqrt{3} \\ \sqrt{3} & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}$	$\{\bar{x}, \bar{z}, y\}$
$\mathbf{D}(S_4^{-1}(100))$	(1)	(-1)	$-\frac{1}{2} \begin{pmatrix} -1 & \sqrt{3} \\ \sqrt{3} & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}$	$\{\bar{x}, z, \bar{y}\}$
$\mathbf{D}(S_4(010))$	(1)	(-1)	$\frac{1}{2} \begin{pmatrix} 1 & \sqrt{3} \\ \sqrt{3} & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & -1 \\ 0 & -1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$	$\{\bar{z}, \bar{y}, x\}$
$\mathbf{D}(S_4^{-1}(010))$	(1)	(-1)	$\frac{1}{2} \begin{pmatrix} 1 & \sqrt{3} \\ \sqrt{3} & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{pmatrix}$	$\{z, \bar{y}, \bar{x}\}$
$\mathbf{D}(S_4(001))$	(1)	(-1)	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$	$\{\bar{y}, x, \bar{z}\}$
$\mathbf{D}(S_4^{-1}(001))$	(1)	(-1)	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$	$\{y, \bar{x}, \bar{z}\}$

TABLE A.2: T_d representation matrices for 90° improper rotations about the six equivalent (001) axes for single group irreps

$\mathbf{D}(g)$	Γ_1	Γ_2	Γ_3	Γ_4	Γ_5	$\hat{P}_g\{x, y, z\}$
$\mathbf{D}(\sigma_v(011))$	(1)	(-1)	$-\frac{1}{2} \begin{pmatrix} -1 & \sqrt{3} \\ \sqrt{3} & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$	$\{x, z, y\}$
$\mathbf{D}(\sigma_v(01\bar{1}))$	(1)	(-1)	$-\frac{1}{2} \begin{pmatrix} -1 & \sqrt{3} \\ \sqrt{3} & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix}$	$\{x, \bar{z}, \bar{y}\}$
$\mathbf{D}(\sigma_v(101))$	(1)	(-1)	$\frac{1}{2} \begin{pmatrix} 1 & \sqrt{3} \\ \sqrt{3} & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 \\ 0 & -1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{pmatrix}$	$\{\bar{z}, y, \bar{x}\}$
$\mathbf{D}(\sigma_v(\bar{1}01))$	(1)	(-1)	$\frac{1}{2} \begin{pmatrix} 1 & \sqrt{3} \\ \sqrt{3} & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & -1 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$	$\{z, y, x\}$
$\mathbf{D}(\sigma_v(110))$	(1)	(-1)	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\{y, x, z\}$
$\mathbf{D}(\sigma_v(1\bar{1}0))$	(1)	(-1)	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\{\bar{y}, \bar{x}, z\}$

TABLE A.3: T_d representation matrices for mirror operations about the six equivalent (001) axes for single group irreps

Representation matrices for the Γ_5 irrep are completely compatible with $L=1$ eigenstates, so return appropriate coordinate transformations for the cartesian basis.

$\mathbf{D}(g)$	Γ_1	Γ_2	Γ_3	Γ_4	Γ_5	$\widehat{P}_g\{x, y, z\}$
$\mathbf{D}(C_3(111))$	(1)	(1)	$-\frac{1}{2} \begin{pmatrix} 1 & -\sqrt{3} \\ \sqrt{3} & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 \\ -1 & 0 & 0 \\ 0 & -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 \\ -1 & 0 & 0 \\ 0 & -1 & 0 \end{pmatrix}$	$\{z, \bar{x}, \bar{y}\}$
$\mathbf{D}(C_3(11\bar{1}))$	(1)	(1)	$-\frac{1}{2} \begin{pmatrix} 1 & \sqrt{3} \\ -\sqrt{3} & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 & 0 \\ 0 & 0 & 1 \\ -1 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 & 0 \\ 0 & 0 & 1 \\ -1 & 0 & 0 \end{pmatrix}$	$\{\bar{y}, z, \bar{x}\}$
$\mathbf{D}(C_3(1\bar{1}1))$	(1)	(1)	$-\frac{1}{2} \begin{pmatrix} 1 & \sqrt{3} \\ -\sqrt{3} & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$	$\{y, z, x\}$
$\mathbf{D}(C_3(\bar{1}11))$	(1)	(1)	$-\frac{1}{2} \begin{pmatrix} 1 & \sqrt{3} \\ -\sqrt{3} & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & -1 \\ -1 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & -1 \\ -1 & 0 & 0 \end{pmatrix}$	$\{y, \bar{z}, \bar{x}\}$
$\mathbf{D}(C_3(1\bar{1}\bar{1}))$	(1)	(1)	$-\frac{1}{2} \begin{pmatrix} 1 & -\sqrt{3} \\ \sqrt{3} & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & -1 \\ 1 & 0 & 0 \\ 0 & -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & -1 \\ 1 & 0 & 0 \\ 0 & -1 & 0 \end{pmatrix}$	$\{\bar{z}, x, \bar{y}\}$
$\mathbf{D}(C_3(\bar{1}\bar{1}1))$	(1)	(1)	$-\frac{1}{2} \begin{pmatrix} 1 & -\sqrt{3} \\ \sqrt{3} & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$	$\{z, x, y\}$
$\mathbf{D}(C_3(\bar{1}\bar{1}\bar{1}))$	(1)	(1)	$-\frac{1}{2} \begin{pmatrix} 1 & -\sqrt{3} \\ \sqrt{3} & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & -1 \\ -1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & -1 \\ -1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$	$\{\bar{z}, \bar{x}, y\}$
$\mathbf{D}(C_3(11\bar{1}\bar{1}))$	(1)	(1)	$-\frac{1}{2} \begin{pmatrix} 1 & \sqrt{3} \\ -\sqrt{3} & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 & 0 \\ 0 & 0 & -1 \\ 1 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 & 0 \\ 0 & 0 & -1 \\ 1 & 0 & 0 \end{pmatrix}$	$\{\bar{y}, \bar{z}, x\}$

TABLE A.4: T_d representation matrices for the 120° symmetry operations about the eight equivalent (111) axes for single group irreps

The notations for labelling S_4 and C_3 should be compared, since there is a subtle difference. $\mathbf{D}(S_4^{-1}(100))$ is equivalent to $\mathbf{D}(S_4(\bar{1}00))$, however the angle ϕ used are different; $-\pi/2$ and $+\pi/2$ respectively. Similarly $\mathbf{D}(C_3(\bar{1}\bar{1}\bar{1}))$ is equivalent to $\mathbf{D}(C_3^{-1}(111))$, with angles $+\pi/3$ and $-\pi/3$ respectively.

