AC
801
73
1991
No. 62
Cop 2

PKC
ADZ - 5527
JAL 2/9/93

ACKNOWLEDGEMENTS

I am deeply indebted to my advisor, Dr. Charles W. Myles, for his patient and helpful guidance during the research and preparation of this dissertation. I thank the other members of my committee, Dr. Gibson, Dr. Lamp, Dr. Lichti, and Dr. Peters for their helpful criticism. I would also like to thank the many faculty and staff members at the Physics Department who have helped me in these years. I thank the Physics Department for their support in the form of teaching assistantships and a part-time instructorship. I thank Texas Tech University for a grant of computer time to perform the calculations. Finally, I would like to thank my wife and my family for their support during this time.

CONTENTS

ACKNOWLEDGEMENTS	ii
ABSTRACT	v
LIST OF TABLES	vi
LIST OF FIGURES	vii
CHAPTER	
I. INTRODUCTION	1
II. THEORY BACKGROUND	12
2.1 Vogl Band Structure for the Host Semiconductors	12
2.2 Hjalmarson et al. Deep Level Theory	14
2.3 Wavefunction of Deep Levels	18
III. EFFECTS OF NEAREST-NEIGHBOR LATTICE RELAXATION ON DEEP LEVELS	21
3.1 Qualitative Effects of Lattice Relaxation	22
3.2 Deep Levels with Lattice Relaxation	23
3.3 Form for α_i	27
3.4 Results for Chemical Trends with Lattice Relaxation	30
3.4.1 Results for GaP	32
3.4.2 Results for Si	39
3.4.3 Results for Other Materials	41

IV. A SIMPLE MODEL TO CALCULATE THE AMOUNT OF NEAREST-NEIGHBOR LATTICE RELAXATION	64
V. MOLECULAR DYNAMICS FORMALISM FOR NEAREST NEIGHBOR LATTICE RELAXATION	71
5.1 Theory	71
5.2 Results	77
5.3 Total Energy Versus Impurity Bond Length	83
VI. FORMALISM FOR INCLUDING THE EFFECTS OF BOTH FIRST- AND SECOND-NEIGHBOR RELAXATIONS	93
6.1 Defect Potential	93
6.2 Forces and Molecular Dynamics	95
VII. RESULTS FOR DEEP LEVELS DUE TO SPECIFIC IMPURITIES: COMPARISON WITH EXPERIMENT AND OTHER THEORIES	109
7.1 Comparison with Experiment	112
7.2 Comparison with Other Theories	116
VIII. EFFECTS OF LATTICE RELAXATION ON THE DEEP LEVEL WAVEFUNCTION	121
IX. SUMMARY AND CONCLUSIONS	140
REFERENCES	147
APPENDIX	153

ABSTRACT

A formalism for investigating the effects of lattice relaxation on the deep levels associated with substitutional impurities in semiconductors is developed. This theory includes the effects of both first- and second-neighbor relaxation. It combines a tight-binding Green's function method for calculating deep levels with a molecular dynamics technique for determining the magnitude and direction of the host atom relaxation around an impurity. The results of applying this theory to various impurities in eight semiconductors are presented and compared with experiment and other theories. Chemical trends in deep levels and the effects of varying amounts of relaxation are explored with this formalism. In addition, deep energy levels including the effects of lattice relaxation for specific impurities are predicted. The corresponding deep level wavefunctions are also computed using this theory. The results show that the effects of lattice relaxation have a strong influence on the electronic properties of deep levels. In particular, both the positions of deep levels in the band gap and the deep level wavefunction are sensitive to such effects.

LIST OF TABLES

4.1	Covalent radii and the bond lengths calculated from them.	69
4.2	Bond lengths, covalent radii, and parameters α_{A_1} and α_{T_2} for various impurities in 8 semiconductors.	70
5.1	Constant A for various materials.	86
5.2	The host bond length d_H , the impurity bond length d_I and the relaxation distance Δd for various impurities in GaP, Si, GaAs and Ge.	87
6.1	The labeling convention for the nearest-neighbor and second-neighbor host atoms to the impurity.	103
6.2	Bond lengths d_I and d_{II} for various impurities in GaP, Si, GaAs and Ge, and the corresponding values of Δd , α , $\Delta d'$, and β .	104
6.3	Relationships between pairs of nearest- and second-neighbor host atoms to the impurity.	105
7.1	Deep energy levels of A_1 -symmetry for various impurities in GaP, Si, GaAs and Ge.	117
7.2	The percentage improvement Δ of the deep level predictions of the present theory over the Hjalmarson et al. theory in comparison with experiment.	118
7.3	Comparison of the predicted A_1 -symmetric deep levels from the present theory with those from the Talwar et al. theory and with experimental data.	118
8.1	Magnitudes of the on-site and nearest-neighbor parts of the wavefunction for various impurities in Si, GaP and GaAs.	132

LIST OF FIGURES

3.1	Energy levels of A_1 symmetry produced by an impurity substitutional for P in GaP	45
3.2	Energy levels of A_1 symmetry produced by an impurity substitutional for Ga in GaP.	46
3.3	Energy levels of T_2 symmetry produced by an impurity substitutional for P in GaP.	47
3.4	Energy levels of T_2 symmetry produced by an impurity substitutional for Ga in GaP.	48
3.5	Energy levels of A_1 symmetry produced by N and O substitutional for P in GaP as a function of d_I/d_H .	49
3.6	Energy levels of A_1 symmetry produced by a substitutional impurities in Si.	50
3.7	Energy levels of T_2 symmetry produced by substitutional impurities in Si.	51
3.8	Energy levels of A_1 symmetry produced by Te, Se, and S in Si as a function of d_I/d_H .	52
3.9	Energy levels of A_1 symmetry produced by an impurity substitutional for As in GaAs.	53
3.10	Energy levels of A_1 symmetry produced by an impurity substitutional for Ga in GaAs.	54
3.11	Energy levels of A_1 symmetry produced by a substitutional impurity in Ge.	55
3.12	Energy levels of A_1 symmetry produced by an impurity substitutional for P in AlP.	56
3.13	Energy levels of A_1 symmetry produced by an impurity substitutional for Al in AlP.	57
3.14	Energy levels of A_1 symmetry produced by an impurity substitutional for As in AlAs.	58
3.15	Energy levels of A_1 symmetry produced by an impurity substitutional for Al in AlAs.	59

3.16	Energy levels of A_1 symmetry produced by an impurity substitutional for Sb in GaSb.	60
3.17	Energy levels of A_1 symmetry produced by an impurity substitutional for Ga in GaSb.	61
3.18	Energy levels of A_1 symmetry produced by an impurity substitutional for P in InP.	62
3.19	Energy levels of A_1 symmetry produced by an impurity substitutional for In in InP. .	63
5.1	Time dependence of the magnitude of the total force and of the bond length for N substitutional for P in GaP.	88
5.2	Time dependence of the magnitude of the total force and the bond length for O substitutional for P in GaP.	89
5.3	Force on one of the four Ga nearest neighbors as a function of distortion distance for N and O substitutional for P in GaP.	90
5.4	Time dependence of the magnitude of the total force and of the bond length for a substitutional impurity S in Si.	91
5.5	Total energy versus the change of the bond length for an O substitutional for P in GaP.	92
6.1	Symmetric geometrical relationships between the impurity and its nearest neighbors and second neighbors.	107
6.2	Determinant $D(E)$ as a function of energy E in the bandgap for A_1 symmetric levels due to Si:Se.	108
7.1	Determinant $D(E)$ as a function of energy E in the bandgap for the A_1 symmetric levels of O substitutional for P in GaP.	119
7.2	Determinant $D(E)$ as a function of energy E in the bandgap for the A_1 symmetric levels of the impurities S, Se, and Te in Si.	120
8.1	Dependence of the on-site part of the A_1 -symmetric impurity wavefunction for impurities in Si.	134
8.2	Dependence of the nearest-neighbor part of the A_1 -symmetric impurity wavefunction for impurities in Si.	135
8.3	Dependence of the on-site part of the A_1 -symmetric impurity wavefunction for impurities substitutional for Ga in GaP.	136

8.4	Dependence of the nearest-neighbor part of the A_1 -symmetric impurity wavefunction for impurities substitutional for Ga in GaP.	137
8.5	Dependence of the on-site part of the A_1 impurity wavefunction for impurities substitutional for Ga in GaAs.	138
8.6	Dependence of the nearest-neighbor part of the A_1 impurity wavefunction for impurities substitutional for Ga in GaAs.	139

CHAPTER I

INTRODUCTION

Semiconductors are very important materials in the electronic industry because their properties can be manipulated over a wide range through the control of impurities and other imperfections. They are insulators at zero temperature and their energy band gap is relatively narrow, with typical values being of the order of 1 to 2 eV. Impurities and other lattice defects, such as vacancies and antisite defects, may form energy levels which lie within the fundamental band gap and these levels can strongly affect both the electrical and the optical properties of such materials. These defect levels in the band gap fall into two general classes. These are "shallow" levels and "deep" levels. As their names imply, "shallow" levels usually lie within 0.1eV of the valence- or conduction-band edge, and "deep" levels often lie well within the band gap. However, for the last several years, semiconductor theorists have used alternate definitions for these two kinds of defect levels. Rather than emphasizing the level energies, these definitions refer to the type of potential which produces the levels. In particular, the term "shallow levels" is now used to describe those which are produced by the long-ranged Coulomb potential of the defect. On the other hand, the term "deep levels" is now used to denote those which are produced by the central cell potential of the defect. This potential is more

localized and short-ranged than the Coulomb potential. Thus, for example, utilizing this definition, even though the A_1 -symmetric defect level produced by N substitutional for P in GaP is energetically very shallow (within a few meV of the lowest conduction band), it is still considered a “deep” level because it is known to be produced by a short-ranged central cell potential.¹ This definition of deep levels is used throughout this dissertation.

The purpose of this dissertation is to study the electronic properties of deep levels in semiconductors, such as their symmetries, their positions in the band gap and their wavefunctions. Specifically, the main interest is the effects of lattice relaxation on deep levels. In this dissertation, I develop two formalisms. The first is designed to predict the positions of deep levels in the band gap including the effects of lattice relaxation and to investigate the chemical trends associated with lattice relaxation. This formalism is applied to the calculations of the effects of lattice relaxation on deep levels due to substitutional impurities in 8 semiconductors. The second formalism, which is based on the molecular dynamics technique, is designed to compute the magnitude and the direction of the lattice relaxation produced by substitutional impurities in host semiconductors. This formalism is also applied to various impurities in several semiconductors. The results obtained by applying these formalisms are compared with other theories and available experimental data. With these formalisms and the results obtained using them, I hope that the theoretical

understanding of deep levels, especially the understanding of the effects of lattice relaxation on them, will be improved. In addition, I hope that the theory developed here will give experimentalists some theoretical guidance. I will briefly introduce some background in this chapter, and give more detailed theory background in the next chapter.

It is known that impurities which produce shallow levels in the band gap, so called "shallow impurities," generally contribute extra charge carriers to the host material. Their role, therefore, is to primarily control the type and the magnitude of the conductivity of the material. Unlike shallow impurities, impurities which produce deep levels in the band gap, so-called "deep impurities," act primarily as carrier traps or recombination centers. As such, they are undesirable in devices where carriers must have long lifetimes, for example, in solar cells. However, they are useful when the carrier concentration needs to be reduced sharply on a short-time scale, as in a fast switch. In addition, when the recombination or carrier capture energy is released as light, deep impurities are used in making light-emitting diodes(LEDs).²

The microscopic properties and the roles of shallow impurities in semiconductors were well understood many years ago through a combination of theory (effective mass theory) and experiments (primarily optical absorption spectra).³ The main point of this theory is that an electron in the conduction band or a hole in the valence band can be treated analogously to an electron in a

hydrogen atom with an effective mass m^* . Then, the physical picture of a shallow impurity in a semiconductor becomes that of an electron with mass m^* under the action of the screened Coulomb potential (produced by the crystal lattice). The energy levels of shallow impurities in the band gap can then immediately be given by

$$E_n = E_c - e^4 m_e^* / 2 \hbar^2 \epsilon^2 n^2 \quad (1.1)$$

for donor levels, and

$$E_n = E_v + e^4 m_h^* / 2 \hbar^2 \epsilon^2 n^2 \quad (1.2)$$

for acceptor levels, where n is an integer, E_c is the edge of the conduction band, E_v is the edge of the valence band, m_e^* and m_h^* are, respectively, the effective masses of the electron and hole, e is the charge of the electron, $\hbar$ is Planck's constant, and ϵ is the dielectric constant of the material.³

Deep impurities have proven far more difficult to investigate than shallow impurities. Deep levels can never be predicted by simple equations as shallow levels are by the above equations. Since deep levels were discovered in 1952,⁴ many experimental techniques and theories have been developed and applied to investigate these phenomena.⁵ For example, experimental techniques, such as electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR) were often used to investigate the properties of deep levels in the 1960's and 1970's.⁶ These techniques, with more sophisticated electronics, are

still used today.^{7,8} Since the mid-1970's, people have developed many other experimental techniques to study deep levels. Among these are deep level transient spectroscopy (DLTS),⁹ and optical detected magnetic resonance (ODMR).¹⁰

Theorists working on deep impurities usually focus their attention on one of two main theoretical techniques. One technique is called the cluster method, and another is called the Green's function method. The cluster method, which was pioneered by Messmer and Watkins,¹¹ attempts to simulate the infinite crystal by a limited number of atoms. This cluster of atoms is treated as a large molecule for which Schrodinger's equation is solved as exactly as possible using various quantum chemical methods based on the many-electron approximation. Among these methods are extended Huckel theory,¹¹ the CNDO (Complete Neglect of Differential Overlap) method and MNDO (Modified Neglect of Differential Overlap) method.¹² Although these methods do an excellent job of predicting the equilibrium geometry of the lattice around a defect,^{12,13} they cannot easily yield the correct band structure of the host,¹⁴ especially the positions of the conduction bands. This method, thus, cannot be easily used for accurately predicting the positions of deep levels in the energy band gap. For this reason, the formalisms which I develop in this dissertation are based on Green's function methods.

Modern deep level theories based on Green's function techniques were only developed in the late 1970's to the early 1980's.¹⁵⁻¹⁹ These theories are based on the one-electron approximation. The primary advantage of Green's function theories is that they treat an isolated defect in an infinite crystal with the same accuracy that one chooses to treat the corresponding perfect crystal. That is, for a given defect potential, their accuracy is identical to that of the band structure one uses to describe the host crystal. The key to their success is the fact that one first treats the infinite perfect crystal, taking the advantage of the periodicity and Bloch's theorem.²⁰ The changes induced by the impurity are then calculated by taking advantage of the fact that they are produced by a central cell potential which is localized in the lattice, so that the calculations of the perfect crystal and the crystal containing the impurity can be done separately. Since these theories usually give quite accurate band structures of semiconductors, they are easily used to predict the positions of deep levels in the band gaps.

There are two basic types of Green's function methods, both of which have their uses for understanding the basic physics of deep levels. The first of these are often called "first principles" deep level theories,¹⁵⁻¹⁷ and are based on the local density approximation²¹ and the theory of pseudopotentials.²² These theories usually concentrate on the accurate predictions of deep levels for a few specific defects (such as vacancies and antisite defects) in a few host semiconductors (such as Si, GaAs, and GaP).^{15-17,23} The advantages of these

methods are that they can be made self-consistent and parameter free, and that they often yield accurate results for deep levels in comparison with experimental data. Their disadvantages are that they require tremendous amounts of computer time and that they are not easily able to predict the chemical trends in data because of their computational complexity.

The second Green's function method was first introduced by Hjalmarson, Vogl, Wolford and Dow in 1980.¹⁸ It is based on a tight-binding formalism. The advantages of this method are (1) that one can use it to easily predict the chemical trends in deep levels as a function of defect and host for numerous defect-host systems, (2) that these trends usually do remarkably well in comparison with both experimental data and "first principles" theory results, and (3) that the absolute deep level energies obtained by this method are also often qualitatively and semi-quantitatively correct. However, because of its semi-empirical nature, absolute level depths obtained by this method are not expected to be as reliable in comparison with experimental data as those obtained by "first principles" theories. Generalizations of this theory to treat various types of defects and impurities in semiconductors have been successful in their predictions of chemical trends in the defect related properties of numerous materials. For example, this theory and its modifications have been successful (in comparison with experimental data) in their treatments of (a) isolated, pairs, and triplets of impurity and vacancy associated defects in Group IV and III-V

semiconductors,^{18,24-25} (b) core excitons in bulk materials,²⁶ (c) Schottky-barrier heights in III-V semiconductors,²⁷ (d) energy levels of impurities at semiconductor-semiconductor interfaces,²⁸ (e) pressure dependences of deep levels,²⁹ (f) charge-state splittings of deep levels,³⁰ (g) deep level wavefunctions and magnetic hyperfine parameters of deep levels,³¹⁻³³ (h) the alloy composition dependence of deep levels in semiconductor alloys,³⁴ (i) alloy broadening of deep levels in semiconductor alloys,³⁵ and (j) deep levels in semiconductor superlattices.³⁶ Obviously, this of type Green's function method is very flexible and powerful for investigating various deep level properties. Further, some of these properties are very difficult to study by "first principles" theories because of their computational complexity. I will discuss this theory in detail in the next chapter.

This theory does, however, suffer from the drawback that it neglects the effects of lattice relaxation in the calculations. Thus, while it is useful for predicting chemical trends, the quantitative accuracy of this theory is limited. It is known that when a defect is added to a semiconductor, it will interact with the surrounding host atoms, the lattice stability around it will be altered, and the surrounding host atoms will be displaced.³⁷ Because deep levels are produced by a localized, short-ranged defect potential, the distortion of the lattice around a defect will strongly affect them. In order to improve the accuracy of the predictions, the effects of lattice relaxation on deep levels clearly have to be

included. In fact, Hjalmarson et al. mentioned such effects in their original paper,¹⁸ and argued that lattice relaxation is usually very small and thus could be neglected to a first approximation. Thus, they did not study such effects further.

This theory, thus, left some significant problems and open questions which should be discussed in a more complete theory. Among these questions are: (a) What is the size of the lattice relaxation? (b) In which direction do the surrounding atoms around an impurity move, inward or outward? (c) How does the lattice relaxation depend on the host and defect? (d) How will the lattice relaxation affect the properties of deep levels? That is, how will a deep level be shifted due to the lattice relaxation? Obviously, correctly answering these questions will strongly improve this type of Green's function theory, and make it more realistic and complete. This is what I try to do in this dissertation.

In this dissertation, what I am primarily doing is generalizing the Hjalmarson et al. theory to include lattice relaxation effects on deep levels. To do this, I develop formalisms (i) to investigate the properties of deep levels including the effects of lattice relaxation using the Hjalmarson et al. theory as a starting point, and (ii) to calculate the lattice relaxation due to particular defects in semiconductors using molecular dynamics techniques. By studying such effects systematically, I hope to answer the questions which were unanswered by Hjalmarson et al. theory. These formalisms retain much of the simplicity of this

earlier theory. However, as I show in this dissertation, its quantitative accuracy can be considerably improved in comparison with experimental data by including lattice relaxation. Using this theory, I calculate the chemical trends in deep levels and the trends associated with varying amounts of lattice relaxation in eight semiconductors for various impurities. The magnitudes and directions of the lattice relaxation for particular impurities in several materials are also computed. I also predict the positions of deep levels in the energy band gap for specific impurities in these materials, and these results are compared with experimental data and other theories, such as "first principles" theories.

The remainder of this dissertation is organized as follows. In Chapter II, I present a brief discussion of the Hjalmarson et al. theory and the Vogl et al. band structure theory which I use to characterize the host crystals. The combinations of these two theories form the starting point of my theory. In Chapter III, I present an outline of the formalism which I use to investigate the properties of deep levels associated with varying amounts lattice relaxation. In this chapter, only the effects of lattice relaxation of the nearest-neighbor host atoms are considered. This formalism is applied to eight semiconductors for various impurities. In Chapter IV, I present a simple model based on the covalent radius approximation to calculate the magnitudes and directions of the nearest-neighbor lattice relaxation for various impurities in these materials. Chapter V contains a formalism based on the molecular dynamics approach to

calculate the amounts of nearest-neighbors lattice relaxation. In this chapter, the results obtained using this formalism for impurities in GaP, Si, GaAs, and Ge are also presented. In Chapter VI, a formalism for calculating the effects of lattice relaxation including both the first and the second nearest-neighbor host atoms is presented. Chapter VII contains the predicted deep levels for specific impurities in GaP, Si, GaAs and Ge obtained from this formalism. These predicted deep levels are also compared with experimental data and other theories where they are available. In Chapter VIII, a formalism for calculating the impurity wavefunction including nearest-neighbor relaxation effects is presented and used to predict wavefunctions for various impurities in Si, GaP and GaAs. Where data is available, these predictions are compared with wavefunctions obtained (indirectly) from ENDOR data. A summary and conclusions are presented in Chapter IX.

CHAPTER II

THEORY BACKGROUND

In this chapter, I briefly describe the Vogl et al. semi-empirical tight-binding theory of electronic energy bands in zincblende and diamond structure materials,³⁸ and the Hjalmarson et al. theory of deep levels due to substitutional impurities.¹⁸ I also briefly describe the theory of deep level wavefunctions which is based on these theories. I do this here because these theories form the starting point for my theory. I also include this chapter as a review for the readers who are already familiar with deep level theory and as an introduction for the readers who are new to this field.

2.1 Vogl Band Structure for the Host Semiconductors

I have mentioned in Chapter I that, in order to use Green's function methods to deal with deep level problems, one must first calculate the band structure for the host crystal. The band structure theory which is best suited for my deep level calculations should be computationally simple and rapidly reproducible on a repeated basis for numerous defect calculations. That is, it must be simply parameterized. Furthermore, it should produce band structures which are accurate in comparison both with experimental data and with very accurate band structures obtained by "first principles" techniques.

