A Supercell, Bloch Wave Method for Calculating Low-Energy Electron Reflectivity with Applications to Free-Standing Graphene and Molybdenum Disulfide

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ABSTRACT

A Supercell, Bloch Wave Method for Calculating Low-Energy Electron Reflectivity with Applications to Free-Standing Graphene and Molybdenum Disulfide

by

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This dissertation reports on a novel theoretical and computational framework for calculating low-energy electron reflectivities from crystalline surfaces and its application to two layered systems of two-dimensional materials, graphene and molybdenum disulfide. The framework provides a simple and efficient approach through the matching of a small set of Fourier components of Bloch wave solutions to the Schrödinger Equation in a slab-in-supercell geometry to incoming and outgoing plane waves on both sides of the supercell. The implementation of this method is described in detail for the calculation of reflectivities in the lowest energy range, for which only specular reflection is allowed. This implementation includes the calculation of reflectivities from beams with normal or off-normal incidence. Two different algorithms are described in the case of off-normal incidence which differ in their dependence on the existence of a symmetry with a mirror plane parallel to the crystal surface. Applications to model potentials in one, two, and three dimensions display consistent results when using different supercell sizes and convergent results with the density of Fourier grids.

The design of the Bloch wave matching also allows for the accurate modeling of crystalline slabs through the use of realistic potentials determined via density functional theory. The application of the method to low-energy electron scattering from free-standing systems of a few layers of graphene, including the use of these realistic potentials, demonstrates this ability of the method to
accurately model real systems. It reproduces the layer-dependent oscillations found in experimental, normal incidence reflectivity curves for a few layers of graphene grown on silicon carbide. The normal incidence reflectivity curves calculated for slabs consisting of few-layer graphene on 10 layers of nickel show some qualitative agreement with experiment. General incidence reflectivity spectra for free-standing few-layer graphene predict free-electron-like dispersion for the location of the lowest energy oscillations as a function of the in-plane Bloch wave vector, as well as other interesting features. The application of the method to scattering from free-standing systems of molybdenum disulfide predicts that low-energy electron reflectivities can provide a means for layer counting, especially in 2H- and 3R-molybdenum disulfide, and structural differentiation, especially between 1T- and 2H-molybdenum disulfide, in few-layer systems. An investigation of the issues and limitations of the method suggests that some modifications and improvements are likely necessary before widespread application is possible.
CHAPTER 1

INTRODUCTION

1.1 Thesis Motivation

An understanding of material surfaces is crucial to the discovery of new materials and the design of new devices for energy and electronics applications. The most important processes in solar cells and batteries occur at surfaces. Displays and touch screens are surfaces through which we interact with devices filled with components built from many layers of materials (with two surfaces at each interface). Progress in materials science and device technology relies on the characterization of surfaces in terms of their structural and electronic properties. It provides the certainty necessary for reproducing experiments, reveals useful information in the search for new materials, and allows for the detailed monitoring of the growth of layered materials and the assembly of nanostructures. There is an array of imaging and probing techniques that contribute to this characterization, each with its advantages and areas of applicability.

The bulk of this dissertation consists of the explanation of a novel theoretical and computational framework for modeling one type of experimental probe of crystalline surfaces: low-energy electron diffraction (LEED), especially in the lowest energy ranges that are most accessible via low-energy electron microscopes (LEEMs). We have developed a method for calculating the intensities of reflected electron beams that has a fairly simple implementation yet can make use of the highly accurate potentials produced by density functional theory (DFT). The ability to use
realistic potentials allows for the study of more materials, especially those with strongly directional bonding, and for the accurate computation of reflectivities to lower energies than many previous methods allow. The simplicity may allow for larger systems to be studied, for easier integration into many different DFT packages, and for some straightforward interpretations of reflectivity spectra features in terms of wavefunctions.

An important class of materials in modern material and surface science is the class of two-dimensional materials. The term ‘two-dimensional material’ is usually used to refer to a single-layer system in which the confinement of electrons to such a small area in one-dimension leads to special properties, but these materials can have interesting properties when a few layers are present as well. There is also a great deal of excitement around Van der Waals heterostructures or layered materials in which two-dimensional materials are stacked on top of one another. LEEM reflectivity is a good tool for studying these systems, and our method is best-suited for studying free-standing systems (with no substrate). Thus, we have used our approach to study free-standing, few-layer systems of the two-dimensional materials graphene and molybdenum disulfide (MoS$_2$). I will demonstrate that these applications to real systems provide evidence that our method can produce useful and interesting insights into the scattering of low-energy electrons from crystal surfaces, including supporting and augmenting experimental studies. I will also show that the method can create predictions of what can be expected in potential experimental studies and the types of information that can be gained from them. Finally, I will discuss the limitations of the method and the improvements that may be necessary to make it viable technique for widespread use.

1.2 Content Arrangement

The following chapter (Ch. 2) contains brief explanations of electron diffraction and the low-energy electron microscope, and a significant review of the various techniques that have been developed to
model low-energy electron diffraction. On first reading, especially for those unfamiliar with LEED calculation techniques, all of the descriptions of specific calculations that constitute Sections 2.3.4 and 2.3.5 can be omitted. Chapter 3 is the heart of the dissertation, describing our theoretical framework for modeling low-energy electron diffraction and deriving and explaining our method for calculating low-energy electron reflectivities in the lowest energy range for incident beams at both normal and off-normal angles. Ch. 4 presents the results of applying this calculation technique to low-energy electron scattering from free-standing systems of few-layer graphene (FLG), specifically, one to eight layers of graphene. In it, I also discuss the agreement with experimental results, a comparison with related theoretical results, and some understanding of the reflectivity spectra in terms of the electronic structure of graphite. Ch. 4 also describes the mixed results of a preliminary attempt to study a system with a substrate: few-layer graphene on top of nickel. Ch. 5 presents the results of applying our calculation technique to low-energy electron scattering from free-standing systems of one to three layers of MoS$_2$ in a few different polymorphs (crystal structures). Finally, Ch. 6 discusses a few of the limitations and unresolved issues with our technique, along with some suggestions on how they might be overcome. Ch. 7 contains my conclusions. Appendix A provides a compressed background on solid state physics, especially electronic structure, with a focus on concepts important to this dissertation, most notably electrons in periodic potentials, Bloch’s Theorem, and band structure. It may be read first for those without much background in solid state physics. Appendix B elaborates on the algorithms described in Ch. 3 by supplying some details of the computational process for calculating reflectivity spectra using the open source DFT package QUANTUM ESPRESSO and our Matlab code.
Chapter 2

Low-Energy Electron Diffraction and Microscopy

2.1 Background

The wave-like nature of the electron means that electron beams can constructively or destructively interfere with one another. Thus, when an electron beam is scattered from a crystal (a periodic arrangement of atoms), diffraction occurs: reflected intensity is high in certain directions where all scattering electrons are in phase and very low in all other directions due to destructive interference. The directions of high intensity correspond to outgoing free electrons with wave vectors that differ from wave vectors of the incoming electrons by a vector of the reciprocal lattice.\(^1\) In fact, it was the observation of diffracted electron beams by Davisson and Germer [4] and Thompson and Reid [5] that first proved the wave nature of electrons experimentally, results so significant that they led to a shared Nobel Prize for Davisson and Thompson in 1937. Observations of this diffraction pattern and measurements of the intensity of diffracted beams allow for determinations of lattice structure.

Electrons at low energies (below a few hundred eV) interact strongly with solids. Thus, low-

\(^1\)The reciprocal lattice is the Fourier transform of a sum of delta functions at each point in the lattice or, alternatively, the set wave vectors of Fourier modes with the same periodicity as the lattice.
energy electron diffraction provides rich information about solid surfaces. Some of the only experimental work done with LEED during the 30 years after its discovery included the demonstration by Farnsworth that for silver grown on the (100) surface of gold as little as 90% of diffracted electrons sampled more than two atomic layers of the surface (at 60 eV). LEED has been used since the 1970s to determine the surface structure of materials. (The delay was due to difficulties in preparing clean surfaces and in analyzing the more complicated scattering of electrons.) In the early 1990s, Bauer developed the low-energy electron microscope, which uses low-energy electrons to image solid surfaces as well as record diffraction effects. This allows for the simultaneous observation of real space and reciprocal space properties. LEEM devices are generally able to record at lower energies than traditional LEED devices, including the very low energy range of 0-10 eV.

2.2 Devices and Experiment

A very brief description of the operation of a LEEM device is aided by Fig. 2-1 (a). To start, a low-energy electron microscope focuses a beam of not-so-low-energy electrons (around 15-20 keV) as it is directed towards a sample. Generally, the beam comes in from the side and is deflected into a direction normal or close to normal to the sample surface by a beam splitter. As the beam approaches the sample it passes through an objective lens that focuses it and also decelerates it to the desired low energy, usually 0-150 eV. The energy is determined by the bias between the sample and the electron gun. The reflected/back-diffracted beams are re-accelerated back through the objective lens and the beam splitter which deflects them towards the imaging apparati. LEEM devices can be set to display the diffraction pattern or to produce an image from any of the (low-order) diffraction beams. LEEM devices also have two ways to record the diffracted intensity as a function of incident beam energy or accelerating voltage, known as I(V) curves, for the lowest order diffracted beams, most commonly the specularly reflected beam. They can perform microspot LEED (µLEED), which involves the illumination of areas as small as 250
Figure 2-1: The many sides of LEEM: (a) A simple schematic of a typical LEEM apparatus [1]. (b) A diffraction pattern of monolayer graphene on Ru(0001) [2]. (c) A LEEM image of FLG on Ru(0001) [2]. (d) Two LEEM-IV curves of FLG on Ru(0001), from two points in the LEEM image in (c) [2].
nm in diameter, as opposed to the typical illumination area of square microns in traditional LEED. Alternatively, LEEM images over a range of energies can be analyzed to produce spatially-resolved IV measurements with resolutions close to that of the instrument, about 5 nm, essentially an IV curve for each pixel. The results of this process are usually referred to as LEEM-IV curves. Fig. 2-1 (b)-(d) show examples of three of these types of data produced by LEEM investigations of layers of graphene on ruthenium. [6]

2.3 LEED Theory and Calculation Methods

2.3.1 The Need for Theory

To determine many quantitative details about surface structures, and even some complicated qualitative ones, imaging and diffraction patterns are not enough. This requires the analysis of I(V) curves, which entails the comparison of experimental curves to theoretical curves computed using models of the scattering of electrons from the sample. Details can be determined by adjusting the model until the theoretical curve sufficiently matches the experimental one. For instance, one common method is to define a measure of the difference between the curves and minimize this measure over a lattice parameter of the crystal. Another example is the determination of the way that layers stack on top of one another by calculating theoretical curves for the most likely arrangements and comparing to the experimental curve.

