ELECTRONIC STATES OF ULTRATHIN GaAs/Alas SUPERLATTICES

Timothy George Gilbert

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A thesis submitted for the degree of Doctor of Philosophy 1988

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To Bryony

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How should I know what rice is? How should I know who knows what it is? I've no idea what rice is. I only know its price.

Bertolt Brecht, Die Massnahme.

ACKNOWLEDGEMENTS

It gives me great pleasure to thank those people and institutions without whose assistance, such an undertaking as this would not have been either possible or anywhere near as enjoyable. Any such list is unfortunately bound to contain omissions of which none are deliberate but a compromise has to be made somewhere. Foremost in their contribution to this work is my supervisor Steve Gurman who has my sincere gratitude for his patience and guidance throughout. I would also like to thank Paul Stephenson, Andy Smith, Suresh Parmar and Lee Flight, all of whom have helped me with the project at some stage and SERC and GEC Hirst Research Centre, Wembley for invaluable financial support.

Special thanks go to my mother, brothers and sister, Nicki Kaye, Gill Crawley, Jane Bellam, Paula Radice, Chris Parker, Steve Gilmore, Andy Brookes, Andy Davis and Liz Lomba (in roughly chronological order) who have all contributed something along the way and have (intentionally or otherwise) prevented me from becoming completely sane.

Finally, I would like to thank the last three batches of Knollocks and the members of the Leicester theory group for making my stay here both pleasureable and interesting.

> Tim Gilbert Leicester January 1988.

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INTRODUCTION

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The past decade or so has seen the rapid growth of interest in synthetic semiconductor structures which offer more possibilities than before of controlling the behaviour of charge carriers either by virtue of their size or by the use of interfaces between semiconductor layers. The charge carriers become localised to less than the usual three dimensions and the physics of low-dimensional structures has evolved to meet the needs of this new avenue of endeavour. Much of this work has concentrated on layered structures comprised of gallium arsenide and aluminium arsenide (or the alloy) and these form the basis for the study here.

Prominent in this field has been the interest in superlattice structures which are comprised of alternate layers (a few hundred Å thick) of two semiconductors chosen because of the similarity in their lattice parameters (for the above pair, the difference is less than 0.1%). When the layers are this thick, they retain much of their bulk character so that the bulk energy levels of the constituent materials align at the interfaces to form atomically abrupt potential steps. The most important of these levels are the top of the valence band and the bottom of the conduction band since they are respectively the highest occupied and the lowest unoccupied levels and are therefore relevant in any discussion of electronic transitions. They align at the interface to form the (almost legendary) valence and conduction band discontinuities which act to confine carriers in particular layer types. As they are periodic along the superlattice axis, they give rise to a potential profile similar to that of the Kronig-Penney model (Kronig and Penney, The resulting confinement leads to the formation of 1930).

quantized states, the energies of which can be altered by varying the layer thicknesses as well as using different materials (including alloying), a process often referred to as 'band-gap engineering'. This work is intended as a contribution to the understanding of the mechanisms of charge confinement in these systems.

In any theoretical study, there must be some sort of a compromise made between the accuracy of the work and the versatility and ease of implementation of the particular method used. A simple model will typically be flexible in its approach and will include those features which are thought to have the largest influence on the properties of such systems. Whilst their predictive power may not be great, they do not require large computing resources and are capable of furnishing considerable physical insight. A more sophisticated treatment on the other hand will attempt to include many small but non-negligable effects, making them more cumbersome to implement and more taxing on the available computing resources. The results however may be sufficiently accurate firstly, to permit a comparison with experimental data and secondly, to highlight the shortcomings (if any) of more elementary approaches. Both are necessary in the development of understanding in any branch of science and should be viewed as being complementary to, rather than competing with, each other.

The electronic structure calculations performed here adopt the empirical pseudopotential formalism which is capable of reproducing many of the properties of bulk semiconductors reasonably accurately with the disadvantage of having to use a large basis set. This then falls into the latter category as

discussed above. Electronic structure calculations using the pseudopotential method are discussed in detail in chapter two and examples of the band structures of the two semiconductors of interest in this thesis, gallium arsenide and aluminium arsenide, are calculated at the end of the chapter to illustrate it.

One of the fundamental difficulties encountered in studying such systems is that of actually growing them. Controlling the growth conditions (temperature, pressure, the ambient concentration of atomic and molecular species etc.) on the atomic level is very expensive, usually quite slow and necessarily implies paying careful attention to all pertinent These however have been overcome to a large extent matters. by several methods including molecular beam epitaxy (MBE), metalorganic vapour phase epitaxy (MOVPE) and others which have been able to obtain high quality (relatively defect free) materials and, in the case of layered structures, interface widths of less than two atomic layers. The two methods of growth mentioned here are briefly described in chapter three. This chapter also contains details relating to the effects of the band line-up on the resulting electronic properties and an outline of how such offsets are measured by both theory and experiment. The chapter ends by discussing some of the issues still unresolved and briefly mentioning some of the more detailed aspects of the electronic structure of superlattices, some of which play an important role in the systems studied here.

Chapter four begins by illustrating the geometric considerations which are important in the ultrathin systems studied here. These include the crystal structure of all the

superlattices and the reciprocal space details which are relevant to the understanding of the electronic states. For such thin systems, any effects related to and occurring at the interface are of crucial importance since the interface regions take up so large a part of these structures. To model accurately the effects of this periodic array of interfaces, a rigorous self-consistency requirement is employed to account for their effects. The general philosophy and the theoretical details of the self-consistent method are described in chapter four which also includes details of the special points method of performing the required Brillouin zone integrals. The chapter ends by parametrizing the method so that the band structures of both bulk materials are accurately reproduced and a test of the accuracy of the scheme is also included.

The primary object of this work is the calculation of the electronic properties of $(GaAs)_n(AlAs)_n$ superlattices from n=1 to 4 and their variation with n. These are presented in chapter five where the usual crystal properties such as the self-consistent potential, the valence charge density etc. are included and compared with those obtained from the starting (empirical) potential to illustrate the effects and importance of self-consistency. Also, those superlattice states where significant confinement effects occur are described in detail as the behaviour of these states will be used to estimate the size of the valence band offsets present in these systems.

Chapter six contains the results of subjecting ultrathin superlattices to hydrostatic pressure and is intended not only to illustrate the effects of pressure on ultrathin systems but also hopefully to show the versatility of the method employed here. The self-consistent method is used for both bulk

materials and a comparison of these calculations with experimental findings is included. Similar calculations are performed on the n=3 superlattice and the behaviour of those states here is described in detail. Chapter seven concludes the thesis and includes a critical review of the work described and suggests other possible areas of work which may be useful as an extension to that carried out here.

CHAPTER TWO

ELECTRONIC STRUCTURE CALCULATIONS

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2.1 INTRODUCTION

Condensed matter physics concerns itself with the variety of matter that results on the condensation of atoms or molecules to form a conglomeration. The resulting mass may be liquid or solid and if the latter, may be either crystalline, where the atoms are arranged in a regular fashion, or amorphous, where the structure is essentially random. This thesis is only concerned with crystalline solids where the atomic positions are precisely known.

The study of crystalline solids usually addresses itself to two not unrelated aspects: the exact arrangement of the atoms in the three dimensional array (structural geometry) and the behaviour of the electrons in this crystalline matrix. The former includes both the shape of the basic building block of the solid, the unit cell, and also the atomic layout within the unit cell. The latter will reveal itself in the type of bonding present, e.g. covalent, ionic etc. and through the bonding, will seek to adopt the most favourable atomic configuration possible. The two are then seen to be strongly allied in determining many of the physical properties of the solid.

When atoms coalesce, the electrons near to the atomic core are only slightly perturbed by the new situation but the outer or valence electrons interact strongly with the valence electrons of other atoms and the previously quantized atomic levels broaden into bands. The way and extent to which they do this is fundamental to our understanding of the ways in which electrons behave in solids and the resulting properties are unique to each solid. The electrons, as well as controlling the more obvious conduction properties also play a central role in magnetism, superconductivity and the optical response to

name but a few. The electronic properties thus underpin much of the inherent physics of solids and the calculation of these properties is a natural first choice in understanding their nature. It comes as no surprise then to see the extensive efforts invested along these lines.

The methodology involved in calculating the electronic properties i.e. the band structure, is now well developed, and many computational schemes of differing complexity exist such that it has become a routine exercise in many theory groups. Whilst the language of quantum mechanics provides a useful way of formulating the problem, the different methods vary in size and type of their approximations, some appealing to simple, intuitive methods to provide physical insight and other more complicated theories used to furnish accurate numerical results. With the developments in high speed computers, more complex systems are capable of being studied with greater accuracy than before. By such advances, our understanding of such systems not only improves, but can become modified to a large extent.

From the multitude of techniques used in calculating band structures, the self-consistent pseudopotential method is adopted in this thesis. This method has been applied to the study of semiconductor surfaces, Schottky barriers and semiconductor superlattices with great success (Cohen, 1980). Details on the self-consistent method are to be found in chapter four while pseudopotentials are discussed in section three of this chapter.

2.2 BAND THEORY

Calculating the band structure of a solid means solving the Schrodinger equation

$$[-\frac{1}{2}\nabla^{2} + V(r)]\psi_{n}(k,r) = E_{n}(k)\psi_{n}(k,r) \qquad (2.1)$$

at T=0K, with realistic assumptions about the form of the potential V(r) and the electronic wavefunctions $\Psi_n(\mathbf{k}, \mathbf{r})$ (note that atomic units are used where e=m=n=1, the unit of energy is the Hartree (1Ha=27.2eV) and the unit of length, the Bohr radius, is equal to 0.529Å. They will be used throughout the thesis unless otherwise stated). Here k is the electron wavevector and n labels the electronic bands. The manyelectron problem has been replaced by the one-electron picture where all the other electrons are treated in some average fashion. Many body effects are small in intrinsic semiconductors because of the low electron density. Neglecting them (which does not introduce significant error) is a practical consideration because of their complexity.

The periodic array of atoms which characterises crystalline solids can be exploited to make possible the solution of (2.1). Such systems do not however possess infinite periodicity as they always terminate in surfaces where the periodicity in the direction normal to the surface is broken. The expedient of periodic or Born-von-Karman boundary conditions however imposes an artificial periodicity in this direction. In one dimension, the line of atoms are joined at the ends to make a loop and in two dimensions a torus results. In three dimensions however no topological contortion can satisfy these boundary conditions but it still works admirably as a

mathematical device (Ziman, 1972). They constrain the wavevector to certain quantized values, but since the sample is large compared to the atomic size, the distribution of points in k-space is essentially continuous.

Bloch's theorem (Bloch, 1928) means that the mathematically infinite lattice can then be reduced so that only the unit cell needs to be considered. It states that the wavefunction will be of the form

$$\Psi_{n}(\mathbf{k},\mathbf{r}) = \exp(\mathbf{i}\mathbf{k}\cdot\mathbf{r}) \cdot \mathbf{U}_{n}(\mathbf{k},\mathbf{r}) \qquad (2.2)$$

where $U_n(k,r) = U_n(k,r+L)$, (L being a lattice vector) i.e. it has the periodicity of the lattice. In an analogous way, k or reciprocal space will have similar conditions imposed upon it and we need only consider the first Brillouin zone (often abbreviated to just Brillouin zone or simply BZ) which is the smallest repeat unit in k-space. The shape of the BZ will depend on the Bravais lattice underlying the crystal structure of the solid.

Since the function $U_n(\mathbf{k},\mathbf{r})$ has the periodicity of the lattice, it can be expanded in plane waves

$$U_{n}(\mathbf{k},\mathbf{r}) = (1/\sqrt{\Omega}) \sum_{\mathbf{K}} u_{nk}(\mathbf{K}) \exp(i\mathbf{K}\cdot\mathbf{r}) \qquad (2.3)$$

where the K's are reciprocal lattice vectors (rlv's) and the unit cell volume is Ω . The potential can similarly be expanded in plane waves

$$V(\mathbf{r}) = \Sigma \ v(\mathbf{K}) \ \exp(i\mathbf{K} \cdot \mathbf{r})$$
(2.4)
K

so that the Schrodinger equation becomes equivalent to solving a set of simultaneous equations

$$\left[\frac{1}{2}(k+\kappa)^{2}-E_{n}(k)\right]u_{nk}(\kappa) + \sum_{\kappa'}v(\kappa-\kappa')u_{nk}(\kappa') = 0 \qquad (2.5)$$

which can be written as a secular determinant

det
$$\left| \left[\frac{1}{2} (\mathbf{k} + \mathbf{K})^2 - \mathbf{E}_n(\mathbf{k}) \right] \delta_{\mathbf{K}, \mathbf{K}'} + v(\mathbf{K} - \mathbf{K}') \right| = 0$$
 (2.6)

The secular matrix thus requires the calculation of the matrix elements of the potential

$$\mathbf{v}(\mathbf{K}-\mathbf{K'}) = \langle \mathbf{k}+\mathbf{K'} | \mathbf{V}(\mathbf{r}) | \mathbf{k}+\mathbf{K} \rangle \qquad (2.7)$$

where the Dirac brackets are used for notational simplicity. Direct solution of (2.6) using the full potential is however impractical except possibly for very small atoms. Near to the ion cores, the potential is strong enough for it to bind electrons into core states which are strongly localised around the core and play no part in conduction processes. The resulting wavefunctions are profoundly affected by the potential and have strong, short wavelength oscillations near the core region. Such oscillatory behaviour can only be accurately reproduced if the expansions (2.3) and (2.4) contain many plane waves and hence the secular matrix becomes prohibitively large (Heine, 1970). The strength of the potential then makes the plane wave expansions unmanageable for the purpose of solving (2.6).

It is not unsurprising then that nearly free electron (NFE) theory is able to account for the broad features of

semiconductor band structures. NFE theory implicitly assumes that the potential is weak enough so that it can be treated as a small pertubation to the free electron (V(r)=0) situation. Low order perturbation theory then enables one to calculate the band structure which is given by (Ziman, 1972; Ashcroft and Mermin, 1976)

$$E(\mathbf{k}) = \frac{1}{2} \left[E^{0}(\mathbf{k}) + E^{0}(\mathbf{k} - \mathbf{G}) \right] \pm \frac{1}{2} \left\{ \left[E^{0}(\mathbf{k}) - E^{0}(\mathbf{k} - \mathbf{G}) \right]^{2} + 4 \left| v(\mathbf{G}) \right|^{2} \right\}^{1/2}$$
(2.8)

where $E^{0}(\mathbf{k}) = \frac{1}{2}\mathbf{k}^{2}$ and $E^{0}(\mathbf{k}-\mathbf{G}) = \frac{1}{2}(\mathbf{k}-\mathbf{G})^{2}$ are the free electron energies and V(G) is a potential matrix element. The well known result is that far from the Bragg plane where $|\mathbf{k}| = |\mathbf{k}-\mathbf{G}|$, the energy is free electron like but deviations from the free electron parabola become predominant near to them. If the Bragg condition is satisfied exactly then

$$E(k) = E^{U}(k) \pm |v(G)|$$
 (2.9)

so that the band splits to produce a band gap of size 2|v(G)|. The predicted gap is much too large to make two band NFE theory quantitatively useful, but the agreement with the basic shape of the band structures of elemental semiconductors such as Si and Ge poses a problem. In particular, it suggests that the valence electrons experience a potential that is weaker than that which the core electrons see. This point has been put to practical purpose in the case of some metals in order to map out the fermi surface (Ashcroft, 1963) with good agreement with experiment.

That valence electrons do not "see" the full potential was perplexing for a time. Explanations for the relative success

of simple NFE theory were sought after since old ideas about the strength of the interaction between the valence electrons and the ion cores could not still be valid. Much of the initial success of pseudopotential theory was in explaining the good results and limitations of NFE theory and it is to pseudopotentials that we now turn.

2.3 **PSEUDOPOTENTIALS**

One of the first attempts to try to account for the successes of NFE theory was by the formulation of orthogonalised plane waves (OPW's) due to Herring (1940). The OPW's were constructed so as to reproduce both the correct oscillatory form of the wavefunction near to the ion cores and the plane wave nature in between. The OPW's were defined by

$$\psi(\mathbf{k},\mathbf{r}) = |\mathbf{k}\rangle - \sum_{\mathbf{c}} \langle \phi_{\mathbf{c}}(\mathbf{k},\mathbf{r}) | \mathbf{k}\rangle \phi_{\mathbf{c}}(\mathbf{k},\mathbf{r}) \qquad (2.10)$$

where the sum is over all the core states $\phi_{c}(\mathbf{k},\mathbf{r})$ to which the OPW's are made orthogonal, i.e.

$$\langle \psi(\mathbf{k},\mathbf{r}) | \phi_{\mathbf{C}}(\mathbf{k},\mathbf{r}) \rangle = 0 \qquad (2.11)$$

Eigenfunctions can then be constructed from a linear combination of OPW's and a secular determinant similar to (2.6) results which, since the OPW matrix elements converge much more rapidly in k-space than plane wave ones, is much smaller in size. Whilst providing an accurate way of calculating band structures, the OPW method does not illustrate clearly the reasons why NFE theory works so well.

This had to wait until the reformulation of the OPW method

separately by Antoncik (1959) and Phillips and Kleinman (1959) who were responsible for first using the term pseudopotential. They noted that the condition for orthogonalising the eigenfunctions of the hamiltonian to the core states i.e. equation (2.11) was satisfied by

$$\psi(\mathbf{k},\mathbf{r}) = \chi(\mathbf{k},\mathbf{r}) - \Sigma \langle \phi_{\mathbf{C}}(\mathbf{k},\mathbf{r}) | \chi(\mathbf{k},\mathbf{r}) \rangle \phi_{\mathbf{C}}(\mathbf{k},\mathbf{r}) \qquad (2.12)$$

Using this form in (2.1) gives (with reduced notation)

$$H\chi + \Sigma (E-E_C)\phi_C \langle \phi_C | \chi \rangle = E\chi \qquad (2.13)$$

which, when formally compared to (2.1) by writing

$$[H + V_{y}(r)]\chi = E\chi$$
 (2.14)

allows the identification of the pseudowavefunctions χ and the pseudopotential as being the sum of the actual periodic potential V(r) and the core orthogonalisation term

$$V_{ps}(r) = V(r) + \sum_{c} (E - E_{c}) \phi_{c} \langle \phi_{c} | \qquad (2.15)$$

Near to the ion cores, the potential V(r) is negative (attractive) and the second term is positive since E is always greater than E_c i.e. the valence and conduction states of interest lie above the core levels in energy. The partial cancellation that results, sometimes as much as 95% (Heine, 1957), means that the pseudopotential (which the valence electrons see) is weaker than the actual potential which is the justification that we seek for NFE theory. Thus the

pseudowavefunctions are smoothly varying and can be expanded in a small number of plane waves

$$\chi(\mathbf{k},\mathbf{r}) = (1/\sqrt{\Omega}) \Sigma u(\mathbf{K}) \exp[i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}] \qquad (2.16)$$

$$\mathbf{K}$$

The effect of pseudizing is illustrated in figure 2.1 for a model pseudopotential.

Following the same procedure as before, we get

det
$$\left| \left[\frac{1}{2} (\mathbf{k} + \mathbf{K})^2 - \mathbf{E}_n(\mathbf{k}) \right] \delta_{\mathbf{K}, \mathbf{K}'} + \mathbf{v}_{ps}(\mathbf{K} - \mathbf{K}') \right| = 0$$
 (2.17)

where the pseudopotential matrix elements are given by

$$v_{ps}(K-K') = \langle k+K' | V_{ps}(r) | k+K \rangle$$
 (2.18)

analogous to (2.7). The procedure resulting in (2.14) is an exact mathematical transformation of the Schrodinger equation which retains the same valence and conduction eigenvalues but alters the eigenfunctions. The disadvantage is that the pseudopotential, unlike the actual potential, is not a simple function of position but is an integral or non-local operator. This point will be dealt with in section four but for now, the local or on-Fermi-sphere approximation is adopted so that matrix elements like (2.18) become functions of G=|K-K'| only i.e.

$$v_{ps}(G) = \langle k+G | v_{ps}(r) | k \rangle$$
 (2.19)

The total pseudopotential of the solid can then be divided up into contributions from each unit cell and from all basis



Figure 2.1 The effects of pseudizing away the core states in the true potential (a) is shown for a model pseudopotential (b). The oscillations in the original wavefunction (c) near the ion cores (shown as dots) are smoothed over in the pseudowavefunction (d) (from Harrison, 1970).

atoms to give

$$v_{ps}(G) = \sum_{\alpha} S_{\alpha}(G) V_{\alpha}(G)$$
(2.20)

where the sum is over the α atom types present. The structure factor $S_{\alpha}(G)$ depends only on the crystal structure and is given by

$$S_{\alpha}(G) = (1/N_{\alpha}) \sum_{\alpha} \exp(iG.R_{j\alpha}) \qquad (2.21)$$

where the N_{α} atoms of type α are positioned at $R_{j\alpha}$ and the pseudopotential atomic form factor $V_{\alpha}(G)$ is the fourier transform of the atomic pseudopotential

$$V_{\alpha}(G) = (1/\sqrt{\Omega_0}) \int v_{\alpha}(r) \exp(-iG.r) d^3r \qquad (2.22)$$

 Ω_0 being the atomic volume. For semiconductors having the zincblende structure, (2.21) can be rewritten as

$$v_{ps}(G) = s^{S}(G)v^{S}(G) + is^{A}(G)v^{A}(G)$$
 (2.23)

where the symmetric and antisymmetric form factors are the semi-sum and the semi-difference of the two atomic pseudopotentials

$$v^{S}(G) = \frac{1}{2} [v_{1}(G) + v_{2}(G)]$$

$$(2.24)$$

$$v^{A}(G) = \frac{1}{2} [v_{1}(G) - v_{2}(G)]$$

and the structure factors are

$$S^{S}(G) = \cos(G.\tau)$$

$$(2.25)$$

$$S^{A}(G) = \sin(G.\tau)$$

where $\tau = (a_0/8)(1,1,1)$ i.e. half way between the two basis atoms. With a weak pseudopotential, the matrix elements are expected to fall off rapidly in k-space and hence we may truncate at some convenient point G_{+} say and set all $v(G>G_{+})$ equal to zero. In practice, truncation usually depends on the available computing resources since the cutoff point will determine the size of the secular determinant (2.17) which needs to be solved. For the present cutoff of $|G_{+}|^2=11$, only 6 form factors (3 symmetric and 3 antisymmetric) are required since for some reciprocal lattice vectors, the structure factors (2.25) can be zero. This cutoff means that 51 plane waves are used as a basis set corresponding to a matrix size of 51 X 51. These form factors are usually treated as adjustable parameters so that the resulting band structures reproduce prominent energy gaps as measured by experiment. Empirical pseudopotentials are often quoted in this way (Cohen and Bergstresser, 1966; Baldereschi et al., 1977) and have proved to be both useful and versatile in solid state physics.