The Vogl et al. sp^3s^* semi-empirical tight-binding structure theory meets all of these criteria. This theory uses an s , p_x , p_y , p_z , and s^* orbital basis on each atom. The use of excited s^* orbitals allows a description of the conduction bands that is flexible enough to treat both direct and indirect band gap semiconductors.³⁸ The host crystal Hamiltonian in this theory is written as

$$H_0 = \sum_{i,\vec{R}} (|ia\vec{R}\rangle E_i^a \langle ia\vec{R}| + |ic\vec{R}\rangle E_i^c \langle ic\vec{R}|) + \sum_{i,j,\vec{R},\vec{R}'} [|ia\vec{R}\rangle V_{ij}(\vec{R},\vec{R}') \langle ic\vec{R}'] + h.c.], \quad (2.1)$$

where $i=s, p_x, p_y, p_z$ or s^* labels the orbital, a and c denote anion and cation. $\vec{R}$ specifies the unit cell, h.c. denotes the Hermitian conjugate, and the transfer matrix elements $V_{ij}(\vec{R},\vec{R}')$ are nonzero only if $\vec{R}$ and $\vec{R}'$ are nearest neighbors. Thus, this Hamiltonian only includes the effects of the nearest neighbors around a host atom. The on-site and nearest-neighbor interaction parameters, E_i^a , E_i^c and $V_{ij}(\vec{R},\vec{R}')$, can be found in Table I of Ref. 38 for 16 different semiconductors. They were obtained by an empirical fit to accurate pseudopotential band structures, such as those from Ref. 39. The states $|ia\vec{R}\rangle$ and $|ic\vec{R}\rangle$ in Eq.(2.1) are localized basis orbitals centered on the anion at $\vec{R}$ and cation on $\vec{R}+\vec{d}$, respectively, where $\vec{d}$ is the nearest-neighbor vector. The tight-binding parameters of the Vogl et al. Hamiltonian have the properties that the on-site matrix elements E_i^a and E_i^c are proportional to the corresponding atomic energies of the host atoms, as first suggested by Harrison.⁴⁰ The nearest

neighbor transfer matrix elements V_{ij} in this Hamiltonian scale roughly according to the inverse square of the bond length d , following Harrison's d^{-2} scaling rule.⁴⁰ That is, Vogl et al. found that $V_{ij} \approx C_{ij}d^{-2}$, where C_{ij} depends on the material. For example, Vogl et al. have calculated that for all materials $V_{ss} \approx -42d^{-2}$ and $V_{p_x p_x} \approx 12d^{-2} \text{ eV}$.³⁸ For all calculations reported in this dissertation, I use this band theory to characterize the host crystal materials. It is also worth stating that this band-structure theory has been widely tested on a variety of problems.^{18,24-36} However, I emphasize here that the formalism I develop in this dissertation is independent of this particular choice and is valid for other tight-binding band-structure models.

2.2 Hjalmarson et al. Deep Level Theory

I now briefly discuss the Hjalmarson et al. theory of deep levels due to substitutional impurities.¹⁸ This theory is based on a method originally developed by Koster and Slater.⁴¹ If one supposes that an atom of the perfect crystal is replaced by an impurity atom, the Schrodinger's equation becomes

$$(H_0 + V)|\Psi\rangle = E|\Psi\rangle, \quad (2.2)$$

where H_0 is the Hamiltonian of the perfect crystal (given by Eq.(2.1)), and the defect potential V is formally given by $V = H - H_0$, where H is the Hamiltonian of the crystal containing the impurity. In Eq.(2.2), $|\Psi\rangle$ is the impurity

wavefunction and E is the impurity energy. The host crystal Green's function is defined as

$$G^0(E) = (E - H_0)^{-1}. \quad (2.3)$$

For impurity energy levels E in the band gap, Eq. (2.2) can be rewritten as

$$|\Psi\rangle = G^0(E)V|\Psi\rangle, \quad (2.4)$$

or

$$(I - G^0(E)V)|\Psi\rangle = 0, \quad (2.5)$$

where I is the unit matrix. More details of the Green's function techniques can be found in Ref. 42. Thus, the impurity energy levels E in the band gap of a semiconductor, which are produced by the defect potential V , are given by the non-trivial solutions of the determinant equation

$$\det[I - G^0(E)V] = 0. \quad (2.6)$$

In principle, the defect potential V describes the many-body interactions of an electron (or a hole) with the host crystal and the impurity atom. For example, because of the size of the impurity atom, it slightly distorts its lattice environment (this effect is called lattice relaxation) and because of its charge, it slightly polarizes neighbor atoms (this effect is called charge state splitting). Thus, these effects should be included in the potential, V . I would also like to point out that, since I am just interested in deep levels, I only include the central

cell potential part of the defect potential V , and neglect the Coulomb potential which produces shallow levels, as Hjalmarson et al. have done. Thus, the solutions of Eq. (2.2) will represent deep levels only.

The Hjalmarson et al. theory makes two approximations about the form of defect potential V .¹⁸ These are (1) that the atomic energy differences between two atoms in a solid are similar to those differences for two free atoms, so that the on-site matrix elements of V are proportional to the atomic energy differences of the impurity and host atoms, and (2) that, since lattice relaxation effects should be small, the transfer matrix elements of V can be taken to be zero. Thus, in this theory, the defect potential matrix is diagonal in the tight-binding representation, and the effects of lattice relaxation are neglected.

For the isolated substitutional impurity in tetrahedrally symmetric zincblende or diamond structure materials, the point group is T_d . Such an impurity can, thus, have defect states with either non-degenerate A_1 (s-like) or triply degenerate T_2 (p-like) symmetry. The determinantal equation (2.6) can then be factored to become

$$\det[I - G^0(E)V] = \prod_{i=0}^3 \det[I_i - G_i^0 V_i] = 0, \quad (2.7)$$

where the subscript i is a symmetry index; $i=0$ corresponds to A_1 states, and $i=1, 2$ and 3 correspond to T_2 states, G_i^0 , V_i and I_i are, respectively, the Green's function submatrix, the defect potential submatrix, and the unit matrix in the subspace i . From now on, unless otherwise noted, the index i will be used only to

stand for A_1 or T_2 symmetric states. Equation (2.7) enables one to calculate the deep levels for A_1 and T_2 states separately. With the two approximations of the Hjalmarson et al. theory and considering only the nearest-neighbor atoms, the defect potential V of an impurity on the anion site at the origin has the form as

$$V = \sum_i V_i = \sum_i |ia\vec{0}\rangle U_i \langle ia\vec{0}|, \quad (2.8)$$

where U_i is the on-site matrix element of submatrix V_i . The basis states $|ia\vec{R}\rangle$ are orthogonalized, symmeterized Lowdin orbitals which are linear combinations of sp^3 hybrid orbitals.⁴³ For an impurity on the cation site, the label a is replaced by c in Eq. (2.8). Using Eq. (2.8), Eq. (2.7) can be written as two scalar equations as

$$U_i = 1/G_{aa}^i(E), \quad (2.9)$$

where $G_{aa}^i(E)$ is the on-site element of the Green's function matrix $G_i^0(E)$. That is

$$G_{aa}^i(E) = \langle ia\vec{0}|G^0(E)|ia\vec{0}\rangle, \quad (2.10)$$

where $\vec{0}$ denotes the origin, and superscript i here has the same meaning as subscript i before. According to the first approximation of the Hjalmarson et al. theory, U_i can be calculated as

$$U_i = \beta_i(E_{imp}^i - E_{host}^i), \quad (2.11)$$

where E_{imp}^i and E_{host}^i are, respectively, the impurity and host atomic energies for states of symmetry i , and β_i is an empirical parameter, which, for fixed i , is a

constant for all defects and all host systems. I note that Eq. (2.11) is consistent with the Vogl et al. bandstructures (Eq. (2.1) for the on-site matrix elements. Hjalmarson et al. have determined that $\beta_{A_1}=0.8$ and $\beta_{T_2}=0.6$.³⁸ I will use many of the ideas which have been briefly discussed here to develop my formalism for including the effects of lattice relaxation on deep levels. The details will be discussed in the next chapter.

2.3 Wavefunction of Deep Levels

As was already discussed, deep levels are produced by a localized, short-range defect potential. This feature should, of course, be presented in the associated wavefunctions. Starting with the Hjalmarson et al. theory, the wavefunctions of deep levels due to substitutional impurities were studied in the absence of lattice relaxation in real space by Ren et al.³¹ and in k space by Dai et al.³². In Ref. 31, the results for deep level wavefunctions as a function of the distance R measured from the impurity site for a S^+ impurity in Si are compared with experimental data which is derived from ENDOR data⁴⁴ and atomic parameters.⁴⁵ From both the theoretical results and the data, it is found that the magnitude of the wavefunction decreases rapidly with R. This confirms the idea that the deep levels are characterized by localized, short-range states.

One can formally write the deep level wavefunction of a substitutional sp^3 bonded impurity as

$$|\Psi\rangle = \sum_{i, \vec{R}} \langle i, b, \vec{R} | \Psi \rangle |i, b, \vec{R}\rangle, \quad (2.12)$$

where i labels the orbital, $\vec{R}$ is a position vector in the lattice, and b can be either the anion (a) site or the cation (c) site.

From Eq. (2.4), the i -symmetric part of the deep level wavefunction on site b at $\vec{R}$ is related to the Green's function as

$$\langle i, b, \vec{R} | \Psi \rangle = \langle i, b, \vec{R} | G^0(E) V | \Psi \rangle. \quad (2.13)$$

For simplicity, consider an impurity on the anion site at the origin, so that its defect potential is given by Eq. (2.4). Then, using Eqs. (2.4), (2.9) and (2.10), one can easily obtain

$$\langle i, b, \vec{R} | \Psi \rangle = \frac{\langle i, b, \vec{R} | G^0(E) | i, a, \vec{0} \rangle}{\langle i, a, \vec{0} | G^0(E) | i, a, \vec{0} \rangle} \langle i, a, \vec{0} | \Psi \rangle. \quad (2.14)$$

In addition, Ren et al. have shown that

$$|\langle i, a, \vec{0} | \Psi \rangle|^2 = -\frac{(\langle i, a, \vec{0} | G^0(E) | i, a, \vec{0} \rangle)^2}{\frac{d}{dE} \langle i, a, \vec{0} | G^0(E) | i, a, \vec{0} \rangle}. \quad (2.15)$$

Using Eqs. (2.15) and (2.14), the part of wavefunction on any site b at position $\vec{R}$ can be determined. It is also interesting to note that these two equations give an expression for the wavefunctions that they are independent of the explicit form of the defect potential. In fact, they express it in terms of host properties

only. In Ref. 31, the very interesting result is found that, for a given symmetry, the wavefunction depends only slightly on the deep level energy E . That is, deep level wavefunctions are hostlike and almost independent of the impurity! This means that, for the same host crystal and for impurity states of a given symmetry, different impurities have similar wavefunctions.

CHAPTER III

EFFECTS OF NEAREST-NEIGHBOR LATTICE RELAXATION ON DEEP LEVELS

In this chapter, I outline my formalism for calculating the effects of lattice relaxation on deep levels. As mentioned before, this formalism is a generalization of the Hjalmarson et al. theory¹⁸ and uses the Vogl et al. band structure theory as input.³⁸ However, any other tight-binding band-structure theory could in principle be used. I only consider isolated sp^3 bonded substitutional impurities in zincblende and diamond structure semiconductors. However, in principle, more complicated defects could also be treated by a generalization of the present theory. Further, in this chapter, only the effects of the relaxation of the nearest-neighbor-host atoms around an impurity are considered. In Chapter VI, the formalism is extended to include the effects of the relaxation of the second-nearest-neighbor-host atoms. Also, in order to focus on the effects of lattice relaxation on deep levels, I only consider neutral impurities. That is, I neglect the effects of charge state splitting. Such charge-state effects could, in principle, be included by combining the present theory with that of Ref. 30.

In this chapter, I also discuss the results of applying this formalism to the deep levels produced by various impurities in eight semiconductors. They are Si, Ge, GaP, GaAs, GaSb, AlP, AlAs, and InP. These materials are among the most

technologically important zincblende and diamond structure materials. Of course, the formalism can easily be extended to other materials.

3.1 Qualitative Effects of Lattice Relaxation

It was mentioned already that the effects of lattice relaxation will strongly affect the properties of deep levels. However, in the past, theorists have usually studied such effects and deep levels separately. For example, the effects of lattice relaxation were studied by cluster methods,^{11-13,46} by the valence force model,^{37,47-48} and by total energy methods.⁴⁹ In these theories, people were mainly interested in the magnitudes and directions of such effects induced by defects, and did not consider such effects on deep levels. Such effects have, however, been studied in some deep level theories, such as "first principles" theories.^{50,51} These approaches, which are certainly more accurate than that outlined in this chapter, have the disadvantages mentioned in Chapter I.

I also note that a previous generalization of the Hjalmarson et al. theory¹⁸ to include lattice-relaxation effects for S, Se, and Te impurities in Si and Ge was made by Talwar et al. using a theory of total energy.⁵² However, despite the fact that the approximations used in Ref. 52 to calculate such effects are very sophisticated, the resulting deep levels fail to improve on the results obtained by the Hjalmarson et al. theory¹⁸ in comparison with experimental data.

Lattice relaxation falls into two general classes. These are breathing-mode relaxations, which preserve the point group symmetry of the deep impurities

during the relaxation, and symmetry breaking relaxation. One major cause for symmetry breaking lattice relaxation is the Jahn-Teller instability. The Jahn-Teller theorem states that a localized system in an orbitally degenerate state distorts spontaneously to lower its symmetry until the resulting state has no orbital degeneracy.⁵³ The proof of this theorem is straightforward, and readers can find more details in Ref. 53. Jahn-Teller effects play a very important role in the case of vacancies in Si, because some of their deep levels are produced by an orbitally triply degenerate state (a T_2 state).⁵⁰⁻⁵¹ However, in this dissertation, I mainly consider the non-degenerate A_1 symmetric deep levels. Although a few cases where symmetry breaking distortions occur even though the undistorted configuration has no orbital degeneracy can be related to Jahn-Teller effects,⁵⁴ for most of the cases in which I am interested, the lattice relaxation due to the impurities can be exactly or approximately described by a symmetry conserving "breathing-mode" relaxation. Thus, in rest of this dissertation, only this type of lattice relaxation is considered.

3.2 Deep Levels with Lattice Relaxation

In order to include the effects of lattice relaxation on deep levels, I modify the second approximation of the Hjalmarson et al. theory¹⁸ and allow for non-zero off-diagonal matrix elements of the defect potential. Using a tight-binding band-structure representation and the same basis used in Eq. (2.1) in the nearest-neighbor approximation, the defect potential V should have a form

similar to that of the Hamiltonian of Eq. (2.1). That is, for an impurity on the anion site at the origin in a zincblende crystal, the defect potential including the off-diagonal matrix elements which can be used to represent the effects of the nearest-neighbor-lattice relaxation can formally be written as

$$V = \sum_i |ia\vec{0}\rangle U_i^a \langle ia\vec{0}| + \sum_{ij\vec{d}} [|ia\vec{0}\rangle V_{ij}^{ac} \langle jc\vec{d}| + h.c.], \quad (3.1)$$

where a and c refer to the anion and cation, $\vec{R}=\vec{0}$ is the unit cell at the origin, the sum on $\vec{d}$ is taken over the four nearest-neighbor cations, U_i^a is the diagonal matrix element of the potential at the anion site for symmetry i , V_{ij}^{ac} is the off-diagonal matrix element, which couples the orbital i at the anion site to orbital j at the cation site, and h.c. denotes the Hermitian conjugate. Formally, $V=H-H_0$, where H is the Hamiltonian of the defect containing crystal and H_0 is the perfect crystal Hamiltonian given by Eq. (2.1). Thus, U_i^a is a difference in the on-site matrix elements of the Hamiltonian for the defect containing and perfect crystals, and V_{ij}^{ac} is a difference in transfer-matrix elements. For a similar impurity on the cation site, the labels a and c are interchanged in Eq. (3.1). In the case of diamond-structure semiconductors, the labels a and c lose their meanings except to denote the atoms at the origin and their nearest neighbors.

This defect potential can be simplified by symmetry considerations. As mentioned earlier, I only consider symmetric lattice relaxation of the host atoms around an impurity. In this type of relaxation, the host atoms relax either inward or outward in a symmetric fashion, and the impurity will stay at the

origin without any movement. Thus in this case, the T_d symmetry is conserved in the relaxation, the impurity still has either non-degenerate A_1 states or triply-degenerate T_2 states and Eq. (2.7) remains valid. Since only effect of the nearest-neighbor relaxation around the impurity is considered in this chapter, only the four nearest-neighbor-host atoms around the impurity are allowed to move either inward or outward. The other host atoms stay at their original positions. Thus, each of the submatrices in Eq. (2.7) are of size 5×5 . In addition, the defect potential in subspace i has the form

$$V_i = |ia\vec{0} \rangle U_i \langle ia\vec{0}| + \sum_{\vec{d}} [|ia\vec{0} \rangle \alpha_i \langle ic\vec{d}| + h.c.], \quad (3.2)$$

where U_i is a shorthand notation for U_i^a , α_i is a linear combination of the V_{ij}^{ac} , and $i=A_1$ and T_2 . By adopting a defect potential of the form given by Eq. (3.2), in effect, I have enlarged the defect from an isolated substitutional impurity to a five atom cluster consisting of the impurity and its four nearest-neighbor atoms. Unlike the so-called cluster methods, however, the Green's function technique allows the calculations to be done for the infinite crystal (containing this 5 atom cluster). For each symmetry i , this means that the determinantal equation (Eq. (2.7)) (and all matrices in it) become of size 5×5 . I will show below that the effects of lattice relaxation are included in parameters α_i . With similar considerations, the Green's function can be block-diagonalized, so that one of

the submatrices of the host Green's function $G_i^0(E)$, which enters Eq. (2.7) can be written as

$$G_i^0(E) = \begin{matrix} & \begin{matrix} a & c & c & c & c \end{matrix} \\ \begin{matrix} a \\ c \\ c \\ c \\ c \end{matrix} & \begin{pmatrix} G_{aa} & G_{ac} & G_{ac} & G_{ac} & G_{ac} \\ G_{ca} & G_{cc} & G' & G' & G' \\ G_{ca} & G' & G_{cc} & G' & G' \\ G_{ca} & G' & G' & G_{cc} & G' \\ G_{ca} & G' & G' & G' & G_{cc} \end{pmatrix} \end{matrix}, \quad (3.3)$$

where a and c again label the anion and cation site. $G_{aa} = G_{aa}(E)$ is given by Eq. (2.10), for convenience, the superscript i has been suppressed, and the other matrix elements are given by

$$G_{ac} = G_{ac}(E) = \langle ia\vec{0} | G^0(E) | ic\vec{d} \rangle, \quad (3.4)$$

$$G_{ca} = G_{ca}(E) = \langle ic\vec{d} | G^0(E) | ia\vec{0} \rangle, \quad (3.5)$$

$$G_{cc} = G_{cc}(E) = \langle ic\vec{d} | G^0(E) | ic\vec{d} \rangle, \quad (3.6)$$

and

$$G' = G'(E) = \langle ic\vec{d}' | G^0(E) | ic\vec{d}' \rangle. \quad (3.7)$$

Here $\vec{d}$ is the vector between the impurity on the anion site and a nearest-neighbor atom on the cation site, and $\vec{d}'$ is the vector between two nearest-neighbor atoms (which are second neighbors each other). By solving Eq.

(2.7) with Eq. (3.3) as input, one can find a relation between the parameters U_i and α_i and the elements of Green's function matrix $G_i^0(E)$ which has the form

$$U_i = \frac{1}{G_{aa}} - \frac{G_{ca} + G_{ac}}{G_{aa}} 4\alpha_i + \frac{4G_{ac}G_{ca} - G_{cc}G_{aa} - 3G_{aa}G'}{G_{aa}} 4(\alpha_i)^2. \quad (3.8)$$

When $\alpha_i=0$ (no lattice relaxation), the above equation becomes the result of Hjalmarson et al. theory given by Eq. (2.9). Since all of the Green's function matrix elements are the functions of energy E , for those elements corresponding to energy E in the band gap, Eq. (3.8) is an implicit equation for the i -symmetric deep levels E as a function of the parameters U_i and α_i for a particular host material band structure. For $\alpha_i=0$, it can then be used to generate level energy E versus diagonal defect potential elements U_i as Hjalmarson et al. have done.¹⁸ For fixed $\alpha_i \neq 0$, which includes the effects of lattice relaxation, one can also use Eq. (3.8) to generate such E versus U_i . Alternately, for fixed U_i , one can also generate deep level energy E versus α_i diagrams from Eq. (3.8). Such diagrams allow one to explore the chemical trends in the deep levels (by varying U_i for fixed α_i) or to explore the trends in the deep levels with varying amounts of lattice relaxation (by varying α_i for fixed U_i). Clearly, both A_1 and T_2 symmetric deep levels can be treated in this way by choosing $i=A_1$ or $i=T_2$ in Eq. (3.8). Most of the results discussed below were obtained for A_1 symmetric levels.

3.3 Form for α_i

As mentioned above, the off-diagonal elements of the defect potential matrix, α_i , represent, in the nearest-neighbor approximation, the effects of lattice relaxation around an impurity in a host crystal. In order to calculate the deep levels including such effects, α_i must be specified. Hjalmarson et al. have suggested that α_i may be calculated by a generalization of Harrison's inverse-bond-length-squared approximation.¹⁸ Here, I present a formalism to calculate α_i based on this approximation. In the Appendix, another form for α_i is discussed, which, following Menon and Allen,⁵⁵ is based on an exponential form for the off-diagonal matrix elements.

Harrison showed that the nearest-neighbor-transfer-matrix elements of the host Hamiltonian scale approximately as the inverse bond length squared.⁴⁰ Vogl et al. have used this approximation to partially determine the off-diagonal parameters in their sp^3s^* host band structure theory (see section 2.1).³⁸ I assume that this same scaling rule holds for the transfer-matrix elements of both the defect containing and the perfect crystals. Since the off-diagonal elements, α_i , of the defect potential matrix are differences in such transfer matrix elements ($V=H-H_0$), this allows them to be written as

$$\alpha_i = -C_i \left(\frac{1}{d_I^2} - \frac{1}{d_H^2} \right), \quad (3.9)$$

where d_I is the bond length between the impurity and a nearest-neighbor-host atom, and d_H is the bond length of the host crystal. The first minus sign has been chosen for convenience. Following Vogl et al.,³⁸ C_i is a proportionality constant which depends on i but is independent of material. It is shown in Ref. 38 that C_i (for perfect crystals) can be determined by fitting to experimental data. However, the values of C_i in Eq. (3.9) are different by a factor four from those of the similar constants in Ref. 38. This is because Vogl et al. define the host off-diagonal elements as $4\langle i\vec{a}_0 | H^0 | i\vec{c}\vec{d} \rangle$, so that the contributions of the four nearest neighbors can be included simultaneously. However, the host off-diagonal elements in my theory are $\langle i\vec{a}_0 | H^0 | i\vec{c}\vec{d} \rangle$ which only contain the contributions of one of the four nearest-neighbor atoms. The values of C_i in Eq. (3.9) are thus chosen to be the same as those found by Vogl et al. (divided by four). This results in the numerical values $C_{A_1} = 10.5 \text{ eV}(\text{\AA})^2$, and $C_{T_2} = -3 \text{ eV}(\text{\AA})^2$. Because C_i is independent of material, I also assume that this quantity has the same value for the impurity containing and the perfect crystal. It is shown later that using these two constants in my formalism produces very good deep levels in comparison with experimental data.