In a somewhat different vein, density functional theory allows for structural prediction without a heavy dependence on input parameters, and a LEED I(V) curve calculated from the DFT results allows for a check of these predictions and a method for understanding differences from other structural predictions. Since structural determination at the nanoscale is a very tricky business, the more independent approaches for investigating and verifying structures that are available, the more reliable the findings. A DFT approach can also provide a deeper understanding of the interaction of electrons with a material and the electronic states and band structure of the material.
2.3.2 General Quantum Scattering Theory

In the generic scattering problem for a quantum particle (i.e., in the realm where quantum effects dominate), one seeks a solution to the single-particle Schrödinger Equation for which the form is known far from the scattering center. For a time-independent potential, the relevant Schrödinger Equation is the time-independent Schrödinger Equation, which in Rydberg units looks like:

\[
(-\nabla^2 + V(r)) \psi_j(r) = E_j \psi_j(r).
\]  

(2.1)

(See A.1 for derivation from full Schrödinger Equation via basic separation of variables and for a justification of the use of the single-particle Schrödinger Equation.) For an electron scattering from a target with fixed, time-independent potential, \( V(r) \), the form of the wavefunction for the electron, \( \psi(r) \), (infinitely) far from the scattering center is a solution to the Schrödinger Equation for a free particle, i.e., a linear combination of plane waves,

\[
\psi(r) = \sum_{j=1}^{N} A_je^{i\mathbf{q}_j \cdot \mathbf{r}}.
\]  

(2.2)

The experimental setup for a scattering problem typically demands that the amplitude of the incoming beam, say, \( A_1 \), is the only known amplitude. The scattering problem is solved by appropriately patching together solutions found for the area near the target with solutions far from the target with the asymptotic form,

\[
\psi(r) = A_1e^{i\mathbf{q}_1 \cdot \mathbf{r}} + \sum_{j=2}^{N} A_je^{i\mathbf{q}_j \cdot \mathbf{r}}.
\]  

(2.3)

With targets with finite scattering domains, typically, the solutions near the target are found within a large sphere and and plane waves are expanded in terms of spherical harmonics. Then, one of two approaches is used for patching solutions to the asymptotic form: 1) the asymptotic forms are derived from the form of the solution inside and some parameters adjusted to make the solution
approach the known form asymptotically or 2) the values of the interior solution are matched to the known form at points in some region far from the target. As we will see, sometimes the scattering from a crystal is computed as the sum of scattering from atoms, starting by treating each as a finite scattering domain. Our method, along with other Bloch wave methods, avoids this by treating scattering from the whole system at once. In the end, however, all analyses of scattering from crystal surfaces involve a target that is essentially infinitely extended in two dimensions, and the known form exists far from the surface in the single direction perpendicular to the surface (on one or both sides of the surface).

2.3.3 A Brief History of LEED Calculation Methods

The scattering of low-energy electrons requires taking into account ‘multiple scattering’ - the interaction between an atom in the solid and an electron that has already scattered off another surface atom. The multiple scattering effects can be handled explicitly by calculating the effects of one scattering event and then the effects of the scattering of one of the results of the first scattering event, and so on, or implicitly through full solution of the Schrödinger Equation for the surface. The 1960s and '70s saw the development of a variety of methods for solving problems involving the multiple scattering of electrons, with a healthy mix of explicit and implicit (and even some hybrid-like) techniques. A narrowing down of the variety of methods and improvements in the computational efficiency of the associated programs produced a surface structure determination boom during the 1970s and '80s. The most widely-used approaches to solving this problem involve an assumption that the scattering potential is a ‘muffin tin’ potential: spherically symmetric in a ball around each nucleus and constant in regions in between (interstitial regions) [7]. This assumption of muffin-tin potentials is likely justified for many materials for electron energies from 10 to 30 eV [7]. However, below these energies and for materials with anisotropic electron density, like strongly covalently bonded materials, a way around this assumption is necessary. Our approach
moves away from this assumption, as has some recent work of other groups.

The following two sections constitute a literature review of LEED calculation methods and will illustrate the large variety of ways that researchers have sought to improve, expand, speed up, and simplify these methods. While there is a dizzying mix of approaches described, there are a few overarching ideas about the state of LEED calculation methods to take away from it.

- Muffin-tin potentials have been combined with perturbative, layer techniques to create some of the most widely-used computational packages for surface structure determination.

- However, the assumption of a muffin-tin potential is a serious restriction that does fail in the lowest energies ranges, so that full-potential techniques are needed.

- Bloch wave methods are the favored choice for incorporation of full-potentials.

- Bloch wave methods automatically take into account multiple scattering through the solution of the Schrödinger Equation for the entire crystal at once.

- Bloch wave methods allow for interpretations of LEED spectra and experiments in terms of band structure.

- Bloch wave matching techniques must be handled carefully due to stability issues, especially when the method involves the propagation in real space of a solution represented in Fourier space perpendicular to the propagation and/or when including high-order evanescent states.

- Complex band structures are an accurate and useful but involved approach to solving the scattering problem.

2.3.4 Early Methods: Mostly Muffin-Tin Approaches

The numerous methods developed in the ‘60s and ‘70s differed in the basis sets used to expand the solutions to the Schrödinger equation, the forms of potentials assumed, how they handled intralayer and interlayer scattering, and in their inclusion of thermal vibrations, other temperature
effects, and inelastic scattering. As hinted at above, even just the distinction between explicit and implicit methods is not crystal clear. In 1971, Shen saw the division as being between the ‘band-structure-matching formalism’ and the non-Bloch wave approaches. For Shen, the first class all involve computing the total wavefunction inside the crystal in terms of Bloch waves and matching these Bloch waves to incoming and outgoing beams in the surface region, and the majority use pseudopotentials. Representatives include Bethe [8], Heine’s work on complex band structure and surface states [9], Boudreaux’s and Heine’s use of nearly-free-electron complex band structure and wavefunction matching in LEED calculations [10], Marcus’s and Jepsen’s propagation matrix method using Bloch waves [11], and Pendry’s matrix formulation of Boudreaux’s and Heine’s Bloch wave method to include surface layers different from the periodic substrate [12]. The second class are methods based on multiple scattering using muffin-tin potentials and Green’s functions, which automatically entail the matching at the surface. Examples include the work of McRae, Kambe, and Shen [13, 14, 15, 16]. (However, Shen also mentions the need to combine Bloch waves and Green’s functions in order to handle scattering from a semi-infinite crystal, by which he seems to mean arbitrary, two-dimensionally periodic surface layers with a simple periodic substrate.)

More explicitly, an example of the first class is given by Pendry’s matrix formulation of the Bloch wave method of Boudreaux and Heine [12]. Pendry describes a process in which solutions in the crystal are written in three-dimensional Bloch wave form approximated by a finite number of Fourier components in the in-plane directions. Including Bloch waves that decay into the crystal, there are infinitely many Bloch waves with in-plane wave vectors that match that of the incoming wave. If \( n \) Fourier components are kept, \( 2n \) of these Bloch solutions are used (to have a determined system of matching equations). Then, Bloch wave solutions and plane wave solutions are matched at interfaces between different regions, producing a large matrix system to be solved for the amplitudes of the Bloch and plane waves. An example of the second class can be found in Beeby’s creation of one of the earliest explicit multiple scattering methods by breaking planes of atoms, assumed to be
infinitely periodic, into subplanes with identical structures and computing scattering matrices for each layer and accounting for both in-plane and between-plane scattering using Green’s functions [17].

Pendry also emphasizes the difference between Bloch wave methods and non-Bloch wave methods, but classifies things somewhat differently in his 1974 book on LEED. For Pendry, Bloch wave methods come in two types: layer approaches and pseudopotential approaches, and in non-Bloch wave methods Pendry includes not just basic Green’s function approaches but those that take advantage of absorption to treat the semi-infinite crystal as a slab and perturbative techniques, like Renormalized Forward Scattering.

In the book, Pendry describes a layer, Bloch wave method as the primary example of non-perturbative LEED calculation methods. Pendry distinguishes between two stages in the Bloch wave methods: calculating Bloch wave solutions and expanding wavefunctions in terms of those Bloch wave solutions. This is common to all Bloch wave methods, including modern methods. There is the initial problem of computing Bloch wave solutions for the crystal, meaning almost by definition determining at least pieces of the band structure. Then, solutions for the whole space must be created using the Bloch waves as some sort of basis for the solution space, along with representations of the wavefunctions in the vacuum. For solving for Bloch waves, first, Pendry allows for in-plane scattering using spherical-wave multiple scattering from muffin-tin potentials to create the scattering for a full plane or layer in terms of phase shifts. Then, he shows how to solve for Bloch waves for a semi-infinite crystal composed of those layers, using the layer scattering matrices to set up a matrix eigenvalue problem for the band structure. This layer approach for calculating Bloch waves leads to a form of eigenvalue problem especially useful for analyzing LEED, which is an equation that for fixed energy, $E$, and parallel wave vector, $k_\parallel$, gives eigenvalues that specify $k_z$. Pendry opposes this to pseudopotential methods which the author claims “involve hunting about the complex-wave vector plane for zeros of a determinant.” This is a significant point whose full
force will be appreciated upon reading Sec. 3.2.3. After finding the Bloch waves, Pendry applies a simple method for obtaining reflected plane wave amplitudes from incident plane wave amplitudes, via Bloch wave amplitudes, by matching amplitudes of appropriate combinations of beams.

This method is very similar to the work of Marcus, Jepsen, and Jona in 1972 [18], in which the authors use a layer-KKR (Korringa-Kohn-Rostoker) method that they originally designed for complex band structure calculations [19] to compute LEED spectra for FCC metal. The authors use a setup in which they start with solutions written in the ‘beam representation’ (also called the Laue or mixed representation), meaning in a finite Fourier series expansion in two dimensions for the periodic part of the Bloch wave form:

\[
\psi_{k}(r) = e^{i\mathbf{k}_{\parallel} \cdot r} \sum_{n=1}^{N} \psi_{k}^{n}(z)e^{i\mathbf{G}_{\parallel} \cdot r}. \tag{2.4}
\]

They then write the \(z\)-dependent coefficients in the odd form,

\[
\psi_{k}^{n}(z) = \alpha_{n}^{+}(z)e^{ik_{nz}z} + \alpha_{n}^{-}(z)e^{-ik_{nz}z}, \tag{2.5}
\]

to derive a scattering (‘propagation’) matrix approach to scattering between layers based on generalized Bloch functions in \(z\) (a type of discrete form of the complex band structure). For scattering within a layer, they transform from the ‘beam representation’ to a spherical-wave representation so that they can use the phase-shift-based KKR method, taking advantage of the assumption of muffin-tin potentials, then transform back to the ‘beam representation’ [18].

These layer, Bloch wave methods, can handle top layers that differ from the bulk (due to relaxation, reconstruction, or even just the potential barrier at the surface) by computing scattering matrices for those layers first and computing Bloch states only for the semi-infinite system beyond that surface region. However, Pendry points out the computing requirement limitations of Bloch wave methods, saying, “Certainly structural analysis would be limited to rather simple systems if
the Bloch-wave method were to be used, because of computing time involved” [20]. Van Hove [7] suggests that Bloch wave methods actually cannot deal very well with surface layers, or at least offer nothing new for them, saying, “The Bloch-wave and transfer-matrix methods have the virtues of both providing a connection with the familiar band-structure theory of bulk materials and of giving a simple interpretation of the electron-diffraction process at elementary surfaces. However, these advantages have not been particularly useful in treating more complex surfaces involving adsorbates or reconstructions.”

Pendry also discusses layer methods that do not compute Bloch states. Bloch wave methods provide much more complete information about the electronic structure of the system, including the band structure, which can allow for a deeper understanding of LEED scattering, however, it is sometimes advantageous to forego this information to simply compute reflectivities in an efficient fashion. Pendry offers a brief description of the matrix doubling method, which requires finite absorption so that the semi-infinite crystal can be modeled by a slab of finite thickness. As in all the layer methods, planes of atoms are first combined into layers. Then, a pair of layers is combined in the same fashion to form a new layer, then a pair of those pairs are combined, etc., until the scattering from a thick slab has been computed.

Finally, Pendry describes his perturbative approaches, especially the Renormalized-Forward-Scattering (RFS) approach which assumes weak reflection by any given layer, so that the total reflectivity is expanded in terms of the reflectivity produced by a given (odd) number of reflections. This method is very efficient, but it has difficulties at the lowest energies (<10 eV) due to the strong layer reflections in this range and when interlayer spacing is small due to the need to include many evanescent waves [7]. Van Hove, who played a large part in laying the groundwork for some of the most widely-used LEED calculation codes, together with co-authors explain that while RFS is a very efficient method, matrix-doubling is the more reliable option [7]. Pendry adds that perturbation approaches do not necessarily converge, while the other layer (and pseudopotential) methods can be
made to converge with the proper increase in Fourier components and phase shifts (from spherical scattering from muffin-tins).