A.2 Double Group Representation Matrices

Evaluation of double group irreducible representation matrices for Γ_6 , Γ_7 , and Γ_8 is obtainable through the total angular momentum generators J_i , and symmetrised basis functions that block diagonalise Euler rotations into compatible irreps. The 24 single group operations representation matrices, with double group operations the opposite sign, since $e^{iJ_i\phi} = -e^{iJ_i(\phi+2\pi)}$ for half integer spin particles are shown in Tables A.5 ... A.8. Like in the single group case, O_h representation matrices are obtainable through compatibility relations, with signs of inversion class representation matrices pertaining to the parity of the irrep. $\mathbf{D}(C_2(010))$ sets the choice of phase on basis through time reversal symmetry.

$\mathbf{D}(g)$	Γ_6	Γ_7	Γ_8
$\left. \begin{array}{l} \mathbf{D}(E) \\ -\mathbf{D}(\widehat{E}) \end{array} \right\}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$
$\left. \begin{array}{l} \mathbf{D}(C_2(100)) \\ -\mathbf{D}(\widehat{E}C_2(100)) \end{array} \right\}$	$\begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 0 & i \\ 0 & 0 & i & 0 \\ 0 & i & 0 & 0 \\ i & 0 & 0 & 0 \end{pmatrix}$
$\left. \begin{array}{l} \mathbf{D}(C_2(010)) \\ -\mathbf{D}(\widehat{E}C_2(010)) \end{array} \right\}$	$\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}$
$\left. \begin{array}{l} \mathbf{D}(C_2(001)) \\ -\mathbf{D}(\widehat{E}C_2(001)) \end{array} \right\}$	$\begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix}$	$\begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix}$	$\begin{pmatrix} i & 0 & 0 & 0 \\ 0 & -i & 0 & 0 \\ 0 & 0 & i & 0 \\ 0 & 0 & 0 & -i \end{pmatrix}$

TABLE A.5: T_d representation matrices for the identity and three 180° rotation operations for double group irreps

$\mathbf{D}(g)$	Γ_6	Γ_7	Γ_8
$\left. \begin{array}{l} \mathbf{D}(S_4(100)) \\ -\mathbf{D}(\widehat{E}S_4(100)) \end{array} \right\}$	$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -i \\ -i & 1 \end{pmatrix}$	$\frac{-1}{\sqrt{2}} \begin{pmatrix} 1 & -i \\ -i & 1 \end{pmatrix}$	$\frac{-1}{2\sqrt{2}} \begin{pmatrix} -1 & i\sqrt{3} & \sqrt{3} & -i \\ i\sqrt{3} & 1 & i & \sqrt{3} \\ \sqrt{3} & i & 1 & i\sqrt{3} \\ -i & \sqrt{3} & i\sqrt{3} & -1 \end{pmatrix}$
$\left. \begin{array}{l} \mathbf{D}(S_4^{-1}(100)) \\ -\mathbf{D}(\widehat{E}S_4^{-1}(100)) \end{array} \right\}$	$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 & i \\ i & 1 \end{pmatrix}$	$\frac{-1}{\sqrt{2}} \begin{pmatrix} 1 & i \\ i & 1 \end{pmatrix}$	$\frac{1}{2\sqrt{2}} \begin{pmatrix} 1 & i\sqrt{3} & -\sqrt{3} & -i \\ i\sqrt{3} & -1 & i & -\sqrt{3} \\ -\sqrt{3} & i & -1 & i\sqrt{3} \\ -i & -\sqrt{3} & i\sqrt{3} & 1 \end{pmatrix}$
$\left. \begin{array}{l} \mathbf{D}(S_4(010)) \\ -\mathbf{D}(\widehat{E}S_4(010)) \end{array} \right\}$	$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}$	$\frac{-1}{\sqrt{2}} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}$	$\frac{1}{2\sqrt{2}} \begin{pmatrix} 1 & -\sqrt{3} & \sqrt{3} & -1 \\ \sqrt{3} & -1 & -1 & \sqrt{3} \\ \sqrt{3} & 1 & -1 & -\sqrt{3} \\ 1 & \sqrt{3} & \sqrt{3} & 1 \end{pmatrix}$
$\left. \begin{array}{l} \mathbf{D}(S_4^{-1}(010)) \\ -\mathbf{D}(\widehat{E}S_4^{-1}(010)) \end{array} \right\}$	$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}$	$\frac{-1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}$	$\frac{1}{2\sqrt{2}} \begin{pmatrix} 1 & \sqrt{3} & \sqrt{3} & 1 \\ -\sqrt{3} & -1 & 1 & \sqrt{3} \\ \sqrt{3} & -1 & -1 & \sqrt{3} \\ -1 & \sqrt{3} & -\sqrt{3} & 1 \end{pmatrix}$
$\left. \begin{array}{l} \mathbf{D}(S_4(001)) \\ -\mathbf{D}(\widehat{E}S_4(001)) \end{array} \right\}$	$\frac{1-i}{\sqrt{2}} \begin{pmatrix} 1 & 0 \\ 0 & i \end{pmatrix}$	$\frac{1+i}{\sqrt{2}} \begin{pmatrix} i & 0 \\ 0 & -1 \end{pmatrix}$	$\frac{1+i}{\sqrt{2}} \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -i & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & i \end{pmatrix}$
$\left. \begin{array}{l} \mathbf{D}(S_4^{-1}(001)) \\ -\mathbf{D}(\widehat{E}S_4^{-1}(001)) \end{array} \right\}$	$\frac{1-i}{\sqrt{2}} \begin{pmatrix} i & 0 \\ 0 & 1 \end{pmatrix}$	$\frac{1+i}{\sqrt{2}} \begin{pmatrix} -1 & 0 \\ 0 & i \end{pmatrix}$	$\frac{1+i}{\sqrt{2}} \begin{pmatrix} i & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -i & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$

TABLE A.6: T_d representation matrices for 90° improper rotations about the six equivalent (001) axes for double group irreps