However, all is not a bed of roses: the pseudopotential representation has its own peculiar features which, while not hindering their use, does present problems that need to be acknowledged and taken account of. These are the subject of the next section.

2.4 IDIOSYNCRACIES

2.4.1 Indeterminacy

In section three, it was noted that the condition for the orthogonality of the valence states to the core states (2.11) gave rise to a pseudopotential (2.15). However, Austin et al. (1962) pointed out that a pseudopotential defined by

$$V_{\rm ps}(r) = V(r) + \Sigma F_{\rm c}(k) \langle \phi_{\rm c}(k,r) |$$
 (2.26)

where $F_c(k)$ is an arbitrary function of the core states, produces the same valence eigenvalues as the original hamiltonian but different eigenfunctions. The arbitrary nature of $F_c(k)$ means that it can be defined to suit the purpose of the exercise. For instance, one may define it in such a way so as to produce good cancellation in (2.15) resulting in a smooth, weak pseudopotential and hence a small secular matrix or so that the radial nodes of the wavefunction near to the ion core are eliminated giving rise to a soft core pseudopotential. Such procedures are inevitably somewhat messy and the resulting plethora of pseudopotentials all used to describe the electronic properties of a given system is testament to this.

2.4.2 Non-locality

The pseudopotential defined by (2.15) is a non-local or integral operator and not a simple function of position as is the actual potential V(r). The non-locality means that the pseudopotential operates on states according to their angular momentum quantum number 1 so that s electrons see a different pseudopotential to p electrons and so on. Consequently the matrix elements (2.18) are strictly functions of four variables K, K', G=|K-K'| as well as the energy dependence. The

non-locality however tends to increase with atomic number (Cohen and Heine, 1970) so that for reasonably light elements, the local or on-fermi-sphere approximation is good. It works well provided that the valence bands are well separated from the core states so that the difference $(E-E_C)$ in (2.15) is almost constant and can be replaced by some average energy (usually the fermi level) and that the cancellation in (2.15) is roughly equal for all relevant components of angular momentum (Chelikowsky and Cohen, 1976).

Whilst empirical pseudopotentials have been used to describe many of the electronic properties of semiconductors with satisfactory agreement with experiment, they have found to be deficient in some respects. In particular, the valence band widths and the charge located in the bonding region are incorrectly reproduced. The introduction of non-locality was found to increase the accord with experiment (Chelikowsky and Cohen, 1976; Phillips and Pandey, 1973) although it is not clear whether the deficiency is inherent to local pseudopotentials or whether careful refinement could improve their accuracy (Zunger, 1979).

The effects of non-locality have been systematically studied by Zunger and Ratner (1978) and have found to be important in systems where either the d electrons are predominant e.g. transition metals, or where there aren't many core states to pseudize away as in the first row elements. Semiconductors, falling between the two in the periodic table, are likely to have a small non-local potential and hence the use of the local approximation is at least reasonable.

The next section illustrates the use of local, empirical pseudopotentials to calculate the band structures of both bulk

GaAs and AlAs. The parameter set used is that of Baldereschi et al. (1977) and the necessary adjustments made to use them as inputs in the superlattice calculations are explained.

2.5 EMPIRICAL PSEUDOPOTENTIALS

2.5.1 Geometrical Considerations

Before presenting results of pseudopotential calculations, it is useful to briefly mention pertinent details of the crystal structure i.e. the unit cell and the k-space counterpart the BZ. Both GaAs and AlAs crystallize into the zincblende structure as do most binary semiconductors (some II-VI compounds for example PbSe and PbS however, adopt the sodium chloride structure). Ternary and quaternary alloys based on elements from groups III and V of the periodic table also usually adopt the zincblende structure although there is some evidence in particular cases where crystallization into a different phase has found to be energetically more favourable (Srivastava et al., 1984). Whether this is just a local atomic rearrangement or takes place on a large scale, as has been reported in the case of the (AlGa)As alloy by Kuan et al. (1985), is a matter of considerable importance and debate.

The zincblende unit cell has a face centred cubic space lattice with two basis atoms, one situated at the origin and the other a quarter along the body diagonal. The BZ is a truncated octahedron and has body centred cubic (bcc) symmetry. Use of the symmetry elements permits the definition of the irreducible BZ which is the smallest segment that can be used to reconstruct the whole BZ. The irreducible BZ therefore contains all the information present in the whole BZ since the value of any function F at a position R outside the irreducible



Figure 2.2 The Brillouin zone showing the main symmetry points and directions for the fcc lattice. The irreducible Brillouin zone is also shown.

BZ can be related to the value at a position r within it by

$$\mathbf{F}(\mathbf{R}) = \mathbf{T}_{i} \mathbf{F}(\mathbf{r}) \tag{2.27}$$

where T_i are the symmetry elements of the BZ. The BZ for the fcc lattice as well as the irreducible part are shown in figure 2.2. The band structure E(k) is then calculated with k a vector in the irreducible zone along lines connecting points of high symmetry. Those symmetry points used in this thesis have the following coordinates:

$$\Gamma = (0,0,0)$$

$$L = (1/2,1/2,1/2)$$

$$X = (1,0,0)$$

$$U = (1,1/4,1/4)$$

$$K = (3/4,3/4,0)$$

in units of $2\pi/a_0$.

2.5.2 Band structure calculations

As was mentioned in section three, the matrix elements of the pseudopotential fall off fairly rapidly in k-space and may be truncated so that

$$\mathbf{v}(\mathbf{G} > \mathbf{G}_{+}) = 0 \tag{2.28}$$

With $|G_t|^2=11$, only six form factors are required for zincblende semiconductors and these can be adjusted to reproduce prominent energy gaps to within experimental accuracy. Elemental semiconductors such as Si and Ge have their antisymmetric form factors equal to zero by definition leaving only three to fit. For both GaAs and AlAs, the form factors of Baldereschi et al. (1977), shown in table 2.1, are

g ²	GaAs	AlAs	
3	Symmetric -0.2290 1 -0.2200		
8 11	0.0123 0.0600	0.0260 0.0700	
3 4 11	Antisyr 0.0700 0.0600 0.0100	nmetric 0.0720 0.0625 -0.0075	

Table 2.1 Symmetric and antisymmetric form factors used in the fitting procedure to generate the band structures of GaAs and AlAs from Baldereschi et al., 1977. The form factors are in Rydbergs.

	Gallium a	arsenide	Aluminium arsenide	
	Ga	As	Al As	
a1	21.43160	1.01118	0.60924	1.67088
a2	2.19037	2.92626	2.03195	2.70211
a3	30.41915	0.40849	0.59933	0.35363
a4	-10.98827	-3.08852	-0.85048	-5.02580

Table 2.2 Pseudopotential parameters that result from fitting the analytic form (2.30) to the above form factors. The lattice constant is taken to be 10.6901 atomic units for both materials.

Sym.	Gallium a	rsenide	Aluminium	n arsenide
Point	Theory	Expt.	Theory	Expt.
Г	1.496	1.519	3.013	3.020
Х	1.692	2.010	1.991	2.229
L	1.850	1.840	2.547	2.661

Table 2.3 Comparison of theoretical band gaps calculated from equation 2.30 and experimental values at the principal symmetry points in the Brillouin zone. All are measured in electron volts above the valence band maximum. For experimental sources, see table 4.2. used to calculate the band structure. However, while the form factor representation is convenient for bulk calculations, superlattices having different geometries will have rlv's other than bulk ones and it is useful to replace the discrete form factors by continuous analytic forms for the atomic pseudopotentials. This is so that these pseudopotentials can be used in the superlattice calculations to begin the self-consistent process. The analytic forms must not only reproduce the original form factors but must also tend to the correct asymptotic limits

$$v(G) \rightarrow -(2/3)E_F + O(G^2)$$
 as $G \rightarrow 0$
(2.29)
 $v(G) \rightarrow 0$ as $G \rightarrow \infty$

 E_F being the fermi energy of a free electron gas of the same electron density as the bulk materials. The limit as G tends to zero is obtained for local potentials which contain the Coulomb potential (Harrison, 1966) and is a manifestation of self- consistent screening by the electron gas. A suitable analytic form is that suggested by Cohen and coworkers (Cohen, 1980 and references therein)

$$v(G) = \frac{a_1(G^2 - a_2)}{\{1 + \exp[a_3(G^2 - a_4)]\}}$$
(2.30)

which produces the correct asymptotic limits (2.29). By adjusting the parameters a_i the original form factor set can be reproduced. The same cutoff (2.28) must also be employed here in order to be consistent with the empirical pseudopotential


Figure 2.3 Pseudopotential atomic form factor curves for the Ga (top left) and As (top right) atoms in GaAs and the Al (bottom left) and As (bottom right) atoms in AlAs. The vertical bars show the positions of the bulk reciprocal lattice vectors and the dashed line indicates the continuation of the curve beyond the cutoff described in the text.



Figure 2.4 Energy band structure of GaAs with the top of the valence band set to zero. Notation of the symmetry points is described in the text.

method and because the same limit is used in the selfconsistent calculations. In practice, a least squares method is used to fit the adjustable parameters and the results for GaAs and AlAs are shown in table 2.2 with the resulting analytic forms illustrated in figure 2.3. The positions of the bulk reciprocal lattice vectors corresponding to $|G|^2=3$, 4, 8 and 11 are also shown, but beyond the latter limit, all matrix elements must be set to zero.

The band structures of GaAs and AlAs, shown in figures 2.4 and 2.5 respectively, with the effects of spin-orbit coupling neglected, illustrate broad similarities between the two materials. In the region of interest however, i.e. near to the band gap, there are profound differences not the least of which is that while GaAs is a direct gap semiconductor i.e. the minimum in the conduction band has the same symmetry as the maximum in the valence band, AlAs has an indirect band gap (the conduction band minimum has different symmetry to the valence band maximum). The lowest conduction band in both materials shows other prominent minima at different symmetry points in the BZ characteristic of III-V semiconductors. The energy positions of the minima are summarised in table 2.3 and are compared with present experimental values. The discrepancies between the two sets indicate that the pseudopotentials used here could be further refined in order to better the accord between theory and experiment. Since the positions of the band edges are responsible to a large extent for the nature of the electronic states resulting on the formation of a superlattice, it is crucial to establish them reasonably accurately in order to make quantitative predictions about superlattice states. This will be discussed in more detail later in this thesis.

CHAPTER THREE

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SEMICONDUCTOR JUNCTIONS

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3.1 INTRODUCTION

The use of bulk semiconductors in the electronics industry is now well established. The main reason for this is that their electronic properties are easily tuned by the incorporation of dopant atoms which make the the semiconductor n- or p-type depending on whether the dopants are donors or acceptors respectively. Another degree of freedom arises from the fabrication of semiconductor junction structures which have inevitably arisen since the incorporation of bulk structures in a device necessarily involves making electrical contacts to the semiconductor. The properties of the junction itself were not at first recognised as being important since the dimensions were such that the bulk components predominated. However with the miniaturisation of devices, the properties of the interface became more prominent (Ferry, 1984) and in some cases were the cause of device failure. It soon became clear that including the effects of the interface were important in such cases.

The first interface to come under scrutiny was the metalsemiconductor interface, or Schottky barrier as it is now known first studied by Schottky (1938) and separately by Mott (1938). (Surfaces which can be considered as a solid vacuum interface are not included here). Thermodynamic considerations force the equalisation of the fermi levels across the interface which creates a potential barrier to the flow of electrons. This simple picture produces a Schottky barrier height given by

$$V_{b} = \phi_{m} - \chi_{sc} \tag{3.1}$$

where ϕ_m is the metal work function and χ_{sc} is the semiconductor electron affinity. In reality, this picture turns out to be a limiting case fulfilled by few such systems. Reviews of this topic can be found in Williams (1982) or Brillson (1983).

Semiconductor-semiconductor interfaces or heterojunctions were first investigated theoretically by Anderson (1962) after Shockley had patented the transistor in 1951. The model consisted of two isolated semiconductors characterised by energy gaps and electron affinities. Upon contact, there is a flow of charge from one semiconductor to the other governed by the solution of Poisson's equation which results in the previously flat bands being parabolically bent in the vicinity of the interface. Discontinuities in both the valence and the conduction band result, the latter being given by

$$\Delta E_{c} = \chi_{1} - \chi_{2} \tag{3.2}$$

This electron affinity rule enjoyed widespread acceptance, in the absence of competitors, for over a decade. Modelling heterojunctions by linear theories i.e. those which obtain the barrier height as the difference of two parameters related to the isolated bulk constituents, is an appealing idea and has to some extent been verified by measurements of the transitivity of the GaAs-AlAs-Ge (110) offsets (Katnani and Bauer, 1986). In this context, transitive means that the offsets present in one semiconductor pair can be predicted from those of the other two combinations, something that stresses the influence of the bulk properties rather than those due to the precise atomic arrangement at the interface.

Other linear models of heterojunction band line-ups are described briefly in section three of this chapter.

The question of which constituent semiconductors to use for which device will depend on the purpose of the device under investigation. For the desired electronic properties, the region of interest is near to the band gap since optical transitions take place across it. It is then possible to select those semiconductors having the appropriate size and type (direct or indirect) of band gap which can, to some extent, be varied and controlled by alloying (Jaros, 1985).

The need to guard against interfacial imperfections, for example defects, contaminants, misfit dislocations etc., is also an important consideration here. The level of contamination by unwanted chemical species will depend on the care taken in the growth process although a very small background concentration is difficult to avoid. Minimising the background concentration of contaminants requires the generation of a hard vacuum down to about 10^{-11} Torr as is the case with molecular beam epitaxy. Misfit dislocations can be avoided by selecting semiconductors which have similar (to within 0.5%) lattice constants so that lattice-matching occurs (this is not the case with strained-layer superlattices where the misfit can be up to a few percent but we will not consider The continuity of atoms across the interface ensures these). that the atomic correspondence generates little elastic strain which, if it became too large, would be relieved by the generation of misfit dislocations and charge traps making for a useless device. Great care is then necessary to successfully choose and grow device quality heterojunctions.

Semiconductor superlattices, which can be considered

structurally as a periodic array of thin heterojunctions, are composed of thin (0-300Å) layers of two semiconductors stacked periodically on top of each other. First proposed by Esaki and Tsu (1970), they differ from heterojunctions by virtue of their small dimensions which means that microscopic quantum effects would exert influence on the electronic, optical and transport properties in novel ways. Indeed many of the properties of superlattices proposed by Esaki and Tsu have been observed experimentally as well as others which were not theoretically predicted. Those properties that are relevant to this work will be described in this chapter. Overviews of the subject can be found in review articles by Ando et al. (1982) and Kelly and Nicholas (1985).

3.2 METHODS OF GROWTH

Once it was postulated that quantum well structures would have novel and interesting properties, it became a matter of realising such structures and putting them to the test. Out of the many growth methods that can be used to grow structures to the required precision, molecular beam epitaxy (MBE) and metalorganic vapour phase epitaxy (MOVPE) have come to the fore and now enjoy the widest application. The two methods have certain similarities and very striking differences and because their role in this field is so important, it is worth devoting some space to each.

3.2.1 Molecular Beam Epitaxy

MBE is a refined form of vacuum evaporation in which directed neutral thermal atomic and molecular beams impinge on a heated substrate under ultra-high vacuum $(10^{-10}$ to 10^{-11} Torr) conditions. The MBE apparatus is an expensive and

complicated machine consisting essentially of a growth chamber with several material sources in either atomic or molecular form contained in heated Knudsen effusion cells, which are constructed so that the emitted beam is collimated and can be shut off when required. The cell temperature, which controls not only the beam composition (monatomic, diatomic etc.) but also the flux incident on the substrate, is of vital importance in the growth process. The substrate, which can be introduced without breaking the hard vacuum, is rotated at speeds between 0.3 and 2.0 Hz to ensure uniform growth across the wafer and, in the case of alloy growth, the period of revolution must exceed the time to deposit one monolayer in order to obtain uniform composition in the growth direction. The growth rate is typically between 0.1 and 10 μ/hr (0.1 to 10 monolayers/s). The growth process is controlled by kinetic and thermodynamic factors since impinging species may or may not stick to the surface and typically change site about 10^6 times before incorporation into the bulk (Heckingbottom et al, 1983), implying the existence of kinetic barriers to various physical processes that can occur. In practice, the beam fluxes, substrate and cell temperatures, the opening and closing of cell shutters etc. all play critical roles in determining the quality and subsequent performance of the epilayer and are therefore all controlled by computer.

As well as containing all the elements required for growth, the MBE apparatus also includes analytical tools which are used to analyse the residual gases in order to follow the reaction path as well as monitoring the growth process. The former is usually achieved with a mass spectrometer whereas the latter employs reflection high energy electron diffraction

(RHEED) for the crystal structure and either auger electron spectroscopy (AES) or angle-resolved photoelectron spectroscopy (ARPES) for the electronic structure.

The RHEED arrangement consists essentially of a 5-20 KeV electron gun which emits electrons that are incident at a very shallow angle (1-4°), and a fluorescent screen which detects the diffracted electrons. The diffraction pattern formed provides information on the morphology, symmetry and defect structures, any changes in which during growth can be used to monitor growth dynamics. It has also been found that the intensity of any diffracted spot oscillates and decays, the period of oscillation corresponding to the growth of one complete monolayer and the decay arising from the growth of the next layer before the first is complete (Neave et al., 1983). Annealing, which allows the atoms to readjust to their equilibrium positions, restores the original intensity and layer by layer growth can then recommence.

AES and ARPES are both standard tools for probing the electronic structure and are used extensively for this purpose. For epilayers, it is the electronic structure of the surface that is measured and changes in this are indicative of the formation of new states or the modification of already existing ones. By assigning features corresponding to electronic states in the spectra, it is possible to gain information on the formation of bonds arising from the growth of the epilayer. More details on the importance of the electronic structure and the MBE process can be found in a review article by Joyce (1985).

3.2.2 Metalorganic Vapour Phase Epitaxy

MOVPE, instead of using elemental sources as is the case with MBE, typically uses organometallic compounds for cation sources and non-metal hydrides for the anion source e.g. to grow GaAs, the starting materials are likely to be trimethylgallium (TMG) and arsine. The source gases are purified below the part per 10⁹ level for the growth of undoped samples, and then reacted together in low vacuum (10^{-6} Torr) or at atmospheric pressure to deposit the required semiconductor on to the substrate, which sits on a heated susceptor. As a consequence of the reaction, a large volume of either unreacted material or gaseous biproducts collects around and below the substrate, the former being known as the boundary layer. This backlog may either enhance or inhibit the growth, the usual growth temperatures (600-850°C) using the boundary layer to prevent outward diffusion of unwanted reagents thereby enhancing the reaction and hence growth. Below these temperatures, incorporation and decomposition are the rate limiting steps whilst above them, species rapidly desorb from the surface. The growth rate tends to be quicker than for MBE and can similarly be controlled by computer. Because of the high concentration of background gases, monitoring the growth process is severely impeded and so information that would otherwise have been useful in predicting and understanding the competing interactions that are present is difficult to obtain. This does not however prevent it from being popular and the fact that it produces excellent quality samples at a much lower cost than the MBE arrangement also works in its favour. It is also easier, more versatile and can accommodate larger substrate areas than MBE.

Both methods are equally able to produce good quality materials and, more specifically, abrupt interfaces with interface widths of about one monolayer. Such a stringent requirement is essential for ultrathin superlattices and even for a 100Å quantum-well structure, a monolayer variation in thickness changes energy levels by typically a few meV.

These two processes as well as others have made it possible to study high quality samples in a quantitative fashion and it is no longer the case that poor experimental results can be blamed on poor quality samples. The expertise of the crystal grower is now widely recognised as being of great importance in the study of systems that require accuracy on the atomic scale.

3.3 BAND OFFSETS

Superlattices are frequently described in terms of the effect that the periodic superlattice potential has on the bulk energy levels, usually the band edges (band bending takes place over roughly 1000Å and can therefore be neglected). In conditions of space charge neutrality, the band edges of the two semiconductors are aligned adjacent to each other and repeated in the superlattice direction giving rise to a series of wells and barriers in both the valence and conduction These modify the properties of the carriers (both bands. electrons and holes) in this energy range in a way similar to the square barrier problem in undergraduate quantum mechanics. Most, if not all superlattices are more complicated than this picture would suggest and unravelling the different competing effects can be a very complicated procedure.

3.3.1 Band Alignment

For superlattices with large periods however, the above description is a reasonable one (although still incomplete of course) and it means that there will be three distinct kinds of band line-up that are possible. These will depend only upon the size of the forbidden energy gaps of the semiconductors and where they slot together on an energy scale. They are all shown in figure 3.1 and are discussed briefly below.

(a) Type I. These occur when the band gap of the small gap semiconductor fits entirely inside the gap of the other semiconductor. Both electrons and holes will be confined in the same material and hence the probability of recombination will be high making them excellent candidates for laser devices. The alignment means that the difference in band gaps is equal-to the sum of the band discontinuities

$$\Delta E_{a} = |E_{a}(1) - E_{a}(2)| = \Delta E_{v} + \Delta E_{c} \qquad (3.3)$$

and hence knowing ΔE_g allows the characterisation of the line-up by calculating or measuring either of the band discontinuities. Typical examples are the GaAs/(AlGa)As system for aluminium concentrations in the alloy of less than about 45% (where the alloy changes from a direct gap semiconductor to an indirect one (Baldereschi et al., 1977)) and the GaAs/GaSb system.

(b) Type II. If the complete overlap of band gaps is replaced by a partial overlap, then a type II superlattice results.



Figure 3.1 The three possible band-edge alignments that can occur at a heterojunction interface are shown here with (a) type I, (b) type II and (c) type III. The artificial spatial separation of the valence and conduction band discontinuities in (c) is for presentation purposes only. The line-up can be described by the relation

$$\Delta E_{g} = |\Delta E_{v} - \Delta E_{c}| \qquad (3.4)$$

with the additional constraint that $E_g > \Delta E_v$. Such a staggered line-up is found in the GaAs/(AlGa)As system for aluminium concentrations greater than about 45%. Electrons and holes are thus spatially separated and the probability of recombination is much less than in type I superlattices. By varying the alloy composition, a type I to type II transition can occur and thus the alloy composition is an important variable in determining the properties of such systems. Such a transition has been observed in (AlGa)As/AlAs quantum well structures by Wilson et al. (1986).

(c) Type III. When there is no overlap between the band gaps, type III superlattices result. Unlike the previous two cases which are both semiconducting, these are semi-metallic in behaviour. The line-up, as in the previous case, is described by (3.4) but with the constraint that $E_{g} < \Delta E_{v}$ so that electrons and holes are confined in different layers. However, the overlap of the valence and conduction bands means that both electrons and holes are expected to be able to find conduction channels by mass migration across the interface. Such a phenomena is predicted for the InAs/GaSb superlattice for an InAs layer thickness greater than about 115Å (Sai-Halasz et al., 1978) where a semiconductor-semimetal transition is observed i.e. a type II to type III transition.