Some comments about Bloch wave techniques are in order. First, it should be recognized that they contain all multiple scattering automatically. In his paper on the matrix formulation of Boudreaux’s and Heine’s work, Pendry notes “that in the Bloch function approach, the time consuming device of representing the crystal as a finite number of monolayers, which is inherent in a scattering approach, is eliminated. The Bloch functions have already taken account all of the multiple scattering in the crystal.” (Note that this paper was written before the explicit categorization of Bloch wave approaches into layer-based and pseudopotential-based in Pendry’s 1974 book. In this quote, he is referring to a pseudopotential, Bloch wave approach.) Boudreaux and Heine explain in slightly more detail, “The meaning of multiple scattering in a periodic crystal is to turn a pure plane wave into a Bloch function. If therefore we match the incident beam onto the appropriate Bloch-function solutions of the Schrödinger Equation inside the crystal, we automatically take into account all the multiple scattering effects considered by McRae [referring to [13]].” Bloch wave methods, however, were not used in the most popular computational LEED packages. Indeed, the most popular computational LEED packages make use of the non-Bloch wave methods that Pendry described: layer-doubling and the perturbative Reversed-Forward-Scattering [21, 7, 22].

However, these non-Bloch wave methods were dependent upon the scattering potential of the crystal having the form of non-overlapping spheres of potential connected by regions of constant potential, i.e., the muffin-tin potential. It is also often assumed that the potentials in the spheres are spherically symmetric. At the lowest energies, roughly below 20 eV, these potentials are not adequate for accurately describing electronic interactions with crystals due to the electrons sensitivity to the electron charge distribution in the regions between atomic cores [7]. See Sec. 2.3.5 for specific examples of this failure.
Many Bloch wave methods also had issues. Wachutka [23] claims to have shown in his thesis and in a German publication that a number of previous approaches were ill-posed and, thus, had significant numerical instabilities, including: the propagation matrix approach of Marcus and Jepsen [11], the layer, transfer matrix approach of McRae [24], the step-by-step integration of Bloch waves in the Laue (or beam) representation proposed by Appelbaum and Hamann [25], and the transfer-matrix method of Jepsen that uses spherical wave decompositions of scattering in-between layers to handle materials with more closely packed layers [26]. Wachutka uses rigorous functional analysis to show that two-sided boundary conditions on a linear combination of the wavefunction and its derivative (two-sided Robin conditions) give a well-posed problem. Wachutka claims that the ill-posedness produced by one-sided, separate boundary conditions on the wavefunction and its derivative used in propagation matrix and transfer-matrix methods cause numerical instabilities and lack of convergence when these methods are used to study complex elements and materials with surfaces of limited symmetry [27]. The author suggests that the main issue is the application of Cauchy boundary data to an elliptic partial differential equation. The new method is a layer method that uses Green’s functions for single layer scattering. Wachutka claims that the layer-KKR method and the related Green’s function methods are also well-posed, but points out that they rely crucially on the muffin-tin potential approximation. The new method can use potentials of any form (as long as they are in $L^2$). The author also claims that the method “provides direct access to the complex band structure.”

2.3.5 More Recent, Full-Potential Methods

In a 2000 overview paper on electron scattering states for low-energy spectroscopies [28], Schattke tells a similar story about Cauchy conditions on an elliptical equation, calling it “the most serious problem preventing the application of standard band-structure procedures to electron states, as apparent in electron spectroscopies.” Unfortunately, his only published example of this problem is
the propagator formalism of Marcus and Jepsen. Some of the issues are described in some detail, however. The author argues that the propagator matrix that computes Fourier components at one $z$ from those at the previous $z$ contains strongly increasing waves. Thus, any error due to the finiteness of the Fourier decomposition is amplified by the propagator. But also, any effort to reduce error by increasing the Fourier basis actually makes the propagator more ill-conditioned because the exponent of the growing terms is given by $k_z^{G||} = \sqrt{E - |k|| + G||^2}$, where $G||$ is a reciprocal lattice vector (i.e., a Fourier wave vector). However, these methods did work for some surfaces. Schattke offers that this is explained by the simple representation in a small basis set of the pseudopotentials used.

Schattke goes on to describe three modern approaches to LEED (and other scattering state calculations). First, multiple-scattering approaches that attempt to replace muffin-tin potentials with more realistic anisotropic potentials are discussed. The discussion includes attempts by Nagano and Tong [29] and Zhang et al. (including Van Hove) [30], the incorporation by Rubner, Kottecke, and Heinz of non-spherically symmetric potentials in Tensor LEED [31], the inclusion of full potentials of arbitrary shape in the layer KKR method by Grass, Braun, and Borstel [32], and others. An extended discussion is given on the products of a Ph.D. student in Schattke’s group [33] which incorporate full-potentials into the Tong and Van Hove code [21]. The target current spectra (similar to LEED transmission) of GaAs (100) surface computed with a full-potential and with muffin-tin potential are compared. There is a clear difference from 0 to 10 eV for small off-normal incidence angles, especially the complete absence of a peak in the muffin-tin calculation. Schattke also describes some modern pseudopotential methods in the Laue representation and in full direct-space that make use of local and non-local pseudopotentials and modern numerical analysis techniques [34, 35, 36].
ELAPW $k \cdot p$ Methods with Variational Matching

Finally, Schattke devotes a section to methods that use ‘linear methods of band theory.’ This section is focused on his work with Krasovskii using the linearized augmented plane wave (LAPW) methods, including the $k \cdot p$ formulation and the extended LAPW method. (There are a few versions of these methods developed by Schattke, Krasovskii, and Strocov after Schattke wrote this paper.) These are very accurate, all-electron DFT methods designed for three-dimensional band structure calculations, which are modified to obtain the complex band structure and scattering states. These accurate methods for finding the complex band structure, and thus accurate Bloch wave solutions, improve some of the issues with the wavefunction matching, but the real advance in these methods is the use of a variational approach to the matching. The variational approach produces approximate matching but allows for more controllable errors. The $k \cdot p$ formulation is used for these methods because it is amenable to solution of the ‘inverse band structure’ problem of finding $k_z$’s and the associated Bloch wave solutions given $E$ and $k_\parallel$ (as was Pendry’s layer, Bloch wave method described above). Then, these Bloch solutions are expressed in the Laue representation and ‘matched’ to solutions in the vacuum, written as plane waves and evanescent waves decaying into the vacuum. Now, Krasovskii points out (as have others, including Heine in 1963 [37]) that to match over the entire 2D surface would require infinitely many Bloch solutions [38], and says that “Practical treatment of the semi-infinite crystal problem depends upon the answer to the question: Given a finite set of bulk Bloch waves, what is the best approximation to the function?” Pendry [12] approached this by exactly matching only a given number of Fourier components, which suffers from the matching issues discussed above. Instead, Krasovskii and Schattke choose a certain number of Bloch solutions and a certain number of parallel Fourier components for the Laue representation. For each Fourier component, they smoothly continue it as a function of $z$ into the vacuum with a linear combination of an outgoing wave and an evanescent wave decaying into the vacuum, except for the $(0,0)$ component which is continued by an incoming and an outgoing wave. Then, these
functions are used as a basis for the minimization of the energy deviation, \( \| (\hat{H} - E) \Phi \| \), in the surface region.

The method of Krasovskii and Schattke also has a way of determining (and using) the extent to which current is carried by certain Bloch solutions into the crystal (partial absorption currents or PACs), essentially identifying which bands play the biggest parts in LEED. This method has been used to study graphite [39] and the layered dichalcogenides niobium diselenide [40], titanium disulfide [41], and vanadium diselenide and titanium ditelluride [42] with a focus on determining the unoccupied band structure via band mapping and photoemission spectra. Strocov portrays the ability to compute the partial absorption currents and subsequently identify the bands with highest PACs, which the author refers to as coupling bands, as crucial to performing band mapping since it is the critical points of coupling bands that correspond to extrema in the derivative of the reflectivity curve with respect to energy, \( \frac{dR}{dE} \). The method is illustrated with copper as an early example [43], but the need for finding PACs in non-free-electron materials, like those above, is emphasized [44]. Strocov’s early work was performed with pseudopotentials, but Krasovskii and Schattke claim that an all-electron method should be better than a pseudopotential method at low energies “where scattering by the singular potential is strong and the electron absorption is small” [45], and the later papers of Krasovskii and Schattke include results from all-electron potentials. Krasovskii and Strocov also demonstrate the importance of using a full-potential over a muffin-tin potential in their work on TiS\(_2\) [41]. The spectrum computed by employing a muffin-tin potential in the authors framework (calculated via averages in and outside a muffin-tin sphere of their self-consistent potential) differs qualitatively from the spectrum computed with the same method and a full, self-consistent potential.

All of the above Bloch wave methods treat the crystal as a semi-infinite system, meaning that it extends infinitely in one direction, say +z. For the occupied band structure of surfaces, using a slab-in-supercell approach is a common alternative to the semi-infinite crystal, however it is rarely
used for scattering. Schattke actually quickly dismisses supercell approaches in his review paper, saying that they are 'bulk-like calculations' and do not permit scattering boundary conditions [28]. However, Krasovskii eventually developed a method in which a slab calculation is used to handle the top few layers and the solutions are incorporated into the variational method by extending the bulk solutions (from the complex band structure) by the slab solutions [46, 38].

A Supercell, Bloch Wave Matching Method Like Ours

There is also another group working on an approach very similar to ours. A group at Carnegie Mellon has published a few papers [47, 48, 49, 50] describing a supercell, Bloch wave matching approach to calculating low-energy electron reflectivity in the lowest energy range. Like our method, this method uses the Kohn-Sham wavefunctions of a system with a self-consistent potential calculated using density functional theory, but the details of the matching technique are quite different. The group has studied free-standing graphene systems, graphene on substrates, and graphene-boron nitride systems. They have incorporated inelastic scattering into their method but have only calculated the reflectivity of normal incidence beams. Like that group, we have studied free-standing graphene, but we have also studied free-standing layers of a different layered material, molybdenum disulfide. We have only made a small attempt at graphene on substrates and have not incorporated inelastic scattering, but we have computed spectra for general angles of electron beam incidence.
To simulate electron scattering from a crystal surface, one must have a way to determine electron states near the crystal surface. There are two common methods for computing electronic states (i.e., numerically solving the Schrödinger Equation) near surfaces: semi-infinite methods and supercell or slab methods. In the semi-infinite approach, solutions to the Schrödinger Equation are found for a crystal that extends infinitely in one of the two directions perpendicular to the surface. This usually involves computing complex band structures, which yield both evanescent states, decaying into the crystal, and bulk states inside the crystal. Matching these evanescent and bulk states to evanescent states outside the crystal can lead to the surface valence electronic structure of the system (states with energy below the Fermi level), consisting of bulk states and surface states. For states above the Fermi energy (conduction and scattering states), when semi-infinite electron states are used, the problem consists of matching free-electron states to the evanescent and bulk states in the crystal on the vacuum side of the semi-infinite system.