As can be seen in Eq. (3.9), α_i is simply and directly related to the impurity-host bond length d_I , which represents the magnitude of lattice relaxation. Further, from Eq. (3.9) and the numerical values of C_i , it can be seen that for an outward relaxation ($d_H < d_I$), α_{A_1} (α_{T_2}) is positive (negative),

while for an inward relaxation ($d_H > d_I$), α_{A_1} (α_{T_2}) is negative (positive). Thus, the off-diagonal elements of the defect potential matrix, α_i , are a measure of the lattice relaxation produced in a state of symmetry i by an impurity. The effects of nearest-neighbor lattice relaxation can thus be completely characterized in both magnitude and direction by the parameters α_{A_1} and α_{T_2} .

3.4 Results for Chemical Trends with Lattice Relaxation

The results for the deep level energies E in the band gap as functions of the appropriate on-site defect potential energy, U_{A_1} or U_{T_2} , and the appropriate off-diagonal parts of the defect potentials, α_{A_1} or α_{T_2} , are summarized in Figs. 3.1-3.19, for the case where only nearest-neighbor-lattice relaxation is considered. If A_1 (T_2) symmetric levels are considered in the figure, the appropriate parameters are U_{A_1} (U_{T_2}) and α_{A_1} (α_{T_2}). For convenience, in what follows, I often refer to these parameters as U and α when the symmetry of the corresponding deep levels is clear from the context of the discussion.

The figure numbers which correspond to the predictions for deep levels in various materials are as follows: GaP, Figs. 3.1-3.5; Si, Figs. 3.6-3.8; GaAs, Figs. 3.9 and 3.10; Ge, Fig. 3.11; AlP, Figs. 3.12 and 3.13; AlAs, Figs. 3.14 and 3.15; GaSb, Figs. 3.16 and 3.17; and InP, Figs. 3.18 and 3.19.

Figures 3.1-3.4, 3.6, 3.7, and 3.9-3.19 show diagrams for deep level energies E versus U . The various curves in these figures correspond to the solutions of Eq.

(3.8) for the various values of the parameter α shown in the figure labels. In these figures, the zero on vertical scale corresponds to the top of the valence band, and the maximum energy corresponds to the bottom of the conduction band. The horizontal scale corresponds to the on-site defect potential U calculated from atomic energy differences via Eq. (2.11). The corresponding impurities are labeled at the appropriate U on the top of the figures. Chemical trends (variation in E for fixed α , as the impurity is changed) can, thus, be obtained from these figures as is usual in the Hjalmarson et al. approach.¹⁸ Since the parameter α is a measure of lattice relaxation, the trends for varying amounts of relaxation (varying in E for fixed U as α is changed) can also be extracted from these figures by comparing the E versus U curves for different values of α . In these figures, the curves for $\alpha=0$, which correspond to the case of no lattice relaxation, are the same as the results obtained in Ref. 18.

The deep levels for a particular impurity with a particular value of α can be obtained from these figures by finding the intersection with the curve for that value of α with a vertical line drawn from the label for that impurity at the top of the figure. If there is no intersection for a particular case, then no deep level of the appropriate symmetry is predicted in the band gap for that impurity with that value of α .

Figures 3.5 and 3.8 show predictions for the dependences of A_1 -symmetric deep levels due to specific impurities (fixed U) on the impurity-bond-length to

host-bond-length ratio (d_I/d_H). Figure 3.5 shows such results for N and O substitutional for P in GaP and Fig.3.8 shows similar results for S, Se, and Te in Si. In these figures, the ordinate is the energy in the band gap, measured from the top of the valence band, and abscissa is the ratio d_I/d_H .

Specific results for deep levels in particular materials will now be discussed in more detail.

3.4.1 Results for GaP

Figures 3.1-3.4 display diagrams for the deep levels energies E versus the diagonal part of defect potential U for the deep levels produced by substitutional impurities in GaP. Figures 3.1 and 3.2 show the results for A_1 -symmetric levels due to impurities on the anion site (substitutional for P) and on the cation site (substitutional for Ga), respectively. Figures 3.3 and 3.4 display the similar results for T_2 -symmetric levels due to impurities on the anion and cation sites.

Inspection of Figs. 3.1 and 3.2 reveals the qualitative effects of lattice relaxation on A_1 -symmetric deep levels. First, it can be seen that the $\alpha \neq 0$ curves all have chemical trends which are similar to the $\alpha = 0$ (no lattice relaxation) curves. This result can be understood by noting that the chemical trends of deep levels for $\alpha = 0$ are determined by Eq. (2.9), and when $\alpha \neq 0$, they are determined

by Eq. (3.8). However, if the terms proportional to α and α^2 in Eq. (3.8) are moved from the right side to the left side, that equation has the form

$$U' = 1/G_{aa} \quad (3.10)$$

which is the same form as Eq. (2.9). Here U' is defined as

$$U' = U + \frac{G_{ca} - G_{ac}}{G_{aa}} 4\alpha - \frac{4G_{ac}G_{ca} - G_{cc}G_{aa} - 3G_{aa}G'}{G_{aa}} 4\alpha^2. \quad (3.11)$$

Thus, by adding the effects of lattice relaxation ($\alpha \neq 0$), the predicted deep level energy for a specific impurity will change, but their chemical trends will be similar to the case without relaxation ($\alpha = 0$).

It can also be seen that the deep levels for a fixed U are shifted up toward the conduction-band edge as α becomes increasingly negative and down toward the middle of the band gap (Fig.3.1) or the valence-band edge (Fig.3.2) as α becomes more positive. As discussed in the last section, for A_1 states, negative α corresponds to inward relaxation ($d_H > d_I$), and positive α corresponds to outward relaxation ($d_H < d_I$). These results, thus, show that inward relaxation about an impurity moves its A_1 -symmetric deep levels toward the conduction band, while outward relaxation moves it toward the valence band. This behavior can also be understood by comparing Eq. (3.8) with Eq. (2.9), that is by using Eqs.(3.10) and (3.11). From the detailed calculations, I find that for inward relaxation ($\alpha < 0$), U' is always larger (in magnitude) than U for the same impurity. This means that a predicted deep level with a given amount of

inward relaxation is equivalent to that level without relaxation ($\alpha=0$) for a larger (more negative) U . From Figs. 3.1 and 3.2, one can see that a larger (more negative) U gives a higher energy level in the band gap along the $\alpha=0$ curve. Thus, inward relaxation moves energy levels upward in the same way as a larger (more negative) U without lattice relaxation would. A similar consideration can be used for the case of outward relaxation. In particular, I find that, for outward relaxation, U' is always smaller (in magnitude) than U , so outward relaxation moves the deep levels downward in the band gap in the same way as a smaller (less negative) U without relaxation would.

This behavior can also be explained from a different viewpoint using tight-binding theory. In this theory, the A_1 - and T_2 -symmetric states are linear combinations of the sp^3 hybrids.⁴⁰ When the nearest-neighbor-host atoms around an impurity move inward or outward, two changes occur. First, the hybrid energy changes because the state is no longer made up of pure sp^3 orbitals.⁴⁰ The energy associated with this change is called the dehybridization energy E_d by Harrison. The hybrid energy is lowered by this amount when the nearest-neighbor atoms move toward the impurity, and is increased by it when they move out.⁴⁰ The second change occurs in the potential V_{ij} , (Harrison's notation) which describes the interaction between two hybrid orbitals. This potential, called the "covalent energy" by Harrison⁴⁰ is enhanced for an inward relaxation and weakened for an outward relaxation. Of course, these changes of

E_d and V_r will affect the A_1 - or T_2 -symmetric energy levels in the band gap, and could move them upward or downward depending on the ratio of E_d to V_r .^{50,51}

It is also worth noting that one-dimensional model calculations for A_1 -symmetric antibonding states⁵⁶ yield similar results. In particular, in these model calculations, it was found that such states are pushed toward the conduction band (valence band) for inward (outward) relaxation. Since Hjalmarson et al.¹⁸ have shown that the A_1 -symmetric states associated with substitutional impurities are conduction band derived antibonding hostlike states, this simple model result lends further support to the results of the present calculations. I note that the opposite trend has been predicted by Talwar, Suh, and Tang,⁵² who included both first- and second-neighbor relaxation in their theory. In particular, they found that inward relaxation moves A_1 -symmetric deep levels downward, while outward relaxation moves them upward. Since, in the results presented in this chapter, I have only considered the first-neighbor relaxation, one might think that such higher neighbor relaxation might reverse the trend predicted here. However, based on results I have obtained using molecular-dynamics simulations where second-neighbor relaxation is included, I do not believe this to be the case. These results are discussed in Chapter VI. Further, as is discussed below, the agreement of the present theory with experimental data and "first principles" theories also tends to confirm my predicted trend.

This behavior can be seen more clearly in Fig. 3.5. In this figure, results are shown for the A_1 -symmetric deep levels produced by the impurities O and N substitutional for P in GaP. This is equivalent to fixing U for O and N in Fig. 3.1. In Fig. 3.5, the predicted deep levels as a function of the ratio d_I/d_H are shown. In that figure, the ordinate is the deep level energy measured from the top of the valence band and the abscissa is the ratio d_I/d_H . The trends of the curves in that figure are in agreement with the above discussion. In particular, it can be seen that inward relaxation moves the deep levels towards the conduction band and outward relaxation moves them deeper into the band gap. Also from Fig. 3.5, it can be seen that the deep levels are almost the linear functions of d_I . I note that a first-order perturbation treatment would predict a linear dependence of E on the parameter α . Thus, this predicted linear dependence on d_I is somewhat unexpected. However, I have noted that some similar results were found using "first principle" Green's function methods.^{50,51}

These predicted trends can be further illustrated by discussing a specific case in detail. For example, consider the N impurity substitutional for P in GaP. From Fig. 3.1, it can be seen that this impurity is predicted to have a deep level which changes from about 1.88 eV above the valence band for $\alpha=1.0$ eV (corresponding to an outward relaxation with $d_I=1.46d_H$), to about 2.10 eV for $\alpha=0.0$ eV (no relaxation, or $d_I=d_H$). Similarly, this deep level moves further toward the conduction band as α is decreased below zero, occurring at about

2.21 eV for $\alpha = -0.5$ eV (corresponding to an inward relaxation with $d_I = 0.89d_H$) and becoming conduction band resonant for $\alpha < -0.9$ eV ($d_I < 0.82d_H$).

Similar trends can be obtained for Ga-site impurities in GaP by examination of Fig. 3.2. For example, consider the P at Ga antisite defect "impurity". First, from Fig. 3.2, it can be seen that a large variation in the associated deep levels is predicted, depending on the amount of lattice relaxation. In fact, by varying α , this level can be made to move across a significant fraction of the band gap. Specifically, this level changes from about 0.71 eV above the valence band edge for $\alpha = 1.0$ eV (corresponding to an outward relaxation with $d_I = 1.46d_H$) to about 1.10 eV for $\alpha = 0.0$ eV (no relaxation, or $d_I = d_H$), and to about 1.63 eV for $\alpha = -1.0$ eV (corresponding to an inward relaxation with $d_I = 0.81d_H$).

In Figs. 3.3 and 3.4, the deep energy levels E versus U_{T_2} diagrams for T_2 -symmetric levels due to impurities substitutional for P and Ga respectively in GaP are shown. One can see from these figures that the chemical trends of T_2 -symmetric levels in Fig. 3.3 are predicted to be very different from those of the corresponding A_1 -symmetric levels shown in Figs. 3.1. In particular, the predicted A_1 levels in Fig. 3.1 are all located in the top half of the band gap and near the left corner of the figure. Also, the values of U_{A_1} are all negative. The smaller the magnitude of U_{A_1} is, the closer the deep levels are to the conduction band. By contrast, the corresponding T_2 levels in Fig. 3.3 are mainly located in the bottom half of the band gap and near right side of the figure, and the values

of U_{T_2} are all positive. The smaller the magnitude of U_{T_2} is, the closer the deep levels are to the valence band. Comparing Fig. 3.1 to Fig. 3.3, one also finds that negative α in Fig. 3.3 moves the curves towards the conduction-band edge, and positive α moves them towards valence-band edge. The predicted variation with α for the T_2 levels in Fig. 3.3, thus, is the same as for the A_1 levels in Fig. 3.1. That is, increasingly negative α moves the predicted deep levels towards the conduction band, while increasingly positive α moves them towards the valence band.

However, from the discussion following Eq. (3.9), it is clear that α_{A_1} and α_{T_2} have opposite signs. That is, for T_2 states, $\alpha < 0$ corresponds to outward relaxation ($d_I > d_H$), while $\alpha > 0$ corresponds to inward relaxation ($d_I < d_H$). Thus, in the case of GaP with an impurity on the P site, the physical meaning of the predicted trend for T_2 states is opposite to that for A_1 states. In particular, in this case, a T_2 deep level should move towards the conduction band with outward relaxation, and it should move towards the valence band with inward relaxation. The reason for this difference is that A_1 and T_2 deep levels in GaP with an impurity on the p site have the opposite chemical trends discussed above. It is also interesting to compare Fig. 3.2 with Fig. 3.4, which are both for Ga site impurities in GaP. In these two figures, the values of U are negative in both cases, and the smaller the magnitude of U is, the closer the deep levels are to the conduction band. That is the A_1 and T_2 levels have similar chemical

trends. In Fig. 3.4, it can be seen that positive α moves the deep levels towards the conduction band, and negative α moves them towards the valence band. The predicted variation with α for T_2 levels is, thus, opposite to that for A_1 levels in the case of an impurity on the Ga site in GaP. However, from the discussion following Eq. (3.9), this means that in this case, T_2 levels move towards the conduction band with inward relaxation, and they move towards the valence band with outward relaxation. This trend is the same as that for the A_1 levels shown in Fig. 3.2.

3.4.2 Results for Si

Figures 3.6 and 3.7 show the predictions for A_1 - and T_2 -symmetric deep level energies E due to substitutional impurities in Si. These are plotted versus U_{A_1} and U_{T_2} , respectively, for the values of α shown in the figure labels. Figure 3.8 shows the predicted dependences of the A_1 -symmetric deep levels on the ratio d_I/d_H for the impurities S, Se, and Te in Si.

It can be seen that the predicted chemical trends of the A_1 -symmetric levels in Fig. 3.6 are similar to those of Fig. 3.2 for Ga-site impurities in GaP, but different from those in Fig. 3.1 for P-site impurities in GaP. However, the above predicted trends with varying amounts of relaxation (as a function of α) are similar in this case to those in both Figs. 3.1 and 3.2. In particular, from this figure, it is clear that A_1 levels are predicted to move upward towards the

conduction band for an inward relaxation ($\alpha < 0$) and downward for an outward relaxation ($\alpha > 0$). This trend can again be seen in Fig. 3.8, which shows the trends of the A_1 levels versus the ratio d_I/d_H for S, Se, and Te in Si. Similar to Fig. 3.5, it is clear from Fig. 3.8 that the predicted deep levels have an almost linear dependence on d_I . It can also be seen that the predicted chemical trends and trends in α in Figs. 3.6 and 3.7 are similar to the predictions for an impurity on Ga site in GaP in Figs. 3.2 and 3.4. In particular, in Fig. 3.7, T_2 levels are predicted to move towards the valence band as α becomes more negative, while they move towards the conduction band as α becomes more positive. This is opposite to the predicted variation with α for A_1 levels shown in Fig. 3.6. However, following the discussion in Fig. 3.4, this means that T_2 levels in Fig. 3.7 move towards the conduction band with inward relaxation, and they move towards the valence band with outward relaxation. This predicted trend is the same as that for the A_1 levels shown in Fig. 3.6.

To be more specific, I discuss a numerical example here. Consider a S substitutional impurity in Si. From Fig. 3.6, this impurity is predicted to have an A_1 -symmetric deep level which changes from about 0.39 eV above the valence band for $\alpha = 0.6$ eV (corresponding to an outward relaxation with $d_I = 1.2d_H$), to about 0.56 eV for $\alpha = 0.0$ eV (no relaxation or $d_I = d_H$). Similarly, this deep level is predicted to move further towards the conduction band as α is decreased below zero, occurring in Fig. 3.6 at about 0.66 eV for $\alpha = -0.3$ eV (corresponding

to an inward relaxation with $d_I=0.9d_H$) and at about 0.74 eV for $\alpha=-0.6$ eV (corresponding to an inward relaxation with $d_I=0.87d_H$). That is, when α changes from 0.6 eV to 0.0 eV, the deep level moves upward by 0.18 eV. This is almost equal to the predicted shift of the deep level when α changes from 0.0 eV to -0.6 eV. It appears from this that same amount outward or inward relaxation (as measured by a change in α) shifts the deep levels by about the same amount. This feature is found to be true for most cases. Further, if one considers the case of Si:C, from Fig. 3.6, one finds that this impurity is predicted to have an A_1 -symmetric deep level which changes from 0.97 eV above the valence band for $\alpha=0.6$ eV to 1.1 eV for $\alpha=0.0$, which is a shift of 0.1 eV. This shift is about half of the predicted shift for the case of Si:S. That is, for different impurities in the same material, the same change in α will shift the deep levels by different amount. In the case of Si:C, from Fig. 3.6, it can be seen that when $\alpha<-0.28$ eV (corresponding to an inward relaxation with $d_I<0.93d_H$), the deep level is predicted to be resonant with the conduction band.

3.4.3 Results for Other Materials

Figures. 3.9-3.19 display the energy E versus U diagrams for A_1 -symmetric deep levels due to substitutional impurities in GaAs, Ge, AlP, AlAs, GaSb, and InP. From these figures, it can be seen that the predicted chemical trends for the deep levels can mainly be divided into two groups. The first group displays

trends similar to the chemical trends for A_1 symmetric deep levels due to impurities on the P site in GaP shown in Fig. 3.1 and it consists of the results for most impurities on the anion site in compound materials. For example, for the A_1 deep levels produced by impurities on the As site in GaAs, the P site in AlP, the As site in AlAs, and Sb site in GaSb, they all have similar chemical trends. The second group displays trends similar to the chemical trend for deep levels due to impurities on the Ga site in GaP shown in Fig. 3.2 and it consists of the results for most deep levels due to impurities on the cation site in compound materials. Impurities in diamond structure materials also display this trend. For example, the A_1 levels produced by impurity on the Ga site in GaAs, the Al site in AlP, the Al site in AlAs, the Ga site in GaSb, In site in InP, and impurity site in Si and Ge all display this trend. The only exception occurs for A_1 levels due to impurities on the P site in InP. In Fig. 3.18, it can be seen that, in this case which does not fall into either category, deep levels are all located in the right side of the figure, the values of U are all positive, and the smaller the magnitude of U is, the closer the deep levels are to the valence band. Further, when the α is increasingly positive (corresponding to outward relaxation), the deep levels move towards the conduction band, and when α is increasingly negative (corresponding to inward relaxation), they move towards the valence band. All these features are opposite to those in Fig. 3.1.

Comparing Figs. 3.9 and 3.10, which show the A_1 -deep levels for impurities on As site and Ga site in GaAs, with Figs. 3.1 and 3.2 for impurities on the P site and Ga sites in GaP, it can be seen that the levels in these both materials are predicted to have almost the same the chemical trends and trends with varying amounts lattice relaxation (varying α). To be more specific, I show a numerical example here for the case of GaAs:As_{Ga}. That is As on Ga, an antisite defect "impurity" in GaAs. From Fig. 3.10, it can be seen that, similar to the case of GaP:P_{Ga} in Fig. 3.2, by varying α , this deep level can be made to move across a significant fraction of the band gap. Specifically, this level changes from about 0.5 eV above the valence band for $\alpha=1.0$ eV (corresponding to an outward relaxation with $d_I=1.5 d_H$) to about 0.95 eV for $\alpha=0.0$, and to about 1.48 eV for $\alpha=-1.0$ eV (corresponding to an inward relaxation with $d_I=0.80d_H$). Thus, as α varies between 1.0 eV and -1.0 eV, this deep level is predicted to have a total shift of about 0.98 eV. This is almost equal to 0.92 eV shift of the analogous deep level for GaP:P_{Ga}.

It is also seen that the general features which I have discussed for GaP hold qualitatively for all these materials. For example, in all of the materials studied, an inward relaxation ($\alpha<0$) moves their A_1 -deep levels upward towards the conduction band, while an outward relaxation ($\alpha>0$) moves them downward towards the valence band. The only exception is the case of an impurity on P site in InP.

Figure 3.2: Energy levels of A_1 symmetry produced by an impurity substitutional for Ga in GaP. The remainder of the interpretation is as in Fig.3.1.

Figure 3.3: Energy levels of T_2 symmetry produced by an impurity substitutional for P in GaP. The abscissa is the diagonal part of T_2 state defect potential U_{T_2} , and p is a shorthand notation for T_2 symmetry. The sp^3 -bonded impurities are shown at the top of the figure at the values of U_{T_2} . The $\alpha = 1.0, 0.5, 0.0$, and -0.5 eV correspond to the host-bond-length to impurity-bond-length ratios d_H/d_I of 1.7, 1.4, 1.0, 0.3, respectively. The remainder of the interpretation is as in Fig. 3.1.

Figure 3.4: Energy levels of T_2 symmetry produced by an impurity substitutional for Ga in GaP. The remainder of the interpretation is as in Fig.3.3.

Figure 3.5: Energy levels of A_1 symmetry produced by N and O substitutional for P in GaP as a function of d_I/d_H . The abscissa is the ratio d_I/d_H . The ordinate is the band-gap energy with the zero of energy equal to the top of the valence band. Since d_I/d_H is a measure of the nearest-neighbor-lattice relaxation around the impurity, this figure gives the dependence of the deep levels on this relaxation.

Figure 3.6: Energy levels of A_1 symmetry produced by a substitutional impurity in Si. The $\alpha=0.6$ -, 0.3 -, 0.0 -, -0.3 -, and -0.6 -eV results are shown, respectively, as dashed, dotted, solid, chained, and dotted-dashed curves. These values of α correspond to impurity-bond-length to host-bond-length ratio d_I/d_H of 1.21, 1.09, 1.00, 0.93, and 0.87, respectively. The remainder of the interpretation is as in Fig.3.1.

Figure 3.7: Energy levels of T_2 symmetry produced by a substitutional impurity in Si. The $\alpha = 0.6$ -, 0.3 -, 0.0 -, -0.3 -, and -0.6 -eV corresponds to host-bond-length to impurity-bond-length ratio d_H/d_I of 0.7 , 0.8 , 0.0 , 1.5 , and $3i$ (meaningless), respectively. The remainder of the interpretation is as in Fig.3.3.