$\mathbf{D}(g)$	Γ_6	Γ_7	Γ_8
$\left. \begin{array}{l} \mathbf{D}(\sigma_v(011)) \\ -\mathbf{D}(\hat{E}\sigma_v(011)) \end{array} \right\}$	$\frac{1}{\sqrt{2}} \begin{pmatrix} -i & -1 \\ 1 & i \end{pmatrix}$	$\frac{-1}{\sqrt{2}} \begin{pmatrix} -i & -1 \\ 1 & i \end{pmatrix}$	$\frac{1}{2\sqrt{2}} \begin{pmatrix} i & \sqrt{3} & -i\sqrt{3} & -1 \\ -\sqrt{3} & i & -1 & i\sqrt{3} \\ -i\sqrt{3} & 1 & -i & \sqrt{3} \\ 1 & i\sqrt{3} & -\sqrt{3} & -i \end{pmatrix}$
$\left. \begin{array}{l} \mathbf{D}(\sigma_v(01\bar{1})) \\ -\mathbf{D}(\hat{E}\sigma_v(01\bar{1})) \end{array} \right\}$	$\frac{1}{\sqrt{2}} \begin{pmatrix} i & -1 \\ 1 & -i \end{pmatrix}$	$\frac{-1}{\sqrt{2}} \begin{pmatrix} i & -1 \\ 1 & -i \end{pmatrix}$	$\frac{1}{2\sqrt{2}} \begin{pmatrix} -i & \sqrt{3} & i\sqrt{3} & -1 \\ -\sqrt{3} & -i & -1 & -i\sqrt{3} \\ i\sqrt{3} & 1 & i & \sqrt{3} \\ 1 & -i\sqrt{3} & -\sqrt{3} & i \end{pmatrix}$
$\left. \begin{array}{l} \mathbf{D}(\sigma_v(101)) \\ -\mathbf{D}(\hat{E}\sigma_v(101)) \end{array} \right\}$	$\frac{-i}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}$	$\frac{i}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}$	$\frac{i}{2\sqrt{2}} \begin{pmatrix} 1 & \sqrt{3} & \sqrt{3} & 1 \\ \sqrt{3} & 1 & -1 & -\sqrt{3} \\ \sqrt{3} & -1 & -1 & \sqrt{3} \\ 1 & -\sqrt{3} & \sqrt{3} & -1 \end{pmatrix}$
$\left. \begin{array}{l} \mathbf{D}(\sigma_v(\bar{1}01)) \\ -\mathbf{D}(\hat{E}\sigma_v(\bar{1}01)) \end{array} \right\}$	$\frac{i}{\sqrt{2}} \begin{pmatrix} -1 & 1 \\ 1 & 1 \end{pmatrix}$	$\frac{-i}{\sqrt{2}} \begin{pmatrix} -1 & 1 \\ 1 & 1 \end{pmatrix}$	$\frac{i}{2\sqrt{2}} \begin{pmatrix} 1 & -\sqrt{3} & \sqrt{3} & -1 \\ -\sqrt{3} & 1 & 1 & -\sqrt{3} \\ \sqrt{3} & 1 & -1 & -\sqrt{3} \\ -1 & -\sqrt{3} & -\sqrt{3} & -1 \end{pmatrix}$
$\left. \begin{array}{l} \mathbf{D}(\sigma_v(110)) \\ -\mathbf{D}(\hat{E}\sigma_v(110)) \end{array} \right\}$	$\frac{1-i}{\sqrt{2}} \begin{pmatrix} 0 & -i \\ 1 & 0 \end{pmatrix}$	$\frac{1+i}{\sqrt{2}} \begin{pmatrix} 0 & 1 \\ i & 0 \end{pmatrix}$	$\frac{1-i}{\sqrt{2}} \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & i & 0 \\ 0 & -1 & 0 & 0 \\ -i & 0 & 0 & 0 \end{pmatrix}$
$\left. \begin{array}{l} \mathbf{D}(\sigma_v(1\bar{1}0)) \\ -\mathbf{D}(\hat{E}\sigma_v(1\bar{1}0)) \end{array} \right\}$	$\frac{1-i}{\sqrt{2}} \begin{pmatrix} 0 & 1 \\ -i & 0 \end{pmatrix}$	$\frac{1+i}{\sqrt{2}} \begin{pmatrix} 0 & i \\ 1 & 0 \end{pmatrix}$	$\frac{1-i}{\sqrt{2}} \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & -1 & 0 \\ 0 & i & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}$

TABLE A.7: T_d representation matrices for mirror operations about the six equivalent (001) axes for double group irreps

$\mathbf{D}(g)$	Γ_6	Γ_7	Γ_8
$\left. \begin{array}{l} \mathbf{D}(C_3(111)) \\ -\mathbf{D}(\widehat{EC}_3(111)) \end{array} \right\}$	$\frac{1-i}{2} \begin{pmatrix} 1 & -i \\ 1 & i \end{pmatrix}$	$\frac{1-i}{2} \begin{pmatrix} 1 & -i \\ 1 & i \end{pmatrix}$	$\frac{1-i}{4} \begin{pmatrix} -i & -\sqrt{3} & i\sqrt{3} & 1 \\ -i\sqrt{3} & -1 & -i & -\sqrt{3} \\ -i\sqrt{3} & 1 & -i & \sqrt{3} \\ -i & \sqrt{3} & i\sqrt{3} & -1 \end{pmatrix}$
$\left. \begin{array}{l} \mathbf{D}(C_3(11\bar{1})) \\ -\mathbf{D}(\widehat{EC}_3(11\bar{1})) \end{array} \right\}$	$\frac{1-i}{2} \begin{pmatrix} i & -i \\ 1 & 1 \end{pmatrix}$	$\frac{1-i}{2} \begin{pmatrix} i & -i \\ 1 & 1 \end{pmatrix}$	$\frac{1-i}{4} \begin{pmatrix} -1 & \sqrt{3} & -\sqrt{3} & 1 \\ i\sqrt{3} & -i & -i & i\sqrt{3} \\ \sqrt{3} & 1 & -1 & -\sqrt{3} \\ -i & -i\sqrt{3} & -i\sqrt{3} & -i \end{pmatrix}$
$\left. \begin{array}{l} \mathbf{D}(C_3(1\bar{1}1)) \\ -\mathbf{D}(\widehat{EC}_3(1\bar{1}1)) \end{array} \right\}$	$\frac{1-i}{2} \begin{pmatrix} 1 & 1 \\ -i & i \end{pmatrix}$	$\frac{1-i}{2} \begin{pmatrix} 1 & 1 \\ -i & i \end{pmatrix}$	$\frac{1-i}{4} \begin{pmatrix} -i & -i\sqrt{3} & -i\sqrt{3} & -i \\ -\sqrt{3} & -1 & 1 & \sqrt{3} \\ i\sqrt{3} & -i & -i & i\sqrt{3} \\ 1 & -\sqrt{3} & \sqrt{3} & -1 \end{pmatrix}$
$\left. \begin{array}{l} \mathbf{D}(C_3(\bar{1}11)) \\ -\mathbf{D}(\widehat{EC}_3(\bar{1}11)) \end{array} \right\}$	$\frac{1-i}{2} \begin{pmatrix} 1 & -1 \\ i & i \end{pmatrix}$	$\frac{1-i}{2} \begin{pmatrix} 1 & -1 \\ i & i \end{pmatrix}$	$\frac{1-i}{4} \begin{pmatrix} -i & i\sqrt{3} & -i\sqrt{3} & i \\ \sqrt{3} & -1 & -1 & \sqrt{3} \\ i\sqrt{3} & i & -i & -i\sqrt{3} \\ -1 & -\sqrt{3} & -\sqrt{3} & -1 \end{pmatrix}$
$\left. \begin{array}{l} \mathbf{D}(C_3(1\bar{1}\bar{1})) \\ -\mathbf{D}(\widehat{EC}_3(1\bar{1}\bar{1})) \end{array} \right\}$	$\frac{1-i}{2} \begin{pmatrix} i & 1 \\ -i & 1 \end{pmatrix}$	$\frac{1-i}{2} \begin{pmatrix} i & 1 \\ -i & 1 \end{pmatrix}$	$\frac{1-i}{4} \begin{pmatrix} -1 & i\sqrt{3} & \sqrt{3} & -i \\ \sqrt{3} & -i & 1 & -i\sqrt{3} \\ -\sqrt{3} & -i & -1 & -i\sqrt{3} \\ 1 & i\sqrt{3} & -\sqrt{3} & -i \end{pmatrix}$
$\left. \begin{array}{l} \mathbf{D}(C_3(\bar{1}1\bar{1})) \\ -\mathbf{D}(\widehat{EC}_3(\bar{1}1\bar{1})) \end{array} \right\}$	$\frac{1-i}{2} \begin{pmatrix} i & -1 \\ i & 1 \end{pmatrix}$	$\frac{1-i}{2} \begin{pmatrix} i & -1 \\ i & 1 \end{pmatrix}$	$\frac{1-i}{4} \begin{pmatrix} -1 & -i\sqrt{3} & \sqrt{3} & i \\ -\sqrt{3} & -i & -1 & -i\sqrt{3} \\ -\sqrt{3} & i & -1 & i\sqrt{3} \\ -1 & i\sqrt{3} & \sqrt{3} & -i \end{pmatrix}$
$\left. \begin{array}{l} \mathbf{D}(C_3(\bar{1}\bar{1}1)) \\ -\mathbf{D}(\widehat{EC}_3(\bar{1}\bar{1}1)) \end{array} \right\}$	$\frac{1-i}{2} \begin{pmatrix} 1 & i \\ -1 & i \end{pmatrix}$	$\frac{1-i}{2} \begin{pmatrix} 1 & i \\ -1 & i \end{pmatrix}$	$\frac{1-i}{4} \begin{pmatrix} -i & \sqrt{3} & i\sqrt{3} & -1 \\ i\sqrt{3} & -1 & i & -\sqrt{3} \\ -i\sqrt{3} & -1 & -i & -\sqrt{3} \\ i & \sqrt{3} & -i\sqrt{3} & -1 \end{pmatrix}$
$\left. \begin{array}{l} \mathbf{D}(C_3(\bar{1}\bar{1}\bar{1})) \\ -\mathbf{D}(\widehat{EC}_3(\bar{1}\bar{1}\bar{1})) \end{array} \right\}$	$\frac{1-i}{2} \begin{pmatrix} i & i \\ -1 & 1 \end{pmatrix}$	$\frac{1-i}{2} \begin{pmatrix} i & i \\ -1 & 1 \end{pmatrix}$	$\frac{1-i}{4} \begin{pmatrix} -1 & -\sqrt{3} & -\sqrt{3} & -1 \\ -i\sqrt{3} & -i & i & i\sqrt{3} \\ \sqrt{3} & -1 & -1 & \sqrt{3} \\ i & -i\sqrt{3} & i\sqrt{3} & -i \end{pmatrix}$