In contrast, in the supercell approach, a crystal slab consisting of a finite number of layers of the crystal is surrounded by layers of vacuum on both sides, and this vacuum-slab-vacuum ‘supercell’ is treated as the unit cell of a periodic system. The electronic states of the supercell system can be found by computing only the real band structure. If the vacuum region on both sides of the slab
is large enough, then the potential is nearly zero near the supercell boundaries, and so electrons outside the slab in the supercell should behave the same as they would near a surface bordering a semi-infinite vacuum. If the slab is thick enough so that surface states do not interact, then this method can give good approximations of the surface states. It also provides information about bulk states, especially for thick slabs. However, the Bloch boundary conditions implied by the artificially periodic potential restricts the bulk solutions that will be produced due to the artificial band gaps discussed in Sections 3.1 and 3.4. To relate supercell solutions to scattering, we realize that because the potential is near zero by the supercell boundary, solutions inside the supercell are essentially the same whether the potential outside the supercell is zero or is a periodic extension of the unit cell potential. Thus, the solutions found inside the supercell using the repeated supercell potential can be used in the scattering problem. The solution of the scattering problem in the supercell geometry requires matching of the supercell solutions to other solutions on two boundaries. This can involve matching to vacuum solutions (incoming and outgoing electron beams) on both supercell boundaries [51, 47], as illustrated in Fig. 3-3 (a), or matching to vacuum solutions on one boundary of the supercell and to bulk solutions at some point within the crystal slab [47]. Our method performs matching to electron beams on both sides of the supercell, meaning that it is modeling the scattering from a free-standing slab. Thus the results computed with it are best compared to the experimental scattering from a suspended, microscopically thin sample (a number of layers that can be modeled in a slab). However, they can also be compared to that from a macroscopic system in the case that the scattering is strong enough that the back-diffracted electrons are mostly being scattered by the top few layers of the sample.

We have designed our supercell method with standard DFT packages that use plane wave bases in mind, so that it can be easily incorporated into an open source, widely-used DFT package. The interplay between the DFT package and our algorithm is as follows: the core package functionality is used to find the self-consistent potential (and the optimized structure, if desired) given the input
structure specifications for a slab in a supercell. Then the package is used to solve for the scattering, Bloch states in the crystal for the appropriate Bloch wave vectors. Finally, our supercell, Bloch wave-matching algorithm uses the Kohn-Sham wavefunctions produced by the package to calculate electron reflectivities over a range of energies. (Appendix B contains many more details of this interplay.)

The supercell approach has a few advantages over muffin-tin, layer methods and semi-infinite crystal methods. There is really no restriction on the form of the potential, except that it decay quickly enough away from the surface. The screening effects in most real crystal systems produce an exponential decay of the potential, so this is not a serious restriction. Thus, the supercell approach can incorporate full potentials, including those determined from self-consistent DFT calculations, some of the most accurate potentials available. For many systems, especially those with strong covalent bonding, these potentials will differ significantly from muffin-tin form. This gives the supercell approach a clear advantage over layer methods using muffin-tin potentials, especially at the lowest energies where the electrons are most affected by the deviation from muffin-tin potentials.

In addition, the supercell method can easily take into account any image potential or other surface distortions of the potential, as well as complex surface structures because it treats everything within the supercell as a single unit. Complex band structure methods rely on the periodicity in the scattering direction of the sample, and thus must be augmented to include changes in structure (or even composition) at the surface. We must also keep in mind that the solutions needed for solving the scattering problem in the supercell geometry are simply found by computing the real band structure of the supercell system. This is a much simpler and more standard process than computing complex band structures.

The supercell method is a Bloch wave method, and so it has some of the advantages that come along with that. Multiple scattering is automatically accounted for through the solution of the Schrödinger Equation for a full system of multiple layers. It allows for the relation to the band
structure of the sample, although in the supercell approach, the band structures calculated are the supercell band structures. Thus, in some cases it is necessary to relate the supercell band structures to the bulk band structure before relating the reflectivity to the band structure. In the study of few-layer systems, however, this an advantage because the supercell band structure is one of the best ways to access the band structure of the few-layer system, which is really only two-dimensional.

Finally, the stability issues that have been claimed to be concerns for some Bloch wave matching techniques have not been an issue in our supercell method. We do not use a propagation based method. The solution’s $z$-dependence in the supercell is found in Fourier space, rather than by integration in real space. Then, two-sided, matching boundary conditions are applied, not the one-sided Cauchy boundary conditions of the propagation methods. As will be explained in Sec. 3.2, we do not perform matching on a large number of in-plane Fourier components. Because the matching is performed far from the slab, the components of the wave function that are not associated with the relatively small set of diffracted beams should decay to very small values at the supercell boundary. Therefore, what is sometimes referred to as the residual mismatch, the mismatch in the derivatives of unmatched Fourier components when the values are matched in semi-infinite methods, should be negligible. For matching performed at the crystal boundary this mismatch can be substantial [45], but for matching performed at the edge of a supercell, it is not a concern. The supercell method can have problems when the solutions do not have the expected form at the supercell boundary, as we shall see, but for many solutions (and so at many energies) it entails a very simple and effective matching system.

### 3.1 One-Dimensional Model

As a first, illustrative example of the supercell matching method, we study the analytically solvable one-dimensional square well. (See any introductory reference on quantum mechanics for details, e.g., [52].) The potential of this system is shown in Fig. 3-1, having constant value $-V_0$ for $z \in (0, L)$
and zero otherwise. The time-independent Schrödinger Equation in one dimension (working in Rydberg units) is:

\[-\frac{d}{dz}\psi(z) + V(z)\psi(z) = E\psi(z).\] (3.1)

This case is fundamentally different from the higher dimension problems in that there is no periodicity in the true problem at all (since there is no dimension perpendicular to the direction of the incident beam). Still, it is a first step to investigate the enforcement of the artificial periodicity of the potential and the ability to produce consistent results with different supercells. For this problem, our algorithm is very similar to the standard algorithm found in undergraduate quantum mechanics textbooks, the difference being that we are using Bloch boundary conditions and perform the matching at a distance away from the square well rather than at the edge of the well. With these boundary conditions, one is able to find the general solution to the time-independent Schrödinger Equation for most energies, however, at certain energies (in the gaps in the band structure of this periodic system) there are no Bloch solutions. We find that by changing the width of the supercell we are able to cover all energies. It is also one of few systems for which an analytic result exists, allowing for a check of accuracy. We find that the supercell method produces accurate results, in very good agreement with the analytic results.

In the standard approach, the domain is split into three regions, inside the well and to the right and left of the well, as in Fig. 3-1. Thus the potential in each region is constant and the solutions are simply exponentials (real or complex depending on the energy). Matching arbitrary linear combinations of these solutions at the boundaries of the well leads to the result for the transmission coefficient:

\[T^{-1} = 1 + \frac{V_0^2}{4E(E + V_0)}\sin^2\left(L\sqrt{(E + V_0)}\right),\] (3.2)

where \(V_0\) is the depth of the well and \(L\) is the width.
Figure 3-1: **1D square well potential with matching locations**: The standard approach matches solutions inside the well to those outside the well at the well boundaries. The supercell approach matches solutions at a distance from the boundary. A variety of distances can be used.
Our algorithm splits the real line into three regions also, but the central region includes the square well and some of the vacuum on either side, as in Fig. 3-1. In this case, the solutions in the central region are not of the simplest form; they are given piecewise by complex exponentials. In order to find the solutions numerically, we study a system in which the region is periodically repeated. Since the potential is a function with support on a strict subset of the supercell, this repetition will not effect the solution inside one supercell. This periodic potential implies that Bloch’s Theorem applies and the Schrödinger Equation will have a basis of Bloch wave solutions. Looking for solutions with Bloch wave boundary conditions allows us to use a plane wave (Fourier) basis and turns the Schrödinger equation into a linear system of equations in wave vector (reciprocal) space for each value of the Bloch wave vector parameter. More explicitly, we look to solve the one-dimensional version of the Schrödinger Equation in Fourier space, Eq. A.10. Letting the reciprocal lattice points be \( G_m = \frac{2\pi m}{a} \), the Bloch form of the wavefunction be

\[
\psi_k(z) = e^{ikz} \sum_{m=-N}^{N} c_m(k)e^{\frac{2\pi m}{a}z}, \tag{3.3}
\]

and the Fourier expansion of the potential be \( V(z) = \sum_{m=-N}^{N} V_m e^{\frac{2\pi m}{a}z} \), the eigenvalue problem to solve is:

\[
\begin{pmatrix}
  k^2 + V_0 & V_{-1} & \cdots & V_{-N} & V_N & \cdots & V_1 \\
  V_1 & (k + \frac{2\pi}{a})^2 + V_0 & V_{-1} & \cdots & V_2 \\
  \vdots & \vdots & \ddots & \vdots & \vdots \\
  V_N & \cdots & \vdots & \ddots & \vdots \\
  V_{-N} & \vdots & \vdots & \ddots & \vdots \\
  V_{-1} & \cdots & V_1 & (k - \frac{2\pi}{a})^2 + V_0
\end{pmatrix}
\begin{pmatrix}
  c_0 \\
  c_1 \\
  \vdots \\
  c_N \\
  c_{-N} \\
  \vdots \\
  c_{-1}
\end{pmatrix} =
\begin{pmatrix}
  E c_0 \\
  E c_1 \\
  \vdots \\
  E c_N \\
  E c_{-N} \\
  \vdots \\
  E c_{-1}
\end{pmatrix}. \tag{3.4}
\]

Solving for a set of Bloch wave vectors, \( \{k_j\}_{j=1}^J \), in the positive half of the first Brillouin zone,
[0, π/a], we find a collection of \( J(2N - 1) \) solutions. Now, there is a symmetry in Eq. 3.4 that allows us to find a degenerate solution simply by conjugating the first. Let us assume a solution with wave vector \(-k\), not a priori related to \( \psi_k(z) \), and written with a different ordering of Fourier components:

\[
\psi_{-k}(z) = e^{-ikz} \sum_{m=-N}^{N} \xi_m(k)e^{-i\frac{2\pi m}{a}z}.
\]  

(3.5)

Then, the matrix equation that it solves is much like Eq. 3.4, except that \( k \) has been replaced by \(-k\) and the basis has been rearranged such that \( e^{i\frac{2\pi m}{a}z} \) and \( e^{-i\frac{2\pi m}{a}z} \) are interchanged:

\[
\begin{pmatrix}
(-k)^2 + V_0 & V_1 & \cdots & V_N & V_{-N} & \cdots & V_{-1} \\
V_{-1} & (-k - \frac{2\pi}{a})^2 + V_0 & V_1 & \cdots & V_{-2} \\
\vdots \\
V_{-N} & \vdots \\
V_N & \vdots \\
V_1 & \cdots & V_{-1} & (-k + \frac{2\pi}{a})^2 + V_0
\end{pmatrix}
\begin{pmatrix}
\xi_0 \\
\xi_1 \\
\vdots \\
\xi_N \\
\xi_{-N} \\
\cdots
\end{pmatrix}
= E
\begin{pmatrix}
\xi_0 \\
\xi_1 \\
\vdots \\
\xi_N \\
\xi_{-N} \\
\cdots
\end{pmatrix}.
\]  

(3.6)

Now, because \( V(z) \) is real, \( V_{-n} = V^*_n \). Thus, Eq. 3.6 is the same as

\[
H^*\xi = E\xi.
\]  

(3.7)

Thus, conjugating, we must have

\[
H\xi^* = E\xi^*.
\]  

(3.8)

Thus, for any solution to Eq. 3.4, \( c_m \), associated with the solution,

\[
\psi_k(z) = e^{ikz} \sum_{m=-N}^{N} c_m(k)e^{i\frac{2\pi m}{a}z},
\]  

(3.9)

to the Schrödinger Equation in real space, we have a degenerate solution to the Schrödinger Equa-
tion in real space given by the complex conjugate of the first,

\[ \psi_{-k}(z) = e^{-ikz} \sum_{m=-N}^{N} c_m^*(k)e^{-i\frac{2\pi m}{a}z} = \psi_k^*(z). \]  

(3.10)

(It is also possible to appeal to time-reversal symmetry as a means to show that the complex conjugate of a wavefunction is a degenerate solution, and, indeed we invoke that in the three-dimensional case. In this simple, one-dimensional case, however, it is possible to see the symmetry in the matrix form of the Schrödinger Equation in Fourier space.)