Figure 3.8: Energy levels of A_1 symmetry produced by Te, Se, and S in Si as a function of d_I/d_H . The remainder of the interpretation is as in Fig. 3.5.

Figure 3.9: Energy levels of A₁ symmetry produced by an impurity substitutional for As in GaAs. The $\alpha=1.0$ -, 0.5 -, 0.0 -, -0.5 -, and -1.0 -eV correspond to the ratio d_I/d_H of 1.53, 1.20, 1.00, 0.90, and 0.81, respectively. The remainder of the interpretation is as in Fig.3.1.

Figure 3.10: Energy levels of A₁ symmetry produced by an impurity substitutional for Ga in GaAs. The remainder of the interpretation is as in Fig.3.9.

Figure 3.11: Energy levels of A_1 symmetry produced by a substitutional impurity in Ge. The $\alpha = 0.6$ -, 0.3 -, 0.0 -, -0.3 -, -0.6 -eV correspond to the ratio d_I/d_H of 1.23, 1.11, 1.00, 0.92, and 0.86, respectively. The remainder of the interpretation is as in Fig.3.1.

Figure 3.12: Energy levels of A₁ symmetry produced by an impurity substitutional for P in AlP. The $\alpha=1.0$ -, 0.5 -, 0.0 -, -0.5 -, and -1.0 -eV correspond to the ratio d_I/d_H of 1.47, 1.17, 1.00, 0.91, and 0.83, respectively. The remainder of the interpretation is as in Fig.3.1.

Figure 3.13: Energy levels of A_1 symmetry produced by an impurity substitutional for Al in AlP. The remainder of the interpretation is as in Fig.3.12.

Figure 3.14: Energy levels of A₁ symmetry produced by an impurity substitutional for As in AlAs. The $\alpha=1.0$ -, 0.5 -, 0.0 -, -0.5 -, and -1.0 -eV correspond to the ratio d_I/d_H of 1.52, 1.18, 1.00, 0.88, and 0.79, respectively. The remainder of the interpretation is as in Fig.3.1.

Figure 3.15: Energy levels of A_1 symmetry produced by an impurity substitutional for Al in AlAs. The remainder of the interpretation is as in Fig.3.14.

Figure 3.16: Energy levels of A_1 symmetry produced by an impurity substitutional for Sb in GaSb. The $\alpha=1.0$ -, 0.5 -, 0.0 -, -0.5 -, and -1.0 -eV correspond to the ratio d_I/d_H of 1.70, 1.22, 1.00, 0.87, and 0.77, respectively. The remainder of the interpretation is as in Fig.3.1.

Figure 3.17: Energy levels of A_1 symmetry produced by an impurity substitutional for Ga in GaSb. The remainder of the interpretation is as in Fig.3.16.

Figure 3.18: Energy levels of A_1 symmetry produced by an impurity substitutional for P in InP. The $\alpha=1.0$ -, 0.5 -, 0.0 -, -0.5 -, and -1.0 -eV correspond to the ratio d_I/d_H of 1.26, 1.11, 1.00, 0.92, and 0.85, respectively. The remainder of the interpretation is as in Fig.3.1.

Figure 3.19: Energy levels of A_1 symmetry produced by an impurity substitutional for In in InP. The remainder of the interpretation is as in Fig. 3.18.

CHAPTER IV

A SIMPLE MODEL TO CALCULATE THE AMOUNT OF NEAREST-NEIGHBOR LATTICE RELAXATION

In the last chapter, I predicted results for the trends in deep levels as a function of α , which was the off-diagonal matrix element of the defect potential. In those calculations, α was considered as a parameter and the variation of the deep levels with varying α was predicted. For a particular impurity, α takes the form given by Eq. (3.9). Thus, in order to calculate α for a particular impurity in a particular host and to predict the deep levels for this impurity, the bond lengths d_I and d_H must be specified. The host bond length d_H is well known for all of the common semiconductors and experimental data can, thus, be used for this purpose.⁵⁷ By contrast, the determination of the impurity-host bond length d_I is more difficult. For some impurities in some semiconductors, it might be possible to infer these bond lengths experimentally.⁵⁸ However, for most of impurities of interest, no experimental data exists which can be used for this purpose. In this chapter, I present a simple model for calculating d_I , which utilizes the concept of covalent radius,^{40,57} originally proposed by Pauling.⁵⁹ In the next chapter, I will develop a more accurate and general formalism to compute d_I based on a molecular dynamics technique.

In this simple model, I assume that

$$d_I = r_I - r_H, \quad (4.1)$$

where r_I and r_H are, respectively, the covalent radii of the impurity atom and the nearest-neighbor-host atom. Such radii are tabulated for most atoms in Ref. 40 and 57. I believe that Eq. (4.1) is a reasonable assumption for a number of reasons. First, a similar assumption for the host crystal, which is

$$d_H = r_H^a - r_H^c, \quad (4.2)$$

where r_H^a and r_H^c are, respectively, the anion and the cation host atom covalent radii, yields the host bond lengths d_H within 1% of the experimental values. Second, the d_I computed by Eq. (4.1) are within 5% of the experimental data for the appropriate material (if it exists) formed from the impurity atom-host atom molecular unit. Table 4.1 shows the results obtained using Eqs. (4.1) and (4.2) for some semiconductors and impurities in which I am interested. In addition, molecular dynamics calculations, which will be discussed in the next chapter, yields impurity-host bond lengths d_I within 10% of those predicted by Eq. (4.1) for many impurity-host systems (with the exceptions discussed below). Finally, the values of d_I obtained by Eq. (4.1) are also within 5% of those obtained in the valence force model of Martins and Zunger.⁴⁸

Using the experimental data for d_H from Table 4.1 and the d_I computed by Eq. (4.1), the values of α_{A_1} and α_{T_2} can be computed from Eq. (3.9). Table 4.2

displays these results for various impurities in 8 semiconductors. One can, thus, predict the deep levels for A_1 - and T_2 -symmetric states including the effects of lattice relaxation using this table along with Figs. 3.1-3.19. The positions of deep levels for particular impurities in the band gap can be predicted by using the α_i from Table 4.2 and fixing U_i for that impurity in the appropriate figure. From this table, it can be also seen that $|\alpha_{A_1}|$ is always larger than the corresponding $|\alpha_{T_2}|$ by a factor of 3.5. This is because, in Eq. (3.9), $|C_{A_1}|=3.5|C_{T_2}|$. This means that, for all systems, the effects of lattice relaxation are greater for A_1 -symmetric states than for T_2 -symmetric states. Furthermore, most of experimental data on deep levels produced by substitutional impurities in the materials in which I am interested is available for A_1 -symmetric states only. For these reasons I mainly discuss A_1 -symmetric deep levels in this dissertation.

I note, however, that T_2 symmetric deep levels are very important for vacancies in semiconductors.^{50,51} For example, a vacancy in Si will produce both A_1 - and T_2 -symmetric deep levels.^{50,51} Further, results obtained by self-consistent Green's function methods show that these T_2 -symmetric vacancy levels are also sensitive to lattice relaxation.^{50,51} In addition, as already noted, since they are orbitally degenerate, T_2 -symmetric levels will be expected to display Jahn-Teller distortions under the relaxation of the host atoms.⁵³ Since I only discuss deep levels produced by substitutional impurities and breathing

mode distortions in this dissertation, I will not discuss the problems of T_2 symmetric states any further.

It is worth discussing a very interesting and special case of an oxygen (O) impurity substitutional for P in GaP when one uses the above model to compute d_I . For this case, GaP:O, one finds from Eq. (4.1) that $d_I=1.92$ Å, similar to the Ga-O bond length in Ga_2O_3 .⁵⁷ This thus corresponds to an inward relaxation of the nearest-neighbor Ga atoms. However, Baraff et al. have performed calculations using a pseudopotential Green's function technique for this case and they found that the nearest-neighbor Ga atoms relax away from the oxygen impurity instead of inward.⁶¹ Later, Morgan investigated this problem in more detail and gave a more physical discussion of Baraff's results.⁶² He pointed out that the Ga atoms should relax away from oxygen impurity due to the fact that O is a very electronegative atom in GaP. In addition, due to the small radii of the O orbital in comparison with those of Ga, there is a very small overlap between the Ga and O orbital. Thus, the Ga-O bond is very weak and the nearest-neighbor Ga atoms are pulled away by the second nearest-neighbor atoms.⁶² Morgan estimated that the nearest-neighbor Ga-O bond length in GaP:O is about 0.85 Å larger than that in Ga_2O_3 , or a $d_I=2.77$ Å which corresponds to an outward relaxation.⁶² The molecular dynamics calculation, which I will discuss in the next chapter, yields $d_I=2.78$ Å. It thus tends to support Morgan's model⁶² and Baraff's theory.⁶¹ Since GaAs has a similar

electronic structure as GaP, one can expect that this discussion for GaP:O should also be qualitatively correct for GaAs:O. Using the simple model discussed here, the bond length of Ga-O in GaAs:O is also 1.92 Å, which corresponds to an 0.53 Å inward relaxation. However, from the molecular dynamics calculation discussed below, this bond length is predicted to be 2.73 Å, which corresponds to an 0.28 Å outward relaxation. Thus, on the basis of this calculation, one can conclude that the case of GaAs:O is indeed similar to the case of GaP:O.

Comparison of the molecular dynamics calculations for d_I , which will be discussed in the next chapter, with that from the simple covalent radius model discussed here shows that this simple model can, with a few exceptions like GaP:O, easily be used to determine the directions of the relaxation. Further, it usually gives the magnitude of the relaxation to within about 10% for many impurities in various materials. Of course, this simple model can only include the effects of nearest-neighbor-lattice relaxation. In order to include the effects of higher neighbors, one must use the method I will discuss below (Chapters V and VI), the molecular dynamics approach.

Table 4.1: Covalent radii and the bond lengths calculated from them. All quantities are in Å.

system	$r_H(\text{cation})^a$	$r_H(\text{anion})^a$	d_H	
			cal.	exp. ^b
GaP	1.25	1.10	2.35	2.36
GaAs	1.25	1.21	2.46	2.45
GaSb	1.25	1.41	2.66	2.64
GaN	1.25	0.70	1.95	1.95
AlP	1.25	1.10	2.35	2.37
AlAs	1.25	1.21	2.46	2.44
AlSb	1.25	1.41	2.66	2.66
InP	1.50	1.10	2.60	2.54
InAs	1.50	1.21	2.71	2.62
C	0.77	0.77	1.54	1.54
Si	1.17	1.17	2.34	2.35
Ge	1.22	1.22	2.44	2.45
impurity-host			d_I	
system			cal.	exp.
GaAs:In	1.50	1.21	2.71	2.59 ^c
InAs:Ga	1.25	1.21	2.46	2.47 ^c

a. Ref. 60

b. Ref. 57

c. Ref. 58

Table 4.2: Bond lengths, covalent radii, and parameters α_{A_1} and α_{T_2} for various impurities in 8 semiconductors.

system	$d_H(\text{\AA})^a$	$r_H(\text{\AA})^b$	$r_I(\text{\AA})^b$	$d_I(\text{\AA})$	$\alpha_{A_1}(\text{eV})$	$\alpha_{T_2}(\text{eV})$
GaP:N	2.36	1.26	0.70	1.96	-0.85	0.24
GaP:O ^c		1.26	0.66	1.92	-0.96	0.27
GaP:O ^d		1.26	1.51	2.77	0.52	-0.15
GaP:P _{G_a}		1.10	1.10	2.20	-0.28	0.08
GaP:Ge		1.10	1.22	2.32	-0.07	0.02
GaP:Sb		1.26	1.36	2.62	0.36	-0.10
GaP:C		1.26	0.77	2.03	-0.66	0.19
Si:S	2.35	1.17	1.04	2.21	-0.25	0.07
Si:Se			1.14	2.31	-0.07	0.02
Si:Te			1.32	2.49	0.21	-0.06
Si:N			0.70	1.87	-1.10	0.31
Si:C			0.77	1.94	-0.89	0.25
Ge:S	2.44	1.22	1.04	2.26	-0.31	0.09
Ge:Se			1.14	2.36	-0.14	0.04
Ge:Te			1.32	2.54	0.12	-0.03
GaAs:O	2.45	1.26	0.66	1.92	-1.10	0.31
GaAs:As _{G_a}	2.45	1.21	1.21	2.42	-0.04	0.01
AlP:N	2.37	1.25	0.70	1.95	-0.89	0.25
AlAs:N	2.44	1.25	0.70	1.95	-0.99	0.28
InP:Ga	2.54	1.10	1.25	2.35	-0.27	0.08
GaSb:In	2.64	1.41	1.50	2.91	0.27	-0.08

a. Ref. 57

b. Ref. 40, 60

c. Without correction from Ref. 62

d. With correction from Ref. 62

CHAPTER V

MOLECULAR DYNAMICS FORMALISM FOR NEAREST-NEIGHBOR LATTICE RELAXATION

In order to develop a more accurate and general model to calculate the effects of lattice relaxation, one must consider the entire process in more detail. As is well known, a defect in a semiconductor will interact with the surrounding host atoms, the lattice will be distorted, and the surrounding atoms will be displaced.³⁷ That is, these atoms will experience a net force and move either inward or outward under this force until they achieve a new configuration where that force is zero. If one can accurately determine this configuration, one can obtain an accurate impurity-host bond length d_I . This can then be used in the formalism discussed in Chapter III to determine the deep levels produced by that defect.

In this chapter, I discuss a formalism by which this bond length d_I can be determined using forces derived (mostly) from electronic structure along with standard molecular dynamics techniques. I begin with a discussion of the form of the forces. Again, for simplicity, I only consider the nearest-neighbor relaxation around the impurity in this chapter. This approximation will be modified in the next chapter where both nearest- and second-neighbor relaxation is considered.

5.1 Theory

For an ideal impurity, the four nearest-neighbor-host atoms remain in their perfect crystal positions. In a more realistic treatment, these atoms experience a net force and the lattice distorts to a new configuration where that net force is zero. The total force acting on each of these nearest-neighbor-host atoms can be divided into attractive and repulsive parts, so that it can be written schematically as

$$F_x = F_x^a + F_x^r, \quad (5.1)$$

where the subscript x is the impurity-host atomic bond direction, and F_x^a and F_x^r represent, respectively, the attractive and repulsive parts of the force. Since in the present chapter, I only consider the relaxation of nearest-neighbor atoms around an impurity in tetrahedrally symmetric materials, there are four forces between those atoms and the impurity. These are independent of each other along the four impurity-host atomic bond directions in a unit cell. Further, from the fact that I consider only symmetry conserving distortions, the net force acting on the impurity equals zero for all time, so that the impurity will stay at the origin.

The origin of F_x^r is the repulsion between electrons in overlapping states. I compute it from a pair potential based on Harrison's model.⁶³ Following this model, the repulsive pair potential $V_0(d)$ has the form as

$$V_0(d) = -2SV_2. \quad (5.2)$$

where V_2 is called covalent energy by Harrison⁶³ and has properties similar to the transfer matrix elements of the host Hamiltonian.⁴⁰ That is, V_2 is also proportional to the inverse bond length squared. In Eq. (5.2), d is the bond length, and S is the overlap integral of the coupled orbitals. In Harrison's model, S is calculated using $V_2 = K\bar{\epsilon}S$, where $\bar{\epsilon}$ is the average energy of the hybrid state and K is a constant depending on the material. Equation (5.2) thus becomes

$$V_0(d) = -2V_2^2/|K\bar{\epsilon}|. \quad (5.3)$$

One can see easily from Eq. (5.3) and the fact that $V_2 \propto 1/d^2$, that $V_0 \propto 1/d^4$. I compute F_x^r by using Eq. (5.3) with $F_x^r = -dV_0/dx$, so that F_x^r has the form

$$F_x^r = -A/x^5, \quad (5.4)$$

if the bond length d is replaced by the variable x . Here A is a constant which, in Harrison's model, has the form

$$A = -\frac{85.2}{K} \left[\frac{\hbar^2}{m} \right]^2 \frac{1}{\bar{\epsilon}}, \quad (5.5)$$

where $\hbar$ is Planck's constant and m is the mass of electron.⁶³ However, I will determine this constant by another method which I think is more natural and accurate. This will be discussed after a discussion of the attractive part of the force.

In my formalism, the attractive part of the force, F_x^a , which originates from the occupied one-electronic levels, is computed from the electronic structure by use of the Hellmann-Feynman theorem.⁶⁴ According to this theorem, if x is a component of the position coordinate of an atom, the x component of the force on that atom can be computed from the derivative of the total quantum mechanical energy E_{tot} as

$$F_x^a = -\frac{\partial E_{tot}}{\partial x} = -\frac{\partial}{\partial x} \int_{-\infty}^{E_f} E \rho(E) dE, \quad (5.6)$$

where E_f is the Fermi energy, and $\rho(E)$ is the electronic density of states in the presence of the impurity. The latter quantity $\rho(E)$ is intimately related to the band structure of the material, and can be computed using a Green's function technique.⁴² Formally, it is given as

$$\rho(E) = -\frac{1}{\pi} \text{Im} \text{Tr} G(E), \quad (5.7)$$

where Im means the imaginary part, Tr means the trace, and $G(E)$ is the Green's function matrix, which includes the effects of the impurity. In my formalism, it can be found from the Green's function matrix of the perfect crystal $G^0(E)$ and the defect potential matrix V , which are discussed in Chapter III, using the Dyson equation

$$G = G^0 + G^0 V G = (I - G^0 V)^{-1} G^0. \quad (5.8)$$

By combining Eqs.(5.6), and (5.7), the attractive force can be written as

$$F_z^a = \frac{1}{\pi} \text{ImTr} \int_{-\infty}^{E_f} E \frac{\partial G}{\partial x} dE. \quad (5.9)$$

From the Dyson equation (5.8), one has

$$\frac{\partial G}{\partial x} = \frac{\partial G^0}{\partial x} (VG) + G^0 \frac{\partial V}{\partial x} G + G^0 V \frac{\partial G}{\partial x}. \quad (5.10)$$

Because G^0 is independent of x , this becomes

$$\frac{\partial G}{\partial x} = G^0 \frac{\partial V}{\partial x} G + G^0 V \frac{\partial G}{\partial x}, \quad (5.11)$$

or

$$(I - G^0 V) \frac{\partial G}{\partial x} = G^0 \frac{\partial V}{\partial x} G. \quad (5.12)$$

Then

$$\frac{\partial G}{\partial x} = (I - G^0 V)^{-1} G^0 \frac{\partial V}{\partial x} G = G \frac{\partial V}{\partial x} G, \quad (5.13)$$

where the last step follows from Eq. (5.8). With this result, Eq. (5.9) becomes

$$F_z^a = \frac{1}{\pi} \text{ImTr} \int_{-\infty}^{E_f} E G \frac{\partial V}{\partial x} G dE. \quad (5.14)$$

For the host crystal in the absence of the impurity, each atom is fixed at its perfect crystal equilibrium position and it must be true that $F_z^a(d_H) = -F_z^r(d_H)$ so that the total $F_z = 0$. By using this condition along with Eqs. (5.4) and (5.14) in the absence of the impurity, the constant A in Eq. (5.4) can be determined. I have found that this constant A is dependent on the material. Table 5.1 shows the values of this constant in various materials. These values differ by about

10% from those determined by Eq. (5.5). When an impurity is placed in the host crystal, $F_x^a(d_I)$ and $F_x^r(d_I)$ will, in general, no longer be equal, so that the total $F_x \neq 0$ and the nearest-neighbor-host atoms around this impurity will move under the net force.

Using Eqs. (5.4) and (5.14) and beginning with the nearest-neighbor-host atoms in their perfect crystal positions, one can calculate the motion of each of these atoms for a small time interval δt using Newton's second law along with standard "molecular dynamics" methods.⁶⁵ In this way, new atomic positions can be determined and a new defect potential matrix V (that is new off-diagonal elements, new α) and a new force can be computed. This process can be repeated for successive intervals δt until the net force acting on each nearest-neighbor-host atom approaches zero. Then, one can determine d_I and V (or α) for the relaxed lattice. The magnitude and direction of the relaxation depend on the competitions between the attractive and the repulsive parts of the force. If the initial net force is large, one can expect a large amount relaxation. If the initial net force is negative, an inward relaxation will occur, while if the initial net force is positive, an outward relaxation will occur.

In order to obtain a clearer physical picture of this approach, I consider a numerical example which will give the orders of magnitude of the relevant quantities. For this case, I assume an impurity is substitutional in a Si host crystal, so that the nearest-neighbor Si atoms around the impurity will relax to

new equilibrium positions under the net force due to the impurity from their perfect crystal positions. For a very small interval δt , I assume that the net force is a constant, so that the relaxed distance x along one of the bond lengths is

$$x = \frac{1}{2}a(\delta t)^2 = \frac{1}{2}\frac{F_z}{m}(\delta t)^2, \quad (5.15)$$

where F_z is the net force, m is the mass of a Si atom, and a is the acceleration due to F_z . The initial force has a typical order of magnitude about $1\text{eV}/\text{\AA} = 1.602 \times 10^{-9}\text{N}$, (although sometimes it can be as much as 10 times this value).³⁷ The relaxed distance x is typically $0.1\text{\AA}$ in the first δt due to this force. Since the mass m of a Si atom is $28.086\text{ au} = 4.66 \times 10^{-26}\text{kg}$, from Eq. (5.15), one can obtain $\delta t \approx 2.4 \times 10^{-14}\text{s}$. In practical calculations, I have found that, while the best choice of δt depends on the particular case, it is always of this order of magnitude. Since the acceleration $a = F_z/m$, using those values of F_z and m , one can obtain the rather large initial acceleration of $a \approx 3.435 \times 10^{16}\text{m/s}^2$. Letting the initial velocity be $v_0 = a\delta t$, this yields $v_0 \approx 8 \times 10^2\text{m/s}$. Thus, even for a very small initial force, both the initial acceleration and velocity are still very large. However, as discussed below, I find that the acceleration and velocity decrease rapidly with time as does the net force.

5.2 Results

In Figs. 5.1 and 5.2, I present the results for the time dependence both of the magnitude of the total force along an impurity atom-host atom bond and of the

bond length for the N and O substitutional for P in GaP. In the results presented in these figures, only the relaxation of the nearest neighbors has been considered, so the total force shown is that between the impurity (N or O) and one of the nearest-neighbor Ga atoms along an impurity-host atomic bond. Under this force, the Ga atoms move inward or outward with respect to the impurity, and the impurity stays at its original position. In these figures, the force and d_I are plotted versus $t^*=t/(\delta t)$, where $\delta t=0.35\times 10^{-14}$ s for N and $\delta t=0.8\times 10^{-14}$ for O. This choice of δt was obtained by trial and error. A smaller δt uses considerably more computer time to achieve similar results and a larger value can cause an "overshoot" of the final equilibrium position and an oscillatory behavior of d_I versus t^* .