TABLE A.8: T_d representation matrices for the 120° symmetry operations about the eight (111) axes for double group irreps

Appendix B

Maple Routines

There are many numerical implementation procedures and routines that were done in Maple 13 programming language, so for the benefit of the reader, several Maple source codes are included.

B.1 Clebsch-Gordan Coefficient Calculator

This maple procedure [70] computes Clebsch-Gordan coefficients for the completely general case $C_{J_1, m_{J_1}, J_2, m_{J_2}}^{J_3, m_{J_3}}$. The formula given in Equation 3.19 is implemented;

```
> cg:=proc(j1,m1,j2,m2,j,m)
> local faila, failb, failc, c1, c2, c3, c4, c5, z, zmin, zmax, cgsum, cgcoeff,
term1, term2, ans;
> ans:=0;
> faila:= evalb(j1<abs(m1)) or evalb(j2<abs(m2)) or evalb(j<abs(m));
> failb:= evalb(j>j1+j2) or evalb(j<abs(j1-j2));
> failc:= not evalb(m=m1+m2);
> if faila or failb or failc then RETURN(ans) fi;
> c1:=j1+j2-j: c2:=j1-m1: c3:=j2+m2:
> zmax:=min(c1,c2,c3):
> c4:=j2-j-m1: c5:=j1-j+m2:
> zmin:=max(0,c4,c5):
> cgsum:=0:
> for z from zmin to zmax do
> cgsum:=%+(-1)^z/(z!*(c1-z)!*(c2-z)!*(c3-z)!*(-c4+z)!*(-c5+z)!)
```

```

> od:
> term1:=(2*j+1)*(j1+j2-j)!*(j1-j2+j)!*(-j1+j2+j)!:
> term2:=(j1+m1)!*(j1-m1)!*(j2+m2)!*(j2-m2)!*(j+m)!*(j-m)!:
> cgcoeff:=sqrt(term1*term2/(j1+j2+j+1)!):
> if evalb(m1+m2=m) then ans:=cgcoeff*cgsum else ans:=0 fi:
> ans: end:

```

B.2 Unitary Matrix Generation

This Maple procedure generates the unitary matrix [71] used to convert $\{x, y, z\} \otimes \{\uparrow, \downarrow\}$ into a $J = 3/2 \oplus 1/2$ basis, as quoted in Equation 3.23 in accordance with the Condon-Shortley phase convention [65].

```

> temp := Matrix([[ -1/sqrt(2), 0, +1/sqrt(2) ],
>
>                  [ +I/sqrt(2), 0, +I/sqrt(2) ],
>
>                  [ 0, +1, 0 ]]):
> for n1 from +1 by -1 to -1 do
>   for n2 from +3/2 by -1 to -3/2 do
>     A1[5/2 - n2, 2 - n1] := cg(1,+n1,+1/2,+1/2,+3/2,+n2):
>     B1[5/2 - n2, 2 - n1] := cg(1,+n1,+1/2,-1/2,+3/2,+n2):
>   od:
>   for n2 from +1/2 by -1 to -1/2 do
>     A2[3/2 - n2, 2 - n1] := cg(1,+n1,+1/2,+1/2,+1/2,+n2):
>     B2[3/2 - n2, 2 - n1] := cg(1,+n1,+1/2,-1/2,+1/2,+n2):
>   od:
>   od:
> Matrix([[A1, B1], [A2, B2]]).HermitianTranspose(Matrix([[temp, Matrix(3)],
> [Matrix(3), temp]]));

```

$$\begin{bmatrix}
-1/\sqrt{2} & -i\sqrt{2} & 0 & 0 & 0 & 0 \\
0 & 0 & \sqrt{2}/\sqrt{3} & -1/\sqrt{6} & -i\sqrt{6} & 0 \\
1/\sqrt{6} & -i/\sqrt{6} & 0 & 0 & 0 & \sqrt{2}/\sqrt{3} \\
0 & 0 & 0 & 1/\sqrt{2} & -i/\sqrt{2} & 0 \\
0 & 0 & -1/\sqrt{3} & -1/\sqrt{3} & -i/\sqrt{3} & 0 \\
-1/\sqrt{3} & i/\sqrt{3} & 0 & 0 & 0 & 1/\sqrt{3}
\end{bmatrix}$$