Now, for a fixed energy, the one-dimensional time-independent Schrödinger Equation (Eq. 3.1) is a second-order, linear, ordinary differential equation, so the two solutions that we have found for each energy, \( E \), form a fundamental set of solutions, i.e., a basis for the solution space on the domain of the supercell. Thus, at given energy, if a solution exists that can match the incoming and outgoing beam solutions at the supercell boundary in value and derivative, it can be found as a linear combination of \( \psi_k \) and \( \psi_{-k} \):

\[ \psi_S(z) = f_1 \psi_k(z) + f_2 \psi_{-k}(z). \]

Of course, we only have a basis of the solution space as long as the functions are linearly independent. At \( k = 0 \) and \( k = \frac{\pi}{a} \), \( \psi_k \) is actually the same function as \( \psi_{-k} \). For \( k = 0 \), this is obvious, and for \( k = \frac{\pi}{a} \), it is a consequence of the fact that \( k \) and \(-k\) differ by a reciprocal lattice vector;

\[ \psi_{-\frac{\pi}{a}}(z) = e^{-i\frac{\pi}{a}z} \sum_m b_m(k)e^{i\frac{2\pi m}{a}z} = e^{i\frac{\pi}{a}z} \sum_m b_m(k)e^{i\frac{2\pi (m-1)}{a}z}, \]

(3.11)

which is a Bloch solution with wave vector \( k = \frac{\pi}{a} \), \( \psi_{\frac{\pi}{a}}(z) \). Thus, when computing solutions we choose sets of Bloch wave vectors away from \( k = 0 \) and the Brillouin zone boundary. In fact, even choosing Bloch wave vectors too close to these points can create distorted reflectivity curves.

Given two linearly independent solutions, the matching conditions consist of setting the values and derivatives of \( \psi_S \) equal to the values and derivatives of a combination of the incoming beam and the reflected beam (\( e^{i\sqrt{E}z} + re^{-i\sqrt{E}z} \)) at the left boundary and equal to an outgoing beam at
the right boundary ($t e^{i \sqrt{E} z}$). This can be rearranged into the matrix equation:

$$
\begin{pmatrix}
1 \\
i q_z \\
0 \\
0
\end{pmatrix}
= \begin{pmatrix}
-1 & \psi_k(0) & \psi_{-k}(0) & 0 \\
i \sqrt{E} & \psi'_k(0) & \psi'_{-k}(0) & 0 \\
0 & \psi_k(L) & \psi_{-k}(L) & -e^{i \sqrt{E} L} \\
0 & \psi'_k(L) & \psi'_{-k}(L) & -i \sqrt{E} e^{i \sqrt{E} L}
\end{pmatrix}
\begin{pmatrix}
r \\
f_1 \\
f_2 \\
t
\end{pmatrix}
$$

(3.12)

Solving this linear system, yields $r$, whose squared amplitude, $|r|^2$, is the fraction of incoming electrons reflected by the square well.

Fig. 3-2 shows a comparison of the exact result with the combined results of our algorithm run for five different supercell sizes as well as the contribution of each of three selected results (shifted upward for clarity). The square well used had a width of 6 units and a depth of 15 units below zero. These results demonstrate three things. First, the supercell, Bloch solutions can indeed be used to match the incoming and outgoing beams to produce accurate and consistent results. Except for a slight variation likely caused by the discontinuous nature of the square well, the results from all supercell sizes agree with one another and with the exact, analytical solution. Secondly, for a given supercell, there are certain energies for which Bloch solutions are not found. This is a consequence of the artificial periodicity of the potential, enforced through the Bloch boundary conditions. The requirement that each eigenfunction have the form of a function with the period of the supercell, modulated by a plane wave, can create energy gaps in the supercell band structure for which solutions that meet the requirement cannot be found. In fact, larger supercells lead to smaller Brillouin zones and more Brillouin zone boundaries, at which gaps typically form. However, the last thing that Fig. 3-2 reveals is that these gaps can be overcome. For one thing, as the supercell size gets larger, while the gaps become more frequent, they also become smaller. The top curve was computed with the largest supercell size and has the most frequent but smallest gaps. Also, the gaps occur at different energies for different supercell sizes, so by combining reflectivities computed
Figure 3-2: **Reflectivity curve for 1D square well potential**: The bottom solid curve shows the analytical solution with numerical results of five different runs overlaid. The three top curves consist of numerical results for three different supercell widths which are included in the combined curve.
for various supercell sizes, gaps can be filled. The only exception in this figure is in the very lowest energy range, where there are two very small gaps, not filled by any of the five supercell sizes. Between gaps, i.e., within a band of solutions, the density of computed reflectivities is determined by the grid of \( k \)-points in the Brillouin zone for which solutions are computed. Thus, the curve shown at the bottom, which combines all three results, could be made arbitrarily dense. While these facts about overcoming the band gaps are not proven, the behavior found in this simple system is partially representative of what we have seen in more complicated systems.

### 3.2 Three-Dimensional Matching Algorithm

In higher dimensions, the problem changes in fundamental ways. For one thing, diffraction is actually possible. The electrons scattering from a regular arrangement of atoms destructively interfere except in certain, specific directions related to the periodicity of the surface. Secondly, we are now studying a partial differential equation and do not have the same guarantees that we have for ODE's regarding general solutions. Lastly, in higher-dimensions there are some scattering solutions, i.e., solutions with energies above the vacuum energy, that are localized in the scattering dimension and so cannot be used to compute reflectivities. However, we shall see that for the lowest energy range, the physics restricts the scattering so that the higher-dimensional problem simplifies to one very similar to the one-dimensional case. This section outlines the general form for our supercell, Bloch wave matching theory and then discusses the simplification to the case of the lowest energies for which electrons are not diffracted but only specularly reflected. Then, the matching algorithm is described in more detail for normal incidence scattering and for two cases of off-normal scattering. Results for normal incidence scattering from some model potentials are shown, including convergence with denser Fourier grids and increasing supercell sizes. Finally, the section ends with a brief discussion of a few difficulties for the algorithm, leaving more details for Chapter 6.
The schematic of our scattering setup is shown in Fig. 3-3(a). The surface normal is the $-\hat{z}$ direction and there is one incident wave from $z < 0$ with a wave vector $\mathbf{q} = (q_\parallel, q_z)$ and energy $E = |\mathbf{q}|^2$. The boundary of the supercell consists of the unit cell of the slab on each of the planes $z = 0$ and $z = L$ and the planes created by dragging the unit cell from $z = 0$ to $z = L$. The ‘in-plane’ direction is parallel to the slab surface and normal to the $z$-direction. In this in-plane direction, true periodicity of the crystal potential is assumed, so that the wavefunction within the supercell is extended through all of $\{\mathbf{r} = (x, y, z) \in \mathbb{R} | 0 < z < L\}$ by the Bloch relation. Thus, the scattering problem consists of finding the amplitudes of those parts of the solution that approach left-moving plane waves as $z \to -\infty$ (the outgoing beams) relative to the amplitude of the part that approaches a right-moving plane wave in the same limit (the incoming beam). In practice, this is done by matching the solutions in and around the crystal to solutions of the form

$$\psi_{-\infty}(\mathbf{r}) = e^{i\mathbf{q} \cdot \mathbf{r}} + \sum_{\mathbf{q}'} r_{\mathbf{q}'} e^{i(\mathbf{q}'_\parallel \cdot \mathbf{r} - q'_z z)} \quad (3.13)$$

over a certain set of wave vectors $\{\mathbf{q}'\}$ with $\{q'_z\}$, $q'_z > 0$ on the left, and to solutions of similar form on the right.\(^1\) (Compare to Eq. 3.27.) The size of the set $\{\mathbf{q}'\}$, i.e., the number of reflected waves, depends on the energy and the incident angle of the electron beam.

By using the supercell construction, we can use Bloch’s Theorem in all three dimensions. Thus, as shown in Section A.4.1, for any energy $E$, a basis for the eigenstates of the crystal (in the supercell) can be found with each member written in Bloch form:

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} \sum_{\mathbf{G}} d_{\mathbf{k}}(G_\parallel, G_z) e^{i\mathbf{G} \cdot \mathbf{r}}, \quad (3.14)$$

where $\mathbf{G}$ are the reciprocal lattice vectors for the supercell lattice and $\mathbf{k}$ is a vector in the first Bril-
Figure 3-3: Scattering diagram and demonstration of artificial band gap filling: (a) Schematic showing the wave matching configuration. Black (solid) arrows represent plane waves involved in the specular energy regime. Grayed (dashed) arrows represent higher-order diffraction beams that are relevant at higher energies. (b) Reflectivity of 3 layers of free-standing graphene, calculated using 4 different supercell sizes: 9 (red circle), 10 (green diamond), 14 (blue cross), and 15 (black square) in-plane lattice constants.
louin zone. We can compare this to the discussion in Ch. 2 (Eq. 2.4) about how the two-dimensional periodicity of the crystal leads to a natural representation of the Bloch wave solutions inside the supercell in terms of Fourier series in the plane of the crystal surface, the Laue representation:

\[ \psi_k(r) = e^{i\mathbf{k}_\parallel \cdot \mathbf{r}} \sum_{\mathbf{G}_\parallel} \phi_k(\mathbf{G}_\parallel, z) e^{i\mathbf{G}_\parallel \cdot \mathbf{r}}, \]  

where \( \mathbf{G}_\parallel \) are the in-plane reciprocal lattice vectors and \( \mathbf{k}_\parallel \) is a vector in the first Brillouin zone of the two-dimensional lattice of the crystal. Thus, whereas for a stand-alone slab or a semi-infinite crystal, Bloch’s Theorem only implies a Bloch wave with a two-dimensional wave vector, the use of a supercell makes the Bloch wave vector \( k_z \) relevant. In fact, we shall see that the Bragg condition for surface diffraction makes \( k_z \) the most relevant index, in a sense. This Laue representation can still be useful in the case of the supercell, though, we need to be more explicit about the \( k_z \) dependence:

\[ \phi_k(\mathbf{G}_\parallel, z) = e^{i k_z z} c_k(\mathbf{G}_\parallel, z). \]  

Then, the coefficients \( c_k(\mathbf{G}_\parallel, z) \) are calculated in terms of Fourier components of the full Bloch form, \( d_k(\mathbf{G}_\parallel, G_z) \),

\[ c_k(\mathbf{G}_\parallel, z) = \sum_{G_z} d_k(\mathbf{G}_\parallel, G_z) e^{i G_z z}, \]  

where \( G_z \) are the reciprocal lattice vectors along \( z \).

Now, a wave function inside the supercell, \( \psi_S(r) \), with energy \( E \) can be constructed as a linear combination of these Bloch energy eigenstates,

\[ \psi_S(r) = \sum_{n=1}^D f_n \psi_{\mathbf{k}_n}(r), \]  

where \( D \) is the degeneracy at this energy. (As mentioned before, we have a basis of Bloch solutions
for each energy.)