These figures reveal the details of the dynamics of the process of lattice relaxation, and several interesting features can be found by inspection of them. First, the magnitude of the initial force between the N and the nearest-neighbor Ga atoms is quite different than that between the O and the Ga atoms. A N impurity causes the magnitude of the initial force to be about 21 eV/Å, but an O impurity causes this initial force to have the much smaller value of only about 4.6 eV/Å. The difference of the size of the initial forces will obviously affect the relaxation time, $t=t^*(\delta t)$. In Fig. 5.1 for GaP:N, after about 16 time steps, the force approaches zero, giving a relaxation time about 0.06 ps. However, from Fig. 5.2 for GaP:O, one can see that, after about 27 time steps, the force

approaches zero, corresponding to a relaxation time about 0.22 ps, which is much larger than the time for GaP:N.

From Fig. 5.1, one can also see that the initial force produced by N in GaP causes an inward relaxation, because the atomic bond length of Ga-N at the equilibrium position is smaller than the GaP host bond length. From that figure, as the Ga atoms approach their new equilibrium positions, the Ga-N bond length d_I approaches about 2.15 Å, which gives an inward relaxation distance $\Delta d = d_I - d_H = -0.21$ Å, or a change of about 9% in comparison with the 2.36 Å GaP host bond length. By contrast, the initial force produced by O in GaP causes an outward relaxation, because the bond length of Ga-O at the equilibrium position is larger than the host bond length. I note that an outward relaxation for GaP:O contradicts the analysis based on the covalent radius model discussed in the last chapter. However, it is in qualitative agreement with Morgan's model.⁶² From Fig. 5.2, when the Ga atoms approach their new equilibrium positions, the bond length of Ga-O is 2.78 Å. In this case, the relaxation distance Δd is 0.42 Å, or a change about 18% of the GaP host bond length. The qualitative differences between the results for N and O in GaP are partially due to the fact that O is much more electronegative than N and partially due to the small radii of the O orbitals in comparison with those for Ga, which cause a small overlap between the Ga and O.⁶² Thus, the Ga-O bond is much weaker than the Ga-N bond, so that the Ga atoms relax away from the

O atoms. The fact that the magnitude of the initial force between Ga and N is almost five times as large as that between Ga and O also supports this conclusion.

It is also of interest to study the relationship between the distortion distance, $\Delta d = d_I - d_H$, and the force. In Fig. 5.3, I show results for the total force on one of the four Ga nearest-neighbors as a function of Δd for N and O substitutional for P in GaP. In agreement with Figs. 5.1 and 5.2, it can be seen that N induces an inward relaxation of the nearest-neighbor Ga atoms by about 0.21Å. By contrast, O in GaP induces an outward relaxation by about 0.42eV.

From Fig. 5.2, it can be seen that, as a function of time, the magnitude of the force in the case of GaP:O increases to a maximum value and then decreases to zero. This is different than the case of GaP:N where a smooth decrease in the force with time occurs. This behavior can be understood by noting that the process of lattice relaxation is a competition between the attractive force and the repulsive force. Of course, in the final results of this competition, the net force approaches zero and the atoms approach new equilibrium positions. However, during the process, the net force at a given time step may be either larger or smaller than that at the previous step, depending on the particular case. In my calculations for other impurities in other materials, the curves of force versus time which are similar to both the cases of GaP:N and GaP:O were found.

Figure 5.4 displays a similar diagram to those of Figs. 5.1 and 5.2 for a S substitutional impurity in Si. In that figure, both the magnitude of the force and the bond length d_I are plotted versus $t^*=t(\delta t)$, and I have chosen $\delta t=0.35\times 10^{-14}\text{s}$. From that figure, it can be seen that the S in Si induces an inward relaxation, since the final bond length of $d_I=2.24\text{ \AA}$ is smaller than the Si host bond length $2.35\text{ \AA}$. The corresponding relaxation time is about 0.09s , and the inward relaxation distance Δd is $-0.11\text{ \AA}$ or 5% of the $2.35\text{ \AA}$ Si bond length.

Unfortunately, no experimental data on the relaxation time and distance for these impurities in GaP and Si exists (or for any impurity in any material) to my knowledge. However, the self-consistent Green's function approaches obtain the same orders magnitude for the force and similar trends of the force versus relaxation distance Δd .^{50,51}

The method discussed above can be used to deal with other impurities in other materials. I have used it to calculate the relaxation distance Δd and the impurity-host atomic bond length d_I for various impurities in GaP, Si, GaAs, and Ge. These results are presented in Table 5.2. For comparison, the results for Δd and d_I for the same impurities in these materials calculated from the covalent radius model discussed in the previous chapter are also presented in this table. It can be seen from the table that the results for Δd and d_I from the molecular dynamics approach are usually in qualitative agreement with those from the covalent radius model. In particular, in all cases considered in

Table 5.2, both models predict the same inward or outward relaxation except for the cases of O in GaP (without Morgan's correction) and O in GaAs. Also, the predictions for d_I from these two models are usually within 10% of each other. I will show below that, if d_I from the molecular dynamics approach is used in the deep level formalism, it will produce better results for deep levels than d_I from the covalent radius model in comparison with experimental data.

From Table 5.2, it can be seen that the minimum Δd obtained by the molecular dynamics approach is $-0.08\text{\AA}$ for the case of GaP:P_{Go}. The relaxed bond length in this case is only 3.4% smaller than the host bond length. However, the maximum Δd shown in Table 5.2 is $0.42\text{\AA}$ for the case of GaP:O, where the relaxed distance is about 18% larger than the host bond length. Even though these cases are for the same material, the relaxed distance Δd is very different. Another example is the case of GaP:Ge, where Δd is $-0.12\text{\AA}$, about 5% of GaP bond length. The first reason for these differences, of course, is the fact that different impurities have different covalent radii, so that they will produce different relaxation distances. However, in some cases, the atomic energy difference between the impurity and the host atom which is replaced plays a more important role in the effects of lattice relaxation. For example, oxygen has a very small covalent radius. However, when an oxygen is substitutional for P in GaP, as was discussed above, the Ga atoms will relax away from it instead towards it. As also discussed above, this is due to the large electronegativity of

O in comparison to P, which weakens the Ga-O bond. Another example is the case of Si:Se. Although Se has almost the same covalent radius as Si, Se and Si have a large difference of atomic energies. Thus, Se in Si will produce a quite large attractive force, so that the inward relaxation distance Δd induced by Si:Se is quite large. In these two examples, the covalent radius approximation fails to predict the correct results. This fact confirms that a molecular dynamics approach is necessary.

5.3 Total Energy Versus Impurity Bond Length

In the previous sections in this chapter, I have used molecular dynamics method to determine the impurity bond length d_I . This can also be done using a total energy approach. That is, in a perfect crystal system, the total electronic energy has a minimum value, the total force on each atom vanishes. However, this total energy will change when an impurity is placed in the host crystal, and, after relaxation, it will approach a new minimum value where the total force vanishes again. If one can calculate the total energy as a function of the bond length between the impurity and the nearest-neighbor host atoms, the impurity-bond length d_I at the new equilibrium configuration (corresponding to a new minimum energy value) can then be determined. As a test of the molecular dynamics formalism developed in this chapter, I present an example in this section which uses this total energy approach to determine d_I . I find that the result for d_I obtained using this approach is almost the same as that

obtained by the molecular dynamics method. In particular, the percent difference of d_I obtained from these two methods differs less than 1%. This result confirms the results discussed in the last section.

The interaction between two atoms can be regarded following the discussions in Sec. 5.1 as consisting of (1) an attractive bonding interaction involving the one-electron energies E_{el} and (2) a repulsive interaction due to overlap of electron states. The total energy thus can be modeled by

$$E_{Tot} = E_{el} + E_{rep}. \quad (5.16)$$

Here E_{el} is the sum of the one-electron energies E in the occupied states, and has the form

$$E_{el} = \int_{-\infty}^{E_f} E \rho(E) dE, \quad (5.17)$$

where E_f is the Fermi energy, and $\rho(E)$ is the electronic density of states in the presence of the impurity which is given by Eq.(5.7). Thus,

$$E_{el} = \frac{-1}{\pi} \text{ImTr} \int_{-\infty}^{E_f} E \rho(E) dE. \quad (5.18)$$

Again using Harrison's overlap interaction model,⁶³ E_{rep} can be computed from a pair potential as

$$E_{rep} = A'/d^4, \quad (5.19)$$

where A' can be determined from the Values of A .

Figure 5.5 illustrates the results of a calculation of the total energy versus d_I for an O substitutional for P in GaP. In this figure, the abscissa is $\Delta d = d_I - d_H$,

and the ordinate is the total energy computed by Eq.(5.16). It can be seen that the total energy has a minimum value at $\Delta d=0.41\text{\AA}$, which corresponds to $d_I=2.77\text{\AA}$. This value is almost the same as the value of $d_I=2.78\text{\AA}$ calculated by the molecular dynamics method. The molecular dynamics results are, thus, consistent with the total energy results.

Table 5.1: Constant A for various materials

system	A (eV(Å) ⁴)
Si	199
GaP	152
GaAs	146
Ge	190

Table 5.2: The host-bond length d_H , the impurity-host-bond length d_I and the relaxation distance Δd for various impurities in GaP, Si, GaAs and Ge. All distances are in Å.

system	d_H	d_I		Δd	
		molecular dynamics	covalent radius	molecular dynamics	covalent radius
GaP:N	2.36	2.15	1.96	-0.21	-0.4
GaP:O		2.78	1.92 ^a	0.42	-0.44
GaP:O			2.77 ^b		0.41
GaP:P _{Ga}		2.28	2.22	-0.08	-0.14
GaP:Ge		2.24	2.32	-0.12	-0.04
GaP:Se		2.22	2.24	-0.14	-0.12
Si:S	2.35	2.23	2.21	-0.12	-0.14
Si:Se		2.03	2.31	-0.32	-0.04
Si:Te		2.60	2.49	0.25	0.14
Si:C		1.98	1.94	-0.37	-0.41
GaAs:O	2.45	2.73	1.92	0.28	-0.53
GaAs:As _{Ga}		2.39	2.42	0.04	0.07
Ge:S	2.44	2.32	2.26	-0.12	-0.18
Ge:Se		2.04	2.36	-0.4	-0.08
Ge:Te		2.88	2.54	0.44	0.1

a. Without Morgan's correction. Ref. 62

b. With the correction. Ref. 62

Figure 5.1: Time dependence of the magnitude of the total force (solid curve) along an impurity-atom host-atom bond and of the bond length (dashed curve) for N substitutional for P in GaP. The abscissa is the time step $t^* = t/\delta t$, where $\delta t = 0.35 \times 10^{-14} \text{ s}$. The left ordinate is the magnitude of the total force, and the right ordinate is the bond length.

Figure 5.2: Time dependence of the magnitude of the total force and the bond length for O substitutional for P in GaP. Here $t^* = t/\delta t$, where $\delta t = 0.8 \times 10^{-14} \text{ s}$. The remainder of the interpretation is as in Fig.5.1.

Figure 5.3: Force on one of the four Ga nearest neighbors as a function of distortion distance for N (dashed curve) and O (solid curve) substitutional for P in GaP. The negative values of Δd correspond to an inward relaxation, and the positive values of it correspond to an outward relaxation.

Figure 5.4: Time dependence of the magnitude of the total force (solid curve) along an impurity-atom host-atom bond and of the bond length (dashed curve) for a substitutional impurity S in Si. The remainder of the interpretation is as in Fig.5.1.

Figure 5.5: Total energy versus the change of the bond length for an O substitutional for P in GaP. The minimum value of energy indicates the change of the bond length required for a new equilibrium configuration.

CHAPTER VI

FORMALISM FOR INCLUDING THE EFFECTS OF BOTH FIRST- AND SECOND-NEIGHBOR RELAXATIONS

In the previous chapters, I have only considered the relaxation of the nearest-neighbor host atoms around an impurity. Using the molecular dynamics approach, it is straightforward to extend that formalism to include the relaxation of the second-neighbor atoms. However, it would be difficult to generalize the simple covalent radius model to do that. This is one of the advantages of the molecular dynamics approach. To develop such a formalism, one begins by considering a cluster consisting of 17 atoms (an impurity and 16 host atoms; 4 nearest-neighbor atoms and 12 second-nearest-neighbor atoms) instead of a 5 atoms cluster, as was discussed above. I remind the reader that, even though I am considering a defect cluster, due to my Green's function formalism, my calculations are done for the infinite crystal (containing this cluster).

6.1 Defect Potential

In order to easily describe the problem, I use the labeling convention for the lattice positions of each of the 17 atoms in the cluster that was defined by Ford in his dissertation.⁶⁶ These atom positions are displayed in Table 6.1, which is borrowed directly from Ford's dissertation. In that table, the nearest-neighbor

atoms of the impurity are labeled as 1, 2, 3 and 4, the second-nearest neighbors of the impurity are labeled from 5 to 16. The impurity itself is labeled as 0 and is not shown in the table. The quantity "a" in the table is the lattice constant. In Ref.66, Ford has shown that the nearest neighbors of the impurity are second neighbors each other (as is well known). In addition, he has shown that the nearest neighbors of the impurity have relationships to the impurity's second-nearest neighbors which make them either nearest neighbors, third neighbors, or fifth neighbors of these atoms. Also, he has shown that the second-nearest neighbors of the impurity have relationships among themselves which make them second neighbors, fourth neighbors, sixth neighbors, and eighth neighbors of each other. For example, the second-nearest-neighbor atoms of the impurity which are labeled by 5, 6 and 7 in Table 6.1 are the nearest-neighbors of the atom labeled by 1, and either third neighbors or fifth neighbors of other nearest neighbors of the impurity which are labeled by 2, 3 and 4. Figure 6.1 (a) illustrates the tetrahedrally symmetric geometrical relationships between the impurity (atom 0) and its nearest neighbors (atoms 1, 2, 3, and 4). Similarly, Fig.6.1 (b) shows the geometric arrangement between one of these nearest neighbors (atom 1) to the impurity and its own nearest neighbors (atom 5, 6, and 7), which are the second neighbors of the impurity. For simplicity, I have reoriented the atoms in Fig.6.1 (b), the coordinates x' , y' , and z' are thus different than those in Fig.6.1 (a). All of these relationships

between the 16 host atoms in the 17-atom cluster are presented in Table 6.3.

which is also borrowed from Ford's dissertation.⁶⁶ These relationships are needed in order to properly determine the Green's function matrix elements of the host crystal for the formalism described below.

In the case of the 17-atom cluster, Eq. (2.7) can still be used to determine the deep levels, but each submatrix in that equation, G_i^0 , V_i and I_i , is of size 17×17 instead of 5×5 . For example, the host Green's function matrix G_i^0 in this case includes the effects of 17 atoms in contrast to Eq. (3.3) where only 5 atoms are included. Thus, in effect, by considering the 17-atom cluster, the size of the defect has increased to that size. Clearly, the form of defect potential matrix which is presented by Eq. (3.2) must be modified to include the second-nearest-neighbor relaxation. For example, for an A_1 symmetric state, the form of V_{A_1} is now (for an impurity on the anion site)

$$\begin{aligned}
 V_{A_1} = & |A_1 a \vec{0} \rangle U \langle A_1 a \vec{0}| \\
 & + \alpha \sum_{\vec{d}} (|A_1 a \vec{0} \rangle \langle A_1 a \vec{d}| + |A_1 c \vec{d} \rangle \langle A_1 a \vec{0}|) \\
 & + \beta \sum_{\vec{d}, \vec{d}'} (|A_1 c \vec{d} \rangle \langle A_1 a \vec{d}'| + |A_1 a \vec{d}' \rangle \langle A_1 c \vec{d}|), \\
 & + \gamma \sum_{\vec{d}'} (|A_1 a \vec{0} \rangle \langle A_1 a \vec{d}'| + |A_1 a \vec{d}' \rangle \langle A_1 a \vec{0}|)
 \end{aligned} \tag{6.1}$$

where $\vec{d}$ and $\vec{d}'$, respectively, are the position vectors of the nearest-neighbor and the second nearest-neighbor atoms of the impurity. Here, U and α are shorthand

for U_{A_1} and α_{A_1} , which have been used in Eq. (3.2). The quantity β represents the off-diagonal element of the defect potential matrix which couples the impurity's first-neighbor atoms to those atoms in the second-neighbor shell which are nearest neighbors to them. For example, the coupling between the atom labeled by 1 and the atoms labeled by 5, 6, and 7 in Fig. 6.1 (b) is denoted by β . The quantity γ represents the off-diagonal elements of the defect potential which couple the impurity to the second-neighbor-host atoms. There are other couplings between atoms in the first-neighbor shell and those in the second-neighbor shell, which I assume are very small and can be neglected. Thus, in my approximation, the parameters β and γ represent the effects of lattice relaxation due to the second-neighbor-host atoms of the impurity. The quantity β can be calculated using a method similar to the generalization of Harrison's inverse bond length squared rule which I have used to calculate α (Eq. (3.9)). That is, in this approximation, β can be written as

$$\beta_i = -C_i \left(\frac{1}{d_{II}^2} - \frac{1}{d_H^2} \right), \quad (6.2)$$

where C_i and d_H have the same meanings as in Eq. (3.9), in my calculations, I assume that this C_i has the same numbers as in Eq. (3.9). d_{II} is the bond length between one of the impurity's nearest neighbor and one of its nearest neighbor in the second-neighbor shell of the impurity. For example, d_{II} is the bond length between atoms such as atom 1 and atom 5, 6, and 7 in Fig. 6.1 (b). The quantity γ can be easily calculated using a similar rule. However, in my

calculations, I have found that γ , which is a second-neighbor coupling energy, is very small in comparison with α and β , so it can be neglected in the calculations. I, thus, set it to zero in what follows.

6.2 Forces and Molecular Dynamics

In order to include the effects of second-neighbor relaxation, the 16 host atoms around the impurity are allowed move inward or outward simultaneously instead of only 5 atoms moving as was true for the case of the nearest-neighbor relaxation. To analyze this case, I first consider the net force acting on the second-neighbor-host atoms of the impurity. In general, one needs to consider the interactions between each these atoms and other 16 atoms (including the impurity). However, because the net force acting on these atoms is mainly induced by the changes of the bond length in tight-binding theory, one can approximately consider only the interactions between these atoms and the atoms which are bonded to them. This is analogous to keeping only α and β and neglecting all other coupling in the above discussion of the defect potential. For example, because the atom labeled by 1 is bonded to the atoms labeled by 5, 6 and 7 (see Fig. 6.1 (b)), the net force acting on each of these atoms is induced by the changes of the bond lengths between atom 1 and atoms 5, 6 and 7. From Fig. 6.1 (b), one can see that atoms 1, 5, 6, 7 and the impurity form a 5 atom cluster so that one can use a formalism similar to that discussed in the last chapter to compute the net force acting on atoms 5, 6 and 7.

In the present case, however, the form of the force acting on each of the nearest-neighbor host atoms of the impurity (atoms 1, 2, 3 and 4) needs to be modified in comparison with its form for nearest-neighbor relaxation only. Because I use a “breathing-mode” model for the relaxation, the nearest-neighbor atoms will move only along the bond directions to the impurity (inward or outward), so that one needs to compute the force components in these directions. Of course, the net forces acting on the nearest-neighbor atoms 1, 2, 3 and 4 due to the impurity are already in these directions. The formal expressions for these forces have been shown in the last chapter. However, for example, the force acting on atom 1 due to atoms 5, 6 and 7 needs to be multiplied by a factor of $\cos(\pi - \theta)$ to project it onto the bond direction between atom 1 and the impurity. Here θ is the bond angle, which is formed by, for example, the impurity, atoms 1 and 5 (see Fig. 6.1 (b)). When the host atoms are in their perfect crystal positions (the initial time of the molecular dynamics simulation), the bond angle is $\theta = 109.5$ degrees. However, the angle θ will change during the relaxation process. From lattice symmetry considerations, the components of force due to atoms 5, 6 and 7 in the direction of the bond length between the impurity and atom 1 are equal. The net force in the z direction acting on atom 1 can thus be written as

$$F_z = F_{1z} - 3F_2 \cos(\pi - \theta), \quad (6.3)$$

where F_{1z} is the net force caused by the impurity, which has the same form as the force computed in the last chapter, and F_2 is the net force produced by one of the atoms 5, 6 and 7. The latter force has the same magnitude but opposite sign as the force acting on one of the atoms 5, 6 or 7. As mentioned above, F_2 can be calculated using a method similar to that discussed in the last chapter. All forces which enter the calculations, such as F_{1z} and F_2 in Eq. (6.3) can, of course, be decomposed into attractive and repulsive parts, as in Eq. (5.1). In addition, in my formalism, each repulsive part has a form similar to that of Eq. (5.4) and each attractive part is computed from the electronic structure using the Hellmann-Feynman theorem.⁶⁴

After an analysis of the force as just discussed, and beginning with all host atoms in their perfect crystal positions, one can use standard "molecular dynamics" methods⁶⁵ to find the new equilibrium positions for 17 atoms in the cluster. This is done in essentially the same manner as was described for first-neighbor relaxation in the last chapter. From this equilibrium configuration, one can determine the nearest-neighbor-bond length d_I and the bond length d_{II} . The results for d_I and d_{II} for various impurities in GaP, Si, GaAs, and Ge are summarized in Table 6.2, and the corresponding values of α and β calculated from Eqs. (3.9) and (6.2), and the quantities $\Delta d = d_I - d_H$, and $\Delta d' = d_{II} - d_H$ are also shown in Table 6.2. From the table, it can be seen that signs of α and β are always opposite. This can be understood by noting the fact that $|\Delta d|$ is always

much larger than $|\Delta d'|$. For example, if the nearest neighbors move toward the impurity, the second neighbors will also move toward it. However, if Δd is much larger than $|\Delta d'|$, d_{II} will be larger than the host bond length d_H . Thus, α , Eq. (3.9), and β , Eq. (6.2) will have opposite signs. From Table 6.2, it can also be seen that the magnitude of α is much larger than that of β for the same system. The reason for this is again that $|\Delta d| > |\Delta d'|$. Physically, the reason that this is true is that the total force acting on a nearest-neighbor atom is much larger than that on a second-nearest-neighbor atom. From the viewpoint of tight-binding theory, this is easily understood. For the same reason, the d_I in Table 6.2 are almost same as those in Table 5.1, where only the nearest-neighbor relaxation was considered.