B.3 Linearly Independent Matrix: $A_{\mathbf{k}, \hat{\pi}}^{\Gamma_8^{\pm}; \Gamma_6^{\mp}}$

This Maple procedure generates the linearly independent matrix $A_{\mathbf{k}, \hat{\pi}}^{\Gamma_8^{\pm}; \Gamma_6^{\mp}}$, used in the construction of the matrix Hamiltonian. Note that there is a scaling of $\sqrt{6}$ to return the exact form in Equation 4.4.

```
> for n1 from +3/2 by -1 to -3/2 do
>   for n2 from +1/2 by -1 to -1/2 do
>     A[5/2 - n1, 3/2 - n2] := k['+']*cg(+1,-1,+3/2,+n1,+1/2,+n2)/sqrt(2)
>                                     + k[z]*cg(+1,+0,+3/2,+n1,+1/2,+n2)
>                                     - k['-']*cg(+1,+1,+3/2,+n1,+1/2,+n2)/sqrt(2);
>   od:
> od:
```

$$\frac{-1}{2\sqrt{3}} \begin{bmatrix} -\sqrt{3}k_+ & 0 \\ 2k_z & -k_+ \\ k_- & 2k_z \\ 0 & \sqrt{3}k_- \end{bmatrix}$$

The Löwdin term may be evaluated through multiplication with the Hermitian transpose. Operator ordering is retained through the introduction of the non-commuting k_z . This matrix is scaled by $\zeta_{\Gamma_8^+; \Gamma_8^+}^{\Gamma_7^-} \equiv \sigma$ in accordance with the equivalence relation $\Gamma_6^+ \equiv \Gamma_7^-$. The interfacial C term is returned, but there is no Z term in accordance with both single and double group formulations.

```
> algsubs(conjugate(k['+']) = k['-'], algsubs(conjugate(k['-']) = k['+'],
algsubs(conjugate(k[z]) = k[z] , 12*(A.HermitianTranspose(A)))));
```

$$\begin{bmatrix} 3k_+k_- & -2\sqrt{3}k_+k_z & -\sqrt{3}k_+^2 & 0 \\ -2\sqrt{3}k_zk_- & 4k_zk_z + k_+k_- & 2(k_zk_+ - k_+k_z) & -\sqrt{3}k_+^2 \\ -\sqrt{3}k_-^2 & 2(k_-k_z - k_zk_-) & 4k_zk_z + k_-k_+ & 2\sqrt{3}k_zk_+ \\ 0 & -\sqrt{3}k_-^2 & 2\sqrt{3}k_-k_z & 3k_-k_+ \end{bmatrix}$$

Bibliography

- [1] Douglas J. Paul. Si/SiGe Heterostructures: from Material & Physics to Devices & Circuits. *Semicond. Sci. Technol.*, 19:R75 – R108, September 2004.
- [2] Peter Y. Yu and Manuel Cardona. *Fundamentals of Semiconductors*. Springer, 3rd edition, 2005.
- [3] G. E. Pikus and G. L. Bir. *Symmetry and Strain-Induced Effects in Semiconductors*. Wiley, english edition, 1974.
- [4] J. P. Dismukes, L. Ekstrom, and R. J. Paff. Lattice Parameter & Density in Germanium-Silicon Alloys. *J. Phys. Chem.*, 68(10):3021 – 3027, October 1964.
- [5] P. Hohenberg and W. Kohn. Inhomogeneous Electron Gas. *Physical Review*, 136(3B):864 – 871, November 1964.
- [6] J. C. Slater. The Theory of Complex Spectra. *The Physical Review*, 34(10):1293 – 1322, November 1929.
- [7] W. Kohn and L. J. Sham. Self-Consistent Equations Including Exchange & Correlation Effects. *Phys. Rev.*, 140(4):1133 – 1138, November 1965.
- [8] W. Tom Wenckebach. *Essentials of Semiconductor Physics*. Wiley-Blackwell, 1999.
- [9] D. J. Chadi and Marvin L. Cohen. Tight-Binding Calculations of the Valence Bands of Diamond & Zincblende Crystals. *Phys. Stat. Sol. (b)*, 68:405 – 419, 1975.
- [10] M. G. Burt. An Exact Formulation of the Envelope Function Method for the Determination of Electronic States in Semiconductor Microstructures. *Semicond. Sci. Technol.*, 3:739 – 753, 1988.
- [11] M. G. Burt. A new Effective-Mass Equation for Microstructures. *Semicond. Sci. Technol.*, 3, 1224 - 1226 1988.
- [12] M. G. Burt. The Justification for Applying the Effective-Mass Approximation to Microstructures. *J. Phys.: Condens. Matter*, 4:6651 – 6690, 1992.
- [13] M. G. Burt. On the Validity & Range of Applicability of the Particle in a Box Model. *Appl. Phys. Lett.*, 65(6):717 – 719, August 1994.
- [14] Lok C. Lew Yan Voon and Morten Willatzen. *The $\mathbf{k} \cdot \hat{\mathbf{p}}$ Method: Electronic Properties of Semiconductors*. Springer, 2009.

- [15] Léon Brillouin. *Wave Propagation in Periodic Structures*. The McGraw-Hill Book Company, Inc, 1946.
- [16] J. F. Nye. *Physical Properties of Crystals*. Oxford Science Publications, 2nd edition, 1985.
- [17] R. Beresford. Full-zone $\mathbf{k} \cdot \hat{\mathbf{p}}$ method of Band Structure Calculation for Wurtzite Semiconductors. *Journal of Applied Physics*, 95(11):6216 – 6224, June 2004.
- [18] Arthur P. Cracknell. Corepresentations of Magnetic Point Groups. *Progress of Theoretical Physics*, 35(2):196 – 213, February 1966.
- [19] Charles Kittel. *Introduction to Solid State Physics*. John Wiley & Sons, Inc, 8th edition edition, 2004.
- [20] Brillouin zone, May 2011. URL http://www.thefullwiki.org/Brillouin_zone.
- [21] Gregory H. Wannier. The Structure of Electronic Excitation Levels in Insulating Crystals. *Physical Review*, 52:191 – 197, August 1937.
- [22] Simon L. Altmann. *Band Theory of Solids: An Introduction from the Point of View of Symmetry*. Oxford University Press, 1994.
- [23] R. de L. Kronig and W. G. Penney. Quantum Mechanics of Electons in Crystal Lattices. *Proc. R. Soc. Lond. A*, 130:499 – 513, November 1931.
- [24] Leon van Hove. The Occurence of Singularities in the Elastic Frequency Distribution of a Crystal. *Physical Review*, 89(6):1189 – 1193, March 1953.
- [25] Eugene P. Wigner (translated from the German by J. J. Griffin). *Group Theory and its application to the Quantum Mechanics of Atomic Spectra*. Academic Press, 1959.
- [26] Eugen Merzbacher. *Quantum Mechanics*. John Wiley & Sons, Inc, 3rd edition, 1998.
- [27] J. J. Sakurai. *Modern Quantum Mechanics*. Addison-Wesley, 1994.
- [28] Manuel Cardona and Fred H. Pollak. Energy-Band Structure of Germanium & Silicon: The $\mathbf{k} \cdot \hat{\mathbf{p}}$ Method. *Physical Review*, 142(2):530 – 543, February 1966.
- [29] Gene Dresselhaus. Spin-Orbit Coupling Effects in Zinc Blende Structures. *Physical Review*, 100(2):580 – 586, October 1955.
- [30] Yositaka Onodera and Makoto Okazaki. Tables of Basis Functions for Double Point Groups. *Journal of the Physical Society of Japan*, 21(11):2400 – 2408, November 1966.
- [31] D. Rideau, M. Feraille, L. Ciampolini, M. Minondo, C. Tavernier, H. Jaouen, and A. Ghetti. Strained Si, Ge, and SiGe alloys modeled with a first-principled-optimized full-zone $\mathbf{k} \cdot \hat{\mathbf{p}}$ method. *Physical Review B*, 74(195208):1 – 20, November 2006.
- [32] Per-Olov Löwdin. A Note on the Quantum-Mechanical Perturbation Theory. *The Journal of Chemical Physics*, 19(11):1396 – 1401, November 1951.