Now, we shall show that, for the scattering problem, only a certain subset of these solutions will play a part, or in other words, only a subset is excited by an incoming beam. This is a proof of the two-dimensional Bragg condition, a standard result in surface science. However, it will make clear a fact not always explicitly discussed along with the Bragg condition. Assuming that the potential is essentially zero outside of the supercell, the wavefunction in the vacuum region to the left of the supercell consists of the incoming beam and some linear combination of scattered plane waves, just as in Eq. 3.13, except that we rename the function to indicate that we assume this form at all points left of the supercell, rather than in the limit as $z \to -\infty$:

$$
\psi_L(r) = e^{i q \cdot r} + \sum_{q'} r_{q'} e^{i (q'_\parallel \cdot r_{\parallel} - q'_z z)}, \quad (3.19)
$$

We require that the solution be in $C^1(\mathbb{R}^3)$, so we must match the solutions inside and outside the supercell over the pieces of the supercell boundary normal to the $z$-direction, focusing only on the left side now: $\psi_L(r_{\parallel}, 0) = \psi_S(r_{\parallel}, 0)$. (We must also match normal derivatives, but that is unnecessary for the current argument.) More explicitly, we enforce:

$$
e^{i q_{\parallel} \cdot r_{\parallel}} + \sum_{q'} r_{q'_{\parallel}} e^{i (q'_{\parallel} \cdot r_{\parallel})} = \sum_{n=1}^{D} f_n e^{i k_{\parallel} \cdot r_{\parallel}} \sum_{G_{\parallel}} \phi_{k_n}(G_{\parallel}, 0) e^{i G_{\parallel} \cdot r_{\parallel}}. \quad (3.20)
$$

Then, we use the fact that the functions must match over the entire plane, $z = 0$, to take advantage of the orthogonality of plane waves. Multiplying each side by $e^{-i K_{\parallel} \cdot r_{\parallel}}$ and integrating over $z = 0$ yields:

$$
\int e^{i (q_{\parallel} - K_{\parallel}) \cdot r_{\parallel}} dA + \sum_{q'} \int r_{q'_{\parallel}} e^{i (q'_{\parallel} - K_{\parallel}) \cdot r_{\parallel}} dA = \sum_{n=1}^{D} f_n \sum_{G_{\parallel}} \phi_{k_n}(G_{\parallel}, 0) e^{i (k_{\parallel} + G_{\parallel} - K_{\parallel}) \cdot r_{\parallel}} dA. \quad (3.21)
$$
or

\[
\delta_{q \parallel K \parallel} + \sum_{q'} r_{q'} \delta_{q' \parallel K \parallel} = \sum_{n=1}^{D} f_n \sum_{G \parallel} \phi_{k_n}(G \parallel, 0) \delta_{k_n + G \parallel K \parallel}.
\]  

For a given \( K \parallel \), this is a discrete set of equations linking the amplitudes of the incoming and outgoing beams to a discrete set of certain coefficients, namely \( \phi_{k_n}(K \parallel - k \parallel, 0) \), of those solutions for which \( k \parallel = K \parallel - G \parallel \) for some in-plane reciprocal lattice vector, \( G \parallel \). If we multiply instead by \( e^{-iK' \parallel \cdot r} \) with a different \( K' \parallel \neq K \parallel + G \parallel \) for any in-plane reciprocal lattice vectors, \( G \parallel \), and integrate, we get a discrete set of equations involving a completely different set of Bloch solutions.

Now, if \( K \parallel \neq q \parallel + G \parallel \), then this system of equations admits the zero solution: \( r_{q'} = f_n = 0 \).

Thus, for a system with one incoming beam, we must only solve the system of equations produced by \( K \parallel = q \parallel + G \parallel \) and thus must have that \( k \parallel = q \parallel + G \parallel' \) for some reciprocal lattice vectors, \( G \parallel \) and \( G \parallel' \). Finally, the set of wave vectors for diffracted beams in this system of equations is \( q' \parallel = q \parallel + G \parallel'' \), for some reciprocal lattice vector, \( G \parallel'' \). Thus, we see that only certain solutions are excited in the crystal by an incoming beam and only certain beams are then back-diffracted.

This is a statement of the two-dimensional Bragg condition for surfaces, typically stated for the back-diffracted beams: the difference between the in-plane components of the wave vectors of the incoming and outgoing beams, \( q \parallel \) and \( q' \parallel \), respectively, must be a vector in the two-dimensional reciprocal lattice of the crystal:

\[
q \parallel - q' \parallel = G \parallel.
\]  

This is true for the outgoing beams on the right side in the supercell scattering geometry, as well. Again, one finds the zero solution (and that no states are excited) for \( K \parallel \neq q \parallel + G \parallel \), since there is no beam with fixed amplitude on the right side. However, when \( K \parallel = q \parallel + G \parallel \), the \( f_n \)'s are not zero due to the non-zero amplitude of the incoming beam, and so the coefficients of the
outgoing beams on the right side are also non-zero (generically - total reflection is a possibility but it does not come from a complete zero solution for all coefficients). For experiment, it is the two-dimensional Bragg condition for the outgoing waves that is most important, but for computing electron reflectivities and diffraction intensities, it is equally important that the condition holds inside the crystal (supercell) as well: the difference between the in-plane components of the wave vectors of the incoming beam and the Bloch solutions inside the crystal, \(q_\parallel\) and \(k_\parallel\), respectively, must be a vector in the two-dimensional reciprocal lattice of the crystal:

\[
k_\parallel = q_\parallel + G_\parallel.
\]  

(Compare this to the three-dimensional Bragg condition for the location of diffraction spots, or, in other words, the existence of diffracted beams: \(q - k = G\). Typically, for the kinematic treatment of x-ray or electron diffraction, this is derived from scattering arguments involving structure factors and lattice sums which find infinite scattered intensity when the Bragg condition is satisfied. See Marder [53], for instance. This argument can be adapted to surfaces, as well. See Van Hove [7]. However, for the dynamical (multiple scattering) treatment necessary for low-energy electrons, this argument is not valid. Van Hove and Tong [21] discuss the needed adjustments for the explicit scattering argument. More general arguments based on the Schrödinger Equation are a simple way to handle the multiple scattering implicitly. Van Hove offers such an argument in [7], but it is rather opaque. Pendry [20] has a thorough argument using change of variables and symmetry, which does not even assume Bloch’s Theorem. The above argument is illustrative in the context of our Bloch wave matching computation scheme.)

The Bragg condition for inside the supercell restricts the sum in Eq. 3.18 for the general form of the solution inside the supercell to solutions that are degenerate and have Bloch wave vectors, \(k_n\), that satisfy this condition. In fact, we work in the reduced zone scheme, so \(k_n\) is in the first Brillouin zone. (The number of such solutions is from here on the new definition of D.) The Bragg
condition for outside the supercell allows us to rewrite the general solution in this region, Eq. 3.19, with explicit in-plane wave vectors in terms of the incoming beam and the reciprocal lattice:

\[
\psi_L(r) = e^{i\mathbf{q} \cdot \mathbf{r}} + \sum_{\mathbf{G}} r_{\alpha,\beta} e^{i(\mathbf{q} + \mathbf{G}) \cdot \mathbf{r} - iq'_z(\alpha,\beta)z}, \quad (3.27)
\]

\[
\psi_R(r) = \sum_{\mathbf{G}} t_{\alpha,\beta} e^{i(\mathbf{q} + \mathbf{G}) \cdot \mathbf{r} + iq'_z(\alpha,\beta)z}, \quad (3.28)
\]

where \(r_{\alpha,\beta}\) and \(t_{\alpha,\beta}\) are the amplitudes of reflection and transmission, respectively, for each reciprocal lattice vector \(\mathbf{G} = \alpha \mathbf{b}_1 + \beta \mathbf{b}_2\) in terms of the primitive basis for reciprocal space, \(\{\mathbf{b}_1, \mathbf{b}_2\}\), and

\[
q'_z(\alpha, \beta) = \sqrt{q_z^2 - |\mathbf{G}|^2 - 2\mathbf{q}_z \cdot \mathbf{G}}, \quad (3.29)
\]

This last equation simply enforces that the energies of the incoming and outgoing beams are equal:

\[
E_{in} = |\mathbf{q}|^2 = |\mathbf{q}_z|^2 = E_{out} = |\mathbf{q}_z + \mathbf{G}_z|^2 + |q'_z|^2. \quad (3.30)
\]

It determines the number of reflected (and transmitted) beams. If \(q_z^2 - |\mathbf{G}_z|^2 - 2\mathbf{q}_z \cdot \mathbf{G}_z < 0\), then the wavefunction in this region is evanescent, decaying away from the supercell boundary. However, since each supercell boundary is a significant distance from the slab, evanescent solutions will have decayed nearly to zero at the supercell boundary, and so we do not need to match solutions outside the unit cell to them. Thus, the sums in Eqs. 3.27 are over the small finite set of reciprocal lattice vectors for which \(q_z^2 - |\mathbf{G}_z|^2 - 2\mathbf{q}_z \cdot \mathbf{G}_z < 0\), which we will say has \(N_{\mathbf{G}_z}(E)\) elements.

Now, we must repeat the matching along the supercell boundary that was used in the derivation of the two-dimensional Bragg condition to construct full solutions of the Schrödinger Equation in the supercell geometry and compute reflectivities. Again, the solution must be in \(C^1(\mathbb{R}^3)\), so we must match the solutions inside and outside the supercell over the supercell boundaries parallel to
the slab surface: \(\psi_L(\mathbf{r}_\parallel, 0) = \psi_S(\mathbf{r}_\parallel, 0)\) and \(\psi_R(\mathbf{r}_\parallel, L) = \psi_S(\mathbf{r}_\parallel, L)\). This yields:

\[
e^{i\mathbf{q}_\parallel \cdot \mathbf{r}_\parallel} + \sum_{\mathbf{G}_\parallel} r_{(\alpha, \beta)} e^{i(\mathbf{q}_\parallel + \mathbf{G}_\parallel) \cdot \mathbf{r}_\parallel} = \sum_{n=1}^{D} f_n e^{i\mathbf{k}_n \parallel \cdot \mathbf{r}_\parallel} \sum_{\mathbf{G}_\parallel} \phi_{\mathbf{k}_n}(\mathbf{G}_\parallel, 0) e^{i\mathbf{G}_\parallel \cdot \mathbf{r}_\parallel}
\]

(3.31)

\[
\sum_{\mathbf{G}_\parallel} t_{(\alpha, \beta)} e^{i(\mathbf{q}_\parallel + \mathbf{G}_\parallel) \cdot \mathbf{r}_\parallel + iq_z'(\alpha, \beta) L} = \sum_{n=1}^{D} f_n e^{i\mathbf{k}_n \parallel \cdot \mathbf{r}_\parallel} \sum_{\mathbf{G}_\parallel} \phi_{\mathbf{k}_n}(\mathbf{G}_\parallel, L) e^{i\mathbf{G}_\parallel \cdot \mathbf{r}_\parallel}.
\]

(3.32)

Again, we multiply by an in-plane Fourier component (with wave vector \(\mathbf{K}_\parallel = -\mathbf{q}_\parallel - \mathbf{G}_\parallel'\)) and integrate over the parallel supercell boundary to find a separate equation for each in-plane reciprocal lattice vector, for each boundary:

\[
\delta_{\mathbf{G}_\parallel} \mathbf{0} + \sum_{\mathbf{G}_\parallel} \delta_{\mathbf{G}_\parallel} \mathbf{G}_\parallel r_{(\alpha, \beta)} = \sum_{n=1}^{D} f_n \sum_{\mathbf{G}_\parallel} \phi_{\mathbf{k}_n}(\mathbf{G}_\parallel, 0) \delta_{(\mathbf{k}_n + \mathbf{G}_\parallel)(\mathbf{q}_\parallel + \mathbf{G}_\parallel')} \]

(3.33)

\[
\sum_{\mathbf{G}_\parallel} t_{(\alpha, \beta)} \delta_{\mathbf{G}_\parallel} \mathbf{G}_\parallel e^{iq_z'(\alpha, \beta) L} = \sum_{n=1}^{D} f_n \sum_{\mathbf{G}_\parallel} \phi_{\mathbf{k}_n}(\mathbf{G}_\parallel, L) \delta_{(\mathbf{k}_n + \mathbf{G}_\parallel)(\mathbf{q}_\parallel + \mathbf{G}_\parallel')}.
\]

(3.34)