In order to investigate the trends in the effects of the second-neighbor atoms on deep levels, one can plot diagrams of deep level energies E versus U for varying β and α , similar to what I have done in Figs. 3.1 to 3.19. However, to do that, one needs to algebraically solve a 17×17 determinantal equation to obtain an equation analogous to Eq.(3.8), which would express U as a function of α , β , and various Green's function matrix elements. Of course, this is very difficult to do. Instead, however, for deep levels of symmetry i , one can plot curves of the determinant

$$D(E) = \det[I_i - G_i^0(E)V_i] \quad (6.4)$$

as a function of E for various fixed values of U , α , and β . The value of E where

$$D(E) = 0 \quad (6.5)$$

is, of course, the predicted deep level for those values of U , α , and β . By plotting such curves for various values of these parameters, and noting the changes in the deep level energy E which causes $D(E)$ to vanish, trends in deep levels as a function of these parameters can be explored. For example, Fig. 6.2 displays such results for $D(E)$ versus E for various combinations of α and β in the case of A_1 -symmetric levels produced by Si:Se (fixed U).

In Fig. 6.2, there are three groups of curves containing three members each. Within each group, these curves are, from left to right, dashed, solid and dotted. Each group of three curves corresponds to a different value of α . From left to right in the figure, the groups represent results for $D(E)$ with $\alpha=0.3$ eV, 0.0 eV and -0.3 eV, respectively. Within each group, the three curves correspond to three different values of β . From left to right, they are -0.3 eV, 0.0 eV and 0.3 eV. The intersections of these curves with the horizontal line at $D(E)=0.0$ gives deep levels in the band gap for the values of α and β quoted. One can see from the figure that, within each group, as β becomes more positive, the deep levels will move towards the conduction band (to the right), while as β becomes more negative, this level will move towards the valence band (to the left). One can also see from the figure that, for a similar change in both β and α , the corresponding shift in the deep levels is quite different. For example, in the right

most group ($\alpha = -0.3$ eV), when β changes from 0.0 eV to 0.3 eV, the deep level is predicted to move towards the conduction band with a shift of about 0.03 eV. Almost the same shift in the other direction is predicted when β changes from 0.0 eV to -0.3 eV for that same value of α . However, when α changes from 0.0 eV to 0.3 eV, the predicted deep level shifts by about 0.14 eV, and when α varies from 0.0 eV to -0.3 eV, the deep level shift is about 0.12 eV. Obviously, the first neighbor-matrix element α plays a more important role in the effects of lattice relaxation than does the second neighbor-matrix element β . In addition, one again should note the fact that in the practical cases listed in Table 6.2, the magnitude of α is always larger than the magnitude of β for the same impurity-host system. I have found similar results for other impurities in Si and in other materials. These facts, taken together, show that the effects of the second-neighbor relaxation on deep levels are much smaller than those of the nearest neighbors.

By taking a larger defect cluster, which contains higher-neighbor shells of the impurity, one could consider higher-neighbor atoms in the calculations using an extension of the same method discussed here. However, the discussion above lends support to the assumption that higher-neighbor relaxation should usually produce even smaller effects on the deep levels. Thus, considering the effects of the relaxation of the higher-neighbor atoms should not be necessary.

Table 6.1: The labeling convention for the nearest-neighbor and second-neighbor host atoms to the impurity. This table is borrowed from Ref. 66.

Nearest-Neighbor Atoms	
Atom Number	Lattice Position
1	$(111)a/4$
2	$(\bar{1}\bar{1}1)a/4$
3	$(1\bar{1}\bar{1})a/4$
4	$(\bar{1}1\bar{1})a/4$
Second-Neighbors Atoms	
Atom Number	Lattice Position
5	$(011)a/2$
6	$(101)a/2$
7	$(110)a/2$
8	$(\bar{1}01)a/2$
9	$(0\bar{1}1)a/2$
10	$(\bar{1}\bar{1}0)a/2$
11	$(1\bar{1}0)a/2$
12	$(0\bar{1}\bar{1})a/2$
13	$(10\bar{1})a/2$
14	$(\bar{1}10)a/2$
15	$(\bar{1}0\bar{1})a/2$
16	$(01\bar{1})a/2$

Table 6.2: Bond lengths d_I and d_{II} for various impurities in GaP, Si, GaAs and Ge, and the corresponding values of Δd , α , $\Delta d'$, and β .

system	$d_I(\text{\AA})$	Δd	$\alpha(\text{eV})$	$d_{II}(\text{\AA})$	$\Delta d'$	$\beta(\text{eV})$
GaP:N	2.15	-0.24	-0.39	2.41	0.05	0.08
GaP:O	2.78	0.42	0.53	2.28	-0.08	-0.21
GaP:P _{Ga}	2.28	-0.08	-0.14	2.40	0.04	0.06
GaP:Ge	2.24	-0.12	-0.21	2.40	0.04	0.06
GaP:Se	2.22	-0.14	-0.25	2.43	0.07	0.11
Si:S	2.23	-0.12	-0.21	2.41	0.06	0.09
Si:Se	2.03	-0.32	-0.65	2.48	0.13	0.19
Si:Te	2.60	0.25	0.35	2.28	-0.09	-0.12
Si:C	2.09	-0.26	-0.50	2.47	0.12	0.11
GaAs:O	2.73	0.28	0.34	2.36	-0.09	-0.14
GaAs:As _{Ga}	2.39	-0.06	-0.09	2.47	0.02	0.03
Ge:S	2.32	-0.13	-0.20	2.48	0.03	0.04
Ge:Se	2.06	-0.39	-0.73	2.56	0.11	0.15
Ge:Te	2.88	0.43	0.48	2.61	0.16	0.21

Table 6.3: Relationships between pairs of nearest- and second-neighbor host atoms to the impurity. This table is borrowed from Ref. 66.

Nearest- and Second-Neighbor Pairs			
Third-Neighbors			
1 and 8	2 and 5	3 and 6	4 and 5
1 and 9	2 and 6	3 and 7	4 and 7
1 and 11	2 and 11	3 and 9	4 and 8
1 and 13	2 and 12	3 and 10	4 and 10
1 and 14	2 and 14	3 and 15	4 and 12
1 and 16	2 and 15	3 and 16	4 and 13
Fifth-Neighbors			
1 and 10		3 and 5	
1 and 12		3 and 8	
1 and 15		3 and 14	
2 and 7		4 and 6	
2 and 13		4 and 9	
2 and 16		4 and 11	
Second-Neighbor Pairs			
Second-neighbors			
5 and 6	6 and 11	9 and 10	12 and 13
5 and 7	7 and 13	9 and 11	12 and 15
5 and 8	7 and 16	10 and 12	13 and 16
5 and 14	8 and 9	10 and 15	14 and 15
6 and 7	8 and 10	11 and 12	14 and 16
6 and 9	8 and 14	11 and 13	15 and 16
Fourth-Neighbors			
5 and 9	6 and 13	8 and 15	10 and 14
5 and 16	7 and 11	9 and 12	12 and 16
6 and 8	7 and 14	10 and 11	13 and 15

Table 6.3: Continued

Sixth-neighbors			
5 and 10	6 and 14	8 and 11	10 and 13
5 and 11	6 and 16	8 and 12	10 and 16
5 and 13	7 and 8	8 and 16	11 and 15
5 and 15	7 and 9	9 and 13	11 and 16
6 and 10	7 and 12	9 and 14	12 and 14
6 and 12	7 and 15	9 and 15	13 and 14
Eighth-Neighbors			
5 and 12		8 and 13	
6 and 15		9 and 16	
7 and 10		11 and 14

Figure 6.2: Determinant $D(E)$ as a function energy E in the bandgap for A_1 symmetric levels due to Si:Se. In this case, $U = -6.5$ eV. The values of E where $D(E) = 0$ are the predicted deep levels for specific values of α and β . The abscissa is the band-gap energy with the zero of energy equal to the top of the valence band. The ordinate is the value of $D(E)$. The quantity α is a measure of the nearest-neighbor-lattice relaxation, and β is a measure of the second-neighbor relaxation. The cases of $\alpha = 0.3, 0.0$, and -0.3 eV correspond to ratios d_I/d_H of 1.09, 1.00, and 0.93, respectively. The cases of $\beta = 0.3, 0.0$, -0.3 eV correspond to ratios d_{II}/d_H of 1.09, 1.00, and 0.93, respectively.

CHAPTER VII

RESULTS FOR DEEP LEVELS DUE TO SPECIFIC IMPURITIES: COMPARISON WITH EXPERIMENT AND OTHER THEORIES

In order to predict a deep level produced by a specific impurity in a host semiconductor using my theory, one first needs to calculate d_I and d_{II} . However, as mentioned before, if only the effects of the nearest-neighbor relaxation on deep levels are considered, both the covalent radius model and the molecular dynamics approach can be used to calculate d_I and in this case, $d_{II} = d_H$. The values of α can then be computed from Eq. (3.9) using this bond length. One can, thus, obtain deep levels from Figs. 3.1-3.19 for the impurity of interest with that value of α in a specific material. However, if one wants to consider both the effects of relaxation of the nearest and second neighbors on deep levels, one must use the molecular dynamics approach to calculate d_I and d_{II} . Then α and β must be calculated with these values of d_I and d_{II} . Afterwards, in order to predict the deep levels including the effects of relaxation of the second neighbors, one needs to plot a diagram similar to Fig. 6.2. That is a diagram of $D(E)$ versus E for the specific values of α and β as well as for fixed diagonal defect potential U is needed. The energy E corresponding to $D(E)=0$ on the curve then gives the

deep level. Of course, this can not only be done graphically, but also can be done numerically.

As an example, I now consider the case of the A_1 -symmetric deep level produced by an oxygen atom substitutional for a P atom in GaP. Using the covalent radius model, the bond length of Ga-O, d_I , is 1.92 Å, and d_{II} with Morgan's⁶² correction is 2.77 Å. These bond lengths give $\alpha = -0.96$ eV and 0.52 eV, respectively. From Fig. 3.1, one can find the A_1 deep level by drawing a vertical line from potential for the impurity O labelled on the top of the figure. This potential is $U = -11.9$ eV. The intersection of that line with the curves for the appropriate values of α gives the deep level predictions for these two values of d_I in this approximation. For $d_I = 1.92$ Å, a deep level is found by this method at 2.08 eV above the valence band, and for $d_I = 2.77$ Å, a deep level is found at 1.70 eV. On the other hand, using the molecular dynamics method, one obtains d_I and d_{II} equal to 2.78 Å and 2.23 Å, respectively. These give values of α and β equal to 0.53 eV and -0.21 eV. From Fig. 7.1, which shows $D(E)$ versus E in this case ($\alpha = 0.53$ eV and $U = -11.9$ eV) for $\beta = 0$ and -0.21 eV, one obtains deep level at 1.71 eV for $\beta = 0$, and at 1.70 eV for $\beta = -0.21$ eV by noting where $D(E) = 0$ in these cases.

In summary, it is clear that the deep levels for specific impurities can be obtained by the following procedure: (1) calculate U using Eq. (2.11), (2) compute d_I and d_{II} using the molecular dynamics method described in Chapter

VI, (3) calculate α using Eq. (3.9) along with the experimental data of d_H and the computed values of d_I , (4) calculate β using Eq. (6.2), and (5) compute the resulting deep level either graphically or numerically using Eq. (6.5). Another example using this method is displayed in Fig. 7.2, which shows graph of $D(E)$ versus E for the A_1 levels produced by S, Se, and Te in Si. In this figure, the values of U are -7.4, -6.5, and -3.5 eV, the values of α are -0.21, -0.65, and 0.35 eV, and the values of β are 0.09, 0.19, and -0.12 eV for Si:S, Si:Se, and Si:Te, respectively. From Fig. 7.2, it can be seen that the deep levels are predicted to occur at 0.65 eV, 0.84 eV, and 1.04 eV for Si:S, Si:Se, and Si:Te, respectively.

7.1 Comparison with Experiment

I have used my theory to compute the A_1 -symmetric deep levels produced by various impurities in GaP, Si, GaAs, and Ge. These results are summarized in Table 7.1. In the second and third columns of that table, I display the results of these calculations obtained from the covalent radius model, which includes the effects of relaxation of the nearest-neighbors only and the molecular dynamics model which includes the effects of both the first and second neighbors. Shown for comparison in the fourth and the fifth columns of Table 7.1 are the experimental deep levels for the same impurities, along with the predicted deep levels obtained by the Hjalmarson et al. (no relaxation) theory¹⁸.

As can be seen from Table 7.1, in most cases, the predictions of deep levels from both the covalent radius model and the molecular dynamics approach

improve upon those of the Hjalmarson et al. theory in comparison with experimental data. Exceptions to this are O in GaP using the covalent radius model without Morgan's correction and O in GaAs in the covalent radius model. In addition, in all cases considered, except for GaP:N and Si:S, the deep level predictions of the molecular dynamics method are better than those of the covalent radius model in comparison with experiment. In the cases of GaP:N and Si:S, both models predict nearly the same results. I conclude that, even though the molecular dynamics method requires more computational effort than the covalent radius model, it gives better predictions of deep levels in comparison with experimental data. Therefore, in the following discussion, I use the predictions of deep levels from molecular dynamics approach. I also note that the predictions for deep levels in Ge are the worst in comparison with experiment of all cases considered. This is because the inaccuracies in the host bandstructure I have used for Ge.^{38,73} This point will be discussed in more detail later.

From Table 7.1, it can be seen that for different specific impurities, the differences in the predicted deep levels due to the effects of lattice relaxation from those obtained by the Hjalmarson's theory, where such effects are neglected, depend on the case. For example, after considering such effects, the deep level produced by N substitutional for P in GaP is predicted to be higher in the band gap at 2.25 eV than the prediction from the Hjalmarson's theory of 2.10 eV. There is, thus, a change in the predicted energy of $\Delta E = E_r - E_0 = 0.15$ eV,

where E_r represents the deep levels obtained with relaxation (shown in the second column in Table 7.1), and E_0 represents the deep levels obtained without relaxation (shown in the last column of that table). From Table 7.1, one can also see that, in the case of GaP:O, the deep level computed with relaxation is predicted to be deeper in the band gap, at 1.70 eV, than the deep level obtained from Hjalmarson's theory at 1.85 eV. This change is also 0.15 eV, but is of the opposite sign of that for N. From Table 7.1, it can be seen that the magnitude of the maximum difference in the A_1 deep levels predicted by my theory and those predicted by Hjalmarson's theory is 0.19 eV, which occurs in the case of Si:Se. On the other hand, the magnitude of the minimum difference is 0.04 eV which occurs in the case of GaAs:As_{Ga}, except for that in the case Ge:S.

To obtain a feeling for the significance of including the effects of lattice relaxation in the theory of deep levels, it is worthwhile to make a quantitative calculation of the improvement in comparison with experimental data, by using my theory (with relaxation effects included) rather than the Hjalmarson et al. theory (with no relaxation). To do this, I have computed the quantity

$$\Delta = \frac{|E_0 - E_{exp}| - |E_r - E_{exp}|}{|E_0 - E_{exp}|} \times 100, \quad (7.1)$$

where E_0 represents the predicted deep level of the Hjalmarson theory, E_{exp} represents experimental deep levels, and E_r is the deep level prediction of my theory. The quantity Δ represents the percentage improvement of my theory over the Hjalmarson et al. theory in comparison with experimental data. It is

clear from Table 7.1 that the predictions of my theory are closer to the experimental data than that of the Hjalmarson et al. theory. Using Eq.(7.1), however, one can quantify exactly how much closer they are. The results of Δ for all cases shown in Table 7.1 are summarized in Table 7.2. As can be seen from this table, my predictions for deep levels including the effects of lattice relaxation show great improvement to the Hjalmarson et al. theory in comparison with experimental data. In particular, the percentage improvement ranges from 19.6% to 90.5%, except for the case of Ge:S.

7.2 Comparison with Other Theories

As mentioned in Chapter I, self-consistent pseudopotential Green's function methods^{15-17,50-51} have been used to accurately predict deep level properties for specific impurities in some materials. From the following example, it can be seen that the results obtained from my theory often compare quite favorably, both qualitatively and quantitatively with results from this more sophisticated theory. Scheffler, Vigneron and Bachelet have studied the effects of lattice relaxation on the deep levels produced by the Ge impurity substitutional for Ga in GaP using this method.⁵⁰ These calculations have predicted that the nearest-neighbor P atoms around the Ge should relax inward towards the Ge_{Ga} center, and that an A_1 deep level should be produced in the energy band gap. Further, they predict that the impurity bond length d_I is reduced by 3.5% compared to the GaP bond length of 2.36 Å, that is they predict $d_I=2.28$ Å. My theory is qualitatively and

quantitatively in remarkable agreement with all of these predictions. For example, I find both inward relaxation and an A_1 level in the gap. In addition, I predict (in Table 6.2) that the relaxed bond length d_I is 2.24 Å, a 5% reduction compared to the host bond length. In addition, Scheffler et al.⁵⁰ predict the deep level at 2.26 eV, which differs by 0.1 eV from the experimental data of 2.16 eV. I predict the deep level at 1.95 eV (in Table 7.1), which differs from experimental data by 0.11 eV. This is almost same absolute error, but in the opposite direction, as that obtained in Ref. 50. Comparison of my predictions with other results obtained by this method give similar agreement.

As mentioned earlier, the orders of magnitude of initial force due to substitutional impurities found by my theory are the same as found by the self-consistent pseudopotential Green's function methods. Also, the trends of the force versus relaxation distance obtained from my theory are similar to the predictions from this approach. All of these facts give me confidence that the theory outlined here is reasonably reliable.

As also mentioned in Chapter I, Talwar et al. have studied the effects of lattice relaxation on deep levels for the chalcogen defects S, Se, and Te in Si based on a generalization of the Hjalmarson's theory,⁵² which has a similar starting point to my theory. Their predictions for the deep levels for these cases are summarized in Table 7.3 along with the results of my theory and the experimental data. The values in the second column of that table are their

predicted deep levels obtained without considering the effects of relaxation, the values in the third column are their predictions considering such effects. Even though Talwar et al. have used a sophisticated total energy method to calculate the amount of the lattice relaxation, and included second-neighbor interactions in their band structure model, it can be seen from Table 7.3 that their theory (with relaxation) fails to improve on their predictions for deep levels without relaxation in comparison with experimental data. In fact, their deep levels obtained with relaxation included have a larger discrepancy with the experimental data than their predicted levels without relaxation. In addition, the shifts of deep levels found by Talwar et al. after considering the effects of lattice relaxation in comparison with those obtained without such effects are much smaller than I have found. For example, the maximum shift they found is only 0.05 eV in the case of Si:Se. On the other hand, I predict a shift about 0.19 eV in Si:Se. Thus, although Talwar et al. theory has the same starting point as the theory outlined here, the results obtained from it are very different than those of the present theory. The reason that these two theories yield qualitatively and quantitatively different results is not clear.

Table 7.1: Deep energy levels of A_1 -symmetry for various impurities in GaP, Si, GaAs, and Ge. All energies are in eV, measured from the top of the valence band. The abbreviation V.B. (C.B.) means that the predicted level is valence band (conduction band) resonant.

system	mol.dyn.	cov.rad.	experiment	Hjalmarson ^a
GaP:N	2.25	2.27	2.34 ^b	2.10
GaP:O	1.70	2.08	1.46 ^b	1.85
GaP:P _{Ga}	1.09	1.11	1.10 ^c	1.03
GaP:Ge	1.95	1.90	2.16 ^d	1.85
Si:S	0.64	0.66	0.85 ^e	0.58
Si:Se	0.84	0.70	0.86 ^e	0.65
Si:Te	1.04	1.09	1.01 ^e	1.12
GaAs:O	1.16	C.B.	0.75 ^f	1.26
GaAs:As _{Ga}	0.74	0.73	0.75 ^c	0.70
Ge:S	V.B.	V.B.	0.6 ^f	V.B.
Ge:Se	0.28	0.12	0.64 ^f	0.07

a. Ref. 18

b. Ref. 67

c. Ref. 68

d. Ref. 69

e. Refs. 6-8

f. Ref. 70

Table 7.2: The percentage improvement Δ of the deep level predictions of the present theory over the Hjalmarson et al. theory in comparison with experiment. The results are for various impurities in GaP, Si, GaAs, and Ge.

system	$\Delta(\%)$
GaP:N	62.5
GaP:O	61.5
GaP:P _{Ga}	85.7
GaP:Ge	32.3
Si:S	22.2
Si:Se	90.5
Si:Te	72.7
GaAs:O	19.6
GaAs:As _{Ga}	80.0
Ge:S	0.0
Ge:Se	46.0

Table 7.3: Comparison of the predicted A_1 -symmetric deep levels from the present theory with those from the Talwar et al. theory and with experimental data. The results are for impurities S, Se, and Te in Si. All levels are in electronic volts, and measured from the top of the valence band. The experimental data is from Refs.6-8.

System	Talwar		present theory	experiment
	unrelaxed	relaxed		
Si:S	0.51	0.46	0.65	0.85
Si:Se	0.64	0.59	0.84	0.86
Si:Te	1.18	1.18	1.04	1.01

Figure 7.1: Determinant $D(E)$ as a function of energy in the bandgap for the A_1 symmetric levels for O substitutional for P in GaP. In the case of GaP:O, the value of α is 0.53 eV and $U = -11.9$ eV. The remainder of the interpretation is as in Fig. 6.2.

Figure 7.2: Determinant $D(E)$ as a function of energy E in the bandgap for the A_1 symmetric levels for the impurities S, Se, and Te in Si. The remainder of the interpretation is as in Fig.7.1.

CHAPTER VIII

EFFECTS OF LATTICE RELAXATION ON THE DEEP LEVEL WAVEFUNCTION

In this chapter, I develop a formalism to investigate the effects of lattice relaxation on deep level wavefunctions using a generalization of the Ren et al. wavefunction theory,³¹ which was briefly outlined in Chapter II. For simplicity, I consider only nearest-neighbor relaxation in this formalism. The results of applying this formalism to impurities in Si, GaP, and GaAs are also discussed.

Formally, the deep level wavefunction in the localized orbital basis $|ib\vec{R}\rangle$ has the form given by Eq. (2.12), repeated here for convenience,

$$|\Psi\rangle = \sum_{i,\vec{R}} \langle ib\vec{R}|\Psi\rangle |ib\vec{R}\rangle, \quad (8.1)$$

where b can be either the anion site (a) or the cation site (c), i labels the symmetry (A_1 or T_2) of the states, and $\vec{R}$ is position vector in the lattice. Also from Eq. (2.3), another formal expression for the deep level wavefunction is

$$|\Psi\rangle = G^0(E)V|\Psi\rangle. \quad (8.2)$$

The i symmetric part of the wavefunction on site b at position $\vec{R}$ can thus be written as

$$\langle ib\vec{R}|\Psi\rangle = \langle ib\vec{R}|G^0V|\Psi\rangle. \quad (8.3)$$

To be specific, here I only discuss the wavefunction for A_1 -symmetric states. Those for T_2 states can be studied in a similar manner. The on-site part of the wavefunction for an impurity on an anion site at $\vec{R}=\vec{0}$, will thus have the form

$$\langle A_1 a\vec{0} | \Psi \rangle = \langle A_1 a\vec{0} | G^0 V_{A_1} | \Psi \rangle. \quad (8.4)$$

where V_{A_1} is the defect potential given by Eq. (3.2) with $i=A_1$. Because it is difficult to determine $\langle A_1 a\vec{0} | \Psi \rangle$ from the above equation directly, I use another method to do it.