- [33] Evan O. Kane. Energy Band Structure in p-type Germanium & Silicon. *J. Phys. Chem. Solids.*, 1:82 – 99, 1956.
- [34] Gene Dresselhaus, A. F. Kip, and Charles Kittel. Cyclotron Resonance of Electrons and Holes in Silicon & Germanium Crystals. *Physical Review*, 98(2):368 – 384, April 1955.
- [35] J. M. Luttinger and W. Kohn. Motion of Electrons & Holes in Perturbed Periodic Fields. *Physical Review*, 97(4):869 – 883, February 1955.
- [36] W. Kohn and J. M. Luttinger. Theory of Donor States in Silicon. *Physical Review*, 98(4):915 – 922, May 1955.
- [37] J. M. Luttinger. Quantum Theory of Cyclotron Resonance in Semiconductors: General Theory. *Physical Review*, 102(4):1030 – 1041, May 1956.
- [38] R. N. Dexter, H. J. Zeiger, and Benjamin Lax. Cyclotron Resonance Experiments in Silicon & Germanium. *Physical Review*, 104(3):637 – 644, November 1956.
- [39] L. Esaki and R. Tsu. Superlattice & Negative Differential Conductivity in Semiconductors. *IBM J. Res. Develop.*, pages 61 – 65, January 1970.
- [40] R. I. Taylor and M. G. Burt. Continuity Conditions for Envelope Functions at Semiconductor Interfaces Derived from the Bastard Model. *Semicond. Sci. Technol.*, 2:485 – 490, 1987.
- [41] Yu-Hsuan Kuo, Yong Kyu Lee, Yangsi Ge, Shen Ren, Jonathan E. Roth, Theodore I. Kamins, David A. B. Miller, and James S. Harris. Strong Quantum-Confined Stark Effect in Germanium Quantum-Well Structures on Silicon. *Nature*, 437:1334 – 1336, October 2005.
- [42] G. E. Pikus and G. L. Bir. Cyclotron & Paramagnetic Resonance in Strained Crystals. *Physical Review Letters*, 6(3):103 – 105, February 1961.
- [43] Moustafa El kurdi, Sebastien Sauvage, Guy Fishman, and Phillipe Boucaud. Band-edge alignment of SiGe/Si Quantum Wells & SiGe/Si Self-Assembled Islands. *Physical Review B*, 73(195327):1 – 9, May 2006.
- [44] G. Dehlinger, L. Diehl, U. Gennser, Hans Sigg, J. Faist, K. Ensslin, D. Grutzmacher, and E. Muller. Intersubband Electroluminescence from Silicon-Based Quantum Cascade Structures. *Science*, 290:2277 – 2280, December 2000.
- [45] G. Bastard. *Wave Mechanics Applied to Semiconductor Heterostructures*. Wiley, 1988.
- [46] Bradley A. Foreman. Effective-Mass Hamiltonian and Boundary Conditions for the Valence Bands of Semiconductor Microstructures. *Physical Review B - Rapid Communications*, 48(7):4964 – 4969, August 1993.
- [47] Douglas J. Paul. 8-band $\mathbf{k} \cdot \hat{\mathbf{p}}$ Modeling of the Quantum Confined Stark Effect in Ge Quantum Wells on Si Substrates. *Physical Review B*, 77(155323):1 – 7, April 2008.
- [48] Chris G. Van de Walle. Band Lineups and Deformation Potentials in the Model-Solid Theory. *Physical Review B*, 39(3):1871 – 1883, January 1989.

- [49] Matteo Bonfanti, E. Grilli, M. Guzzi, Daniel Chrastina, G. Isella, Hans von Känel, and H. Sigg. Direct Gap Related Optical Transitions in Ge/GeSi Quantum Wells. *Physica E*, pages 1 – 4, 2008.
- [50] Matteo Bonfanti, Emanuele Grilli, Mario Guzzi, Michele Virgilio, Giuseppe Grosso, Daniel Chrastina, Giovanni Isella, Hans von Känel, and Antonia Neels. Optical Transitions in Ge/GeSi Multiple Quantum Wells With Ge-rich Barriers. *Physical Review B - Rapid Communications*, 78(041407):1 – 4, July 2008.
- [51] David A. B. Miller, D. S. Chemla, T. C. Damen, A. C. Gossard, W. Weigmann, T. H. Wood, and C. A. Burrus. Band-Edge Electroabsorption in Quantum Well Structures: The Quantum-Confined Stark Effect. *Physical Review Letters*, 53(22): 2173 – 2176, November 1984.
- [52] Rebecca K. Schaevitz, Jonathan E. Roth, Shen Ren, Onur Fidaner, and David A. B. Miller. Material Properties of Si-Ge/Ge Quantum Wells. *IEEE Journal of Selected Topics in Quantum Electronics*, 14(4):1082 – 1089, Jul/Aug 2008.
- [53] Leon Lever, Zoran Ikonc, Alex Valavanis, Jonathan D. Cooper, and Robert W. Kelsall. Design of Ge-SiGe Quantum-Confined Stark Effect Electroabsorption Heterostructures for CMOS Compatible Photonics. *Journal of Lightwave Technology*, 28(22):3273 – 3281, November 2010.
- [54] Mildred S. Dresselhaus, Gene Dresselhaus, and Ado Jorio. *Group Theory; Application to the Physics of Condensed Matter*. Springer, 2008.
- [55] Melvin J. Lax. *Symmetry Principles in Solid State and Molecular Physics*. Wiley, 1974.
- [56] G. F. Koster. Matrix Elements of Symmetric Operators. *The Physical Review*, 109(2):227 – 231, January 1958.
- [57] C. J. Bradley. Space Groups and Selection Rules. *Journal of Mathematical Physics*, 7(7):1145 – 1152, July 1966.
- [58] D. E. Littlewood. Invariant Theory, Tensors & Group Characters. *Phil. Trans. R. Soc. Lond. A*, 239:305 – 365, February 1944.
- [59] George F. Koster, John O. Dimmock, Robert G. Wheeler, and Hermann Statz. *Properties of the Thirty-two Point Groups*. M.I.T. Press, 1963.
- [60] P. H. Butler. Coupling Coefficients and Tensor Operators for Chains of Groups. *Phil. Trans. R. Soc. Lond. A*, 277(1272):545 – 585, January 1975.
- [61] Jean-Marie Normand and Jacques Raynal. Relations between Cartesian & Spherical Components of Irreducible Cartesian Tensors. *J. Phys. A: Math. Gen.*, 15: 1437 – 1461, 1982.
- [62] Mary L. Boas. *Mathematical Methods in the Physical Sciences*. Wiley, 2nd edition, 1983.
- [63] S. L. Altmann and C. J. Bradley. On the Symmetries of Spherical Harmonics. *Phil. Trans. R. Soc. Lond. A*, 255(1054):199 – 215, January 1963.
- [64] Conyers Herring. Effect of Time Reversal Symmetry on Energy Bands of Crystals. *Physical Review*, 52:361 – 365, August 1937.