These then span the range of structures that are possible and choice between them depends on the device requirements. Such structures are often analysed in terms of models derived

from the simple idea of band alignment using an effective mass treatment (see for example Bastard, 1981) and while encompassing the major features involved, omit certain complexities which can have profound consequences (Jaros, 1985).

3.3.2 Role of Band Offsets

The band offsets are, without doubt, the most important parameter used to characterise systems which result when two semiconductors are lattice-matched to each other (Margaritondo, 1986). This is because they are often larger than the kinetic energy of the electrons in the superlattice direction and so quantum confinement occurs. The height and width of the confining barrier play a major role in determining the degree of confinement (which increases with both variables) and are therefore important in considering device possibilities. The operation of modern electronic devices, the high electron mobility transistor (HEMT) for example, critically depend on the line-up geometry. It is desirable that for good operation, the conduction parallel to the interface be optimised and at the same time, the conduction perpendicular to the interface be minimised (Kroemer, 1983). The operation of the HEMT as well as other novel devices made possible by modern growth techniques can be found in the review by Board (1985).

Precise knowledge of the band offsets for a variety of semiconductor pairs enables the selection of appropriate ones for the particular desired purpose. Determining these offsets, both theoretically and experimentally, has proved to be a difficult task and even on the most commonly studied system, the GaAs/(AlGa)As interface, there is still

controversy although a consensus has almost been reached.

3.3.3 Determination of Band Offsets.

3.3.3.1 Theoretical Determination

By far the most common method used to predict band offsets is to use a linear theory which subtracts two bulk related parameters which are calculated or measured in some fashion. The Anderson model (1962), described in section one of this chapter, uses electron affinities to obtain the conduction band discontinuity and has in its time received widespread support which probably reflects both the lack of competition and the variability of structures grown using (by modern standards) primitive growth technologies. With the increasing availability of high quality samples, it has been relegated to the status of "rule of thumb" because of its consistent disparity with the growing body of reliable experimental data.

Other linear theories that have received much interest are those due to Harrison (1977), Frensley and Kroemer (1977) and Tersoff (1984b). Harrison's LCAO (linear combination of atomic orbitals) model evaluates the position of the top of the valence band by using atomic state energies and matrix elements between p states on adjacent sites. By aligning these energies, one can obtain the valence band discontinuity for as many semiconductor pairs as are studied. The method of Frensley and Kroemer (1977) uses self-consistent bulk energy levels and average potentials calculated by the pseudopotential method and also includes an ionic part apportioning the ionic charge according to the semiconductor electronegativities. The presence of interfacial dipoles is ignored, contrary to Tersoff (1984b) where the interface

dipole is taken to be the dominant driving force determining the band offsets. Tersoff's method has the added advantage in that it can also be applied, with equally good results, to Schottky barriers (1984a) thus identifying common features between the two systems anticipated on intuitive grounds by many workers in this field. His premise, that there is a level in semiconductors that plays the same role as the fermi level in metals and that differences in these values inevitably leads to charge transfer and hence a dipole which acts to oppose further charge transfer when a heterojunction is formed, stresses the importance of the dipole in the formation of band offsets. The method has been compared with reliable experimental data and found to be accurate to 0.1eV (Margaritondo, 1985).

Linear theories have the advantage in that they provide a conceptually simple way of understanding and calculating band offsets. They are accurate to no better than about 0.1eV and a limit on their accuracy of 0.15eV has been arrived at by Katnani and Margaritondo (1983) which is met (or even bettered) only by Tersoff's method (1984b). From the point of view of superlattices however (since band offsets are usually measured for heterojunctions where there is only one interface), there is evidence for example on the InAs/GaSb system that a semiconductor-semimetal transition takes place at a certain critical layer thickness (Sai-Halasz et al., 1978) which implies that the offsets change with superlattice period, a conclusion backed up by experiment (Esaki, 1981). Such a dependence of the offsets in superlattices upon layer thickness cannot be accounted for by linear theories which can only propose a single value for each semiconductor pair

corresponding to the heterojunction, and so care must taken when using these values for superlattices.

It is also possible in fully self-consistent calculations to make predictions about the band offsets. The method essentially consists of calculating the difference in average potential between the two constituents in the superlattice and then using these reference levels as the average potentials in the isolated bulks. By aligning the valence and conduction band edges with these reference levels, it is then possible to estimate the band offsets. This is expected to produce good results for systems with large layer thicknesses because the individual layers will begin to resemble the properties of the corresponding bulk material if they are sufficiently thick. The question of how thick an epilayer must be so that both the bulk properties are reproduced and the band offsets stabilize at a constant value is a difficult one, although an answer of three layers or atom pairs has been tentatively reported (Bauer and Sang, 1981) although it may differ from system to The procedure is somewhat less exact for small layer system. thicknesses and its accuracy will be commented upon in chapter five where it is used for the superlattices studied here.

3.3.3.2 Experimental Determination

Experimental techniques used in the evaluation of band offsets divide roughly into two distinct groups: those which rely upon measuring device characteristics using engineering methods and those which attempt to understand the physical nature of the system by using physicist's techniques. The former group includes measuring the I-V characteristics, the C-V intercept method and C-V profiling which model the interface and hence the electronic behaviour in a simple,

intuitive way. Some of these techniques have been shown to be fairly unreliable producing data with a large scatter. For more details on these methods and their limitations, see Kroemer (1983). The latter group includes a vast number of techniques many of which either probe electronic states or transitions between states. Only those relevant to this work or those which have produced accurate and reproducible results are described.

Developing out of the recent growth in surface science, photoelectron spectroscopy (under several acronyms usually describing the photon beam energy for example, UPS, XPS etc.) is a process whereby incident photons have sufficient energy to eject electrons out of a system. By monitoring the angle and energies of the emitted electrons, it is possible to gain information on the occupied electronic states (Williams et al., 1980). Since photons interact strongly with matter, those electrons ejected will have originated from the surface layers and it is this surface sensitivity that makes it useful in following epilayer growth. The position of the valence band maximum shows up as an edge on energy distribution curves (Margaritondo, 1983) and if the shift in the position of the edge during growth is large, resolution of the features due to the different valence band edges is good and errors smaller than 0.1eV are possible. The presence of surface states and core level shifts complicate the analysis but can be taken account of fairly accurately.

Optical experiments such as infrared absorption and photoluminescence excitation spectroscopy monitor transitions between excitonic states i.e. between hole and electron states, and the spectra show peaks at positions corresponding

to the energy difference between the participating states. The first determination of the band offsets in the technologically important GaAs/(AlGa)As system used the former technique (Dingle et al., 1974) and obtained a valence band offset equal to 15% of the total direct energy gap difference. Optical methods usually assume a particular model typically including values for the electron and hole effective masses (usually those of the bulk constituents) and may include the effects of band non-parabolicity etc. which is used to analyse the experimental measurements. Comparing the model against the experimentally observed transitions allows the determination of the offset which best fits the data. However for the above determination, it was found that other values may fit the data better and more significantly, that the fit is fairly insensitive to the choice of offset (Wolford et al., 1986). As a result, the "15% rule" has now been discarded with many recent determinations of the valence band offset being close to 40% of the total direct energy gap difference (see for example Wilson et al., 1986 for a graph of recent determinations of the valence band offset for a variety of aluminium concentrations in the alloy).

As well as predicting offsets, photoluminescence can also furnish estimates of layer thicknesses and thickness fluctuations from the position of the peak and its linewidth, variations in thickness tending to broaden the peaks. This makes it a very useful probe in the understanding of superlattices.

Another method proposed by Langer and Heinrich (1985) is based on the fact that transition metal defects in semiconductors align themselves according to some reference

level common to all semiconductors. The valence band discontinuity is then just the difference in energy positions of the defect in the two semiconductors comprising the heterojunction. It has been suggested that the reference level is the vacuum level (Ledebo and Ridley, 1982; Caldas et al., 1984) in which case something akin to the Anderson rule is recovered. This assumption is not however necessary in predicting offsets using this method which has produced results in line with present trends.

The above list is by no means exhaustive and one other method which has recently come to the fore is also worth mentioning. The use of hydrostatic pressure has recently become a useful probe of the band structure because like alloy composition, it can be used to move band edges and hence change band gaps. Consequently, the band offsets will also change with pressure so that by monitoring the photoluminescence associated with various transitions and extrapolating back to atmospheric pressure, the offsets can be determined once the binding energies of the excitonic states are correctly taken account of. More details on this topic are given by Venkateswaran et al. (1986) and Wolford et al. (1986) and in chapter six.

Experimental data have also shown that there are potentially many other effects that affect the size of band discontinuities. Some of these are more obvious than others and will depend on those semiconductors comprising the interface. Much of this work has concentrated on the GaAs/(AlGa)As system and is the topic of the next section. 3.3.4 Contentious Issues

The current interest in interface systems is such that

data for the band offsets of most semiconductor pairs are available. The list is continually updated and the scatter in published data on a single system is typically large. Band offsets, sensitive as they are to the exact environment at the interface, will be affected if the method of growth does not result in atomically abrupt interfaces (which is usually desired) and forms a test of interface quality. Reliable determinations of offsets then require as a stringent prerequisite that the method of growth (MBE, MOVPE etc.) should be as closely controlled as is possible so that an "ideal" interface results.

Even when the most up-to-date growth techniques are employed, unexpected results have been found to occur. The offsets may depend upon the crystallographic orientation so that different crystal faces produce different offsets. Experimental evidence for independence in the GaAs/(AlGa)As system is provided by Wang et al. (1985) who find that the (110) and (311) interfaces have, to within experimental error, the same offset (the linearity of most theoretical models forces independence since they calculate bulk related levels independent of the specific atomic structure at the interface). Independence of the offsets upon orientation suggests that offsets are predominantly bulk determined and that the atomic environment plays only a minor (or possibly no) role in determining offsets.

It has also been found that the offsets can depend upon the sequence of growth so that the properties of interfaces grown later differs from those grown earlier (Miller et al., 1982; Kroemer, 1983). Waldrop et al. (1981) measured a valence band offset of 0.15eV when AlAs is grown on GaAs and

0.40eV when GaAs is grown on AlAs. Such a dependence upon the growth sequence is indicative of different interfacial structures possibly due to different atomic reconstructions at the substrate surfaces. Different growth conditions can stabilise a different reconstruction (Joyce, 1985) and hence determine the properties of the interface once growth is complete. Such a technology dependence illustrates the complexity and importance of the growth process and must be controlled or understood (or preferably both) to a large extent before real progress can be made (Voos, 1986).

For some systems, (InGa)As/Ga(SbAs) for instance, it has been found that the offsets depend not only upon alloy composition but also layer thickness (Sai-Halasz et al., 1978; Esaki, 1981) in multilayer systems. Such variations are assumed not to exist in the GaAs/(AlGa)As system, the offsets (or more precisely the offsets as percentages of the energy gap difference) being treated as constants. For instance, it has been found experimentally (Batey and Wright, 1986) that the valence band offset is linear in aluminium concentration and theoretically, that it curves downward with aluminium concentration (Ferraz and Srivastava, 1986). It is certainly true that if the direct energy gap of the alloy varies quadratically with aluminium concentration as is commonly assumed (see Adachi, 1985 for instance), then it is most unlikely that the fractional offsets are independent of alloy composition. It is then more likely that the extent of any changes would depend on the particular system being considered.

3.4 REALISTIC FEATURES OF THE ELECTRONIC PROPERTIES

Whilst much understanding of the electronic properties can be deduced from merely treating the superlattice as though it consisted of a periodic array of wells and barriers, it is nearly always more complex than this simple picture would indicate. Some of those features that complicate and enrich these properties are outlined below.

3.4.1 Minibands

That electrons and holes can be confined by conduction and valence band discontinuities respectively means that quantized states can form in the wells. These so-called minibands are analogous to the energy bands in bulk semiconductors but arise because of quantum confinement in particular layers in multilayer systems. They are qualitatively similar to the eigenstates of the familiar particle in a box situation except that the confining potential is finite and superimposed on this picture are the microscopic potentials due to the presence of atoms at particular positions in each layer. A finite potential barrier means that confined (or bound) states can couple to evanescent states in the gap and indeed may "communicate" with states in neighbouring wells by the tunnelling of carriers. This is particularly so for ultrathin barriers (<10 atomic layers) and the resulting electronic properties will reflect this.

Not only is it possible for confined states to occur in the wells but also, resonant states above the confining barriers have been observed (Zucker et al., 1984; Mendez et al., 1986) which are partially confined in the barrier layers. They have also been found in empirical pseudopotential

calculations and have been assumed to be due to the presence of the microscopic atomic potentials (Wong et al., 1985). Such a conclusion was probably arrived at because of the paucity of data to the contrary at that time. However, these resonant states can be produced by the Kronig-Penney model, probably the simplest method for calculating states near superlattice band edges (see Appendix A), thereby contradicting the above.

3.4.2 Excitons

Excitons are formed by illumination from sub-bandgap radiation, the excited electron becoming weakly bound to the hole left behind in the valence band. The excitonic state formed has an energy just below the conduction band edge, this distance being equal to the binding energy of the exciton which for bulk GaAs is a few meV. The excitons are spatially delocalised (the diameter of a bulk GaAs exciton is about 200Å) and hence occupy a small volume in k-space so that they are usually associated with a particular minimum in the If excitons are confined in layers thinner conduction band. than their bulk diameter, then they tend to become squashed and as a result, their binding energy increases. This means that they are apparent (as an abrupt edge in the optical spectra) at room temperature unlike the corresponding bulk feature which is weak due to thermal dissociation (Dingle et al., 1974).

Excitons are also dependent upon the detailed subband structure because of the different effective masses of the degenerate valence band states. The light and heavy hole states give rise to distinct excitons whose binding energy is affected by the amount of hybridisation present and hence the

deviations from parabolicity. The selection rule governing transitions then is seen to be modified and previously forbidden transitions can be observed (Meynadier et al., 1985; Sanders and Chang, 1985).

The one-electron theory used in this thesis cannot include effects due to excitons since they are two-body phenomena (and are therefore neglected). They are however important in that they play a large role in the interpretation of optical spectra since transitions involving them can be observed.

3.4.3 Band Hybridisation

Because the superlattice period is larger than the unit cell dimensions for the bulk constituents (the lengths of the primitive translation vectors are half the lattice constant), the superlattice BZ is much smaller than the bulk one. This gives rise to what has been called by many authors zonefolding although this is somewhat incorrect and misleading. What actually happens, as will be demonstrated in the next chapter, is that those parts of the bulk BZ outside the superlattice BZ are translated by a reciprocal lattice vector of the superlattice so that they fall within the superlattice The process is therefore better described as zone-BZ. translating. The precise geometrical details are left to the next chapter and for now, some of the main consequences for the electronic structure are described.

Electronic states with a given bulk symmetry i.e. associated with a particular symmetry point in the bulk BZ, are on formation of a superlattice, translated to a different point, k say, in the superlattice BZ (a k-point in the superlattice BZ is distinguished from a bulk k-point by a bar

above it). If the translated state is close in energy with states originating at k, then they will hybridize if the two states are of different bulk symmetry and the resulting superlattice states will have mixed character, consistent with first order perturbation theory.

The existence of superlattice states with mixed character is usually ignored in effective mass models which consider only states with a given bulk symmetry (usually zone centre or Γ states). However the effects of the other bulk states which are translated to k will not only strongly affect the effective masses, but also the transition probabilities since the selection rule may be circumvented by the mixed character of the superlattice states. Hence transitions which would have been forbidden in effective-mass theory are now permitted and the matrix elements important in such transitions are found to change (Ninno et al., 1985).

3.5 SUMMARY

The electronic properties of semiconductor multilayer structures present new phenomena that are not only of technological interest but are also a challenge to basic physics. The technologist can grow such structures employing a wide variety of semiconductors using high precision fabrication techniques. The physicist will examine and identify those fundamental features or concepts which allow physical understanding of such systems so as to provide the necessary background knowledge to predict the likely properties of similar systems. The role of the band offsets has been emphasized as being of central importance to the understanding of the electronic properties of multilayer

systems. The difficulties in obtaining accurate and reproducible data for the offsets for a wide enough variety of systems to test available theories has been outlined. Much of that described in section four will be used in the interpretation of the results in chapters five and six.

CHAPTER FOUR

METHOD OF CALCULATION

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4.1 GEOMETRICAL CONSIDERATIONS OF SUPERLATTICES

4.1.1 Atomic Structure

Accurate calculation of the electronic properties of superlattices necessarily includes taking into account the atomic structure within each layer, especially when the layer thicknesses are less than about 10 atomic layers where envelope function treatments are expected to fail. The atomic structure of the AC/BC superlattice can be expected to be similar to that of bulk AC with some of the A atoms replaced by B atoms in such a way as to leave the atomic positions unchanged and to reproduce the superlattice period. This however avoids the issues of lattice matching and of the thermodynamic stability of the resulting superlattice. These will be taken up later.

The above method of describing a superlattice allows the definition of a superlattice unit cell (which will of course depend on the period) and by doing this, one can use the same fourier-space techniques as those used in bulk calculations in chapter two. This is the basis of the slab method which exploits the translational symmetry present not only in the plane normal to the superlattice direction, but also along the superlattice. The slab method has previously been used to invoke an artificial periodicity in single interface systems such as surfaces, Schottky barriers and heterojunctions. If the unit cell that results is too thin in the slab direction, then the adjacent interfaces will interact and degeneracies that ought to occur will be lifted. The layers also might not accurately reproduce the desired bulk properties, thereby necessitating the use of thicker layers. The upper limit on the size will be imposed by the available computing resources

and therefore some compromise will have to be made which does not introduce serious error.

Superlattices, on the other hand, have precisely the geometry specified by the slab method and so no artificial periodicity is imposed. The superlattice (or slab) unit cell is then larger than the bulk unit cell because of the increased period in the superlattice direction. For example, the translation vectors in the case of the primitive unit cell of the bulk

$$a_{1} = a_{0}(0.5, 0.5, 0.0)$$

$$a_{2} = a_{0}(0.5, 0.0, 0.5) \qquad (4.1)$$

$$a_{3} = a_{0}(0.0, 0.5, 0.5)$$

enclose a volume equal to the quarter of a cube of side a_0 , the lattice constant. The (GaAs)_n(AlAs)_n superlattices studied here have their tetragonal unit cells described by

$$a_{1} = a_{0}(0.5, 0.5, 0.0)$$

$$a_{2} = a_{0}(0.5, -0.5, 0.0)$$

$$a_{3} = a_{0}(0.0, 0.0, n)$$

(4.2)

where the superlattice direction is defined to be along the z axis. The volume of the unit cell is then

$$\Omega_{sl} = na_0^3/2 = 2n\Omega_{bulk}$$
(4.3)

provided that the lattice constant remains fixed. This is an excellent approximation here as the lattice constants of GaAs and AlAs differ by only 0.1% (Adachi, 1985). In all

calculations, the average lattice constant of 10.6901 a.u. was adopted for the lattice constant of the superlattice. It could be argued that since it is usual for GaAs to be the substrate and that thin epilayers adopt the lattice constant of the substrate layer, then the lattice constant of the superlattice should be that of GaAs. Whilst the validity of such an argument is not contested here, the effects given the similarity of the lattice constants are likely to be much smaller than other effects neglected such as the non-locality of the pseudopotential and spin-orbit coupling.

There has also been much work to determine whether ultrathin GaAs/AlAs superlattices are structurally stable. Kuan et al. (1985) deduced the existence of long-range order in random (GaAl)As alloys from the appearance of reflections (that would be absent in the random alloy) in x-ray diffraction measurements. They found that although the ordering is never complete, there is a tendency for Ga atoms to occupy certain sites and for Al atoms to occupy certain other sites and concluded that the monolayer superlattice is the thermodynamic equilibrium state of the random alloy. This is in contrast to Phillips (1981) who attributed the stability to oxygen defects and Ourmazd and Bean (1985) who suggested that substrate strain effects may stabilise it. Thermodynamic studies (Bylander and Kleinman, 1986; Wood et al., 1987; Ciraci and Batra, 1987) have shown that although the random alloy is the room temperature equilibrium structure, the monolayer superlattice is metastable and disproportionation into compounds is energetically favoured.

4.1.2 Reciprocal Space Consequences

For the bulk fcc semiconductor previously considered, the

fact that all the primitive lattice translation vectors were of the same length gave rise to a uniform grid of points in k-space. The superlattice however has a different geometry with the translation vector along the superlattice axis being longer than the other two (which are equal to each other and to those of the bulk). This not only means that points will be more closely spaced in the (001) direction in k-space (and therefore that the number of rlv's less than a certain upper limit will increase) but more importantly, that the shape of the BZ is significantly altered. The latter point is not just an observation made for the sake of completeness; its consequences are far-reaching and a full understanding of the way in which the BZ alters its shape can shed light on the nature and behaviour of the superlattice electronic states.

In order to demonstrate the way in which the BZ changes, the fcc BZ will be used as a starting point. On doubling the size of the unit cell in the z direction in forming the monolayer (n=1) superlattice, the width of the BZ in the k_z direction will be halved. Those parts outside the new BZ boundary must be translated (by reciprocal lattice vectors) and be made to fit inside the new BZ in much the same way that the higher BZ's are fitted into the first BZ on going from the extended to the reduced zone scheme (Kittel, 1976). Such a process has been referred to as zone folding although zone translating better describes what actually happens. This process is illustrated in figures 4.1 and 4.2 and shows the BZ for the monolayer superlattice.

The thicker superlattices (n=2,3,4) have their BZ's generated in a similar fashion. It is merely a matter of repeating the above process using this time the monolayer BZ



Figure 4.1 The fcc Brillouin zone with that of the (001) monolayer superlattice shown inlaid.



Figure 4.2 The Brillouin zone of the (001) monolayer superlattice illustrating how all the parts of the fcc Brillouin zone can be made to fit inside it.
as the starting point. They all have the same tetragonal symmetry as the monolayer BZ but have their widths in the k_z direction scaled by 1/n.

Points in the fcc BZ which fall outside the superlattice BZ will become superimposed on points inside the original BZ which may have different symmetry. One important consequence of this is that states at this k-point will therefore have a mixed bulk symmetry. In compound semiconductors where the band structures may exhibit more than one minimum in the conduction band (usually at the Γ , X and L points), there is the possibility that the points where the minima occur will be translated elsewhere in the BZ on the formation of a superlattice. It is therefore important to know the way in which the BZ is constructed so that these points can be located in the new BZ since it is almost certain that the minimum in the conduction band of the superlattice will be at one of these points. Use of illustrations such as figure 4.1 enable the details of the translating process to be unravelled and the location of these points in the new BZ to be found. From this, the following can be concluded

- 1. The superlattice $\overline{\Gamma}$ (0,0,0) point always contains the fcc (0,0,0) and (0,0,1) points.
- 2. The superlattice \overline{K} (1,0,0) point always contains the fcc (1,0,0) and (0,1,0) points.
- 3. The superlattice \overline{R} (1/2,1/2,1/2n) point contains the fcc (1/2,1/2,1/2) and (1/2,1/2,-1/2) points only when n is odd.
- 4. The superlattice \overline{J} (1/2,1/2,0) point contains the fcc (1/2,1/2,1/2) and (1/2,1/2,-1/2) points only when n is even.