For any substitutional impurity with energy E and wavefunction $|\Psi\rangle$, a slight change of the defect potential dV_{A_1} will produce a corresponding change in energy given by

$$dE = \langle \Psi | dV_{A_1} | \Psi \rangle. \quad (8.5)$$

Using the expression for the defect potential given by Eq. (3.2) for $i=A_1$, it is clear that

$$\frac{\partial V_{A_1}}{\partial U} = |A_1 a\vec{0}\rangle \langle A_1 a\vec{0}|, \quad (8.6)$$

where U is the on-site element of the A_1 -symmetric potential matrix. Combining Eqs. (8.5) and (8.6), one has

$$\frac{\partial E}{\partial U} = \langle \Psi | A_1 a\vec{0} \rangle \langle A_1 a\vec{0} | \Psi \rangle, \quad (8.7)$$

or

$$\frac{\partial E}{\partial U} = | \langle A_1 a\vec{0} | \Psi \rangle |^2. \quad (8.8)$$

Thus,

$$\langle A_1 a \bar{0} | \Psi \rangle = \sqrt{\frac{\partial E}{\partial U}}. \quad (8.9)$$

For convenience, I choose the phase of the on-site part of the wavefunction such that the positive sign is used in Eq. (8.9). Then, this wavefunction can be written as

$$\langle A_1 a \bar{0} | \Psi \rangle = \sqrt{1 / \frac{\partial U}{\partial E}}. \quad (8.10)$$

Equation (8.10) is the formal expression for the on-site wavefunction that I have used on my calculations. It is analogous to Eq. (2.15) for $\alpha=0$. However, in contrast to that equation, Eq. (8.10) contains the effects of lattice relaxation. This can be seen by referring to Eq. (3.8), which gives U in terms of various matrix elements of the Green's function $G^0(E)$ and of the off-diagonal defect potential parameter α . In my calculations, I have evaluated $\partial U / \partial E$ by taking the partial derivative of Eq. (3.8). This result has then been inserted into Eq. (8.10) to determine the on-site part of wavefunction.

Once the on-site part of the wavefunction is determined, the projections of the wavefunction on other sites can be obtained by matrix manipulation. For example, from Eq. (8.3), a formal expression for the part of the deep level wavefunction on the nearest-neighbor-cation atom at position $\bar{d}$ (for the impurity on the anion site at the origin) is

$$\langle A_1 c \bar{d} | \Psi \rangle = \langle A_1 c \bar{d} | G^0 V_{A_1} | \Psi \rangle. \quad (8.11)$$

where $\vec{d}$ is a specific one of the nearest-neighbor vectors. Inserting the defect potential, Eq. (3.2) with $i=A_1$, into Eq. (8.3), one obtains

$$\begin{aligned} \langle A_1 c \vec{d} | \Psi \rangle &= \langle A_1 c \vec{d} | G^0 | A_1 a \vec{0} \rangle U \langle A_1 a \vec{0} | \Psi \rangle \\ &+ \sum_{\vec{d}'} [\langle A_1 c \vec{d} | G^0 | A_1 c \vec{d}' \rangle \alpha \langle A_1 a \vec{0} | \Psi \rangle] \\ &+ \langle A_1 c \vec{d} | G^0 | A_1 a \vec{0} \rangle \alpha \sum_{\vec{d}'} \langle A_1 c \vec{d}' | \Psi \rangle, \end{aligned} \quad (8.12)$$

where the sum on $\vec{d}'$ goes over the position vectors for the four nearest-neighbor atoms, including the atom of interest at position $\vec{d}$. For breathing-mode distortions, because of in a tetrahedral symmetry, all four nearest neighbors are equivalent. The above equation can then be simplified to

$$\begin{aligned} \langle A_1 c \vec{d} | \Psi \rangle &= \langle A_1 c \vec{d} | G^0 | A_1 a \vec{0} \rangle \langle A_1 a \vec{0} | \Psi \rangle U \\ &+ 4 \langle A_1 c \vec{d} | G^0 | A_1 a \vec{0} \rangle \langle A_1 c \vec{d} | \Psi \rangle \alpha \\ &+ \langle A_1 c \vec{d} | G^0 | A_1 c \vec{d} \rangle \langle A_1 a \vec{0} | \Psi \rangle \alpha \\ &+ 3 \langle A_1 c \vec{d} | G^0 | A_1 c \vec{d}_1 \rangle \langle A_1 a \vec{0} | \Psi \rangle \alpha, \end{aligned} \quad (8.13)$$

where $\vec{d}_1$ is any one of the nearest-neighbor positions except that for the atom of interest at $\vec{d}$ (i.e. $\vec{d}_1 \neq \vec{d}$). Further manipulation with Eq. (8.13) gives

$$\begin{aligned}
& \langle A_1 c \bar{d} | \Psi \rangle [1 - 4\alpha \langle A_1 c \bar{d} | G^0 | A_1 a \bar{0} \rangle] \\
&= [\langle A_1 c \bar{d} | G^0 | A_1 a \bar{0} \rangle U + 3\alpha \langle A_1 c \bar{d} | G^0 | A_1 c \bar{d}_1 \rangle \\
&\quad + \alpha \langle A_1 c \bar{d} | G^0 | A_1 c \bar{d} \rangle] \langle A_1 a \bar{0} | \Psi \rangle,
\end{aligned} \tag{8.14}$$

or

$$\langle A_1 c \bar{d} | \Psi \rangle = W \langle A_1 a \bar{0} | \Psi \rangle, \tag{8.15}$$

where W has the form

$$W = \frac{U \langle A_1 c \bar{d} | G^0 | A_1 a \bar{0} \rangle + 3\alpha \langle A_1 c \bar{d} | G^0 | A_1 c \bar{d}_1 \rangle - \alpha \langle A_1 c \bar{d} | G^0 | A_1 c \bar{d} \rangle}{1 - 4\alpha \langle A_1 c \bar{d} | G^0 | A_1 a \bar{0} \rangle}. \tag{8.16}$$

Equations (8.15) and (8.16) express the nearest-neighbor part of the wavefunction in terms of the on-site wavefunction $\langle A_1 a \bar{0} | \Psi \rangle$, (given by Eq. (8.10)), the parameter α , and matrix elements of the host Green's function. I note that U occurring in Eq. (8.16) is also expressible in terms of α and these matrix elements by using Eq. (3.11). In the previous chapters, I have discussed on detail the fact that α contains the effects of lattice relaxation on the defect potential. Thus, Eq. (8.15) represents the nearest-neighbor part of the deep level wavefunction including such effects. If one lets $\alpha=0$ in Eq. (8.15), it becomes Eq. (2.14) of Chapter II (with $b=c$ and $\bar{R}=\bar{d}$), which corresponds to the case without the lattice relaxation.

Equations (8.10) and (8.15), are expressions for the projections of the deep level wavefunction on the on-site and the nearest-neighbor site, and they contain the effects of nearest-neighbor relaxation. In principle, following a similar procedure, one can calculate the projections of the impurity wavefunction on higher-neighbor sites.

From Eq. (8.15), it can be seen that the part of wavefunction on the nearest neighbors depends directly on the on-site wavefunction $\langle A_1 a_0 | \Psi \rangle$. It can also be shown that the part of the wavefunction on each higher neighbor has the form similar to Eq. (8.15). This means that each of these functions will have the similar chemical trends as those of the on-site impurity wavefunction. This fact was mentioned in Ref.31 for the case of no lattice relaxation. Further, from the forms of Eqs. (8.10) and (8.15) it can be expected that, the on-site and nearest-neighbor wavefunction will both have similar chemical trends as those no relaxation. From Eqs. (8.10) and (8.15), it can be also seen that including the effects of lattice relaxation in the calculation changes the magnitude of the wavefunction in comparison with that obtained without relaxation. These wavefunction features partially control the properties of deep levels themselves. For example, as was discussed in Chapter III, the chemical trends of deep levels with the effects of lattice relaxation included are similar to those without relaxation, but the deep level positions are changed in comparison with the cases obtained without relaxation.

Although it is probably obvious from the form of Eqs. (8.10) and (8.15), it is perhaps worth emphasizing to the reader that these equations give the dependence of the on-site and nearest-neighbor parts of wavefunction on the deep level energy E . I point this out here because the reader may not be used to seeing wavefunction given as a function of energy. By computing these wavefunctions as a function of the parameter E , they can be computed for all possible deep levels in the band gap. Using Eqs. (8.10) and (8.15), the trends in the impurity wavefunction can thus be predicted as a function of energy and also as a function of the amount of the lattice relaxation (varying α).

Figures 8.1-8.6 illustrate the predicted results for the parts of A_1 -symmetric impurity wavefunction on the impurity site and on the nearest neighbors in Si, GaP, and GaAs. These results are shown as functions of the deep level energy E in the band gap for the various values of α labelled in the figures. In particular, Fig. 8.1 shows the on-site part of the wavefunction for impurities in Si, and Fig. 8.2 shows the nearest-neighbor part of wavefunction for the same case. Figures 8.3 and 8.4 show the on-site and nearest-neighbor parts of wavefunction for impurities on the cation site in GaP, and Figs. 8.5 and 8.6 show the similar wavefunction in GaAs. In these figures, the vertical scale indicates the magnitude of the wavefunction and on the abscissa, $E=0.0$ eV represents the top of the valence band and the maximum E represents the bottom of the conduction band. If one notes that the size of the divisions on vertical scales in

these figures are quite small, it can be seen that the curves for the various values of α in these figures are slowly varying with deep level energy E in the band gap as was found by Ren et al.³¹ for no relaxation ($\alpha=0$). Physically, this means that the deep level wavefunction has mostly host-like character and depends very little on which impurity one considers. Stated another way, for a given host, all substitutional impurities have approximately the same A_1 -symmetric deep level wavefunctions. This is agreement with the results of Ref.31. The $\alpha=0$ curves in these figures are the same as those found by Ren et al..

By comparing the results for various α in Fig. 8.1 for impurities in Si, it can be seen that lattice relaxation does not change the energy dependence of the on-site wavefunction very much in comparison with the no relaxation ($\alpha=0$) case. However, it does change the magnitude of the wavefunction. For example, the magnitude of the wavefunction shifts from 0.35 to 0.38 for α changing from 0.0 to 0.6 eV and to 0.32 for $\alpha=-0.6$ eV at an energy of $E=0.6$ eV in the band gap. Further, it can be seen that the shift induced by a certain amount of relaxation (fixed α) varies with E as it changes from the top of the valence band to the bottom of the conduction band. Since the wavefunction with no relaxation varies somewhat with the deep level energy, it is not surprising that the shifts induced by the lattice relaxation on the wavefunction are also dependent on the deep level energy in some extent. From Fig. 8.1, it can be seen that, for this case, the predicted changes of the wavefunction due to the relaxation which

occur for E near the conduction-band edge are larger than those near the valence band. For example, for E near the valence-band edge, the predicted change in the on-site wavefunction as α varies from 0.0 to 0.3 eV is about 0.01, while for E near the conduction-band edge, the predicted change for the same variation of α is about 0.035. If one notes that $|\langle A_1 a_0 | \Psi \rangle|^2$ represents the probability of an electron occupying this state, these results predict that, on the impurity site, an electron has a larger probability of occupying an impurity level which is near the conduction band than it does for a level near the valence band.

From this figure, one can also see that an inward relaxation ($\alpha < 0$) around the impurity is predicted to decrease the magnitude of the on-site wavefunction, and an outward relaxation ($\alpha > 0$) is predicted to increase the wavefunction. For example, for a level near the middle of the gap ($E = 0.6$ eV), when $\alpha = -0.6$ eV, the magnitude of the wavefunction decreases from its $\alpha = 0$ value of 0.35 to 0.32. When $\alpha = 0.6$, the wavefunction magnitude increases to 0.39 at this same energy. Since $|\langle A_1 a_0 | \Psi \rangle|^2$ represents the probability of an electron occupying this state, these results thus predict that, on the impurity site, for outward relaxation, the electron has a larger probability of occupying the state described by $\langle A_1 a_0 | \Psi \rangle$ than it does with no relaxation. On the other hand, for an inward relaxation, the electron has a less probability of occupying this state than it does with no relaxation.

These results can be understood by the fact that the deep level wavefunction decreases rapidly in magnitude with the displacement vector $\vec{R}$ from the impurity site, as can be seen by comparing the magnitude of wavefunction in Figs. 8.1 and 8.2 and as has been shown in Ref.31 in the absence of relaxation. For outward relaxation, the atoms around the impurity move away and $\vec{R}$ increases. The part of the impurity wavefunction on the neighbors thus decreases. However, since the wavefunction must be normalized, the sum of $|\langle A_1 | b_{\vec{R}} | \Psi \rangle|^2$ over $\vec{R}$ for a given energy level must be equal to unity. Thus, the on-site wavefunction must increase by a corresponding amount. For the same reason, an inward relaxation will cause the on-site wavefunction to decrease.

From Fig. 8.2, it can be seen, in agreement with the above discussion, that the magnitude of the part of the wavefunction on the first neighbors is smaller than that on the impurity site for the same α . For example, in Fig. 8.2, the magnitude of the wavefunction at $E=0.6$ eV for $\alpha=0.6$ eV is 0.09, which is about four times as small as that for the same E and α shown in Fig. 8.1. Further, from Fig. 8.2, it is clear that outward relaxation is predicted to decrease the magnitude of the nearest-neighbor part of the wavefunction in comparison with no relaxation. On the other hand, inward relaxation is predicted to increase this part of wavefunction. This trend is opposite to that found for the on-site part wavefunction in Fig. 8.1. This is to be expected from the discussion in the preceding paragraph. For example, from Fig. 8.2, the magnitude of wavefunction

at $E=0.6$ eV decreases from 0.11 to 0.09 for a change in α from 0.0 to 0.6 eV, while it increases to 0.126 for a variation with $\alpha=0.0$ to $\alpha=-0.6$ eV.

Figures 8.3-8.6 show the similar results for the on-site and nearest-neighbor parts of the impurity wavefunction associated with an impurity substitutional for the cation in GaP and GaAs. The features of the wavefunction in these figures are all in agreement qualitatively with those presented in Figs. 8.1 and 8.2 for Si. In particular, it can be seen from these figures that the curves for the various values of α are slowly varying with deep level energy E in the band gap. The lattice relaxation (corresponding to different α) does not change the energy dependence of the wavefunction very much, but changes its magnitude. It can also be seen that an inward relaxation around the impurity is predicted to decrease the magnitude of the on-site part of the wavefunction and increase the nearest-neighbor part. On the other hand, an outward relaxation is predicted to increase the magnitude of the on-site part of the wavefunction and decrease the nearest-neighbor part. Comparing the wavefunctions in GaP and GaAs, it can be seen that the predicted trends of the dependence of the wavefunction on the impurity levels in the band gap in these figures are very similar. Further, the magnitudes of the wavefunction in GaP and GaAs are almost same for the same value of α and same energy in the band gap. For example, the magnitude of the on-site wavefunction in Fig. 8.3 (for GaP) at $E=1.2$ eV for $\alpha=0.0$ is predicted to be 0.5, and is predicted to be 0.51 in Fig.8.4 for the same α (for GaAs). This

result could be used to explain why deep levels in GaP and GaAs have similar properties.

Experimental data on deep level wavefunctions can be obtained indirectly from ENDOR and ESR spectra. Such data for S, Se, and Te in Si have been obtained by Ludwig⁶ and Grimmeiss⁷. Also, such data for antisite "impurities" P_{Ga} in GaP and As_{Ga} in GaAs have been obtained by Kaufmann and Wagner.⁸ Table 8.1 shows the results for the on-site and the nearest-neighbor part of the wavefunctions for these impurities in Si, GaP and GaAs calculated by the formalism developed in this chapter and by Ren et al.³¹ with no relaxation. The impurity wavefunction with relaxation were obtained for the appropriate impurity using the α obtained by the molecular dynamics approach and the E obtained by the procedure described in the previous chapters. The experimental data is also shown in the table for comparison. From Table 8.1, it can be seen that the theoretical results which include lattice relaxation are in better agreement with experimental data than those with no relaxation for all cases except for Si:Te. In that case, the predicted magnitude of the wavefunction is little larger than that obtained from experimental data. However, the difference between the theoretical result and data is within the experiment error range.^{6,7,8} I note that in the case of the antisite defects, the relaxed and unrelaxed results are very similar, even though the results obtained by including relaxation are a little nearer to the experimental data than those with no relaxation.

Table 8.1: Magnitudes of the on-site and nearest-neighbor parts of the wavefunction for various impurities in Si, GaP and GaAs. Experimental data is from Refs.6-8.

System	Wavefunction					
	Relaxed		Unrelaxed		Experiment	
	on-site	first-neighbor	on-site	first-neighbor	on-site	first-neighbor
Si:S	0.346	-0.121	0.351	-0.108	0.329	-0.128
Si:Se	0.323		0.374		0.335	
Si:Te	0.381		0.360		0.364	
GaAs:As _{Ga}	0.459		0.457		0.461	
GaP:P _{Ga}	0.493	-0.141	0.498	-0.139	0.466	-0.151

Figure 8.1: Dependence of the on-site part of the A_1 -symmetric impurity wavefunction for impurities in Si. The figure shows $\langle A_{1,a,0} | \Psi \rangle$ as a function of the deep level energy E and the varying amounts of lattice relaxation. The abscissa is the impurity energy in the band gap with the zero equal to the top of the valence-band edge. The ordinate is the magnitude of the wavefunction. The $\alpha = 0.6, 0.3, 0.0, -0.3$, and -0.6 eV results are shown, respectively, as dashed, dotted, solid, chained, and dotted-dashed curves.

Figure 8.2: Dependence of the nearest-neighbor part of the A_1 -symmetric impurity wavefunction for impurities in Si. The figure shows $\langle A_1 c d | \Psi \rangle$ as a function of the deep level energy E and the varying amounts of lattice relaxation. The remainder of the interpretation is as in Fig.8.1.

Figure 8.3: Dependence of the on-site part of the A_1 -symmetric impurity wavefunction for impurities substitutional for Ga in GaP. The $\alpha = 1.0, 0.5, 0.0, -0.5$, and -1.0 eV results are shown, respectively, as dashed, dotted, solid, chained, and dotted-dashed curves. The remainder of the interpretation is as in Fig.8.1.

Figure 8.4: Dependence of the nearest-neighbor part of the A_1 -symmetric impurity wavefunction for impurities substitutional for Ga in GaP. The remainder of the interpretation is as in Fig. 8.3.

Figure 8.5: Dependence of the on-site part of the A_1 impurity wavefunction for impurities substitutional for Ga in GaAs. The remainder of the interpretation is as in Fig. 8.1.

Figure 8.6: Dependence of the nearest-neighbor part of the A_1 impurity wavefunction for impurities substitutional for Ga in GaAs. The remainder of the interpretation is as in Fig.8.5.

CHAPTER IX

SUMMARY AND CONCLUSIONS

In summary, I have investigated the effects of lattice relaxation on deep levels in 8 technologically important semiconductors using a formalism I have developed. This formalism is a generalization of the Hjalmarson et al. theory of deep levels due to substitutional impurities in zincblende and diamond structure materials,¹⁸ and it uses the Vogl et al.³⁸ sp^3s^* semi-empirical, nearest-neighbor, tight-binding band structure for perfect semiconductor hosts as input. For simplicity and reality, only the symmetry conserving "breathing-mode" relaxation has been considered here, although my method could be generalized to treat more complicated cases. In this formalism, both first- and second-neighbor-lattice-relaxation effects are included by representing the off-diagonal matrix elements of the defect potential by parameters, which depend on both host and host-impurity bond length. To determine these parameters as a function of these bond lengths, I have used Harrison's inverse-bond-length squared-scaling rule.⁴⁰ By computing deep levels as a function of these parameters, the effects of varying amounts of lattice relaxation on deep levels have been explored. I have found that the parameters which correspond to the effects of the second-neighbor relaxation affect the deep levels by only a small amount in comparison to the first-neighbor effects.

For calculating the directions and magnitude of lattice relaxation, which is necessary to determine these parameters for a particular impurity, two different approaches have been taken. First, in approximation where only the nearest-neighbor relaxation considered, a simple model based on the covalent radius approximation has been used to easily and quickly indicate the direction and magnitude of relaxation. This simple model was found to also give semi-quantitatively correct results for both the lattice relaxation and the deep levels in most cases. Second, for a more accurate calculation, a molecular dynamics method has been used to calculate both the first- and second-neighbor relaxation around an impurity. That is, this method has been used to determine the relaxed bond lengths which enter the off-diagonal defect potential parameters. The attractive part of the force which enters these calculations is computed directly from the electronic structure, using the Hellmann-Feynman theorem.⁶⁴ The repulsive part of this force is obtained from a pair potential based on Harrison's overlap interaction.⁶³ In addition, the effects of lattice relaxation on deep level wavefunctions have also been investigated using a formalism based on these same approximations.

Since both Hjalmarson et al. deep level theory and its generalizations have proven successful in both predicting the chemical trends of deep levels and in making semiquantitatively correct predictions for such levels,^{18,24-36} I believe that the predicted chemical trends, and predicted trends with varying amounts

of lattice relaxation should be reliable. Further, my numerical calculations of the positions of deep levels including such effects have proven accurate in comparison with experiment and have considerably improved the quantitative accuracy of the Hjalmarson et al. theory. Some of these predictions are also in good quantitative and qualitative agreement with those obtained from "first-principles" theories, where such results are available. Due to these facts, I believe that the predicted deep levels in this dissertation are also quantitatively reliable. I hope that these predictions of the properties of deep levels including the effects of lattice relaxation are useful in assisting in the identification of deep levels in semiconductors.

From the results and discussions of previous chapters, some major conclusions can be made. First, under a "breathing-mode" lattice relaxation, deep levels keep the symmetry they had in the absence of such effects. That is, for zincblende and diamond structure materials, deep levels due to sp^3 bonded substitutional impurities including the effects of lattice relaxation still have either A_1 or T_2 symmetric states. However, due to Jahn-Teller distortions, which will affect T_2 states, a breathing-mode model is really not appropriate for such states. Second, lattice relaxation effects do not change the chemical trends of the deep levels appreciably, but shift their positions in the band gap. Third, inward relaxation and outward relaxation will move deep levels in the opposite directions in the band gap. In particular, inward relaxation due to an impurity

generally moves its A_1 -symmetric deep levels towards the conduction band, and moves its T_2 -symmetric deep levels towards the valence band, while outward relaxation moves the deep levels in the opposite directions. Fourth, at least in the breathing-mode model, the effects of lattice relaxation are larger for A_1 deep levels than for T_2 levels. Fifth, the effects of second-neighbor relaxation are much smaller than those due to first-neighbor relaxation. Sixth, the predictions of deep levels including such effects considerably improve the results obtained by Hjalmarson et al. theory in comparison with experimental data.