- [65] E. U. Condon and G. H. Shortley. *The Theory of Atomic Spectra*. Cambridge University Press, 1935.
- [66] Laurence D. Barron. *Molecular Light Scattering & Optical Activity*. Cambridge University Press, 2nd edition, 2004.
- [67] Paul E. S. Wormer. Tetrahedral Harmonics Revisited. *Molecular Physics*, 99(23): 1973 – 1980, 2001.
- [68] Joseph L. Birman, Ting-Kuo Lee, and Rhoda Berenson. Effective Hamiltonians & Clebsch-Gordan Coefficients in Crystals. *Physical Review B*, 14(2):318 – 321, July 1976.
- [69] C. R. Nave. Russell-saunders or $\mathbf{L} \cdot \mathbf{S}$ coupling, May 2011. URL <http://hyperphysics.phy-astr.gsu.edu/hbase/atomic/lcoup.html>.
- [70] Ted Barnes. A clebsch-gordan coefficient “procedure” using maple, December 2010. URL <http://personal.ph.surrey.ac.uk/~phs3ps/mapcg.map>.
- [71] Arthur P. Cracknell and S. J. Joshua. Symmetry Adapted Functions for Double Point Groups ii. Cubic Point Groups. *Proc. Camb. Phil. Soc.*, 67:647 – 656, 1970.
- [72] Warren J. Elder, Robert M. Ward, and Jing Zhang. Double-Group Formulation of $\mathbf{k} \cdot \hat{\mathbf{p}}$ theory for Cubic Crystals. *Physical Review B*, 83(165210):1–23, April 2011.
- [73] Linus Pauling. The Nature of the Chemical Bond. III. the Transition from one Extreme Bond Type to Another. *American Chemical Society*, 54(292):988 – 1003, March 1932.
- [74] J. Weber and M. I. Alonso. Near-Band-Gap Photoluminescence of Si-Ge Alloys. *Physical Review B*, 40(8):5683 – 5693, September 1989.
- [75] Thomas B. Bahder. Eight-Band $\mathbf{k} \cdot \hat{\mathbf{p}}$ Model of Strained zinc-blende crystals. *Physical Review B*, 41(17):11992 – 12001, June 1990.
- [76] Sven E. Harnung. Irreducible Tensors in the Octahedral Spinor Group. *Molecular Physics*, 26(2):473 – 502, 1973.
- [77] Soline Richard, Frederic Aniel, and Guy Fishman. Energy-Band Structure of Ge, Si, and GaAs: A thirty-band $\mathbf{k} \cdot \hat{\mathbf{p}}$ method. *Physical Review B*, 70(235204):1 – 6, December 2004.
- [78] U. Rössler. Non-parabolicity and Warping in the Conduction Band of GaAs. *Solid State Communications*, 49(10):943 – 947, March 1984.
- [79] A. R. Denton and N. W. Ashcroft. Vegard’s law. *Physical Review A*, 43(6):3161 – 3164, March 1991.
- [80] N. Fraj, I. Saïdi, S. Ben Radhia, and K. Boujdaria. Band Parameters of AlAs, Ge & Si in the 34-band $\mathbf{k} \cdot \hat{\mathbf{p}}$ model. *Semicond. Sci. Technol.*, 23(085006):1 – 6, June 2008.
- [81] Freidrich Schäffler. High-Mobility Si & Ge Structures. *Semicond. Sci. Technol.*, 12:1515 – 1549, 1997.

- [82] M. H. Weiler, R. L. Aggarwal, and Benjamin Lax. Warping- & Inversion-Asymmetry-Induced Cyclotron-Harmonic Transitions in InSb. *Physical Review B*, 17(8):3269 – 3283, April 1978.
- [83] A. Baldereschi and Nunzio O. Lipari. Spherical Model of Shallow Acceptor States in Semiconductors. *Physical Review B*, 8(6):2697 – 2709, September 1973.
- [84] P. Lawaetz. Valence-Band Parameters in Cubic Semiconductors. *Physical Review B*, 4(10), November 1971.
- [85] R. Braunstein. Valence Band Structure of Germanium-Silicon Alloys. *Phys. Rev.*, 130(3), May 1963.
- [86] Moustafa El kurdi, Guy Fishman, Sebastien Sauvage, and Phillipe Boucaud. Band Structure and Optical Gain of Tensile-Strained Germanium Based on a 30 Band $\mathbf{k} \cdot \hat{\mathbf{p}}$ Formalism. *Journal of Applied Physics*, 107(013710):1 – 7, January 2010.
- [87] Jian-Bai Xia. Effective-Mass Theory for Superlattices Grown on (11N)-Oriented Substrates. *Physical Review B*, 43(12):9856 – 9864, April 1991.
- [88] Zoran Ikonc, V. Milanovic, and J. Tjapkin. Valence Subband Structure of [100], [110], & [111] Grown GaAs-(Al,Ga)As Quantum Wells & the Accuracy of the Axial Approximation. *Physical Review B*, 46(7):4285 – 4288, August 1992.
- [89] J. C. Hensel and K. Suzuki. Quantum Resonances in the Valence Bands of Germanium. ii. Cyclotron Resonances in Uniaxially Stressed Crystals. *Physical Review B*, 9(10):4219 – 4257, May 1974.
- [90] K. Suzuki and J. C. Hensel. Quantum Resonances in the Valence Bands of Germanium. i. Theoretical Considerations. *Physical Review B*, 9(10):4184 – 4218, May 1974.
- [91] H. R. Trebin, U. Rössler, and R. Ranvaud. Quantum Resonances in the Valence Bands of Zinc-Blende Semiconductors i. Theoretical Aspects. *Physical Review B*, 20(2):686 – 700, July 1979.
- [92] R. H. Henderson and E. Towe. Strain & Crystallographic Orientation Effects on Interband Optical Matrix Elements & Band Gaps of [11/]-Oriented iii-v Epilayers. *J. Appl. Phys.*, 78(4):2447 – 2455, August 1995.
- [93] Woon-Ho Seo and John F. Donegan. 6x6 Effective Mass Hamiltonian for Heterostructures Grown on (11n)-Oriented Substrates. *Physical Review B*, 68(075318): 1 – 8, August 2003.
- [94] Robert Hull and John C. Bean. *Germanium Silicon: Physics & Materials*, volume 56 of *Semiconductors and Semimetals*. Academic Press, 1999.
- [95] Yu-Chang Hsieh. The Vibrational Spectrum and the Specific Heat of Germanium & Silicon. *The Journal of Chemical Physics*, 22(2):306 – 311, February 1954.
- [96] P. N. Keating. Effect of Invariance Requirements on the Elastic Strain Energy of Crystals with Application to the Diamond Structure. *Physical Review*, 145(2):637 – 645, May 1966.
- [97] A. Kahan, M. Chi, and L. Friedman. Infrared Transitions in Strained-Layer GeSi/Si. *J. Appl. Phys.*, 75(12):8012 – 8021, June 1994.