These fcc points are not the only ones to be translated to those in the superlattice BZ. For thicker superlattices, other points of lower symmetry are also translated on to these points allowing the possibility of quite complex states being formed. The translated states will then quite often have a different symmetry to the original fcc bulk states so that the resulting superlattice states will be mixtures of states originating from more than one fcc point. This hybridization is expected to strongly affect the character of such states and will be used in the analysis of the superlattices.

4.2 SPECIAL POINTS IN THE BRILLOUIN ZONE

In calculating the physical properties of semiconductors, one often has to average the properties of quasiparticles over the BZ by performing integrals like

$$I = (\Omega/8\pi^3) \int f(k) d^3k = \overline{f}$$
(4.4)

where the integrand f(k) is a periodic function of wavevector k, e.g., charge density, total energy etc., and Ω is the normalising volume. If one ignores the periodicity, evaluating such integrals then either requires the determination of the functional form of f(k) or at least the generation of f(k) at a large number of points in the BZ (a few thousand is sufficient) in order to accurately sample it. Such procedures whilst accurate are somewhat cumbersome and as we shall see, unnecessary in the present work.

This was the situation until Baldereschi (1973) introduced the mean-value point, defined to be the best approximation to the average value of f(k) over the whole BZ. For the calculation of the charge density along the bonding direction in Ge, it agreed with the 3360 point calculation of Walter and Cohen (1971) to within 1%. The method of Baldereschi was extended by Chadi and Cohen (1973) so that sets of special points could be generated and used to determine crystal properties to an arbitrary degree of accuracy depending on the number of points in the set. Whilst other ways of generating special point sets are now available (see Evarestov and Smirnov, 1983 for instance), the above method is described below and results obtained by this procedure will be used in all subsequent calculations.

The method relies upon the function $f(\mathbf{k})$ being periodic in wavevector space and starts by exploiting this periodicity by means of a fourier expansion

$$\mathbf{f}(\mathbf{k}) = \mathbf{f}_{0} + \sum_{m=1}^{\infty} \mathbf{f}_{m} \mathbf{A}_{m}(\mathbf{k})$$
(4.5)

where the $A_m(k)$ are sums of plane waves

$$A_{m}(k) = \sum_{|R|=C_{m}} \exp(ik.R)$$
 $m = 1, 2, ..., \infty$ (4.6)

The sum is over all m lattice vectors R, of length C_m related to each other by the operations T_i of the lattice point group T. Each $A_m(k)$ then corresponds to a particular star of lattice vectors of length C_m . Using (4.5) and (4.6) in (4.4) then gives

$$\overline{\mathbf{f}} = (\Omega/8\pi^3) \left\{ \mathbf{f}_0 \int_{BZ} d^3 \mathbf{k} + \sum_{m=1}^{\infty} \mathbf{f}_m \int_{BZ} \sum_{|\mathbf{R}|=C_m} \exp(\mathbf{i}\mathbf{k} \cdot \mathbf{R}) d^3 \mathbf{k} \right\}$$
(4.7)

and hence the average value is simply given by f_0 . If there

existed a point \mathbf{k}_{0} such that

$$\sum_{m=0}^{\infty} f_m A_m(k_0) = 0 \qquad m = 1, 2, ..., n \qquad (4.8)$$

for $n=\infty$, then (4.4) would simply be f_0 . However such a point does not exist (satisfying it for the largest value of n possible defines Baldereschi's mean-value point) and so more than one point is necessary to satisfy it for a given value of n. If these points satisfy the following condition

$$\sum_{i=1}^{n} \alpha(k_i) A_m(k_i) = 0 \qquad m = 1, 2, ..., n \qquad (4.9)$$

and moreover, that the weighting factors $\alpha(\mathbf{k}_i)$ sum to unity, then rearranging (4.5) gives

$$f_0 = f(k_i) - \sum_{m=1}^{\infty} f_m A_m(k_i) \qquad (4.10)$$

Multiplying through by $\alpha(k_{\underline{i}})$ and summing over the index i gives

$$f_{0} = \sum_{i=1}^{n} \alpha(k_{i})f(k_{i}) - \sum_{m=1}^{\infty} f_{m} \sum_{i=1}^{n} \alpha(k_{i})A_{m}(k_{i}) \quad (4.11)$$

The terms in which the values of m are less than n vanish by (4.9) leaving only those for which m>n. Since the expansion coefficients f_m drop off rapidly for increasing m (for large $|R_m|$, f_m decreases as $1/|R_m|^3$ for fcc structures), choosing n to be large means that the second term in (4.11) can be neglected and thus, to a good approximation

$$f_{0} = \sum_{i=l}^{n} \alpha(k_{i}) f(k_{i}) \qquad (4.12)$$

$$i = l \qquad 58$$

So BZ averages can be performed for sets of \mathbf{k}_i that satisfy (4.9), the accuracy being limited by the number of points used. The generation of larger sets follows from defining two generating wavevectors \mathbf{k}_1 and \mathbf{k}_2 that satisfy $A_m(\mathbf{k})=0$ for $m = m_1$ and m_2 respectively i.e.

$$A_{m_{1}}(\mathbf{k}_{1}) = \sum_{|\mathbf{R}|=C_{m_{1}}} \exp(i\mathbf{k}_{1} \cdot \mathbf{R}) = 0$$

$$A_{m_{2}}(\mathbf{k}_{1}) = \sum_{|\mathbf{R}|=C_{m_{2}}} \exp(i\mathbf{k}_{2} \cdot \mathbf{R}) = 0$$

$$(4.13)$$

Sets of special points \mathbf{k}_i can then be generated by

$$\mathbf{k}_{i} = \mathbf{k}_{1} + \mathbf{T}_{i}\mathbf{k}_{2}$$
 (4.14)

where T_i are the operations of the lattice point group T. This theorem, first proved by Chadi and Cohen (1973), then allows the generation of new special point sets. The use of suitable values for the generating wavevectors will produce a set that does not contain too many special points, something that is desirable for most practical uses. One can however generate special point sets with a large number of points thereby enabling the calculation of the BZ average to an arbitrary degree of accuracy.

The above procedure, first demonstrated by Chadi and Cohen (1973) for crystals with cubic and hexagonal Bravais lattices, has since been used to calculate special point sets for crystals with a different symmetry. Special point sets for the tetragonal and trigonal lattices have been calculated by Lin-Chung (1978) and Cunningham (1974) has calculated them for the two-dimensional BZ. A comprehensive review of special

points including methods other than that described above can be found in Evarestov and Smirnov (1983). Their use in any fully self-consistent calculations can dramatically reduce the amount of computing required without a corresponding loss of accuracy and so are central to the method described in the next section.

4.3 SELF-CONSISTENCY

In chapter two, it was demonstrated how with the use of empirical pseudopotentials, the electronic properties of bulk semiconductors could be calculated reasonably accurately. The band structure of semiconductors such as Si and Ge were found to be similar to those generated assuming that the electrons were nearly free. The valence electrons experience a weak pseudopotential, which has the periodicity of the underlying crystal lattice.

When however the crystal potential deviates from this periodicity as will be the case near a defect, surface or interface, there will be an accompanying redistribution of charge necessitating an alternative description if these effects are to be included. If the potential associated with the change in environment becomes deeper, then electrons will be attracted to it and screen out its effects. When this has happened and the system attains equilibrium, it is said to be self-consistent. If the region where this charge redistribution takes place is small compared to the size of the system, then reasonable estimates of its properties can be calculated by either ignoring the self-consistency requirements altogether or including them in some simple, intuitive fashion. However, since the layer thicknesses of

the superlattices to be investigated here are of the same size as the distance over which charge transfer effects are likely to be significant, including self-consistency will be an important consideration.

4.3.1 The Self-Consistent Method

Self-consistency within the pseudopotential scheme has been employed by many authors in the past to study a variety of physical systems. The method described here follows to a large extent the formulation of Cohen (1980 and references therein) differing mainly in the calculation of the ionic pseudopotential and the use of a parametrization scheme. It relies on being able to separate the various contributions to the total potential thus

$$V_{tot}(r) = V_{ion}(r) + V_{H}(r) + V_{xc}(r)$$
 (4.15)

where $V_{ion}(r)$, $V_{H}(r)$ and $V_{xc}(r)$ are the ionic, hartree and exchange-correlation potentials respectively. In essence, the method entails keeping the ionic potential constant during the self-consistency procedure and letting the valence electrons, described by the hartree and exchange-correlation potentials, redistribute about the ions until self-consistency is achieved.

The process begins by first expanding the superlattice wavefunctions in plane waves

$$\psi_{n}(\mathbf{k},\mathbf{r}) = (1/\sqrt{\Omega}) \Sigma u_{nK}(\mathbf{k}) \exp[i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}] \qquad (4.16)$$

$$\mathbf{K}$$

where the kinetic energy cutoff is such that all rlv's that satisfy $|G|^2 \le 11$ are included. This means that the number of

plane waves used as a basis set will be different for each superlattice, increasing with the number of basis atoms. The pseudopotential is also expanded as a fourier series

$$V_{ps}(\mathbf{r}) = \sum_{\mathbf{K}} v_{ps}(\mathbf{K}) \exp(i\mathbf{K} \cdot \mathbf{r}) \qquad (4.17)$$

and this leads to the familiar secular equation

det
$$|[\frac{1}{2}(\mathbf{k}+\mathbf{K})^2 - \mathbf{E}_n(\mathbf{k})]\delta_{\mathbf{K},\mathbf{K}'} + \mathbf{v}_{ps}(\mathbf{K}-\mathbf{K}')| = 0$$
 (4.18)

The empirical pseudopotentials for GaAs and AlAs of Baldereschi et al. (1977), modified as in chapter two, are used to initiate the process. In principle, the iterative procedure should converge to the self-consistent result irrespective of the starting point but a good first approximation to the self-consistent potential will reduce the number of iterations required and hence the demand on computing resources. Equation (4.18) is solved using a standard library routine which returns the eigenvalues $E_n(k)$ and the eigenvectors, the fourier coefficients of the wavefunction.

The next stage is to calculate the total valence charge density given by

$$\rho(\mathbf{r}) = 2 \sum_{\mathbf{n},\mathbf{k}} |\psi_{\mathbf{n}}(\mathbf{k},\mathbf{r})|^2 \simeq 2 \sum_{\mathbf{n},\mathbf{k}} \alpha(\mathbf{k}_{\mathbf{i}}) |\psi_{\mathbf{n}}(\mathbf{k}_{\mathbf{i}},\mathbf{r})|^2 \quad (4.19)$$

where the summation is over all special points \mathbf{k}_i which have a weight $\alpha(\mathbf{k}_i)$ associated with them and all states n such that $\mathbf{E}_n(\mathbf{k}_i) \leq \mathbf{E}_f$. The fermi level can either be calculated by invoking charge neutrality i.e. filling states according to

the Pauli exclusion principle until all valence electrons have been accommodated or, since the systems under investigation are known to be semiconducting, it may simply be assigned to the top of the valence band.

Since the pseudopotential representation is being used, the fourier coefficients of the charge density are calculated by

$$\rho(\mathbf{G}) = (2/\Omega) \Sigma \alpha(\mathbf{k}_{i}) \Sigma \mathbf{u}_{n,\mathbf{K}-\mathbf{G}}^{\mathbf{X}}(\mathbf{k}_{i}) \mathbf{u}_{n\mathbf{K}}(\mathbf{k}_{i}) \qquad (4.20)$$

$$\mathbf{k}_{i}^{\mathbf{X}} \mathbf{n}_{\mathbf{K}}^{\mathbf{X}}$$

This valence charge density will produce a potential field since every electron will be coulombically repelled by all the other electrons. The potential generated by all the electrons, the hartree potential, is given by the solution to Poisson's equation

$$\nabla^2 \nabla_{\mathbf{H}}(\mathbf{r}) = -4\pi\rho(\mathbf{r}) \tag{4.21}$$

and its fourier coefficients are given by

$$V_{H}(G) = 4\pi\rho(G)/|G|^{2}$$
 (4.22)

which diverges as G tends to zero. This divergence is however unphysical since $V_{\rm H}(G=0)$ is the average potential due to the presence of the valence electrons which is equal and opposite to that due to the ions because of charge neutrality. For convenience then, both $V_{\rm H}(G=0)$ and $V_{\rm ion}(G=0)$ can be set to zero.

As well as the coulombic repulsion, the electrons also interact according to their spin via the exchange potential due to the Pauli exclusion principle. In Hartree-Fock theory, the exchange potential is non-local, but can be approximated by the local $X\alpha$ statistical exchange potential due to Slater (for a good review of the $X\alpha$ method, see Slater, 1974). The exchange potential is then found to be proportional to the cube root of the charge density

$$V_{x}(r) = -6\alpha[3\rho(r)/\pi]^{1/3}$$
 (4.23)

where α is a parameter lying between 2/3 and 1. The two extreme cases result from statistical approximations to the average exchange energy (α =2/3) by Dirac (1930) and to the average exchange potential (α =1) by Slater (1951) although it is usually taken to lie somewhere between the two thereby partially accounting for the effects of correlation (Kohn and Vashishta, 1983). The value of α can then be fixed by, for instance, making self-consistent X α calculations agree with Hartree-Fock results for the isolated atoms (Schwarz, 1972). A different approach is adopted here, the value of α being used to fit observed energy gaps of both bulk GaAs and AlAs at the principal symmetry points in the fcc BZ, something that reproduces solid-state rather than atomic data.

The fourier coefficients of the exchange potential are then

$$V_{v}(G) = -6\alpha(3/\pi)^{1/3} \rho^{1/3}(G) \qquad (4.24)$$

and are calculated by first evaluating the charge density on a grid of points in the unit cell. The number of points N in the grid is roughly proportional to the number of basis atoms and is about 40 per basis atom for the superlattice calculations. The charge density at each point is then cube-rooted (any negative values because of truncation ripples are set to zero) and the results fourier transformed to give the fourier coefficients of the cube-root of the charge density

$$\rho(G) = (1/\sqrt{N}) \Sigma [\rho(r)]^{1/3} \exp(-iG.r)$$
 (4.25)

This process is checked by missing out the cube-root stage and comparing the emergent set of $\rho(G)$'s with the starting values. The sum of the differences was found to be about 10^{-13} for each self-consistency loop, comparable with the machine accuracy. Confidence in the procedure is therefore established.

The sum of the hartree and exchange potentials is that solely due to the electrons and has been called the screening potential since the valence charge density screens out the potential due to the pseudoions. The screening potential, added to the ionic potential then completes the sum in (4.15). The latter is approximated by the empty-core pseudopotential due to Ashcroft (1966) which is the limiting case of the cancellation theorem in pseudopotential theory discussed in chapter two. It is given by

$$V_{ion}(\mathbf{r}) = 0 \qquad |\mathbf{r}| < r_{c} \qquad (4.26)$$
$$V_{ion}(\mathbf{r}) = -z/\mathbf{r} \qquad |\mathbf{r}| > r_{c}$$

so that the ionic potential is zero inside a sphere of radius

r_c and is coulombic outside. Matrix elements of the ionic potential between plane waves are given by the usual formula

$$V_{ion}(G) = \sum_{\alpha} S_{\alpha}(G) V_{\alpha}(G) \qquad (4.27)$$

where the sum is over all atom types present. The structure factor $S_{\alpha}(G)$ describes the positions of the ions within the unit cell and the ionic pseudopotential form factor is the fourier transform of (4.26) given by

$$V_{\alpha}(G) = -4\pi Z\cos(Gr_{c})/\Omega|G|^{2} \qquad (4.28)$$

where the core radius is treated as an adjustable parameter characterising each ion type and the ionic pseudopotential is normalised to a volume Ω equal to $a_0^3/8$, the same for each ion. Previous self-consistent calculations have either fitted analytical curves to the ionic pseudopotential to reproduce the energy levels of the free ions (i.e. the core states) which are not expected to be much perturbed upon incorporation into a crystal matrix (Pickett et al., 1978; Nakayama and Kamimura, 1985) or have used the local-density approximation (LDA) which underestimates the band gaps (Christensen et al., 1985; Bylander and Kleinman, 1986; Ciraci and Batra, 1987; Nelson et al., 1987). The method used here and described in the next section does not attempt to model the free ions but instead adjusts the values of α and the core radii to reproduce experimentally observed energy gaps in the bulk crystals which to some extent circumvents the deficiencies of the LDA.

Once all the individual contributions to (4.15) have been

calculated, the total can be used to repeat the process until the potential has converged and is then self-consistent. As has been pointed out by Schluter et al. (1975), there are convergence problems associated with the small G components of the potential since both the ionic and the hartree potentials diverge at small G. Physically, these problems are associated with small charge transfers occurring across the interface resulting in fluctuating signs in these small G components. These were taken account of by mixing the fourier coefficients of the input and output potentials to produce the input for the next loop. The condition for self-consistency was chosen so that the average difference between the fourier coefficients of the input and output potentials was less than 10^{-5} Rydbergs. Convergence in the potential was achieved typically within 20 iterative cycles.

4.4 THE PARAMETRIZATION SCHEME

In the previous section, it was stated that the value of α in the exchange potential and the core radii of each ion were to be treated as adjustable parameters to fit the self-consistent bulk properties of GaAs and AlAs. In particular, the energy gaps of both bulk semiconductors at the Γ, X and L symmetry points in the BZ are to be accurately reproduced, since these levels will be important in the formation of superlattice states. Here the method used to fit the gaps is described and the resulting parameter set commented upon in the light of physical expectation.

In order to achieve good correspondence between the calculated and observed gaps, a range of values for each parameter was used. Calculations were performed on both bulk

constituents using a single special point or mean-value point of $k_i = (2\pi/a_0)(0.6223, 0.2953, 0)$ in each cycle of self-consistency. The errors introduced by using just one special point will be examined later in this section. About 15 iterative loops were required to obtain self-consistency and the resulting potential was then used to calculate the energy gaps for comparison with experimental data. For simplicity (although this is not a necessary condition) the core radius of the As ion was taken to be the same in both bulk materials. This should at least be reasonable since the core states are not much perturbed by the surrounding medium and also makes the ionic pseudopotential transferable, which is desirable (Cohen and Heine, 1970).

In carrying out calculations, it was found that all the gaps for both bulks were strongly dependent upon α but that the X point was only weakly dependent upon the core radii, unlike the gaps at Γ and L. The value of α was then fixed within a small range to reproduce the X gaps and the other gaps could be fitted by adjusting the core radii. The resulting parameter set was

> $\alpha = 0.81$ $r_{c}(Ga) = 0.98a.u.$ $r_{c}(Al) = 1.11a.u.$ $r_{c}(As) = 0.936a.u.$

Using this parameter set, the band structures were calculated and the results at the Γ , X and L points are summarised in table 4.1 and compared to the available experimental data. The calculated eigenvalues do show on average a large difference from the experimental ones but the energy gaps at the three principal symmetry point used in the parametrization

S	GaAs			AlAs		
Point	lsp	10sp	Expt.	lsp	10sp	Expt.
r	-12.003 0.000	-12.072 0.000	-13.1 0.00	-11.692 0.000	-11.737 0.000	0.00
	1.522 4.456 8.308	1.490 4.377 8.246	1.519 ^a 4.176 8.33	3.030 4.795 8.405	3.032 4.716 8.304	3.020 ^b 4.34
x	-9.630 -6.477 -2.164	-9.682 -6.580 -2.273	-10.75 -6.70 -2.80	-9.460 -5.647 -2.096	-9.490 -5.722 -2.201	-2.356
	2.069 2.345	1.968 2.342	2.010 ^c 2.58	2.161 2.846	2.172 2.779	2.229 2.428
L	-10.313 -6.129 -0.949	-10.390 -6.140 -1.087	-11.24 -6.70 -1.30	-10.052 -5.619 -0.875	-10.100 -5.618 -0.980	
	1.786	1.691	1.840 ^C	2.833	2.761	2.661 ^d

Table 4.1 Energy positions in eV of bulk bands at Γ, X and L of both GaAs and AlAs comparing the results obtained using the single and ten special point schemes. The vb states are shown separated from the cb states. The experimental data is taken from Semiconductors, Physics of Group IV Elements and III-V Compounds, ed. O. Madelung (1982) except (a) Aspnes, (1976), (b) Pearah et al., (1985), (c) Wolford and Bradley, (1985) and (d) quoted in Gell et al., (1987).

scheme are well reproduced. The valence band width is about 1eV too low, a disparity to be expected from empirical pseudopotentials.

Although the above parameters were obtained assuming that they are all freely adjustable, the values obtained are nonetheless physically reasonable. The value of α lies between 2/3 and 1 as it should from physical arguments, unlike Nakayama and Kamimura (1985) who treat α as the only adjustable parameter in their similar treatment of the same systems and find that a value of 1.15 best fits their calculated gaps to the experimental ones. Not only is this value unphysical but their resulting band structures are less accurate than those calculated here.

Trends in the values of the core radius with atomic number z have been described by Heine and Weaire (1970) who find that

$$r_{c} \sim z^{-1/3}$$
 (4.29)

This is because for increasing z, the higher nuclear charge will tend to pull the core in more tightly thus reducing the core radius. This would predict that the core radius of the arsenic ion should be the smallest and that of aluminium the largest with the gallium somewhere between, which is indeed the case. This agreement has important consequences because the most attractive region of the ionic pseudopotential is just outside the core where the potential just becomes coulombic. A smaller core radius will then have a greater propensity to attract electrons, i.e. a higher electronegativity. Hence the As ion would attract a higher valence

charge than either cation for this reason, consistent with it being anionic, and the Ga ion should do likewise as compared to the Al ion. One would therefore expect a transfer of charge in the superlattices to occur from the AlAs region to the GaAs region although the amount is likely to be small.

The parametrization scheme is then not only successful in accurately accounting for the energy gaps in both semiconductors but also yields a parameter set which is physically reasonable. The results however may be subject to inaccuracies due to the use of a single special point in performing the BZ integrations. The size of possible errors introduced is discussed in the next section.

4.4.1 Accuracy of Special Point Calculations

In order to investigate the errors introduced in the above calculations by using a single special point, the calculations were repeated using the 10 special point set for the fcc Bravais lattice given by Chadi and Cohen (1973). The 10 special points along with their corresponding weights are listed below

$k_1 = (7, 3, 1)$	$\alpha_1 = 3/16$	$k_2 = (7, 1, 1)$	$\alpha_2 = 3/32$
$k_3 = (5, 5, 1)$	$\alpha_3 = 3/32$	$k_4 = (5, 3, 3)$	$\alpha_4 = 3/32$
k ₅ =(5,3,1)	$\alpha_5 = 3/16$	$k_6^{=(5,1,1)}$	$\alpha_6 = 3/32$
k ₇ =(3,3,3)	$\alpha_7 = 1/32$	$k_8 = (3, 3, 1)$	$\alpha_8 = 3/32$
k ₉ =(3,1,1)	$\alpha_9 = 3/32$	$k_{10}^{-(1,1,1)}$	$\alpha_{10} = 1/32$

where the special points k_i are in units of $(\pi/4a_0)$ and their weights sum to unity. This special point set was used to calculate the self-consistent potentials for both bulks and from this, the eigenvalue spectrum and the pseudocharge density along the bonding region were calculated.