The formalism presented here could be extended to treat the effects of lattice relaxation in other situations. For example, an extension of this formalism could be used to study such effects in II-VI semiconductors, such as CdTe, ZnTe, ZnSe, HgTe, and HgSe. These materials are technologically very useful for making infra-red detectors. To extend this theory to them, one needs to both modify the Vogl et al. band structure theory to include the effects of spin-orbit coupling,⁷¹ and to modify the present theory to account for such effects. This means that all matrices treated in this work must be expanded to twice their size. In addition, the present formalism could be extended to treat vacancies and vacancy associated defects in semiconductors. However, I have made an initial attempt to do this and, in preliminary results, found that applying this formalism to this problem beginning with an "ideal vacancy" model fails to improve upon the results obtained by the theory with no relaxation in

comparison with experiment.⁵⁶ A possible approach which might work better would be one beginning with a new vacancy model developed by Xu and Lindefelt.⁷² Also, an extension of my formalism to treat lattice relaxation effects on deep levels associated with paired or more complicated defects, such as triplets of impurities is possible. To do this, one needs to add one or more terms to Eq. (3.2) to describe the interactions within the extended defect. Other extensions and generalizations of this formalism are also possible.

I note that even though the effects of lattice relaxation have been included in the calculations of the deep levels presented here, the discrepancies between theory and experiment still remain. A major factor which contributes to this discrepancy may be inaccuracies of Vogl et al. band structures used in my calculations.^{38,73} This band structure theory only includes interactions between the nearest-neighbor atoms. This theory gives reasonable results for the band structures for many materials. However, Newman and Dow have shown that including some second-neighbor effects improves the accuracies of the band structures, especially for indirect band gap materials with indirect minimum away from the X point of the Brillouin zone, such as Ge, which has its minimum at the L point.⁷³ Also, many alternative tightbinding band models exist which include the effects of second and higher neighbors.⁷⁴

An example where the use of a better bandstructure might improve the results is the case of Ge. For example, experimental data shows that the

impurities S and Se induce deep levels at 0.6eV and 0.64eV, respectively, above the valence band in Ge.⁷⁰ Using the Vogl et al. band structures for Ge, the Hjalmarson et al. deep level theory with no relaxation predicts no impurity levels induced by S in the band gap and a level at 0.07eV above the valence band edge induced by Se. After including the effects of lattice relaxation, and using the same bandstructure, I predict a deep level at 0.28eV for Se, but no impurity levels in the band gap for S (see Table 7.1). However, Newman and Dow⁷³ using their band structure for Ge predict deep levels at 0.17eV for S and 0.25eV for Se with no relaxation. Using their bandstructure and my formalism to include the effects of lattice relaxation in the calculation, I predict deep levels in Ge at about 0.2eV for S and 0.5eV for Se in the band gap. These results compare much more favorably with experimental data than those obtained with the Vogl et al. bandstructure. Due to these facts, I believe that using a more accurate band structure theory in conjunction with my formalism can improve the predictions of the deep levels in the band gap.

Another possibility which could account for some of the discrepancy between my predictions and the experimental data could come from my assumption for the forms of the off-diagonal elements of defect potential matrix and of the repulsive part of the force.^{40,63} These are both taken from Harrison's universal theory and are based, respectively, on the inverse bond length squared scaling rule and the overlap interaction. Jansen and Sankey⁷⁵, using a pseudopotential

based theory, have examined the off-diagonal elements of the tight-binding Hamiltonian in detail, and have found that Harrison's theory is only a crude approximation⁷⁵. However, I have shown that in the Appendix that the formalism developed here is not dependent on Harrison's theory, and that the final results for both of the effects of lattice relaxation and for the positions of deep levels are not affected sensitively by these approximations.

REFERENCES

- [1] D. G. Thomas, J. J. Hopfield and C. J. Frosch, Phys. Rev. Lett. 15, 857 (1965); Phys. Rev. 150, 680 (1966); D. J. Woford, B. G. Streetman, R. J. Nelsen, and N. Holonyak, Jr., Solid State Comm. 19, 741 (1976).
- [2] K. Seeger, Semiconductor Physics-An Introduction (Springer-Verlag, 1989); D. V. Lang, Inst. Phys. Conf. Ser. 31, 70 (1977).
- [3] W. Kohn, and J. M. Luttinger, Phys. Rev. 97, 1721 (1955); 98, 915 (1955); G. W. Ludwig, Phys. Rev. A 137 1520 (1965).
- [4] W. C. Dunlop, Jr., Phys. Rev. 85, 945 (1952).
- [5] S. T. Pantelides, Deep Centers in Semiconductors (Gordon and Breach, New York, 1986).
- [6] G. Feher, Phys. Rev. 114, 1219 (1959); G. W. Ludwig, and H. H. Woodbury, Phys. Rev. Lett. 5, 96 (1962); Solid State Phys. 13, 223 (1962).
- [7] H. G. Grimmeiss, and E. Janzen, J. Appl. Phys. 51, 3740 (1980); *ibid.* 51, 4212 (1980); Phys. Rev. B 23, 1947 (1980); H. G. Grimmeiss, E. Janzen, H. Ennen, O. Schirmer and J. Schneider, Phys. Rev. 24, 4571 (1981).
- [8] U. Kaufmann, J. Schneider, R. Worner, T. A. Kennedy and N. D. Wilsey, J. Phys. C 14, L951 (1981); T. A. Kennedy and N. D. Wilsey, Phys. Rev. B 23, 6585 (1980); R. J. Wagner, J. J. Krebs and G. H. Stauss, Solid State Comm. 36, 15 (1980). Appl. Phys. Lett. 29, 312 (1976); R. J. Wagner, Solid State Comm. 36, 15 (1980); H. G. Grimmeiss, Phys. Rev. B 24, 4571 (1981).
- [9] D. V. Lang, J. Appl. Phys. 45, 3023 (1974).
- [10] B. C. Cavenett, Adv. Phys. 30, 475 (1981).
- [11] R. P. Messmer, and G. D. Watkins, Phys. Rev. Lett. 25, 656 (1970); Phys. Rev. B 7, 2568 (1973).

- [12] P. Masri, A. H. Harker, and A. M. Stoneham, J. Phys. C 16, L613 (1983); G. G. DeLeo, W. B. Fowler, and G. D. Watkins, Phys. Rev. B 29, 3193 (1984); G. G. DeLeo, M. J. Dorogi, and W. B. Fowler, Phys. Rev. B 38, 7520 (1988); G. G. DeLeo, W. B. Fowler, T. M. Sudol, and K. J. O'Brien, Phys. Rev. B 41, 7581 (1990).
- [13] S. K. Estreicher, Phys. Rev. B 41, 9886 (1990); Dj. M. Maric, S. Vogel, P. F. Meiar, and S. K. Estreicher, Phys. Rev. B 40, 8545 (1989).
- [14] S. T. Pantelides, Rev. Mod. Phys. 50, 797 (1978).
- [15] J. Bernholc, and S. T. Pantelides, Phys. Rev. B 18, 1780 (1978); J. Bernholc, N. O. Lipari, and S. T. Pantelides, Phys. Rev. Lett. 41, 895 (1978); Phys. Rev. B 21, 3545 (1980); N. O. Lipari, J. Bernholc, and S. T. Pantelides, Phys. Rev. Lett. 43, 1354 (1979); Phys. Rev. B 21, 3545 (1980).
- [16] G. A. Baraff, and M. Schluter, Phys. Rev. Lett. 41, 892 (1978); Phys. Rev. B 19, 4965 (1980); G. A. Baraff, E. O. Kane, and M. Schluter, Phys. Rev. Lett. 43, 956 (1979).
- [17] M. Jaros, Adv. Phys. 29, 409 (1980); Deep Levels in Semiconductors (Adam Hilger, 1982).
- [18] H. P. Hjalmarson, P. Vogl, D. J. Wolford, and J. D. Dow, Phys. Rev. Lett. 44, 810 (1980); H. P. Hjalmarson, Ph.D. dissertation, University of Illinois (1979).
- [19] D. A. Papaconstantopoulos, and E. N. Economou, Phys. Rev. B 22, 2903 (1980); S. Das Sarma, and A. Madhukar, Phys. Rev. B 24, 2051 (1981).
- [20] F. Bloch, Z. Physik 52, 535 (1928).
- [21] P. Hohenberg, and W. Kohn, Phys. Rev. 136, B864 (1964); W. Kohn, and L. J. Sham, Phys. Rev. 140, A1133 (1965).
- [22] J. A. Appelbaum, and D. R. Hamann, Phys. Rev. Lett. 31, 106 (1973); M. L. Cohen, M. Schluter, J. R. Chelikowsky, and S. G. Louie, Phys. Rev. B 12, 5575 (1975).

- [23] M. Schluter, S. T. Pantelides, N. O. Lipari, and J. Bernholc. Phys. Rev. Lett. 47, 413(1981); J. Bernholc, S. T. Pantelides, N. O. Lipari, and A. Baldereschi, Solid State Comm. 37, 705 (1981); J. Bernholc, N. O. Lipari, S. T. Pantelides, and M. Schluter, Phys. Rev. B26, 5706 (1982); V. A. Singh, A. Zunger, and U. Lindefelt, Phys. Rev. B27, 1420 (1983).
- [24] O. F. Sankey, H. P. Hjalmarson, J. D. Dow, D. J. Wolford, and B. G. Streetman, Phys. Rev. Lett. 45, 1656 (1980); O. F. Sankey, and J. D. Dow, Appl. Phys. Lett. 38, 685 (1981); Phys. Rev. B26, 3243 (1982); C. W. Myles, and O. F. Sankey, Phys. Rev. B29, 6810 (1984); X. J. Wu, M. Z. Huang, and S. Y. Ren, Appl. Phys. Lett. 57, 870 (1990).
- [25] Y.-T Shen, and C. W. Myles, Appl. Phys. Lett. 51, 2034 (1987); J. Appl. Phys. 65, 4273 (1989); Phys. Rev. B40, 6222 (1989); W.-G Li, C. W. Myles, and Y.-T Shen, Phys. Rev. B40, 10425 (1989).
- [26] H. P. Hjalmarson, H. Buttner, and J. D. Dow, Phys. Rev. B24, 6010 (1981).
- [27] R. E. Allen, and J. D. Dow, Phys. Rev. B25, 1423 (1982).
- [28] R. E. Allen, J. P. Buisson, and J. D. Dow, Appl. Phys. Lett. 39, 975 (1981).
- [29] S. Y. Ren, J. D. Dow, and S. F. Sankey, Phys. Rev. B25, 7661 (1985); R. D. Hong, D. W. Jenkins, S. Y. Ren, and J. D. Dow, Phys. Rev. B38, 12549 (1988); D. W. Jenkins, S. Y. Ren, and J. D. Dow, Phys. Rev. B39, 7881 (1989).
- [30] S. Lee, J. D. Dow, and O. F. Sankey, Phys. Rev. B31, 3910 (1985); C. W. Myles, J. Vac. Sci. Technol. A6, 2657 (1988).
- [31] S. Y. Ren, W. M. Hu, O. F. Sankey, and J. D. Dow, Phys. Rev. B26, 951 (1982).
- [32] H.-H Dai, M. A. Gundersen, and C. W. Myles, Phys. Rev. B33, 8234 (1986).
- [33] M. F. Li, D. Q. Mao, and S. Y. Ren, Solid State Commun. 48, 789 (1983); M. F. Li, S. Y. Ren, and D. Q. Mao, J. Phys. C17, 3415 (1984).
- [34] C. W. Myles, P. F. Williams, R. A. Chapman, and E. G. Bylander, J. Appl. Phys. 57, 5279 (1985); E. G. Bylander, C. W. Myles, and Y. T. Shen, J. Appl. Phys. 67, 7351 (1990).

- [35] W. C. Ford, and C. W. Myles. Phys. Rev. B34, 927 (1986); *ibid.* 38, 1210 (1988); 10533 (1988); S. A. Tang, C. W. Myles, and W. C. Ford. *ibid.* 40, 11947 (1989).
- [36] S. Y. Ren, and J. D. Dow, Phys. Rev. B38, 1999 (1988); S. Y. Ren, J. D. Dow, and J. Shen, Phys. Rev. B38, 10677 (1988); S. Y. Ren, and J. D. Dow. J. Appl. Phys. 65, 1987 (1989); Phys. Rev. B39, 7796 (1989).
- [37] F. P. Larkins, and A. M. Stoneham, J. Phys. C4, 143; 154 (1971).
- [38] P. Vogl, H. P. Hjalmarson, and J. D. Dow, J. Phys. Chem. Solids 44, 365 (1983).
- [39] J. R. Chelikowsky, and M. L. Cohen, Phys. Rev. B14, 556 (1976).
- [40] W. Harrison, Electronic Structure, and the Properties of Solids (Freeman, San Francisco, 1980).
- [41] G. F. Koster, and J. C. Slater. Phys. Rev. 95, 1167 (1957).
- [42] E. N. Economou, Green's Functions in Quantum Physics (Springer-Verlag, Berlin, Heidelberg, New York, 1979).
- [43] G. W. Lowdin, J. Chem. Phys. 18, 365 (1950).
- [44] G. D. Watkins, and J. W. Corbett, Phys. Rev. A134, 1359 (1964).
- [45] P. O. Ludwig, Phys. Rev. A137, 1520 (1965).
- [46] R. P. Messmer, and G. D. Watkins. Phys. Rev. B28, 2568 (1973).
- [47] U. Lindfelt, and A. Zunger, Phys. Rev. B28, 4510 (1982); Phys. Rev. B28, 4510 (1983); Phys. Rev. B30, 1102 (1984).
- [48] J. L. Martins, and A. Zunger, Phys. Rev. B30, 6217 (1984).
- [49] J. M. Baranowski, J. Phys. C17, 6287 (1984).

- [50] M. Scheffler, J. P. Vigneron, and G. B. Bachelet. Phys. Re. Lett. 49, 1765 (1982); M. Scheffler, J. Bernholc, N. O. Lipari, and S. T. Pantelids, Phys. Rev. B29, 3269 (1984); M. Scheffler, J. P. Vigneron, and G. B. Bachelet, Phys. Rev. B31, 6541 (1985).
- [51] G. A. Baraff, M. Schluter, and G. Allen. Phys. Rev. Lett. 50, 739 (1983); G. A. Baraff, and M. Schluter, Phys. Rev. B30, 1853 (1984).
- [52] D. N. Talwar, K. S. Suh, and C. S. Tang, Phil.Mag. B54, 93 (1986); B56, 593 (1987).
- [53] H. A. Jahn, and E. Teller, Proc. Roy. Soc. London 161, 220 (1937); R. Englman, The Jahn-Teller Effects in Molecular. and Crystals (Wiley, London, 1972).
- [54] G. B. Bachelet, G. A. Baraff, and M. Schluter, Phys. Rev. B24, 4736 (1981). M. Lannoo, Phys. Rev. B25, 2987 (1982).
- [55] R. E. Allen, and M. Menon, Phys. Rev. B33, 5611 (1986); M. Menon, and R. E. Allen, Phys. Rev. B33, 7099 (1986); Solid State Comm.64, 353 (1988); Phys. Rev. B38, 6196 (1988).
- [56] W.-G. Li and C. W. Myles, (unpublished).
- [57] C. Kittel, Introduction to Solid State Physics Sixth Edition (Wiley, New York, 1986).
- [58] J. C. Mikkelsen, and J. B. Boyce, Phys. Rev. Lett. 49, 1412 (1982). J. Azoulay, E. A. Stern, and D. Shaltiel, Phys. Rev. B25, 5627 (1982); A. Balzarotti, and A. Kisiel, Phys. Rev. B30, 2295 (1984).
- [59] L. Pauling, The Nature of the Chemical Bond (Cornell Univ. Press, Ithaca, 1967).
- [60] R. W. G. Wyckoff, Crystal Structures, 2nd edition, Vol.1 (Interscience, New York, 1963).
- [61] G. A. Baraff, E. O. Kane, and M. Schluter, Phys. Rev. Lett. 47, 601 (1981); Phys. Rev. B25, 548 (1982).

- [62] T. N. Morgan, Phys. Rev. Lett. 49, 173 (1982); Phys. Rev. B25, 548 (1982); B29, 5667 (1984).
- [63] W. Harrison, Phys. Rev. B27, 3592 (1983).
- [64] W. Pauli, Handbuch der Physik (Springer-Verlag, Berlin, 1933); H. Hellmann, Einführung in Die Quantenchemie (Deuticke, Vienna, 1937); R. P. Feynman, Phys. Rev. 56, 340 (1939); J. I. Musher, J. Chem. Phys. 43, 2145 (1965).
- [65] A. Rahman, Phys. Rev. 136, A405 (1964); R. E. Allen, F. W. deWette, and A. Rahman, ibid. 179, 887 (1969); F. H. Stillinger and A. Rahman, J. Chem. Phys. 60, 1545 (1974); R. W. Hockney, and J. W. Eastwood, Computer Simulation Using Particles (McGraw-Hill, New York, 1981).
- [66] W. C. Ford, Jr., Ph.D Dissertation, Texas Tech University (1986).
- [67] A. G. Milnes, Deep Impurities in Semiconductors (Wiley, New York, 1973).
- [68] R. Worner, U. Kaufmann, and J. Schneider, Appl. Phys. Lett. 40, 141 (1982); E. Weber, H. Ennen, U. Kaufmann, J. Appl. Phys. 53, 6140 (1982).
- [69] G. F. Neumark and V. K. Kosai, Semiconductors and Semimetals V19, (Academic, New York, 1983).
- [70] W. W. Tyler, J. Phys. Chem. Solids, 8, 59 (1959).
- [71] A. Kobayashi, O. F. Sankey, and J. D. Dow, Phys. Rev. B25, 6367 (1982); S. N. Ekpenu, and C. W. Myles, J. Phys. Chem. Solids, 51, 93 (1990).
- [72] Hongqi Xu, and U. Lindefelt, Phys. Rev. B41, 5979 (1990).
- [73] K. E. Newman, and J. D. Dow, Phys. Rev. B30, 1929 (1986).
- [74] J. R. Chelckowsky and M. L. Cohen, Phys. Rev. B14, 556 (1976); E. Caruthers and P. J. Lin-Chjung, Phys. Rev. B17, 2705 (1978); A.-B. Chen and A. sher, Phys. Rev. B23, 5360 (1981).
- [75] R. W. Jansen and O. F. Sankey, Phys. Rev. B36, 6250 (1987).

APPENDIX

EXPONENTIAL APPROXIMATION FOR THE OFF-DIAGONAL ELEMENTS AND FOR THE REPULSIVE FORCE

The formalism outlined in the text utilizes a generalization of the inverse-bond-length-squared-scaling rule⁴⁰ for the off-diagonal elements of the defect potential, and of Harrison's overlap interaction model to compute the repulsive force.⁶³ However, this formalism can be easily utilized with any other reasonable assumptions for these quantities. For example, one can use an exponential approximation to replace both the inverse-bond-length squared-scaling rule and the repulsive force, as Menon and Allen have done to model the interaction of impurities and host atoms on a semiconductor surface.⁵⁶ In this Appendix, I modify the Menon and Allen model to obtain a formalism for lattice relaxation effects on deep levels which is based on an exponential approximation for the off-diagonal defect potential and the overlap interaction. The primary reason for developing this alternative formalism is to test the sensitivity of the final numerical results to the forms of these quantities. To do this, one only needs to change the forms of Eq.(3.9) and Eq.(5.4). For simplicity, I only consider nearest-neighbor relaxation in what follows. Extensions to include second-neighbor effects are straightforward.

Following Menon and Allen, I assume that the transfer matrix elements of the host Hamiltonian, V_{ij}^{ac} of Eq.(2.1), vary exponentially with changes in the interatomic separation ($d-d_H$). Then, they can be formally written as

$$V_{ij}^{ac}(d) = V_{ij}^{ac}(d_H) \exp[-\lambda(d - d_H)], \quad (\text{A.1})$$

where d_H is the perfect crystal bond length, and λ is a constant which can be fit using data on the bond stretching force constant of the crystal.⁵⁵ Here, I use the value $\lambda=2/d_H$ following Menon and Allen.⁵⁵ For simplicity, each constant $V_{ij}^{ac}(d_H)$ can be fit to the value obtained from Harrison's inverse-bond-length squared-scaling rule. Because, as discussed in Chapter III, the off-diagonal matrix elements of the defect potential V are differences in the transfer matrix elements of the impurity containing and perfect crystal Hamiltonians, they become

$$\alpha_i = V_i(d_H)(\exp[-\lambda(d_I - d_H)] - 1), \quad (\text{A.2})$$

where $i=A_1$ or T_2 , and d_I is the impurity bond length discussed extensively in the text.

Using a similar approximation, one can find a similar form for the repulsive force. In order to do this, the repulsive potential $V_0(d)$, is also assumed to decrease exponentially with changes in the interatomic separation ($d-d_H$). It thus has the form

$$V_0(d) = V_0(d_H) \exp[-\zeta(d - d_H)], \quad (\text{A.3})$$

where ζ is a constant which I take to $\zeta=2\lambda=4/d_H$ following Menon and Allen.⁵³

The quantity $V_0(d_H)$ can also be fit to values obtained from Harrison's overlap interaction model. The repulsive parts of the force,

$$F_z^r = -\frac{\partial V_0(d)}{\partial d}\bigg|_{d=d_I} \quad (\text{A.4})$$

can thus be written in this approximation as

$$F_z^r = F_0(d_H)\exp\left[-\frac{4}{d_H}(d_I - d_H)\right]. \quad (\text{A.5})$$

By using Eqs.(A.2) and (A.5), the calculations of α and the repulsive force are now based on the exponential approximation.

For A_1 -symmetric states, using $\alpha=\alpha_{A_1}$ and the repulsive force obtained in this manner and keeping the remainder of the molecular dynamics and deep level formalism the same as before, I have calculated d_I and the corresponding deep levels in some specific cases. For all cases considered, I have found that the results for both d_I and the deep levels differ by less than 1% from those obtained using the formalism discussed in the text. This is satisfying, because it indicates that the formalism developed in this dissertation might be more general than it appears at first glance. In particular, my numerical results do not depend on the details of the models used for the off-diagonal matrix elements and the repulsive force.