- [98] K. H. Yoo, J. D. Albrecht, and L. R. Ram-Mohan. Strain in Layered Zinc Blende and Wurtzite Semiconductors Grown Along Arbitrary Crystallographic Directions. *Am. J. Phys.*, 78(6):589 – 597, June 2010.
- [99] Stephen George Turner. *Strain Relaxation Mechanisms & Stress-Balancing of SiGe Heterostructures*. PhD thesis, Imperial College London, 2008.
- [100] J. H. van der Merwe. Crystal Interfaces. part II. Finite Overgrowths. *Journal of Applied Physics*, 34(1):123 – 127, January 1963.
- [101] J. W. Matthews and A. E. Blakeslee. Defects in Epitaxial Multilayers III. Preparation of Almost Perfect Multilayers. *Journal of Crystal Growth*, 32(2):265 – 273, February 1976.
- [102] Paul N. Stavrinou. *A Study of InP-based Strained Layer Heterostructures*. PhD thesis, University College London, 1995.
- [103] J. C. Bean, L. C. Feldman, A. T. Fiory, S. Nakahara, and I. K. Robinson. GeSi/Si strained-layer superlattice grown by molecular beam epitaxy. *J. Vac. Sci. Technol. A*, 2(2):436 – 440, Apr. - June 1984.
- [104] Calvin Yi-Ping Chao and Shun Lien Chuang. Spin-Orbit-Coupling Effects on the Valence-Band Structure of Strained Semiconductor Quantum Wells. *Physical Review B*, 46(7):4110 – 4122, August 1992.
- [105] Y. P. Varshni. Temperature Dependence of the Energy Gap in Semiconductors. *Physica*, 34(1):149 – 154, 1967.
- [106] Shun Lien Chuang. Efficient band-structure calculations of strained quantum wells. *Physical Review B*, 43(12):9649 – 9661, April 1991.
- [107] H. Yaguchi, K. Tai, K. Takemasa, K. Onabe, R. Ito, and Y. Shiraki. Characterisation of Ge/SiGe Strained-Barrier Quantum-Well Structures using Photoreflectance Spectroscopy. *Physical Review B*, 49(11):7394 – 7399, March 1994.
- [108] Gordon E. Moore. Cramming more components onto integrated circuits. *Electronics*, 38(8), April 1965.
- [109] Paul N. Stavrinou and Rob van Dalen. Operator Ordering & Boundary Conditions for Valence-band modeling: Application to [110] Heterostructures. *Physical Review B*, 55(23):15456 – 15459, June 1997.
- [110] Rob van Dalen and Paul N. Stavrinou. General Rules for Constructing Valence Band Effective Mass Hamiltonians with Correct Operator order for Heterostructures with Arbitrary Orientations. *Semicond. Sci. Technol.*, 13:11 – 17, 1998.
- [111] Hai-Bin Wu, S. J. Xu, and Jian Wang. Impact of the Cap Layer on the Electronic Structures & Optical Properties of Self-Assembled InAs/GaAs Quantum Dots. *Physical Review B*, 74(205329):1 – 6, November 2006.
- [112] B. Lassen, L. C. Lew Yan Voon, M. Willatzen, and R. Melnik. Exact Envelope-Function Theory versus Symmetrized Hamiltonian for Quantum Wires: a Comparison. *Solid State Communications*, 132:141 – 149, August 2004.

- [113] Gerard L. G. Sleijpen and Henk A. Van der Vorst. A Jacobi-Davidson Iteration Method for Linear Eigenvalue Problems. *SIAM Review*, 42(2):267 – 293, April 2000.
- [114] Tsuneya Ando. Hole Subband at GaAs/AlGaAs Heterojunctions and Quantum Wells. *Journal of the Physical Society of Japan*, 54(4):1528 – 1536, April 1985.
- [115] Rob van Dalen. *Optimisation of p-type Two-Dimensional Semiconductor Structures for FET Applications*. PhD thesis, University College London, July 1998.
- [116] Claus F. Klingshirn. *Semiconductor Optics*. Springer, 1995.
- [117] Shun Lien Chuang. *Physics of Photonic Devices*. John Wiley & Sons, Inc, 2009.
- [118] R. J. Elliott. Intensity of Optical Absorption by Excitons. *Physical Review*, 108(6):1384 – 1389, December 1957.
- [119] R. Eppenga and M. F. H. Schuurmans. Effect of Bulk Inversion Asymmetry on [001], [110], and [111] GaAs/AlAs Quantum Wells. *Physical Review B - Rapid Communications*, 37(18):10923 – 10926, June 1988.
- [120] K. Takayanagi, Y. Tanishiro, M. Takahashi, and S. Takahashi. Structural Analysis of Si(111)-7x7 by UHV-Transmission Electron Diffraction and Microscopy. *J. Vac. Sci. Technol. A*, 3:1502 – 1506, May/Jun 1985.
- [121] M. C. Payne. An ab initio Investigation of the Takayanagi Reconstruction. *J. Phys. C: Solid State Phys.*, 20:L983 – L987, 1987.
- [122] M. C. Xu, H. F. Ma, W. Ji, B. Yang, and H. J. Gao. Growth of Ge Hexagonal Meshwork Films on Si(111)-7x7. *Nanotechnology*, 17:4413 – 4415, August 2006.