The eigenvalue spectrum shown in table 4.1 illustrates



Figure 4.3 The upper plots show the charge density along the (111) direction for GaAs on the left and AlAs on the right using both single (solid) and ten (dotted) special point schemes. The lower plots show the differences between these two schemes. The units are electrons per cubic atomic unit. that the single and the 10 special point schemes produce similar eigenvalues which differ on average by about 0.05eV and at most by about 0.1eV. The agreement with the experimental data quoted is not then significantly altered by use of more special points.

The pseudocharge density along the bonding direction calculated using both special point schemes for both bulk materials is shown in figure 4.3. The upper plots illustrate the charge density for the two schemes and the lower ones, the difference between them. For both materials, a higher bonding charge results from using more special points although the effect is not large. The bonding charge, like the valence band width, is not described very accurately by empirical pseudopotentials and the results here show significant differences from experimental results obtained using x-ray diffraction techniques (Pietsch, 1986) especially near the core regions where the pseudocharge density is unphysical (because of the neglect of the core charge density which has been orthogonalised away).

The differences between the single and ten special point schemes are not then so large as to invalidate the results of the former method. The results of the parametrization scheme using the single special point will then be used in the superlattice calculations which are presented in the next chapter.

4.5 SUMMARY

The differences between the atomic structure of the superlattices and the bulk materials were investigated and the consequences of this for the shape of the BZ examined. The

self-consistent pseudopotential method has been formally described and was then implemented to develop a scheme which can accurately reproduce some of the properties of those bulk semiconductors which comprise the superlattice. The results obtained here are to be used in the study of the electronic properties of the (GaAs)_n(AlAs)_n superlattices which is the subject of the next chapter. CHAPTER FIVE

CALCULATIONS ON (GaAs) (AlAs) SUPERLATTICES

5.1 INTRODUCTION

We now go on to the main part of the thesis concerning the calculation of the electronic states of $(GaAs)_n(AlAs)_n$ (001) superlattices with n from 1 to 4. In the previous chapter, it was demonstrated how such ultrathin superlattices could be accurately modelled, taking into account charge transfer effects by introducing a rigorous self-consistency requirement. The values of the parameters obtained by fitting the energy gaps of the bulk semiconductors to those experimentally observed will be used for all systems under investigation. Consistency between calculations is then a central tenet of the method adopted here.

As well as using a predetermined parameter set, a suitable special point set must also be chosen for the self-consistency procedure. As in the bulk calculations, a single special point or mean-value point is used. This point is $\mathbf{k}_i = (2\pi/a)(1/4, 1/4, 0)$ which is the mean-value point of the two-dimensional Brillouin zone (2DBZ) given by Cunningham (1974). For large period (001) superlattices, the BZ is thin in the k_{τ} direction and one may assume that the dispersion of bands along this direction is negligible i.e. flat bands. The assumption of a 2DBZ will not then introduce serious error in thick superlattices but will be only approximate here. Ιt will obviously be least accurate for the monolayer case where the BZ is half the width of the fcc BZ in this direction. Α test of the accuracy of this scheme for the monolayer superlattice is therefore included in the next section.

The rest of this chapter is organised as follows. The next section includes the properties of the superlattices resulting from the self-consistency procedure and shows the

effects of self-consistency by comparing the results with those obtained using the starting empirical potential of Baldereschi et al. (1977). Section 5.3 is devoted to the analysis of the near-gap states which are of importance since they will be most affected by the possible existence of band offsets. A study of the origins of these states and their charge distribution in the two layers will then shed light on the confinement effect. Section 5.4 concludes the chapter and includes qualitative predictions for thicker systems.

5.2 SELF-CONSISTENT CRYSTAL PROPERTIES

The (GaAs)_n(AlAs)_n superlattices studied here differ from one another only in the number n of GaAs and AlAs layers comprising the unit cell. Because of the close correspondence of many of the properties of the bulk constituents (Adachi, 1985), it may be expected that the superlattices will show some similarities with those properties of the bulk materials. However, as n increases and the layers become thicker, the individual layers will become more bulk-like so that their differences accompanied by the decoupling of the interfaces will come to the fore. The features associated with both descriptions are important and helpful in the understanding of these systems.

On achieving self-consistency, many of the features expected to illustrate these similarities to bulk-like behaviour can be immediately examined. For example, the self-consistent potential, the valence charge density and the band structure can be used to obtain an overview of these systems. One may also look at the effects that result from introducing a rigorous self-consistency requirement, something

that is expected to be an important consideration in the accurate modelling of ultrathin superlattices.

5.2.1 Total Potential

The self-consistent potentials averaged over the plane perpendicular to the superlattice axis are shown together in figure 5.1 to facilitate a comparison between the different superlattices. They are also compared with the empirical starting potential of Baldereschi et al. (1977) and the differences here serve to illustrate the effects and importance of self-consistency. In all four systems, the amplitude of the starting potential is roughly the same at each cation and each anion site whereas the self-consistent potential shows greater variation. In the GaAs layers, the amplitude of the self-consistent potential is much smaller than that of the starting potential and in the AlAs layers, the difference is small. One of the interesting features arising from the self-consistent results is that the potential in the vicinity of the interface differs from that of adjacent interfaces. The amplitude of the potential is small on going from AlAs to GaAs (left to right in the figures) and significantly larger on going from GaAs to AlAs. These differences are entirely due to self-consistency and reflect the fact that the interfaces are regions where large modifications of the crystal potential are required to "match" the two layers.

As was mentioned in chapter three, the self-consistent potentials can be used to furnish estimates of the band offsets present in superlattice structures. The method requires the calculation of the planar-averaged potential V(z)

$$V(z) = (1/A) \iint V(r) dxdy$$
 (5.1)
76



Figure 5.1 Planar averaged self-consistent. (solid) and empirical (dotted) potentials across a complete period for all four superlattices. The figures are ordered such that the n=1 superlattice is top left, n=2 is top right, n=3 is bottom left and n=4 is bottom right. The atomic positions along the z axis are shown and the units are eV with the origin at the average potential in each case. A being the planar area equal to $a_0^2/2$. The difference in the average potential $\Delta \widehat{V}$ between the GaAs layer and the AlAs layer in the superlattice is then given by

$$\Delta \vec{v} = (2/na_0) \left[\int V(z) dz - \int V(z) dz \right]$$
(5.2)
GaAs AlAs

The limits of integration in (5.2) are half way between those cation and anion positions which completely enclose either layer. By aligning the bulk band edges and shifting them by this difference, band offsets can be deduced. This of course assumes that the average potential in a given layer in the superlattice is the same as in the isolated bulk, something that is admittedly crude in the monolayer case but is expected to become more accurate as the layers thicken.

The values of $\Delta \overline{V}$ obtained are shown in table 5.1. The top of the valence band (vb) was found to lie 0.073eV below the average self-consistent potential in GaAs and 0.385eV below that in AlAs. The difference between these values added to the potential step then gives the valence band offsets which are also shown in table 5.1. In the light of the assumption made to obtain these results i.e. that any layer in the superlattice is precisely bulk-like, it is difficult to estimate the amount of uncertainty present. Comments regarding the accuracy of this procedure will be made in section 5.3 where the individual superlattice states are considered.

5.2.2 Valence Charge Density

Much the same patterns emerge in the results for the total valence charge densities shown in figure 5.2 as in the those of the self-consistent potential. The near-constant



Figure 5.2 Planar averaged self-consistent (solid) and empirical (dotted) charge densities across a complete period for all four superlattices. The units are electrons per cubic atomic unit.

			Charge transfer/e		
n	∆V/eV	∆E _v ∕eV	per layer	per bond	
1 2 3 4	$ \begin{array}{r} -0.274 \\ -0.044 \\ 0.122 \\ 0.080 \end{array} $	0.039 0.269 0.440 0.393	0.076 0.119 0.109 0.112	0.038 0.030 0.018 0.014	

<u>Table 5.1</u> Values for the difference in average pseudopotentials $\Delta \overline{V}$ between the GaAs and AlAs layers, the corresponding valence band offsets ΔE_v and the charge transfer across the interface both per layer and per bond for the four superlattices.

n	Ī	J	ĸ	Ŕ	ĨZ
1	2.072	3.908	2.037	1.953	2.692
2	2.091	2.304	2.169	3.061	2.063
3	1.964	2.575	2.040	2.129	1.957
4	1.910	2.200	2.101	2.416	1.898

<u>Table 5.2</u> The band gaps at various symmetry points in the SBZ for the (GaAs)_n(AlAs)_n superlattices. All results are in eV above the valence band maximum.

N	ī	J	ĸ	R	Z
1	2.072	3.908	2.037	1.953	2.692
3	2.076	3.893	2.047	1.940	2.620

<u>Table 5.3</u> The band gaps at symmetry points in the SBZ with N special points used in the BZ integration. The gaps are in eV.

amplitude of the charge density for the empirical case is changed on achieving self-consistency so that it is smaller in the GaAs layers and remains to a large extent unchanged in the AlAs layers except near to the interfaces. The smaller amplitude in the GaAs layers reflects the fact that the Ga-As bonds are more covalent, something which becomes more apparent in the thicker systems as expected since thicker layers resemble more closely the properties of the bulk.

The charge transfer in all the superlattices given in table 5.1 is calculated using a method similar to the calculation of $\Delta \overline{V}$ above. It is small in all cases, reflecting the similarity of the two materials, and is from the AlAs layers to the GaAs layers as expected from the arguments presented in section 4.4. The direction of charge transfer is consistent with both the Pauling and the Phillips electronegativity values. In addition, the results also suggest that the charge associated with a cation-anion pair differs from 8 electrons (expected from chemical bonding arguments) by less than 0.5%.

5.2.3 Electronic Structure

The band structures are easily calculated from the selfconsistent potential by solving the secular matrix for the eigenvalues at k-points along various symmetry directions. Here, the overall features are described and the analysis of the states near the band edges is left until the next section.

The calculated band structures shown in figures 5.3 to 5.6 all show the states present around the irreducible surface (two-dimensional) BZ as well as the states along $\overline{\Gamma}-\overline{Z}$ (as before, k-points in the SBZ are distinguished from their bulk counterparts by a bar above them) which are the zone







Figure 5.4 Band structure of the n=2 superlattice with the states along the k_z direction shown separate.

cture of the









translated minibands due to the formation of a BZ thinner here than in the fcc BZ. The band structure of the n=1 superlattice also includes the states along $\overline{R}-\overline{Z}$ since the minimum in the conduction band (cb) is found to occur at \overline{R} (equivalent to the zincblende L point) in agreement with other self-consistent calculations (Nakayama and Kamimura, 1985; Bylander and Kleinman, 1986; Ciraci and Batra, 1987) although their gaps of 1.68eV for NK and 1.597eV for BK (CB do not quote a value for this gap) are about 0.3eV below that obtained here (the result of BK's should not be taken too seriously as its accuracy is limited by use of the LDA which is known to underestimate band gaps (Louie, 1986)). The gaps at this and other symmetry points in the SBZ are shown in table 5.2.

Beyond n=1, the superlattices become pseudodirect i.e. the gap lies somewhere along the $\overline{\Gamma}-\overline{Z}$ direction. The lowest conduction miniband in all cases is almost dispersionless with an energy variation of <0.05eV (~2kT at room temperature) along this direction with the absolute minimum lying nearer to \overline{Z} . Some of these results have already been published (Gilbert and Gurman, 1987).

As the superlattices become thicker, the overall trend is for the gaps to decrease since the lowest cb state will tend to the bottom of the well (the energy of the ground state of a one-dimensional infinite square well varies as $1/a^2$ for a well of width a) and similarly for the highest vb state. When the layers are very thin however, states in adjacent wells can interact causing the state to split, moving one up and one down, as in the creation of bonding and antibonding states in diatomic molecules. This may explain why the gap for the n=1

superlattice is smaller than that of the n=2 one. Superimposed on this overall downward trend are fluctuations which reflect the states translated onto the particular symmetry points in the SBZ. The height of the lowest cb state above the vb maximum at the \overline{J} and \overline{R} points shows a large variation because the bulk L point is translated to the \overline{R} point when n is odd and to the \overline{J} point when n is even. When these conditions are satisfied, the gaps here are much smaller than when they are not, indicative of the participation of the L cb minima in forming states. This point will be covered in more detail in the next section.

The minimum gaps obtained here are compared in figure 5.7 to those experimentally determined by Ishibashi et al., (1986). Since excitons are neglected here, the results obtained should be greater than those observed by the unknown binding energy of the exciton (typically a few tens of meV). The good agreement is then not seriously affected by this approximation.

5.2.4 Accuracy of Single Special Point

For all the superlattices studied, the self-consistent method requires that one averages the valence charge density etc. over the whole BZ. As was mentioned in section one of this chapter, a single special point, $\bar{\mathbf{k}} = (2\pi/a)(1/4,1/4,0)$ of the square 2DBZ (Cunningham, 1974) has been used in all the calculations. Since the assumption of a 2DBZ will be least accurate for the monolayer superlattice, the calculations have been repeated with a 3 point set (Cunningham, 1974) of

$$\overline{\mathbf{k}}_{1} = (2\pi/a) (1/8, 1/8, 0)$$

$$\overline{\mathbf{k}}_{2} = (2\pi/a) (3/8, 3/8, 0)$$

$$\overline{\mathbf{k}}_{3} = (2\pi/a) (1/8, 3/8, 0)$$

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Figure 5.8 Comparison of the planar averaged charge density of the n=1 superlattice along the superlattice axis using one (solid) and three (dotted) special points for the BZ integration. The difference between them is shown below. with corresponding weights of 1/4, 1/4 and 1/2 respectively. Although these points also correspond to the 2DBZ, they will to some extent illustrate the accuracy of the single special point calculations. The resulting self-consistent potential was used to calculate the energy gaps at the principal symmetry points of the SBZ and the planar-averaged valence charge density. These are compared to the results obtained using the single special point.

The band structures obtained were so similar that little would be achieved by displaying them. The gaps at symmetry points calculated by the two schemes are given in table 5.3 and differ by less than 1% from each other. The superlattice is seen to remain indirect as a consequence of this accord and the gaps at all cb minima remain ordered as before. The calculated charge densities are shown in figure 5.8 with the difference below. As can be seen from this, they differ similarly by about 1%. Since the 3 point calculation took approximately 3 times as much computer time without significantly affecting the results, the single point is seen to be an efficient way of performing the BZ integrals here.

5.3 ANALYSIS OF SUPERLATTICE STATES

It is well known that states near band edges in superlattice structures behave as though they were subject to a periodic Kronig Penney (KP) type of potential which has the effect of confining the charge in the well layer. This is because the state in the well is matched to a state of the same energy in the barrier where by definition no extended states can exist (because this energy corresponds to the gap). The wavefunction in the well is therefore matched to an

evanescent wave in the barrier and, if the barrier is sufficiently thick, localisation of the charge in the well results. It has only recently been demonstrated that states just above this confining barrier, usually referred to as resonant or virtual bound states, are strongly confined in the barrier (Zucker et al., 1984; Jaros and Wong, 1984) even though such a result is found for the KP model (see Appendix A). Whilst the basic mechanisms responsible for this confinement are well known, there still remains some confusion in the literature. They are briefly reviewed here with the view of both clarifying the picture and to provide a basis for understanding those states resulting from the present calculations.

Superlattice states are formed out of those bulk states which are both near in energy to, and have the same symmetry as, the resulting state. This, because of zone translating, means that at any point in the SBZ \overline{k}_{s} say, the states there will be formed not only out of those states at the same point in the fcc BZ but also from states at other k points which are translated to $\mathbf{\tilde{k}}_{s}^{}$. Large period superlattices will have many such translated points making the situation very complicated. The states contributing to the formation of a given superlattice state can have a very direct influence in determining in which layer the charge will be confined. When these translated states are derived from other cb minima at X and L in the bulk band structures, the effect can be quite profound and may alter the pattern of confinement expected if only one minimum was involved. Their effects, which are neglected in effective mass approaches, limits the accuracy and applicability of such treatments.

Confinement of charge then does occur because the carriers "see" a KP potential but the type of line-up (see chapter three) will depend on the symmetry of the state in question. This may be different from that expected by simply lining up the band edges of the bulk constituents at the same k point firstly because the state may be derived from translated bulk states and secondly (and this also applies to the first point), because the band edges are bulk eigenstates and not those of a given layer in a superlattice. The latter point may be conveniently ignored for thick systems where bulk properties are sufficiently in evidence but in ultrathin systems, the levels that form the KP type of potential are not obviously bulk-like. This then opens up the possibility of band offsets that may be expected to vary with the layer thickness.

Moreover, ultrathin superlattices have been shown to represent a new class of material, unlike either bulk constituent or to thicker systems where band offsets can effect confinement to a large extent. When these effects become significant is still a matter of conjecture although it is obvious that the degree of confinement will increase as the layers become thicker.

5.3.1 Band Edge States

Before going on to present the results, it is worth mentioning some details that are relevant to the analysis here. Only those states at points in the SBZ that contain the bulk Γ , X and L points translated or otherwise will be considered. This will include the $\overline{\Gamma}$ point which includes the fcc Γ and X points, the latter translated, the \overline{K} point which contains the fcc X point and the \overline{J} and \overline{R} points which contain

the fcc L point when n is even and odd respectively. For each state, the planar averaged charge density, the charge density along a chain of bonds in the (110) direction and the bulk states responsible for its formation are calculated. From the first, the charge confined within each layer is calculated in a similar way to that of the charge transfer above. The last is simply obtained from the overlap of the superlattice wavefunction $\psi_n(k)$ with that of bulk ones

$$I_{nk}(n'k') = |\langle \phi_{n'}(k') | \psi_{n'}(k) \rangle|^{2}$$
 (5.3)

This quantity is calculated for a range of bulk states in both GaAs and AlAs for those superlattice states of interest. The wavefunctions of GaAs and AlAs for the same band are found to be almost identical to each other whereas different bands are nearly orthogonal to each other (this is particularly the case with the valence bands and low lying conduction bands which are of interest here). Hence both bulk materials will contribute almost equally to the formation of superlattice states. It is therefore more useful to calculate the total contribution from bulk states at a given symmetry point in the fcc BZ to those states of interest. Each superlattice will be considered in turn and then compared at the end of the section to illustrate the effects of changing the layer thickness.

5.3.1.1 The n=1 Superlattice

The states considered here are those at the superlattice $\overline{\Gamma}$, \overline{K} and \overline{R} points near to the band edges. At $\overline{\Gamma}$, the top three valence and the lowest three conduction band states are examined since their energies are such that they are most likely to be affected by the possible existence of band



Figure 5.9 Planar averages and contour maps of the charge density for n=1 superlattice states at $\overline{\Gamma}$. The maxima in the planar averaged results are set to unity for each state. The contour maps show where the charge is localised with respect to a chain of bonds along the <101> direction, the circles denoting atomic positions. The energies of the states, given in table 5.4, increases upwards.

offsets (the next cb state is a further 2eV higher). At \overline{K} and \overline{R} , only the lowest four and two cb states respectively are considered for similar reasons.

The charge densities of the states at $\overline{\Gamma}$ are shown in figure 5.9 with the corresponding bulk characters and charge confinement results in table 5.4a. The vb states are all Γ -like and would seem to show confinement effects similar to those expected in thicker systems. Charge is partially localised in the GaAs layer with the amount increasing with energy in agreement with the usual picture. This is in contrast to the cb states which, although of mixed character (reflecting strong band hybridisation), do not behave as though they are affected in the same way as states of a similar nature in thicker systems. By lining up the band edges of both bulks so that $\Delta E_{..}$ is 40% of the direct gap at Γ , it is expected that cb states that are Γ - or L-like ought to be confined in GaAs whereas X-like states would "see" a well in AlAs. If such an offset picture were relevant here, the state at 2.072eV, because of its strong X character, would be expected to be partially confined in AlAs, which is not the case.

This behaviour is even more apparent in the cb states at \overline{K} shown in figure 5.10. They are all X derived (no other points are translated here) and the details in table 5.4b show the states to be partially confined alternately in the two layers. These states then show no behaviour consistent with the presence of band offsets and must therefore be due to bulk-like effects.

The two states at \overline{R} in figure 5.11 show a splitting of about leV which has been suggested by Christensen et al.

E(k)/eV	Bulk Character Г X		Charge/layer GaAs AlAs	
-0.044	0.999	0.000	1.006	0.994
-0.043	0.998	0.001	1.042	0.958
0.000	0.995	0.004	1.075	0.925
2.072	0.250	0.736	1.262	0.738
2.365	0.090	0.901	0.791	1.209
2.759	0.657	0.335	0.910	1.090

(b)

(a)

E(k)/eV		Bulk X	Charge,	/layer
		Character	GaAs	AlAs
	2.037	0.992	0.784	1.216
	2.306	0.996	1.287	0.713
	2.410	0.992	0.629	1.371
	2.932	0.991	1.222	0.778

(c)

E(k)/eV	Bulk L Character	Charge, GaAs	/layer AlAs
1.954	0.987	0.973	1.027
2.879	0.988	1.177	0.823

Table 5.4States of the n=1 superlattice showing their bulk
character and the amount of charge confined in each
layer for states at (a) $\overline{\Gamma}$, (b) \overline{K} and (c) \overline{R} in the
SBZ. The dotted line in (a) separates the vb and
cb states. The bulk contributions should be, or
add to, unity, any deviation from which indicates
that small contributions from higher states were
missed.



Figure 5.10 Planar averages and contour maps of the charge density for n=1 superlattice states at \overline{K} .



Figure 5.11 Planar averages and contour maps of the charge density for n=1 superlattice states at \widehat{R} .

(1985) to be a signature of the ordered structure as opposed to the random alloy and may therefore be used to distinguish the two. The lowest state is found to be due to Ga s-orbitals and the higher one to Al s-orbitals in agreement with Bylander and Kleinman (1986) who show this arrangement to be responsible for the large splitting and hence the positioning of the cb minimum here. The influence of the As s-orbitals, clear from the figures, is not noted by them. Again the confinement, shown in table 5.4c is contrary to that observed in thicker systems for L derived states.

This superlattice shows features that are not seen in thicker systems but are more in line with bulk properties. Charge confinement, although present to some extent in all the states examined here, cannot be accounted for by the existence of band offsets and thus marks this system out as a new bulk material in agreement with empirical pseudopotential calculations of Gell et al. (1986). The variations in charge density are due in the main to the atomic orbitals which form the states.