The reciprocal lattice vectors to be included in these systems of equations are the \(N_{\mathbf{G}_\parallel}(E)\) discussed above for which \(q_z^2 - |\mathbf{G}_\parallel|^2 - 2\mathbf{q}_\parallel \cdot \mathbf{G}_\parallel < 0\). We must also match the derivatives over the same boundary. The matching of values over the entire boundaries \(z = 0\) and \(z = L\) (or equivalently over the unit cells in those boundaries) guarantees the equality of the in-plane derivatives, \(\nabla_\parallel \psi_L(\mathbf{r}_\parallel; 0) = \nabla_\parallel \psi_S(\mathbf{r}_\parallel; 0)\) and \(\nabla_\parallel \psi_R(\mathbf{r}_\parallel; L) = \nabla_\parallel \psi_S(\mathbf{r}_\parallel; L)\), so there is only one independent, additional restriction on each boundary, which is on the normal derivatives: \(\frac{\partial}{\partial z} \psi_L(\mathbf{r}_\parallel; 0) = \frac{\partial}{\partial z} \psi_S(\mathbf{r}_\parallel; 0)\) and \(\frac{\partial}{\partial z} \psi_R(\mathbf{r}_\parallel; L) = \frac{\partial}{\partial z} \psi_S(\mathbf{r}_\parallel; L)\). These restrictions lead to:

\[
iq_z \delta_{\mathbf{G}_\parallel} \mathbf{0} - i \sum_{\mathbf{G}_\parallel} \delta_{\mathbf{G}_\parallel} \mathbf{G}_\parallel q_z'(\alpha, \beta) r_{(\alpha, \beta)}
\]

(3.35)

\[
= \sum_{n=1}^{D} f_n \sum_{\mathbf{G}_\parallel} \frac{\partial \phi_{\mathbf{k}_n}(\mathbf{G}_\parallel, 0)}{\partial z} \delta_{(\mathbf{k}_n + \mathbf{G}_\parallel)(\mathbf{q}_\parallel + \mathbf{G}_\parallel')}.
\]

(3.36)
To recap, by the orthogonality of Fourier basis elements, the enforcement of the continuity of the wave function and its normal derivative at each supercell boundary splits into two equations for each of the $N_{G\parallel}(E)$ in-plane reciprocal lattice vectors such that $q'_{\parallel} \geq 0$. Thus, each of these $G_{\parallel}'s$ gives four constraints on the amplitudes $f_n$, $r_{(\alpha,\beta)}$, and $t_{(\alpha,\beta)}$. Now, there is a coefficient, $f_n$, for each of the $D$ Bloch solutions at energy $E$. And there are $N_{G\parallel}(E)$ coefficients, $r_{(\alpha,\beta)}$, of back-diffracted beams and $N_{G\parallel}(E)$ coefficients, $t_{(\alpha,\beta)}$, of the transmitted waves. Thus, we have $4N_{G\parallel}(E)$ equations for $D + 2N_{G\parallel}(E)$ unknowns. This system is only guaranteed to be exactly soluble then when $D = 2N_{G\parallel}(E)$. At the lowest energies, it is actually the typical case that $D = 2N_{G\parallel}(E) = 2$, and so the method is simple to implement. For higher energies, however, it is not clear how commonly this condition is met. Thus, except for a brief discussion in Ch. 6, the remainder of this dissertation deals with the lowest range of energies, for which only one back-diffracted beam is possible ($N_{G\parallel}(E) = 1$), referred to as the specular reflection (only) regime.

### 3.2.1 Algorithm for Specular Reflection

When the energy of the incoming beam is low enough, the only $G_{\parallel}$ allowed by the Bragg conditions (Eqs. 3.26 and 3.25) is $G_{\parallel} = (0,0)$, so that all solutions inside the supercell and all diffracted beams must have $k_{\parallel} = q_{\parallel}$ and $q'_{\parallel} = q_{\parallel}$. This is due to the fact that at these energies, the energies of the states with wave vectors that are shifted by an in-plane reciprocal lattice vector are higher than the energy of the incoming beam. This occurs for energies less than $E_c(q_{\parallel}) = q_c^2$, where 

$$q_c = \min(|q_{\parallel} + \alpha b_1 + \beta b_2|)$$

for all $\alpha, \beta \in \mathbb{Z}$ with $(\alpha, \beta) \neq (0,0)$.

2 To see this, fix $q_{\parallel}$ and assume $E < |q_{\parallel} + \alpha b_1 + \beta b_2|^2$ for some non-zero reciprocal lattice vector. Then, if there is a diffracted

---

2 Note that it is necessary to include all integer pairs, not just some limited set, to handle all possible sets of primitive lattice vectors. For instance, a set of primitive lattice vectors which would require an arbitrarily large $\alpha$, even for $q_{\parallel} = 0$, is given by $\{b_1, b_2\} = \{(1/n, (2n+1)/n), (1, -(2n+1))\}$. 

41
beam related to this reciprocal lattice vector, its energy is $E_d = |q||\alpha b_1 + \beta b_2|^2 + (q_z')^2 > E$, because if $q_z' = 0$ or is imaginary, there is no diffracted beam. Thus, if $E < \min(|q||\alpha b_1 + \beta b_2|^2)$ for all non-zero reciprocal lattice vectors, there can be no diffracted beams. There is also a minimum energy possible for a beam with given $q||$. Because the energy of an electron in vacuum is $E = |q|^2 = |q||^2 + (q_z)^2$, scattering can only be performed at $E > |q||^2$.

In this specular reflection regime, the system of matching equations is quite simple:

$$1 + r_{(0,0)} = \sum_{n=1}^{D} f_n \phi_{k_n}(0)$$  \hspace{1cm} (3.38)

$$t_{(0,0)} e^{iqzL} = \sum_{n=1}^{D} f_n \phi_{k_n}(L).$$  \hspace{1cm} (3.39)

$$iq_z - iq_z r_{(0,0)} = \sum_{n=1}^{D} f_n \frac{\partial \phi_{k_n}}{\partial z}(0)$$  \hspace{1cm} (3.40)

$$iq_z t_{(0,0)} e^{iqzL} = \sum_{n=1}^{D} f_n \frac{\partial \phi_{k_n}}{\partial z}(L)$$  \hspace{1cm} (3.41)

noting that $q_z'(0,0) = q_z$ and defining $\phi_{k_n}(z) = \phi_{k_n}((0,0),z)$. Now, if we limit our matching to only those energies in the generic case $D = 2$, giving two solutions inside the supercell labeled by Bloch vectors $k_1$ and $k_2$, with $k_1|| = k_2|| = q||$, then we can rewrite this as an inhomogeneous $4 \times 4$ matrix equation:

$$\begin{pmatrix} 1 \\ -q_z \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} -1 & \phi_{k_1}(0) & \phi_{k_2}(0) & 0 \\ iq_z & \frac{\partial \phi_{k_1}}{\partial z}(0) & \frac{\partial \phi_{k_2}}{\partial z}(0) & 0 \\ 0 & \phi_{k_1}(L) & \phi_{k_2}(L) & -e^{iqzL} \\ 0 & \frac{\partial \phi_{k_1}}{\partial z}(L) & \frac{\partial \phi_{k_2}}{\partial z}(L) & -iq_z e^{iqzL} \end{pmatrix} \begin{pmatrix} r_{(0,0)} \\ f_1 \\ f_2 \\ t_{(0,0)} \end{pmatrix}$$  \hspace{1cm} (3.42)

The solution is easily computed, and the reflectivity (relative intensity of reflected beam) is then
obtained as $|r_{(0,0)}|^2$.

This is the process for determining the reflectivity for an incident beam with a given in-plane wave vector, $\mathbf{q}_\parallel$, and a given energy, $E$. To produce a reflectivity curve for a fixed $\mathbf{q}_\parallel$, we must compute this over a range of energies. In order to find solutions over a range of energies, the band structure of the system is calculated over a path in the Brillouin zone at fixed $\mathbf{k}_\parallel = \mathbf{q}_\parallel$. Thus, $k_z$, which is a valid parameter in the supercell calculation, varies over the path. The eigenvalue problem for the band structure will produce bands of solutions, the solutions in each band with energies that vary with $k_z$ and different bands producing different energy ranges. Degenerate pairs of solutions produced in this process are matched via Eq. 3.42. To compute the reflectivity for general angles of incidence, this procedure is repeated for a grid of $\mathbf{k}_\parallel$ values, typically along a given direction in the surface Brillouin zone. The details of these aspects of the algorithm are described in more detail for normal and off-normal incidence scattering, including a discussion of how to find pairs of degenerate solutions, in the following two sections.

### 3.2.2 Algorithm for Normal Incidence, Specular Reflection

The above procedure hinges on finding the appropriate two solutions inside the supercell, $\phi_{\mathbf{k}_1}(z)$ and $\phi_{\mathbf{k}_2}(z)$ (when restricting to specular reflection). They must be degenerate and satisfy the Bragg condition for surfaces. For normal incidence scattering, $\mathbf{q}_\parallel = (0, 0)$, so the Bragg condition gives that $\mathbf{k}_\parallel = (0, 0)$ and $\mathbf{q}_\parallel' = (0, 0)$. Now, the time-reversal symmetry of the system implies that for any solution $\psi_\mathbf{k}(\mathbf{r})$, $\psi_\mathbf{k}^*(\mathbf{r}) = \psi_\mathbf{-k}(\mathbf{r})$ is a solution of the same energy. Since $\mathbf{k}_\parallel = -\mathbf{k}_\parallel = (0, 0)$, both of these solutions satisfy the Bragg condition for normal incidence, specular reflection, and the appropriate pair of solutions for a given energy can be found from just one solution at that energy. Thus, an efficient algorithm for Bloch wave matching of normal incidence, specular reflection consists of computing Bloch wave solutions for a grid of $k_z$-points along a path in the first Brillouin zone from $\Gamma$ to $A$, avoiding the $\Gamma$- and $A$-points, as in Fig. 3-4 (a). Then, pairs of degenerate
Figure 3-4: Normal incidence, specular reflection Bloch wave pairs (for hexagonal lattice): (a) $k_z$-points for which Bloch wave solutions are computed in DFT package. (b) $k_z$-points of paired, degenerate, complex conjugate solutions.

solutions satisfying the Bragg condition can be created by pairing each Bloch wave with its complex conjugate, illustrated in Fig. 3-4 (b). Each pair is then used in the system of matching equations, Eq. 3.42, to find the reflectivity. As in the one-dimensional case, the path of $k_z$-points must not get too close to $\Gamma$ and the Brillouin zone boundaries because at those points, there is only one solution, not the two linearly independent solutions needed for the matching. It may be important to avoid maxima and minima of the bands as well, but typically these only occur at $\Gamma$ and the zone boundary for normal incidence scattering.

3.2.3 Algorithm for General Incidence Specular Reflection

Finding the appropriate solutions inside the supercell is more complicated for off-normal incidence because complex conjugate solutions no longer satisfy the surface Bragg condition. In fact, there are two approaches depending on the symmetry of the system. First, I describe the general approach, and then I describe a more efficient method in the case of systems with mirror planes parallel to the surface.