5.3.1.2 The n=2 Superlattice

The states at $\overline{\Gamma}$ considered here are the three at the top of the vb and the lowest four cb states. At \overline{K} and \overline{J} the lowest four and three cb states respectively are analysed since only these states are of interest in ascertaining whether the concept of band offsets is appropriate here and to what extent states (if they exist) are affected by them. The states at $\overline{\Gamma}$ will be considered first.

The charge density of the $\overline{\Gamma}$ states is shown in figure 5.12 and the details regarding the state origins and confinement effects are in table 5.5a. The vb states are all





Ga As Ga As Al As Al As Ga Ga As Ga As Al As Al As Ga

Figure 5.12 Planar averages and contour maps of the charge density for n=2 superlattice states at $\overline{\Gamma}.$

E(k)/eV	Bulk Character		Charge/layer GaAs AlAs	
-0.064	0.995	0.002	1.057	0.943
-0.055	0.977	0.001	1.078	0.922
0.000	0.983	0.000	1.197	0.803
2.091	0.101	0.754	0.575	1.425
2.270	0.279	0.600	1.331	0.669
2.339	0.285	0.580	1.045	0.955
2.694	0.043	0.004	0.878	1.122

(b)

E(k)/eV	Bulk X	Charge,	/layer
	Character	GaAs	AlAs
2.196	0.983	0.883	1.117
2.311	0.981	0.949	1.051
2.507	0.977	0.974	1.026
2.629	0.985	1.091	0.909

(c)

E(k)/eV Bulk L E(k)/eV Character		Charge/layer GaAs AlAs		
2.304	0.963	1.185	0.815	
2.347	0.960	1.016	0.984	
3.693	0.061	0.569	1.431	

Table 5.5States of the n=2 superlattice showing their bulk
character and the amount of charge confined in each
layer for states at (a) $\overline{\Gamma}$, (b) \overline{K} and (c) \overline{J} in the
SBZ. The dotted line in (a) separates the vb and
cb states. The bulk contributions here deviate
from unity primarily because of the participation
of states at points of low symmetry in the bulk BZ.

(a)

partially confined in the GaAs layers as is expected if band offsets similar to those present in thick superlattices existed. The cb states are of mixed origin with the lowest three being predominantly X-like. The next has little Γ or X character and therefore arises from bulk states from other translated points. The lowest state shows a large confinement in AlAs which suggests that, since it is mainly X-like, the effects of band offsets are present. Similar results have been obtained with other self-consistent methods by Nelson et al. (1987) for the highest vb state and the lowest cb state (although they identify the lowest cb state with the X point of AlAs only whereas here it is derived almost equally from both bulk materials) and Nakayama and Kamimura (1985) who find the lowest cb state to be predominantly I-like. The next two states, although having more X than Γ character, are confined in GaAs. Since Γ character confines them in GaAs and X character confines them in AlAs, the pattern of confinement suggests that the Γ barrier is higher than the X barrier and that the two effects oppose each other leading to the small degree of confinement shown.

The states at \overline{K} shown in figure 5.13 are all X derived as can be seen from table 5.5b. The lowest three states are partially confined in AlAs suggesting that they are all below the X barrier and the next one is localised in GaAs, indicative of it being a resonant state just above the X barrier in GaAs. The state at 2.311eV here is at about the same energy as the two states at $\overline{\Gamma}$ discussed above. The small confinement due to the X barrier here means that it is not difficult for the Γ character above to dominate and thus confine states at $\overline{\Gamma}$ in GaAs. Comparing the states at these





Ga As Ga As Al As Al As Ga

Ga As Ga As Al As Al As Ga

Figure 5.13 Planar averages and contour maps of the charge density for n=2 superlattice states at \vec{K} .



Ga As Ga As Al As Al As Ga

Figure 5.14 Planar averages and contour maps of the charge density for n=2 superlattice states at \overline{J} .

two symmetry points allows an estimation for the lower limit of the X barrier height. The lowest $\overline{\Gamma}$ state at 2.091eV is below this barrier as is the \overline{K} state at 2.507eV. The X barrier must then be at least 0.416eV high which by aligning the bulk band edges means that the valence band offset is greater than 0.5eV or $0.33\Delta E_g$, in line with present experimental data. The uncertainty depends upon the distance of these states from their respective bulk band edges (which is difficult to calculate accurately) and the doubt as to whether the bulk band edges are appropriate levels to use here.

The states at \overline{J} in figure 5.14 with the other details in table 5.5c show the lowest two states to be partially confined in GaAs and the third to be confined to a greater extent in This state is more than 1.3eV higher in energy and has AlAs. a very small L character and so will not be affected by the band edges at L. The state must then be derived from bulk states at (1/2, 1/2, 0) since no other point is translated here. These bulk states, just like those at symmetry points, will be aligned to form wells and barriers and it is apparent that the barrier is the GaAs layer. States far above the cb minimum are usually ignored and are assumed to be unaffected by the usual band edge line-up criterion. It must be the case however that any given line-up will affect all states depending on their symmetry and that large confinement effects can and will result from aligning states that are not at bulk symmetry points. This will have important consequences in thicker systems where the number of states translated to $\overline{\Gamma}$ (say) is very large thus making the analysis more difficult than simply having a single KP type potential to confine

charge.

This superlattice then marks the point at which the concept of band offsets becomes appropriate. The confinement effects seen here have been successfully interpreted using such a model and have furnished a lower estimate for the valence band offset of 0.5eV which suggests that the line-up here could be similar to, or the same as, that in thicker systems.

5.3.1.3 The n=3 Superlattice

Those states examined here are the top three vb and the lowest five cb states at $\overline{\Gamma}$ and the lowest four and three cb states at \overline{K} and \overline{R} respectively. The charge density plots of the $\overline{\Gamma}$ states in figure 5.15 and their bulk origins and confinement details in table 5.6a show the vb states to be Γ derived and they are therefore localised in GaAs. The cb states are of mixed character reflecting the strong band hybridisation resulting from the interaction of bulk Γ states and the zone translated bulk states. The lowest state at 1.964eV is predominantly X-like and is confined in AlAs, in agreement with Nelson et al. (1987) but not with Nakayama and Kamimura (1985) who find it localised in GaAs. The next state at 2.164eV shows some X character but is mainly derived from other translated states (at (0,0,1/3) and (0,0,2/3)) which have the effect of exaggerating the localisation in AlAs. The other three states have a very mixed character with contributions from both symmetry points and other translated points. This makes the analysis more difficult since there is the possibility of the state being affected by up to four KP type potentials. It is therefore difficult to say anything definite about these states.





Ga As Ga As Ga As Al As Al As Al As Ga

Ga As Ga As Ga As Al As Al As Al As Ga

 $\begin{array}{c} \hline \textbf{Figure 5.15} \\ \textbf{density for n=3 superlattice states at } \overline{\Gamma}. \end{array}$

E(k)/eV	Bulk Ch F	naracter X	Charge, GaAs	/layer AlAs
-0.087	0.988	0.003	1.144	0.856
-0.081	0.913	0.000	1.237	0.763
0.000	0.938	0.000	1.402	0.598
1.964	0.050	0.799	0.612	1.388
2.164	0.003	0.452	0.430	1.570
2.231	0.423	0.216	1.119	0.881
2.318	0.093	0.254	1.241	0.759
2.387	0.333	0.195	1.425	0.575

(b)

E(k)/eV C		Bulk X	Charge,	/layer
		Character	GaAs	AlAs
	2.040	0.957	0.871	1.129
	2.175	0.958	0.709	1.291
	2.305	0.984	0.894	1.106
	2.573	0.986	1.090	0.910

(c)

E(k)/eV	Bulk L Character	Charge, GaAs	/layer AlAs
2.129	0.963	1.144	0.856
2.358	0.964	1.198	0.802
3.439	0.021	0.651	1.349

Table 5.6States of the n=3 superlattice showing their bulk
character and the amount of charge confined in each
layer for states at (a) $\overline{\Gamma}$, (b) \overline{K} and (c) \overline{R} in the
SBZ. Again, the dotted line in (a) separates the
vb and cb states. Translated states from points of
low symmetry in the bulk BZ make a significant
contribution to some states.

(a)





Ga As Ga As Ga As Al As Al As Al As Ga

Ga As Ga As Ga As Al As Al As Al As Ga

Figure 5.16 Planar averages and contour maps of the charge density for n=3 superlattice states at \overline{K} .



Ga As Ga As Ga As Al As Al As Al As Ga Ga As Ga As Ga As Al As Al As Al As Ga

Figure 5.17 Planar averages and contour maps of the charge density for n=3 superlattice states at \overline{R} .

The states at \overline{K} by contrast, shown in figure 5.16, are almost entirely derived from X as can be seen in table 5.6b. Other translated points make only a small contribution here making the analysis much easier. The lowest three states are localised in AlAs and the next is in GaAs indicating that the first three are bound states of the X well and the last one is a resonant state above the barrier. The top of the X well then lies somewhere between 2.305eV and 2.573eV. Comparing this data with that obtained at $\overline{\Gamma}$, the X well can be seen to encompass both the state at 1.964eV and the state here at 2.305eV implying a lower limit for the X barrier height of 0.341eV. This further gives a lower limit of about 0.44eV (0.29AE_G) for the valence band offset.

The states at \overline{R} in figure 5.17 and the details in table 5.6c show the lowest two cb states to be L-like and largely confined in GaAs whereas the next state has little L character and is confined in AlAs. The results for the first two states show them to be bound in the L well whilst the latter is difficult to characterise since it is derived from points other than bulk symmetry points.

Like the bilayer superlattice, this system shows that the band offset concept is appropriate and can be used to characterise the states at the various symmetry points in the SBZ. In particular, a valence band offset of at least 0.44eV is required to understand the confinement effects observed here.

5.3.1.4 The n=4 Superlattice

The states considered here are the top three vb and the lowest five cb states at $\overline{\Gamma}$ and the lowest four and three cb states at \overline{K} and \overline{J} respectively. The zone-centre states, shown







Ga As Ga As Ga As Ga As A L As A L As A L As A L As Ga

<u>Figure 5.18</u> Planar averages and contour maps of the charge density for n=4 superlattice states at $\overline{\Gamma}$.

in figure 5.18 with their details in table 5.7a, demonstrate the confinement of the Γ -like vb states in the GaAs layer with the degree of confinement increasing with increasing energy i.e. as they approach the bottom of the well. The cb states are of mixed character with bulk translated states from points other than those of high symmetry making significant contributions. The lowest cb state is predominantly X-like and is confined in AlAs in agreement with self-consistent calculations of Ciraci and Batra, (1987) and Nelson et al., The next state has very little Γ or X character and (1987). so is difficult to interpret since it will be derived from other bulk points. The next two have a large X character and show a small localisation in AlAs probably due to the presence of other bulk states which will partially cancel the effect of the X well in AlAs. The state at 2.341eV is mainly Γ -like and is quite strongly confined in GaAs indicating that the Γ well is deeper than the X well.

The states at \overline{K} , illustrated in figure 5.19 with their bulk origin and confinement effects in table 5.7b, are all strongly X-like reflecting the fact that bands from the bulk X point are those of the lowest energy to be translated here. The first two states are confined in the well in the AlAs layer and the next two appear to be resonance states above the X barrier (the state at 2.513eV certainly is but that at 2.374eV shows little resonance effect making such an assignment difficult. This is possibly because it is near to the top of the X barrier). As before, it is possible to obtain a lower limit on the valence band offset since both the $\overline{\Gamma}$ state at 1.910eV and the \overline{K} state at 2.242eV are confined within the X well in AlAs. The X barrier height is then at

E(k)/eV	Bulk Ch F	naracter X	Charge, GaAs	/layer AlAs
-0.129	0.980	0.003	1.184	0.816
-0.109	0.843	0.001	1.552	0.448
0.000	0.835	0.000	1.644	0.356
1.910	0.060	0.440	0.309	1.691
2.082	0.047	0.144	1.178	0.822
2.162	0.048	0.570	0.980	1.020
2.279	0.017	0.712	0.973	1.027
2.341	0.734	0.020	1.313	0.687

(b)	E(k)/eV	Bulk X Character	Charge, GaAs	/layer AlAs
	2.101	0.954	0.710	1.290
	2.242	0.964	0.777	1.223
	2.374	0.966	1.035	0.965
	2.513	0.980	1.095	0.905

(c)

E(k)/eV	Bulk L Character	Charge, GaAs	⁄layer AlAs
2.200	0.949	1.289	0.711
2.239	0.932	1.169	0.831
3.238	0.004	1.205	0.795

Table 5.7States of the n=4 superlattice showing their bulk
character and the amount of charge confined in each
layer for states at (a) $\overline{\Gamma}$, (b) \overline{K} and (c) \overline{J} in the
SBZ. Again, translated states from points of low
symmetry in the bulk BZ make a significant
contribution to some states.

(a)





Ga As Ga As Ga As Ga As Al As Al As Al As Al As Ga

GaAsGaAsGaAsCaAsAlAsAlAsAlAsAlAsGa

Figure 5.19 Planar averages and contour maps of the charge density for n=4 superlattice states at \overline{K} .





CaAsGaAsGaAsGaAsAlAsAlAsAlAsAlAsGa

Ga As Ga As Ga As Ga As Al As Al As Al As Al As Ga

Figure 5.20 Planar averages and contour maps of the charge density for n=4 superlattice states at \overline{J} .

least 0.332eV giving a lower limit on the vb offset of about 0.43eV (0.29 ΔE_v) although if the next \overline{K} state at 2.374eV is used (as it is near to the top of the X barrier), a vb offset of approximately 0.56eV (0.37 ΔE_v) is obtained. This compares favourably with the experimental results obtained for this system with thicker layers (see for example Wilson et al., 1986).

The three cb states at \overline{J} in figure 5.20 and their origin and confinement details in table 5.7c show the lowest two states to be L-like and confined in GaAs whereas the next one is derived from other translated points in the bulk BZ. Its partial confinement in the GaAs layer shows the effect of translated points lining up higher in energy (over 1eV) than the cb minimum and although it would not significantly affect spectroscopic results (which usually concentrate on transitions between states immediately bordering the band gap), does illustrate the physical principles underlying the preferential confinement of charge in particular layers in superlattice structures.

5.3.2 Summary

The analysis of band edge states has been shown to be a potentially useful way of characterising the detailed electronic structure of superlattices. The confinement observed has been shown to be a consequence of the symmetry of the state in question since a state derived from any point (with or without high symmetry) in the fcc BZ will respond to offsets generated by lining up the corresponding bulk states of the two constituents at the same point in this BZ. Using such a procedure has demonstrated that confinement observed in the states of the monolayer superlattice is not consistent

with the existence of band offsets and so must be bulk-like in origin i.e. due to the orbitals that give rise to them. This however is not to say that they do not exist here but rather that their effects are minor. On doubling the layer thickness to form the n=2 superlattice, those band edge states examined did show confinement effects that could be interpreted by the existence of offsets. The confinement was predictably small, considering the layer width, but allowed a lower limit of the vb offset of 0.5eV to be estimated. This value, calculated directly from the confinement effects shown, is expected to be more accurate than the value of 0.27eV obtained in section 5.2.1 from the self-consistent potential because of both the attribution of bulk-like properties for the layers and the non-inclusion of the effects of self-consistency there.

Band offsets first become important in the bilayer system and will therefore be present in systems with thicker layers where they are expected to be accompanied by a greater degree of charge confinement. This is indeed observed for both the n=3 and n=4 superlattices where the states at the top of the vb become more localised in the GaAs layer with the cb states behaving similarly, the symmetry of the state determining in which material confinement occurs. The vb offsets calculated for the two systems are at least 0.44ev and 0.43ev respectively as compared with 0.435eV and 0.392eV respectively from section 5.2.1. Again, there is a disparity between the two sets of results although it is evident that the latter results are becoming more accurate as the layers become thicker (and hence more bulk-like), as would be expected.

The line-ups that result are consistent with those observed in thicker systems with wells for Γ - and L-like cb

states in GaAs and for X-like cb states in AlAs. The results obtained for the vb offset would seem to imply that it is almost independent of layer thickness beyond n=2 reflecting the similarity of the two materials and, coupled with that, a small perturbation to the potential which only extends over those monolayers adjacent to the interface. Those superlattices with n=2 to 4 are of type II and are "indirect" in real space but direct in reciprocal space since the lowest cb state, like the top vb state, is at $\overline{\Gamma}$ but is derived predominantly from X and thus is confined by the well in AlAs.

5.4 CONCLUSION

In concluding this chapter, the results obtained above are briefly reviewed and some predictions for thicker superlattices comprised of the same bulk materials are made. Unfortunately, with the available computing resources, it was found to be difficult to go beyond n=4.

In section 5.2, the self-consistent properties of the four superlattices were examined. The differences in average self-consistent potential led to predictions for the vb offset which showed a marked variation between superlattices. The accuracy of these results was limited (as was made apparent by later results) by having to assume that the layers were effectively bulk-like. The similarity of the two bulk constituents leads to only a small charge transfer from the AlAs layer to the GaAs layer, the direction of which is consistent with electronegativity values. The electronic structure showed the monolayer system to be indirect, in agreement with experiment and other self-consistent calculations and the thicker systems to be pseudodirect with

the gap along the (almost dispersionless) $\overline{\Gamma}-\overline{Z}$ direction. The values for the gaps obtained were also consistent with experiment and for thicker systems are expected to further decrease to the direct gap of GaAs at 1.5eV.

Section 5.3 described in detail the bulk origins of states and how this can be used to understand confinement effects that occur because of the influence of band offsets. The states of the monolayer system could not be interpreted by assuming the existence of band offsets. The states in the other superlattices however demonstrated a consistency with the offset model when care was taken to correctly assign the symmetry of the states studied. The values for the vb offsets were consistent with recent results although it is difficult to pinpoint their magnitude accurately for these systems. Similar calculations on thicker systems are expected to be fruitful however since the differences between the positions of the states and the extrema of the wells should become negligibly small.

These systems were found to be type II superlattices ("indirect" in real space) but were direct in reciprocal space. The lowest state at $\overline{\Gamma}$ was found to be X-like here whereas in thicker systems, the corresponding state is Γ -like making the superlattice type I. A transition must then occur at a critical layer thickness and has been calculated to happen at n=8 (Gell et al., 1986) and n=12 (Nelson et al., 1987) although it is likely to be a gradual rather than an abrupt change.

CHAPTER SIX

EFFECTS OF HYDROSTATIC PRESSURE

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6.1 INTRODUCTION

The use of hydrostatic pressure has recently become a very versatile technique in solid-state physics. It is possibly unique in that up to the point where phase transitions occur, its application preserves the space group symmetry thereby leaving all band degeneracies intact. The main effect is then to decrease the lattice constant which changes all the matrix elements relevant in understanding the electronic structure. As the atoms are pushed closer together, the crystal potential changes and the overlap between orbitals on adjacent atoms increases. If the pressure is high enough it may also be possible for a phase transition to occur giving rise to a crystal structure more stable than the atmospheric pressure one. With the development and use of diamond-anvil cells in producing hydrostatic pressures up to a few hundred kbar, such transitions have been observed in many semiconductors: the final structure may then be determined by in situ x-ray techniques. It is also possible for these transitions to be modelled theoretically with pseudopotential total-energy schemes (Froyen and Cohen, 1983; Chelikowsky, 1987) and provided that the high pressure phase is known, transition pressures can be predicted reasonably accurately. However in order to determine the minimum energy phase, prior knowledge of the structure is required.

The application of high pressure to a solid may lead to a phase transformation. However, lower pressures may produce more subtle effects such as small changes in the electronic properties making this a useful probe of the band structure. Of central interest is the way that the gaps at the principal symmetry points in semiconductors are affected since this will

alter the electronic and the optical response of the system. For instance, if the pressure is large enough, zincblende semiconductors will exhibit metallic properties associated with the lowering of the X cb state below that of the vb maximum at Γ (Froyen and Cohen, 1983). The magnitude of band gaps has been found to vary almost linearly with applied pressure, the slope depending upon the gap in question. By following the movement of states under pressure, a knowledge of the pressure coefficients permits the identification of the symmetry of the states which may permit the determination of the ordering of cb minima in zincblende semiconductors (Welber et al., 1975).

Hydrostatic pressure experiments have also been performed on quantum well structures and superlattices in order to furnish data pertaining to the symmetry of confined states thereby allowing accurate determinations of the band offsets (Wolford et al., 1986; Venkateswaran et al., 1986). It has been found that superlattice states tend to respond to pressure with almost the same pressure coefficient as the bulk states from which they are derived. The energy of Γ states is found to increase whilst that of X states decreases with increasing pressure. There will, at some critical pressure, be a crossover if the Γ -like state is initially below that of the X-like state which is the usual situation in superlattices comprised of reasonably thick layers. For ultrathin layers however, this will in general not happen since the lowest cb state is predominantly X-like (see chapter five) and hence it may be expected that the superlattice should remain type II.

The rest of this chapter is organised as follows. The next section describes the method employed to model the

effects of pressure and includes the calculations on both bulk GaAs and AlAs. This should provide a good test for, and hopefully illustrate the versatility of, the self-consistent method developed in this thesis. Section 6.3 describes the calculations on the (GaAs)₃(AlAs)₃ superlattice and includes an analysis of the band edge states which will reflect in greater clarity the combined effects of pressure and band offsets. Section 6.4 will conclude the chapter.

6.2 BULK SEMICONDUCTORS UNDER HYDROSTATIC PRESSURE

In order to model the changes in bulk GaAs and AlAs under hydrostatic pressure, the lattice constant needs simply to be reduced from a₀ (at atmospheric pressure) to a. The primitive translation vectors then are changed only by this small decrease in lattice constant and the corresponding rlv's increase by the same amount. The change in the lattice constant on application of a pressure P is accurately described by the Murnaghan equation of state (Murnaghan, 1944)

$$P = (B/B')[(\Omega_0/\Omega)^{B'} - 1]$$
(6.1)

where B is the bulk modulus, B' is its pressure derivative (both at atmospheric pressure which is defined to be zero) and Ω_0 and Ω are the volumes at zero pressure and at a pressure P respectively. This is equivalent to the assumption that the bulk modulus is a linear function of pressure although the lattice constant patently is not. The values used for B and B' are 0.747 Mbar and 4.67 respectively (McSkimin et al., 1967) and, whilst these values are strictly for GaAs, they will be used for both materials in the absence of data for

AlAs (the calculated difference of about 3% in the bulk moduli (Adachi, 1985) indicates that they are likely to be similar). It is convenient to assume that the two systems will change similarly with pressure and indeed it has been found that the application of pressure on ultrathin superlattices (with layer thicknesses of about 20Å) illustrates that they may transform as a homogeneous system rather than as two bulk materials (Weinstein et al., 1986). The lattice constant will also be taken to be the same in the two bulks with $a_0=10.6901$ as the zero pressure value, the same as in previous calculations in this thesis.

The range of pressures considered is from zero up to about 80 kbar which reduces the lattice constant by up to 3%. For various lattice constants in this range, the self-consistent method described in chapter four is used to calculate the self-consistent potential of both bulk materials. Again, a single special point is used and the same values for α and the core radii of the ions used in the calculations in the previous chapter are employed. Whilst it is reasonable that α should not change with pressure since the $X\alpha$ method formally treats an atom in a crystal as though it had an infinite lattice constant (Slater, 1974), it may be expected that a smaller lattice constant should imply a smaller core radius although the change would not be large since the core electrons are more rigid than the valence electrons. Welber et al. (1975) used an empty-core form for the ionic pseudopotential screened with the free-electron dielectric function and found that a variation like

$$r_{c} = r_{c}(P=0)[1+b(\Delta a/a_{0})^{2}]^{-1}$$
(6.2)
100

where b is some parameter and $\Delta a=a-a_0$, produced a sublinear variation of the direct energy gap in GaAs with pressure that compared well with their experimental data. Such a variation is consistent with a decrease in ionicity with increasing pressure but, in similar experiments on covalent Ge, a sublinear variation was found and attributed to the effect of the d electrons. The role of ionicity in the changes in energy gaps is then not clear since the d electrons are just as prominent in GaAs as in Ge. Reasons for changing the core radii will be commented upon later in light of the results. **6.2.1 Variation of Electronic Properties**

The principal concerns here are how the energy gaps at the symmetry points in the fcc BZ of both bulks and the average potential change with pressure. The latter will be purely a volume effect related to the variation in the average exchange potential whereas the former will be used to characterise the way in which the energy of the superlattice states change with pressure and also to provide a measure of the accuracy of the scheme by comparing the results obtained here with the (scant) experimental data.

The variations of the energy gaps at the Γ , X and L points with pressure and lattice constant for both GaAs and AlAs are shown in figures 6.1 and 6.2 respectively. The gaps at all symmetry points are found to increase with pressure which is consistent with experimental results for the Γ and L points but contrary to them for the X point. The gap at the Γ point shows the greatest variation with pressure followed by that at the L point and finally the X point. The changes are almost linear with lattice constant and slightly sublinear with pressure. This sublinear variation is in qualitative



Figure 6.1 Pressure and lattice constant dependence of the energy gaps at the principal symmetry points in the fcc BZ for GaAs.



Figure 6.2 Pressure and lattice constant dependence of the energy gaps at the principal symmetry points in the fcc BZ for AlAs.
agreement with experimental results (Welber et al., 1975) although quantitatively, the pressure coefficients (the change in energy gap per unit pressure change) obtained by least-squares fitting are not accurately reproduced. The values calculated here are shown in table 6.1 and those experimentally obtained for GaAs are 10.73meV/kbar for the gap at Γ , -1.34meV/kbar for the gap at X (both by Wolford and Bradley, 1985) and 3.2meV/kbar for the gap at L deduced by Kangarlu et al. (1986) from photoreflectance measurements. No results pertaining to bulk AlAs could be found although Adachi (1985) has offered values of 10.2, -0.8 and 2.8meV/kbar for the **r**, **X** and **L** gaps respectively. The trends for the gaps at Γ and L are therefore correctly reproduced and that at X is at odds with current findings. Given that the main input to the method is the empty-core pseudopotential for the ions, it is instructive to examine it in a little more detail to see whether it contributes to these errors.

For each ion, the core radius is fitted to reproduce bulk energy gaps at atmospheric pressure and hence this fixes the shape of V(G) for a given ion. When pressure is applied, the rlv's increase and hence the matrix elements of this potential will move along this curve. Given that an accurate prediction of the electronic properties can result only from accurate values for the matrix elements, the shape of the curve becomes crucial to the argument. For instance, a more general model pseudopotential has (Cohen and Heine, 1970)

$$V(r) = -A_1$$
 |r|

where the A₁'s are adjustable parameters (different for each

		1	2
GaAs	Г	40.80	14.36
	Х	9.88	3.47
	L	23.51	8.27
AlAs	Г	39.18	13.78
	Х	8.52	3.00
	L	23.23	8.16

Table 6.1 The lattice constant coefficients (1) in eV/au and the pressure coefficients (2) in meV/kbar of the bulk energy gaps for the principal symmetry points.

	Average Potential/Rydbergs				
-100da/a	GaAs	AlAs	Eqn 6.7		
0.0 0.5 1.0 1.5 2.0 2.5 3.0	$\begin{array}{r} -0.6435 \\ -0.6477 \\ -0.6518 \\ -0.6560 \\ -0.6602 \\ -0.6644 \\ -0.6686 \end{array}$	-0.6498 -0.6540 -0.6581 -0.6622 -0.6663 -0.6705 -0.6746	$ \begin{array}{c} -0.7107 \\ -0.7142 \\ -0.7178 \\ -0.7215 \\ -0.7252 \\ -0.7289 \\ -0.7326 \end{array} $		

Table 6.2 Variation with pressure of the average selfconsistent potentials of GaAs and AlAs compared to the predictions of equation 6.7. angular momentum 1) used to reproduce atomic energies and r_m is some radius not necessarily equal to the core radius. It is known that the differences between the A_1 's affects how rapidly V(G) rises to zero (Cohen and Heine, 1970) and since the empty-core model sets all the A_1 's identically equal to zero, it can be seen to be far from satisfactory in this respect.

The ionic potential will be that which the electrons redistribute about on achieving self-consistency and so long as the latter is performed reasonable accurately, discrepancy between experiment and theory must be due to inaccurate modelling of the former. So whilst much physics is built into the empty-core model, it does not allow sufficient freedom since once the core radius is specified, its form is fixed. It is possible to parametrize the core radii at each pressure to reproduce the observed bulk changes and then use these values in superlattice calculations but as has been noted above, there is no obvious physical justification for this.

The values for the average potential for both bulks at various lattice constants are shown in table 6.2. The average potential is due solely to the average exchange potential since the ionic and hartree contributions exactly cancel in the self-consistent procedure because of overall charge neutrality. It is therefore given by

$$V(G=0) = V_{v}(G=0) = -3\alpha(3/\pi)^{1/3} \rho^{1/3}(G=0)$$
(6.4)

where

$$\rho^{1/3}(G=0) = (1/\Omega) \int \left[\sum_{\zeta'} \rho(G') \exp(iG' \cdot r) \right]^{1/3} d^3r \qquad (6.5)$$
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 Ω being the volume of the unit cell. If the G'=0 contribution dominates i.e. the variation in the charge density across the unit cell is small compared with its average value, then

$$V(G=0) \simeq -3\alpha(3/\pi)^{1/3} [\rho(G'=0)]^{1/3}$$
 (6.6)

Since $\rho(G'=0)$ is just the average charge density = n/Ω , this simplifies to

$$V(G=0) \simeq -(6\alpha/a_0) (12/\pi)^{1/3}$$
 (6.7)

where a_0 is the lattice constant and $\alpha=0.81$. The values for the average potential calculated using equation 6.7 are also shown in table 6.2 for comparison with the self-consistent results. Assuming a reciprocal dependence of the average potential on the lattice constant, the coefficient in equation 6.7 is -7.6 Ry a.u. which compares well with the calculated values of -8.7 and -8.6 Ry a.u. respectively for GaAs and AlAs. Given this reciprocal dependence, it is clear that neglecting fourier coefficients other than the first seems to be a reasonable assumption here.

The calculations on the bulk semiconductors are seen to be reasonably successful, predicting the correct trends in the changes in the band gaps at the Γ and L points but not that at the X point. The average potential was found to be inversely proportional to the lattice constant and an attempt to account for this produced reasonable agreement with the self-consistent results. The poor quantitative agreement for the pressure coefficients is not expected to render inappropriate a full analysis of the effects of pressure on

superlattices but merely limit their quantitative accuracy. These will then be useful in accounting for the changes expected to occur in the n=3 superlattice.

6.3 THE n=3 SUPERLATTICE UNDER HYDROSTATIC PRESSURE

This section is intended to illustrate the effects of hydrostatic pressure on the electronic states of an ultrathin superlattice, something which has received much less attention than corresponding investigations on thicker systems. The n=3 superlattice is studied because, like the thicker systems, it has been shown (in the previous chapter) that the concept of band offsets is applicable to the understanding of charge confinement effects and hence that the effects that result from their existence can be readily identified.

The effect of hydrostatic pressure on the superlattice was simulated by decreasing the lattice constant by the amounts used previously in the bulk calculations. It was also assumed that the thicknesses of the GaAs and AlAs layers are changed by the same degree thereby ignoring the small difference in their bulk compressibilities (Adachi, 1985). As for the calculations on this superlattice in the previous chapter, a single special point was used and the values of α and the core radii were assumed to be independent of lattice spacing. The self-consistent potential at different lattice constants was calculated using that calculated for the previous pressure as the starting point, thereby reducing the number of iterations required to achieve convergence. This process was continued until the potential was stable to within 10^{-5} Rydbergs thereby ensuring that charge transfer had been accounted for accurately.

The self-consistent potentials were used to calculate the band gaps at points which contain the bulk Γ , X and L symmetry points and also to follow the changes of states near to the band gap. The bulk character of these states and the resulting degree of charge confinement in each layer were also calculated (at each lattice constant) in order to fully investigate the above changes.

6.3.1 Variation of Electronic Properties

Here, only the variation in the energy gaps at the $\overline{\Gamma},\ \overline{K}$ and \overline{R} points and the average potential will be considered. The gaps, which measure the difference in energy between the highest valence subband at $\overline{\Gamma}$ and the lowest conduction subband at any particular symmetry point, will be simply related to the movement of the bulk states which, when aligned at the interface, give rise to the quantized levels associated with superlattice structures. The movement of one set of bulk levels relative to another will result in a change in the barrier height which will affect the energy of the ground Superimposed on this is the small decrease in lattice state. constant brought about by the application of hydrostatic pressure which will tend to push states away from the bottom of the well. In the absence of zone translation, these two effects are the main ones which will determine the way in which the superlattice states will be affected by pressure.

The energy gaps at the $\overline{\Gamma}$, \overline{K} and \overline{R} points for different lattice constants are shown in table 6.3. All gaps were found to increase at an almost constant rate with the application of pressure, reflecting the similar situation found in the calculations on the bulk materials. Those at $\overline{\Gamma}$ and \overline{K} increased more slowly than that at \overline{R} , the rate of change being

indicative of the former two being controlled by their bulk X character and the latter by its bulk L character. This will be examined in greater detail later in this chapter.

As in the case of the bulk materials, the average potential, also shown in table 6.3, is expected to become more negative on decreasing the lattice constant. It is found to change by 0.025 Ry corresponding to a coefficient of -8.64 Ry a.u. which compares well with the values obtained for the bulk materials and is in reasonable agreement with the coefficient in equation 6.6 quoted in the previous section. This similarity is expected since the electron density here is much the same as that in the bulk materials (given the similarity of the two materials and the small degree of charge transfer) and hence the exchange potential will be much the same.

6.3.2 Band-Edge States

We shall confine the discussion here to those states which, by virtue of their energies, lie close to the band extrema. Other states, as has been mentioned in the previous chapter, are not affected by the presence of band offsets either because they are too high in energy to be affected by them or because they have a different bulk symmetry which means that they will not be affected by those offsets which are due to the vb maximum or the cb minima which are those of interest here. Therefore, only those top three vb states and the lowest five cb states at $\overline{\Gamma}$, the lowest four cb states at \overline{K} and the lowest two cb states at \overline{R} will be considered. These states will be followed as the pressure is increased and, as before, their bulk origins and the amount of charge localised in each material will be examined to fully investigate the response of electronic states in an ultrathin superlattice to

	Ene			
-100da/a	Ĩ	K	R	V(0)/Ryd
0.0 0.5 0.0 1.5 2.0 2.5 3.0	1.964 2.006 2.060 2.080 2.128 2.176 2.225	2.040 2.075 2.121 2.157 2.202 2.248 2.296	2.129 2.225 2.329 2.423 2.528 2.635 2.747	$ \begin{array}{r} -0.6310 \\ -0.6354 \\ -0.6393 \\ -0.6440 \\ -0.6480 \\ -0.6520 \\ -0.6560 \\ \end{array} $

Table 6.3 Variation of the energy gaps at the $\overline{\Gamma}$, \overline{K} and \overline{R} points and of the average self-consistent potential V(0) with pressure for the n=3 superlattice.

	22			22 23			24		
-100da/a	Г	x	Q	Г	x	Q	Г	х	Q
0.0 0.5 1.0 1.5 2.0 2.5 3.0	0.913 0.918 0.919 0.922 0.922 0.923 0.923	$\begin{array}{c} 0.000\\ 0.000\\ 0.000\\ 0.000\\ 0.000\\ 0.000\\ 0.000\\ 0.000\\ 0.000 \end{array}$	1.237 1.230 1.230 1.220 1.219 1.219 1.219	0.988 0.989 0.989 0.988 0.988 0.988 0.988	$\begin{array}{c} 0.003\\ 0.002\\ 0.002\\ 0.002\\ 0.002\\ 0.002\\ 0.002\\ 0.002\\ 0.002 \end{array}$	$1.144 \\ 1.143 \\ 1.146 \\ 1.152 \\ 1.156 \\ 1.160 \\ 1.164$	0.938 0.939 0.938 0.936 0.935 0.933 0.932	$\begin{array}{c} 0.000\\ 0.000\\ 0.000\\ 0.000\\ 0.000\\ 0.000\\ 0.000\\ 0.000\\ 0.000 \end{array}$	1.402 1.397 1.401 1.407 1.411 1.416 1.420

Table 6.4 Pressure induced changes in the bulk Γ and X character and the charge Q confined in the GaAs layer for the top three valence band states at $\overline{\Gamma}$ in the n=3 superlattice. The number used to denote the state increases with its energy.



Figure 6.3 Variation in energy of the states at the Γ point relative to the top of the valence band with fractional decrease in lattice constant.

pressure. Those states at $\overline{\Gamma}$ will be examined first.

The energies of the states at $\overline{\Gamma}$ against pressure are illustrated in figure 6.3 and show the vb states to be almost unchanged except for a small increase in their separation but the cb states to increase almost linearly in energy (relative to the vb maximum) at different rates. The splitting of these vb states is underestimated since spin-orbit coupling has been neglected in all calculations. The bulk character and the charge confined in the two layers for the vb states shown in table 6.4 indicate that they are relatively unaffected by the increase in pressure whereas the cb states show pronounced fluctuations with some of them switching character completely. In this sense, the vb states are of little interest because of these small changes and so only the cb states will be considered further here.

The first two cb states are mainly X-like and increase in energy by about the same amount over the pressure range studied here, an amount similar to the change in the X gap seen in the bulk calculations. The first maintains an almost constant X character while the second shows an overall increase as shown in figure 6.4 which also shows the variations in the Γ character and the charge confinement effects for all of the five states. These two states have very little Γ character (which decreases as the pressure is increased) and are largely confined in the AlAs layer as one would anticipate from their large X character even though other translated states are present here. The next two states also increase in energy at similar rates although faster than the previous two. The Γ character of these states also decays and some of it is replaced by an increase in the X character



Figure 6.4 For the lowest five conduction band states at $\overline{\Gamma}$, this shows the variation with the fractional decrease in lattice constant of (a) the amount of charge confined in the GaAs layer, (b) the bulk Γ character and (c) the bulk X character. The number of the state increases with energy.

and some by the increased contribution from other bulk states (especially state 28 where the X character also decreases). Where large contributions from other translated states occur it is difficult to make any prediction about confinement since they will be subject to a different line-up from the Γ - or X-like states. The fifth state increases in energy at a rate much larger than the others discussed here indicative of a large Γ character, something that can be seen from figure 6.4 where the Γ character begins by increasing and then decreases. The energy of this state reflects this by increasing most when the Γ character is large making it slightly non-linear. The X character is small and decreases rapidly and so the state has its charge mainly confined in the GaAs layer.

The lowest four cb states at \overline{K} are much simpler to understand as their behaviour stems from the fact that they are derived only from one bulk symmetry point. Their energies increase linearly and in pairs with the lowest two and the highest two moving at similar rates as can be seen from figure 6.5. The details on the bulk origins and the confinement effects are shown in table 6.5. They show that all four states have an X character greater than 95% which varies little with pressure and that the first three states are always confined in the AlAs layer and the latter always in GaAs layer illustrating that, as was found before, the first three are confined by the X barrier and the next is a resonant state above it. From the fact that both the lowest cb state at $\overline{\Gamma}$ and the third cb state at \overline{K} are confined by the X barrier, the difference in energy between the two must afford a lower estimate of the height of the X barrier and hence of the valence band offset. These results are shown in table 6.6



Figure 6.5 Variation in energy of the states at the K point relative to the top of the valence band with fractional decrease in lattice constant.

	:	25	26		27		28	
-100da/a	х	Q	х	Q	x	Q	x	Q
0.0 0.5 1.0 1.5 2.0 2.5 3.0	0.957 0.958 0.958 0.959 0.958 0.958 0.958	0.871 0.869 0.865 0.851 0.847 0.843 0.838	0.958 0.960 0.960 0.952 0.950 0.948 0.945	0.709 0.710 0.711 0.692 0.689 0.687 0.686	0.984 0.984 0.983 0.982 0.981 0.980 0.979	0.894 0.896 0.895 0.903 0.903 0.903 0.903	0.986 0.986 0.985 0.984 0.983 0.982 0.981	1.090 1.089 1.083 1.079 1.072 1.064 1.056

Table 6.5 Pressure induced changes in the bulk X character and the charge Q confined in the GaAs layer for the lowest four conduction band states at K in the n=3 superlattice. The number used to denote the state increases with its energy.

	State En		
-100da/a	Lowest T	Highest \overline{K}	∆Ev/eV
0.0 0.5 1.0 1.5 2.0 2.5 3.0	1.964 2.006 2.060 2.080 2.128 2.176 2.225	2.305 2.363 2.423 2.475 2.536 2.597 2.658	0.431 0.435 0.436 0.462 0.467 0.474 0.481

Table 6.6 Estimates of the valence band offset ΔEv from the observed pattern of confinement in the bulk X well.



Figure 6.6 Variation in energy of the states at the \overline{R} point relative to the top of the valence band with fractional decrease in lattice constant.

		25		26
-100da/a	L	Q	L	Q
0.0 0.5 1.0 1.5 2.0 2.5 3.0	0.963 0.962 0.961 0.964 0.964 0.963 0.963	$1.144 \\ 1.146 \\ 1.146 \\ 1.135 \\ 1.133 \\ 1.131 \\ 1.131 $	0.964 0.961 0.960 0.959 0.958 0.955	1.198 1.207 1.208 1.202 1.201 1.199 1.196

Table 6.7 Pressure induced changes in the bulk L character and the charge Q confined in the GaAs layer for the lowest two conduction band states at \overline{R} in the n=3 superlattice. The number used to denote the state increases with its energy.

and although they appear to indicate that the vb offset increases with increasing pressure, there is no way of estimating the errors here which are due to the states not lying at the top and the bottom of the well. To put it another way, this increase in the vb offset will only be real if this variation is greater than that of the distances of the superlattice states from the bulk band edges which comprise the offset profile. Since the positions of the states with respect to the well geometry are not known, little can be concluded.

The two lowest cb states at \overline{R} are also seen, in figure 6.6, to increase linearly in energy at the same rate as each other. This, as can be seen in table 6.7, is due to both states having an almost equal L character (greater than 96%) which changes little with pressure as is also the case with the degree of confinement also shown in table 6.7 which shows the states to be always preferentially confined in the GaAs layer as is expected.

6.4 CONCLUSION

As was stated earlier, the purpose of this chapter was twofold. Firstly, to attempt to predict the changes brought about by hydrostatic pressure in the electronic properties of an ultrathin superlattice, something that had received little theoretical or experimental attention up to now. In the process of understanding these changes, it was necessary to also model the effects of pressure on the two bulk constituents and since experimental data exists for the changes in the energy gap of one of them, it became possible also to fulfil the second purpose of examining the versatility

of the self-consistent method described in this work. Whilst the results on the bulk materials did not show a complete quantitative accord with accepted results, indicative of a shortcoming in the method likely to be related to the use of the empty-core model, we were still able to analyse the results for the superlattice although their quantitative accuracy is obviously in doubt. Even with this disadvantage, it has been possible to extract much of the essential physics and this will be briefly summarised below.

Many of the states examined, particularly those vb states at $\overline{\Gamma}$ and the cb states at \overline{K} and \overline{R} , were to a large extent unaffected by pressure. The only change of note was that the cb states increased in energy at much the same rate as the states at the bulk cb minima from which they are derived. The behaviour of the cb states at $\overline{\Gamma}$ however indicated the subtleties and complexities inherent in the effects of zone translating. They are important because among the points to be translated here are the X point which also contains a minimum in the cb of both bulk materials and as a result, the lowest states have a large X character. As the pressure is increased, the band gaps move at different rates so that the X gaps increase the most slowly and the Γ states the most quickly. Since the low-lying cb states are mainly X-like, they will tend to move at much the same rate as the similar levels in the bulk and will therefore tend to lose their Γ character because these bulk levels increase so rapidly in energy. This was shown to be the case for the first four states here. It can be envisaged as though the bulk Γ levels were "sweeping through" the superlattice states, taking some with them and leaving others behind. Not only is this a very

complicated situation but, as it requires zone translation to account for it, it is something which cannot be accounted for by effective mass theory which can only deal with states at a single symmetry point. Even in thicker systems where such treatments are reasonably accurate at usual pressures because the lowest cb state is typically Γ -like, it has been shown (Wolford et al. 1986) that at some pressure there will be a Γ to X crossover which will necessitate the incorporation of another k point. Effective mass treatments are then not expected to be particularly useful in studies of the effects of hydrostatic pressure on superlattices.

Finally, it may reasonably be said that the X-like states would be expected to decrease in energy in accordance with the behaviour of the bulk X gaps rather than increase as is the case here. The important point here is that the superlattice states derived from a certain k point move at about the same rate as the gaps at the same k point in the bulk materials and since the predictions for the changes in the gaps were in error, the same error was reflected in the movement of the superlattice states.

CHAPTER SEVEN

CONCLUSION

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The purpose of this short summary chapter is twofold; firstly, it is intended as a critical review of the work described and the results obtained in this thesis with the aim of restating its central points and secondly, to suggest possible extensions of and outline modifications to the work performed here.

As was stated in chapter one, the central aim of this work was to accurately model the electronic properties of ultrathin $(GaAs)_n(AlAs)_n(001)$ superlattices so as to clarify the nature of charge confinement effects in systems where the layers are as thin as one atom pair. With such thin systems, there is doubt as to whether confinement effects exist since it is not known whether the concept of band offsets is applicable to characterise them or even whether they can only be described as new materials with properties different from either bulk constituent. In order to accurately model these systems, a quite sophisticated method was employed to include some of those effects which are thought to be more important here than in systems comprised of thicker layers.

The empirical pseudopotential method, described in chapter two, was seen to be a useful way of calculating the electronic properties of bulk semiconductors but needed to be modified in order to treat the superlattices studied here. This was achieved by introducing a rigorous self-consistency requirement to include the effects of charge transfer between the two layer types and the use of a parametrization scheme within it. This included adjustable parameters within the formalism which were used to ensure that the energy gaps at the three principal symmetry points of the two bulk constituents were accurately reproduced. At this point, it is

worth commenting on the successes and limitations of the scheme used here.

The neglect of non-locality and spin-orbit coupling and the use of particular special point sets have been commented upon already. Given the small errors in the fitting procedure, the points on which we wish to concentrate here are

- the G-cutoff used for the termination of the potential in reciprocal space,
- the grid of positions used to determine the exchange potential and
- the use of the empty-core pseudopotential for the ions.

The G-cutoff used in all calculations in this thesis is sufficient to reproduce bulk band structures reasonably accurately and is assumed to be valid in modelling the superlattices. In conjunction with the second point however, this cutoff will affect the calculation of the exchange potential since at each r point where the charge density is calculated, the result will be the actual charge density convoluted with the fourier transform of the "top-hat" function described by this cutoff which will result in truncation errors. Increasing the number of points in the grid will reduce the effect of these ripples and the number used here may be such that this effect is significant. However the same cutoff and a similar number of grid points per atom were used in all calculations to increase the internal consistency and permit comparison between calculations.

The use of the empty-core pseudopotential for the ions is a rather crude approximation which was employed both for its

simplicity and so that a single parameter could be used to describe each ion. Given that results on similar systems using a more rigorous ionic potential than that used here have produced less accord with experimental results particularly in the prediction of band gaps, the use of empty cores for the ions is seen to be a successful way of modelling the ionic potential within a parametrization scheme. In a sense, the inadequacies of the empty-core are minimised by use of the parametrization scheme so that as long as the scheme is used to fit the core radii, the empty-core approximation should be reasonably accurate.

Use of the results of the parametrization scheme for the calculation of the electronic structure of the (GaAs), (AlAs), superlattices in chapter five was seen to be particularly successful. Prediction of energy gaps in good agreement with those experimentally observed reflects this success. From the detailed analysis of those superlattice states near the band edges, relying on correlating the bulk origins with the details of where the charge is preferentially localised, much insight was obtained on the confinement effects present in such thin layers. If the presupposition that states below the top of the barrier are preferentially confined in the wells and that those above it are confined in the barrier layers is accepted, as is the case elsewhere in the literature and as is certainly true for simple models, then this analysis permits a lower limit for the valence band offset to be estimated. The principal drawback with our results was the difficulty in accurately pinpointing the positions of the "bulk" states responsible for the observed pattern of confinement. Hence it was not possible to make precise predictions of the valence

band offsets but the results obtained here are not contrary to the current consensus. In these ultrathin systems, the "15% rule" is consistently violated and apart from the n=1 superlattice where the observed confinement was not due solely to the presence of band offsets, there appeared to be little variation of the valence band offset with n for larger values of n. Extending the study to include superlattices of greater thickness to analyse the changing nature of the lowest conduction band state at $\overline{\Gamma}$ would have been a useful and instructive exercise but, as was noted in chapter five, the limited computer resources made this prohibitive.

The degree of success of the results in chapter five was not present in those obtained for the effects of hydrostatic pressure either on the bulk constituents or the n=3 superlattice. It is difficult to identify the reason(s) for the discrepancies here although, as noted in chapter six, the use of the empty-core pseudopotential to describe the ions is somewhat crude and restrictive. However, once the results for the changes in the energy gaps in the bulk materials were given, similar changes in those of the superlattice could be observed and interpreted in terms of this bulk behaviour. Effects due to zone translating have been shown to be important in such systems, especially for the conduction band states at $\overline{\Gamma}$ which showed quite exotic behaviour. This is something that even with the qualitative agreement present here, could safely be said to be outside the scope of effective mass theories. It is possible that an increase in the agreement with experiment could be achieved if further parametrization were attempted for the core radii of the ions of each bulk materials at each pressure.

One of the most obvious tests and general extensions of the method would be to perform similar calculations on the same systems, changing only the crystallographic orientation. This would provide a useful test of the sensitivity of the electronic properties to the atomic arrangement at the interface and examine the extent to which the bulk properties determine those of systems comprised from them. In addition, systems formed from different bulk materials could be studied although given the lack of data on ultrathin superlattices other than those comprised of GaAs and AlAs, it would be difficult to assess the success of such a study.

The method could also be extended to calculate the optical properties. This would make possible a more complete comparison with experiment thereby enabling a thorough testing of the theory. It would also make possible a prediction of the optical response of devices to see whether semiconductor superlattices could have an important role. This is becoming increasingly the case as our understanding of them becomes more complete and the ability to grow them to a given specification and precision is being realised.

In concluding this chapter, it should be stated that the central aim of this thesis, that of developing a practical formalism which can accurately model the electronic properties of ultrathin semiconductor superlattices, has been achieved and the results obtained by it are, inasmuch as a comparison can be made, in substantial agreement with experiment.

APPENDIX

KRONIG-PENNEY MODEL

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If the offset model of semiconductor superlattices is a tenable one then the simplest way of understanding the basic features of the electronic properties is to use the Kronig-Penney model (Kronig and Penney, 1930). This is frequently used in elementary texts on solid-state physics (see for example Dekker, 1958; Kittel, 1976) to demonstrate the opening of gaps in band theory due to the existence of a periodic (but non-zero) potential. The form of the square well potential, shown in figure A.1, is well suited to the study of superlattice structures, corresponding to either the valence or conduction band offset at a single symmetry point in the superlattice Brillouin zone (SBZ). The model neglects the atomic structure within the layers and hence zone-translating phenomena, important in real structures, are absent in this formalism.

Rather than repeat the derivation of the main results, only those necessary for this description are quoted. Solving the Schrodinger equation gives rise to travelling waves in the wells and evanescent ones in the barriers which describe the tunnelling through the barrier. The cases where the particle has an energy above and below the barrier are sufficiently similar for only the latter to be repeated here. The wavefunctions at an energy E below the barrier are

$$\psi_1(z) = Aexp(ik_1z) + Bexp(-ik_1z) \qquad 0 < z < a$$
(A.1)
 $\psi_2(z) = Cexp(k_2z) + Dexp(-k_2z) \qquad a < z < 2a$

where $k_1 = \sqrt{E}$ and $k_2 = \sqrt{(V-E)}$ in atomic units. Constructing Bloch states U(z) such that $\psi(z) = \exp(iQz)U(z)$ and matching the



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amplitude and derivative of these states at z=0 and z=a (the latter incorporating a phase factor of exp(2iQa)) gives four simultaneous equations which can be written as a matrix times a vector. The determinant of the matrix gives the dispersion relation

$$\cos(2Qa) = [(k^2 - k^2)/2k_1k_2] \sinh(k_2a)\sin(k_1a) + \cosh(k_2a)\cos(k_1a)$$
 (A.2)

which can be solved for the band structure i.e. the E-Q relationship. This is solved by specifying a value of E and calculating the corresponding value of Q. The results shown are restricted to the Γ point (Q=0) of the SBZ.

In order to calculate the wavefunctions, the coefficients A, B, C and D in equation A.1 need to be evaluated. From the matching conditions, only ratios of these can be obtained and it is therefore necessary to specify one further condition to completely determine them. For convenience, the wavefunctions are normalised so that the charge in each state is exactly two electrons which are distributed in some way between the two layers i.e.

$$\int_{0}^{a} |\psi_{1}(z)|^{2} dz + \int_{-a}^{0} |\psi_{2}(z)|^{2} dz = 2a$$
 (A.3)

The algebra here is rather tedious and is not repeated. The charge contained in each layer can then be determined and correlated with the energy position of the state relative to the barrier.

Numerical calculations were carried out with parameters appropriate to the $(GaAs)_A(AlAs)_A$ (001) superlattice which has



Figure A.2 The energy positions of the calculated states relative to the barrier geometry.

Energy/eV	Charge lo GaAs	cated in AlAs
0.092 0.360 0.745 1.084 1.166 1.761 1.854	1.956 1.805 1.282 0.386 0.917 0.804 0.852	0.044 0.195 0.718 1.614 1.083 1.196 1.148

Table A.1 Energy of conduction band states in the Kronig Penney system showing the charge contained in the well (GaAs) and the barrier (AlAs) layers for each state. The height and width of the layers are given in the text.



Figure A.3 The charge densities of the calculated states along the superlattice axis with the energy increasing upwards in the figure.

a period given by 2a = 42.7604a.u. The conduction band offset was assumed to be 60% of the energy gap difference at Γ and is 0.9eV or 66mRy with AlAs the barrier layer. The geometry of the system is then completely specified.

The energy positions of the states at Q=0 relative to this geometry are shown in figure A.2 where it can be seen that the well is strong enough to bind three states. The charge densities associated with these states are shown in figure A.3 and illustrate the occurrence of confinement effects in ultrathin superlattices. These states should be compared with those obtained by envelope function calculations (see for example fig. 1 of Babiker and Ridley, 1986) and illustrate the qualitative similarities between the two methods. The amount of charge confined in each layer for the states calculated here is shown in table A.1. The bound states have their charge confined mainly in the wells as expected since there are no extended states in the barrier layer to match with. The degree of confinement in the well decreases as the states approach the top of the barrier since the effective barrier is made smaller.

However, states above the barrier also show pronounced confinement effects only this time in the barrier layer. These states, called resonant or virtual-bound states, occur because as the electron moves above the well, it is accelerated by the potential well and hence does not spend much time in this region. On going from the well to the barrier layer, it is deccelerated since it has a smaller effective potential and hence, since flux has to be conserved, there is a greater probability of the electron residing in this layer giving a greater charge density. Such states were first observed by Bastard et al., (1984) and Zucker et al., (1984) and transitions involving such states are strong enough to be observed experimentally.

These then show the types of confinement expected, the difference serving to distinguish between those states bound by the well and those above the barrier in the superlattice. This difference is physically important in that it can be used to locate the positions of the band edges leading to estimates of band offsets and is therefore used many times in this thesis to analyse the results. .

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REFERENCES

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- Adachi S. (1985), J. App. Phys. 58, R1.
- Anderson R.L. (1962), Solid State Electron. 5, 341.
- Ando T., Fowler A.B. and Stern F. (1982), Rev. Mod. Phys. 54, 437.
- Antoncik E. (1959), J. Phys. Chem. Solids 10, 314.
- Ashcroft N.W. (1963), Phil. Mag. 8, 2055.
- Ashcroft N.W. (1966), Phys. Lett. 23, 48.
- Ashcroft N.W. and Mermin N.D. (1976), Solid State Physics,

Holt-Saunders, New York.

- Austin B.J., Heine V. and Sham L.J. (1962), Phys. Rev. 127, 276.
- Babiker M. and Ridley B.K. (1986), Superlattices and Microstructures 2, 287.
- Baldereschi A. (1973), Phys. Rev. B 7, 5212.
- Baldereschi A., Hess E., Maschke K., Neumann H., Schulze K.R. and Unger K. (1977), J. Phys. C 10, 4709.
- Bastard G. (1981), Phys. Rev. B 24, 5693.
- Bastard G., Ziemelis O.O., Delalande C., Voos M., Gossard A. and Wiegmann W. (1984), Solid State Commun. **49**, 671.
- Batey J. and Wright S.L. (1986), J. App. Phys. 59, 200.
- Bloch F. (1928), Z. Physik 52, 555.
- Board K. (1985), Rep. Prog. Phys. 48, 1595.
- Bylander D.M. and Kleinman L. (1986), Phys. Rev. B 34, 5280.
- Caldas M.J., Fazzio A. and Zunger A. (1984), App. Phys. Lett. 45, 671.
- Brillson L.J. (1983), J. Phys. Chem. Solids. 44, 703.
- Chadi D.J. and Cohen M.L. (1973), Phys. Rev. B 8, 5747.
- Chelikowsky J.R. and Cohen M.L. (1976), Phys. Rev. B 14, 556.

Chelikowsky J.R. (1987), Phys. Rev. B 35, 1174.

Christensen N.E., Molinari E. and Bachelet G.B. (1985), Solid State Commun. 56, 125.

Ciraci S. and Batra I.P. (1987), Phys. Rev. Lett. 58, 2114. Cohen M.L. and Bergstresser T.K. (1966), Phys. Rev. 141, 789. Cohen M.L. and Heine V. (1970), Solid State Physics, Advances and Applications, 24, 37, eds. H. Ehrenreich, F. Seitz and D. Turnbull, New York. Cohen M.L. (1980), Adv. Elec. and Elec. Phys. 51, 1. Cunningham S.L. (1974), Phys. Rev. B 10, 4988. Dekker A.J. (1958), Solid State Physics, MacMillan, London. Dingle R., Wiegmann W. and Henry C.H. (1974), Phys. Rev. Lett. 33, 827. Dirac P.A.M. (1930), Proc. Camb. Phil. Soc. 26, 376. Esaki L. and Tsu R. (1970), IBM J. Res. Dev. 14, 61. Esaki L. (1981), J. Crystal Growth, 52, 227. Evarestov R.A. and Smirnov V.P. (1983), Phys. Stat. Sol. (b) 119, 9. Ferraz A.C. and Srivastava G.P. (1986), Semicond. Sci. Technol. 1, 169. Ferry D.K. (1984), J. Vac. Sci. Technol. B 2, 504. Frensley W.R. and Kroemer H. (1977), Phys. Rev. B 16, 2642. Froyen S. and Cohen M.L. (1983), Phys. Rev. B 28, 3258. Gell M.A., Ninno D., Jaros M. and Herbert D.C. (1986), Phys. Rev B 34, 2416. Gilbert T.G. and Gurman S.J. (1987), Superlattices and Microstructures, 3, 17. Harrison W.A. (1966), Pseudopotentials in the Theory of Metals, Benjamin, New York. Harrison W.A. (1977), J. Vac. Sci. Technol. 14, 1016.

Heckingbottom R., Davies G.J. and Prior K.A. (1983), Surf. Sci. 132, 375.

Heine V. (1957), Proc. Roy. Soc. 240, 361.

- Heine V. (1970), Solid State Physics, Advances and Applications, eds. H. Ehrenreich, F. Seitz, D. Turnbull, Vol. 24, p1, New York.
- Heine V. and Weaire D. (1970), Solid State Physics, Advances and Applications, eds. H. Ehrenreich, F. Seitz, D. Turnbull, Vol. 24, p249, New York.
- Herring C. (1940), Phys. Rev. 57, 1169.
- Ishibashi A., Mori Y., Itabashi M. and Watanabe M. (1985), J. App. Phys. 58, 2691.
- Jaros M. (1985), Rep. Prog. Phys. 48, 1091.
- Jaros M., Wong K.B., Gell M.A. and Wolford D.J. (1985), J. Vac. Sci. Technol. B 3, 1051.
- Jaros M. and Wong K.B. (1984), J. Phys. C 17, L765.
- Joyce B.A. (1985), Rep. Prog. Phys. 48, 1637.
- Kangarlu A., Chandrasekhar H.R., Chandrasekhar M., Chambers F.A., Vojak B.A. and Meese J.M. (1987), Proceedings of the 18th International Conference on the Physics of

Semiconductors, ed. O. Engström, p569.

Katnani A.D. and Margaritondo G. (1983), Phys. Rev. B 28, 1944. Kelly M.J. and Nicholas R.J. (1985), Rep. Prog. Phys. 48, 1699. Kittel C. (1976), Introduction to Solid State Physics, Wiley,

New York.

- Kohn W. and Vashishta P. (1983), in Theory of the Inhomogeneous Electron Gas, eds. S. Lundqvist and N.H. March, Plenum, New York.
- Kroemer H. (1983), Surf. Sci. 132, 543.
- Kronig R.de L. and Penney W.G. (1930), Proc. Roy. Soc. A **130**, 499.
- Kuan T.S., Kuech T.F., Wang W.I. and Wilkie E.L. (1985), Phys. Rev. Lett. 54, 201.
Langer J.M. and Heinrich H. (1985), Phys. Rev. Lett. 55, 1414. Ledebo L.A. and Ridley B.K. (1982), J. Phys C 15, L961.

Lin-Chung P.J. (1978), Phys. Stat. Sol. (b) 85, 743.

- Louie S.G. (1987), Proceedings of the 18th International Conference on the Physics of Semiconductors, ed. O. Engström, p1095.
- McSkimin H.J., Jayaraman A. and Andreach P. (1967), J. App. Phys. **38**, 2362.

Margaritondo G. (1983), Surf. Sci. 132, 469.

Margaritondo G. (1985), Phys. Rev. B 31, 2526.

- Margaritondo G. (1986), Surf. Sci. 168, 439.
- Mendez E.E., Calleja E., Goncalves da Silva C.E.T., Chang L.L. and Wang W.I. (1986), Phys. Rev. B 33, 7368.
- Meynadier M.H., Delalande C., Bastard G., Voos M., Alexandre F. and Lievin J.L. (1985), Phys. Rev. B **31**, 5539.
- Miller R.C., Tsang W.T. and Munteanu O. (1982), App. Phys. Lett. 41, 374.

Mott N. (1938), Proc. Camb. Phil. Soc. 34, 568.

Murnaghan F.D. (1944), Proc. Nat. Acad. Sci. USA, 30, 244.

- Nakayama T. and Kamimura H. (1985), J. Phys. Soc. Jap. 54, 4726.
- Neave J.H., Joyce B.A., Dobson P.J. and Norton N. (1983), App. Phys. A 31, 1.
- Nelson J.S., Fong C.Y. and Batra I.P. (1987), App. Phys. Lett. 50, 1595.
- Ninno D., Wong K.B., Gell M.A. and Jaros M. (1985), Phys. Rev. B 32, 2700.
- Ourmazd A. and Bean J.C. (1985), Phys. Rev. Lett. 55, 765.
- Pearah P.J., Masselink W.T., Klem J., Henderson T., Morkoc H., Litton C.W. and Reynolds D.C. (1985), Phys. Rev. B 32, 3857.

Phillips J.C. and Kleinman L. (1959), Phys. Rev. **116**, 880. Phillips J.C. and Pandey K.C. (1973), Phys. Rev. Lett. **30**, 787. Phillips J.C. (1981), J. Vac. Sci. Technol. **19**, 545. Pickett W.E., Louie S.G. and Cohen M.L. (1978), Phys. Rev. B **17**,

```
815.
```

- Pietsch U., Tsirelson V.G. and Ozerov R.P. (1986), Phys. Stat. Sol. (b) 138, 47.
- Sai-Halasz G.A., Esaki L. and Harrison W.A. (1978), Phys. Rev. B 18, 2812.
- Sanders G.D. and Chang Y.C. (1985), Phys. Rev. B 32, 5517.
- Schluter J.N., Chelikowsky J.R., Louie S.G. and Cohen M.L. (1975), Phys. Rev. B 12, 4200.
- Schottky W. (1938), Naturwissenschaften, 26, 843.
- Schwarz K. (1972), Phys. Rev. B 5, 2466.
- Slater J.C. (1951), Phys. Rev. 81, 385.
- Slater J.C. (1974), The Self-Consistent Field for Molecules and Solids, Vol. 4, Ch. 1, McGraw-Hill, New York.
- Srivastava G.P., Martins J.L. and Zunger A. (1985), Phys. Rev. B 31, 2561.
- Tersoff J. (1984a), Phys. Rev. Lett. 52, 465.
- Tersoff J. (1984b), Phys. Rev. B 30, 4874.
- Voos M. (1986), Surf. Sci. 168, 852.
- Wang W.I., Kuan T.S., Mendez E.E. and Esaki L. (1985), Phys. Rev. B **31**, 6890.
- Venkateswaran U., Chandrasekhar M., Chandrasekhar H.R., Vojak B.A., Chambers F.A. and Meese J.M. (1986), Phys. Rev. B 33, 8416.
- Waldrop J.R., Kowalczyk S.P., Grant R.W., Kraut E.A. and Miller D.L. (1981), J. Vac. Sci. Technol. **19**, 573.
- Walter J.P. and Cohen M.L. (1971), Phys. Rev. B 4, 1877.

- Weinstein B.A., Hark S.K., Burnham R.D. and Martin R.M. (1987), Phys. Rev. Lett. 58, 781.
- Welber B., Cardona M., Kim C.K. and Rodriguez S. (1975), Phys. Rev. B 12, 5729.
- Williams R.H., Srivastava G.P., and McGovern I.T. (1980), Rep. Prog. Phys. 43, 1357.
- Williams R.H. (1982), Contemp. Phys. 23, 329.
- Wilson B.A., Dawson P., Tu C.W. and Miller R.C. (1986), J. Vac. Sci. Technol. B 4, 1037.
- Wolford D.J. and Bradley J.A. (1985), Solid State Commun. 53, 1069.
- Wolford D.J., Kuech T.F., Bradley J.A., Gell M.A., Ninno D. and Jaros M. (1986), J. Vac. Sci. Technol. B 4, 1043.
- Wong K.B., Jaros M., Gell M.A. and Ninno D. (1985), J. Phys. C 19, 53.
- Wood D.M., Wei S.-H. and Zunger A. (1987), Phys. Rev. Lett. 58, 1123.
- Ziman J.M. (1972), Principles of the Theory of Solids, CUP.
- Zucker J.E., Pinczuk A., Chemla D.A., Gossard A.C. and Wiegmann W. (1984), Phys. Rev. B **29**, 7065.

Zunger A. and Ratner M.A. (1978), Chem. Phys. 30, 413. Zunger A. (1979), J. Vac. Sci. Technol. 16, 1337.

ELECTRONIC STATES OF ULTRATHIN GAAS/ALAS SUPERLATTICES T. G. Gilbert

ABSTRACT 🥣

The continuing refinement of crystal growth techniques has made possible the fabrication of semiconductor superlattices where the period can be as small as one lattice constant. Prediction of many of the properties of such systems requires a detailed description of their electronic structure. In this thesis, a self-consistent pseudopotential method which includes a parametrization scheme has been used to calculate the electronic properties of $(GaAs)_n(AlAs)_n$ superlattices with n ranging from 1 to 4. The parametrization scheme is used to reproduce energy gaps at the principal symmetry points for the bulk constituents and the resulting parameter set is employed in all subsequent calculations.

The n=1 superlattice is found to be indirect with the conduction band minimum at \overline{R} (equivalent to the zincblende L point) and all the thicker systems are pseudodirect in good agreement with experimental results. The lowest conduction band state at the zone centre for all systems is found to be mainly X-derived reflecting the importance of zone translating effects here. By analysing the states near to the band edges, the observed pattern of confinement in states of the n=1 superlattice shows the band offsets to have at most a small role, in contrast to the thicker systems where a definite relationship was established. Moreover, the results suggest that Dingle's "15% rule" is consistently violated and that a valence band offset of about 30-40% is obtained which changes little with layer thickness.

Attempts to study the effects of hydrostatic pressure on the n=3 superlattice were in part successful and predicted quite complex behaviour for the electronic states. Much of the discrepancy between the results obtained and the experimental data was attributed to the inadequacies of the empty-core pseudopotential to model the ions.