The surface Bragg condition for off-normal, specular reflection is $k_\parallel = q_\parallel$. Thus, for a given
Figure 3-5: **Effect of Mirror Symmetry on Band Structure**: Typical band structures for (a) the off-normal scattering from a material without mirror symmetry (2L 2H-MoS\(_2\)), (b) the off-normal scattering of a material with mirror symmetry (1L 1H-MoS\(_2\)), and (c) the normal scattering for any material (in this case one without mirror symmetry: 2L 2H-MoS\(_2\)).
Figure 3-6: Off-normal incidence, specular reflection Bloch wave pairs (for a hexagonal lattice): (a) $k_z$-points for which Bloch wave solutions are computed in DFT package. (b) An illustration of the comparison of energies, after sorting, to find pairs of solutions with energies that differ by less than a specified threshold.
in-plane Bloch wave vector, \( \mathbf{q}_\parallel \), (which along with the energy determines the angle of incidence), the search for appropriate degenerate Bloch waves is over the \( k \)-path \((\mathbf{q}_\parallel, k_z)\), where \( \mathbf{q}_\parallel \) is fixed. Now, in general, the band structure along this path has no clear order, as seen in Fig. 3-5 (a). The identification of degenerate pairs of solutions must be handled in a general way that can find degenerate \( k_z \)-points for any shape of band structure. One approach would be to solve the Schrödinger Equation at a fixed energy, finding all Bloch wave solutions with that energy. This is sometimes referred to as the ‘inverse band structure problem’ [38]. The difficulty here is that \( k \) does not appear in the Schrödinger Equation, in real or reciprocal space, as a simple eigenvalue. It appears as a parameter for which nonlinear methods would need to be used to solve. As mentioned in Ch. 2, certain approaches to the solution of the Schrödinger Equation actually do lend themselves to the inverse band structure problem. See Pendry [20] page 125 for a layer-based method. See the work of Krasovskii [38] for inverse band structure using the \( \mathbf{k} \cdot \mathbf{p} \) approach to Linearized Augmented Plane Wave methods. As our method has been developed with widely-used DFT packages in mind, we developed an algorithm based on the standard band structure calculations which take \( k \)-points as inputs and solve for energy eigenvalues and eigenfunctions. Thus, instead, we take the approach of computing Bloch wave solutions on a fairly dense grid along the path \((\mathbf{q}_\parallel, k_z)\) and sorting all solutions by energy. Then, starting with the lowest energy scattering state, the energies of consecutive solutions are compared to see if they differ by less than a given threshold value. If the two energies differ by less than the threshold, then those two solutions are used in the matching procedure and the energies are removed from the queue. If the energy difference is not within the threshold, the lowest energy is removed from the queue and the higher energy of the pair is compared to the next lowest energy. This process is repeated for all computed solutions with energies less than the specular reflection limit, \( E_c(\mathbf{q}_\parallel) \), and greater than \( |\mathbf{q}_\parallel|^2 \). This procedure is illustrated in Fig. 3-4. As in solving the one-dimensional square well, it is necessary to avoid points for which there is only one solution, since two linearly-independent solutions are required for
the matching. For off-normal incidence, this occurs at the band maxima and minima, which may
or may not be located on the Γ plane or the Brillouin zone boundary. This method works fairly
well, but it does have limitations. Finding the appropriate threshold for the energy difference of
matching pairs can require trial and error and is dependent upon the density of the k-point grid in
the k\_z direction. Some of the errors that can occur are discussed for the example of molybdenum
disulfide in Ch. 6.

In the case of slabs that have a mirror symmetry with mirror plane parallel to the crystal
surface, the relevant band structure is symmetric across Γ, i.e., Bloch wave solutions with Bloch
wave vectors \( k_1 = (q_{\parallel}, k_z) \) and \( k_2 = (q_{\parallel}, -k_z) \) are degenerate. See Fig. 3-5. To see why this is, let
\( M \) denote the symmetry operation of reflection through the mirror plane in variables in which the
mirror plane is located at \( \tilde{z} = 0 \). In other words, \( M \tilde{r} = (\tilde{x}, \tilde{y}, -\tilde{z}) \). (We reserve \( r = (x, y, z) \) for the
coordinates of our scattering set up, shown in Fig. 3-3, in which we define the location of the mirror
plane as \( z = z_M \), typically in the center of the supercell.) We assume that the DFT self-consistency
calculation of a mirror-symmetric atomic configuration will produce a mirror-symmetric potential,
\( V(\tilde{r}) \). Thus, \( \tilde{H} = -\nabla^2 + V(\tilde{r}) \) and \( M \) commute. (Note that \( \nabla^2 \) is the same in \( r \) and \( \tilde{r} \).) Thus, any
Bloch solution, \( \rho_k(\tilde{r}) = e^{i\tilde{k} \cdot \tilde{r}} w_k(\tilde{r}) \), and its image under \( M \), \( M \rho_k(\tilde{r}) \), are degenerate solutions. But

\[
M \rho_k(\tilde{r}) = \rho_k(M^{-1} \tilde{r}) = e^{iM^{-1} \tilde{k} \cdot M^{-1} \tilde{r}} w_k(M^{-1} \tilde{r}) = e^{iM \tilde{k} \cdot \tilde{r}} w_k(M^{-1} \tilde{r}).
\]  

(3.43)

Now, this is a Bloch solution with wave vector \( M \tilde{k} \) and periodic part \( w_{M\tilde{k}}(\tilde{r}) = w_k(M^{-1} \tilde{r}) \). Thus,
already we see that solutions \( \rho_k(\tilde{r}) \) and \( \rho_{M\tilde{k}}(\tilde{r}) \) are degenerate. In other words, Bloch wave solutions
with Bloch wave vectors \( k_1 = (q_{\parallel}, k_z) \) and \( k_2 = (q_{\parallel}, -k_z) \) are degenerate.

The process of finding pairs of solutions to be used in matching can be improved for systems
mirror symmetry using this result. For one thing, it is much more likely that the energy-sorting
process will lead to the exactly correct pairing of degenerate solutions, and the energy difference
threshold can be reduced to a sufficiently small value to ensure this. This is the approach that
Figure 3-7: Off-normal incidence, specular reflection Bloch wave pairs for a mirror symmetric system (for a hexagonal lattice): (a) symmetric path of \( k_z \)-points for which Bloch wave solutions are computed in DFT package. (b) An illustration of the pairing of solutions with opposite \( k_z \)'s.

We have taken in most of our results for consistency and simplicity of explanation. Alternatively, the energy-sorting process can be skipped entirely, and the pairs of solutions can be found by computing band structures along a symmetric \( k_z \)-path and pairing the solutions with \( k_1 = (q_\parallel, k_z) \) and \( k_2 = (q_\parallel, -k_z) \), as illustrated in Fig. 3-7. This was our initial approach, in fact, which worked well until we encountered systems without mirror symmetries, at which point we had to create the energy-sorting process. Ideally, especially in a software package for LEEM reflectivity calculation, one would check for a mirror plane parallel to the crystal surface and choose the exact approach when one is present. In fact, the approach could be made even more efficient, requiring the direct calculation of only one solution per pair, if further analysis of the symmetry is performed.

We can learn more if we change variables back to those of our scattering setup, \( z = \tilde{z} + z_M \). In this case, we look for solutions \( \psi_k(r(\tilde{r})) = \rho_k(\tilde{r}) \) that solve \( H\psi_k = E\psi_k \) with
\[ H = -\nabla^2 + V(\mathbf{r}). \]

Now,

\[
\psi_k(\mathbf{r}(\tilde{\mathbf{r}})) = e^{i\mathbf{k} \cdot \mathbf{r}} u_k(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} e^{ik_z(\tilde{z} + z_M)} u_k(x, y, \tilde{z} + z_M) = e^{i\mathbf{k} \cdot \tilde{\mathbf{r}}} e^{i k_z z_M} u_k(x, y, \tilde{z} + z_M).
\]

(3.44)

(3.45)

But, also, \( \psi_k(\mathbf{r}(\tilde{\mathbf{r}})) = \rho_k(\tilde{\mathbf{r}}) = e^{i\mathbf{k} \cdot \tilde{\mathbf{r}}} w_k(\tilde{\mathbf{r}}). \) Thus, \( w_k(\tilde{\mathbf{r}}) = e^{ik_z z_M} u_k(x, y, \tilde{z} + z_M). \) Now, we can use the simple relationship between \( \rho_k(\tilde{\mathbf{r}}) \) and \( \rho_{Mk}(\tilde{\mathbf{r}}) \) to find the relationship between \( \psi_k(\mathbf{r}(\tilde{\mathbf{r}})) \) and \( \psi_{Mk}(\mathbf{r}(\tilde{\mathbf{r}})). \)

\[
\psi_{Mk}(\mathbf{r}(\tilde{\mathbf{r}})) = \rho_{Mk}(\tilde{\mathbf{r}}) = e^{i M \mathbf{k} \cdot \tilde{\mathbf{r}}} w_k(M^{-1} \tilde{\mathbf{r}}) = e^{i M \mathbf{k} \cdot \tilde{\mathbf{r}}} w_k(x, y, -\tilde{z} + z_M)
\]

(3.46)

(3.47)

\[
= e^{i M \mathbf{k} \cdot (x, y, z - z_M)} e^{i k_z z_M} u_k(x, y, 2z_M - z)
\]

(3.48)

\[
= e^{i M \mathbf{k} \cdot x, y, 2z_M - z}
\]

(3.49)

But, also,

\[
\psi_{Mk}(\mathbf{r}(\tilde{\mathbf{r}})) = e^{i M \mathbf{k} \cdot \mathbf{r}} u_{Mk}(\mathbf{r}).
\]

(3.50)

Thus,

\[
u_{Mk}(\mathbf{r}) = e^{i2k_z z_M} u_k(x, y, 2z_M - z),
\]

(3.51)

and

\[
\psi_{Mk} = e^{i k \cdot \mathbf{r}} e^{i k_z (2z_M - z)} u_k(x, y, 2z_M - z).
\]

(3.52)

Note that this is simply the reflection of \( \psi_k \) through the mirror plane. Thus, for systems with mirror planes parallel to their surfaces, pairs of solutions can be created by computing Bloch wave solutions with wave vectors \( \mathbf{k}_1 = (\mathbf{q}_\parallel, k_z) \) and then using Eq. 3.52 to get a degenerate solution with wave vector \( \mathbf{k}_2 = (\mathbf{q}_\parallel, -k_z). \)
3.3 Two- and Three-Dimensional Models

As a first test of the full matching algorithm, we again investigated model systems, this time in two and three dimensions. Thus, the time-independent Schrödinger Equation looks like:

\[-\nabla^2 \psi(r) + V(r)\psi(r) = E\psi(r),\]

(3.53)

where \( r \in \mathbb{R}^2 \) or \( r \in \mathbb{R}^3 \) and \( V(r) \) is periodic in one or two dimensions. As always, we solve it in Fourier space, after assuming a Bloch solution for the repeating supercell:

\[ \psi_k(r) = e^{ikr} \sum_G d_k(G)e^{iGr}. \]

(3.54)

Thus, we must again solve the Schrödinger Equation in Fourier space, Eq. A.10, now for a two- or three-dimensional model potential. I first studied two-dimensional square wells, but for convergence tests, Gaussian-like wells are more appropriate, in order to avoid the difficulty in approximating a discontinuous function with a Fourier series. I study a system with two rows of Gaussian-like wells perpendicular to the scattering. Each row of wells contributes a term to the potential of the system within a unit cell of the form:

\[ V(y,z) = -V_0e^{-\alpha z^3 + \alpha z^3}, \]

(3.55)

best displayed in Fig. 3-13 (e). The potential is considered to be truly repeated in the \( y \)-direction, but only artificially repeated in the \( z \)-direction for the purposes of using a supercell to compute Bloch solutions. Solving for these Bloch solutions involves writing the wavefunction of multiple dimensions as a vector by choosing an ordering of the multidimensional Fourier coefficients and writing the Hamiltonian operator as a large \( nm \times nm \) matrix analogous to that in Eq. 3.4 for an \( n \times m \) grid in the supercell, for a given \( k_z \) with \( k_y = 0 \) for normal incidence. The eigenvectors give
the Fourier coefficients of the periodic part of the solution. The inverse Fourier transform in the scattering direction then gives the coefficients \( \phi_k(G, z) \) of Eq. 3.16. This \( \phi_k \) and its conjugate can be used in the matching equation, Eq. 3.42 to compute the reflectivity, for each energy eigenvalue for the given \( k_z \). Computing over a path of \( k_z \)-points then creates reflectivity curves like those in Figures 3-9 and 3-14.

Figures 3-8 and 3-9 illustrate the convergence with grid points in the \( z \)-direction of the reflectivity curves for scattering from two rows of these cubic, Gaussian-like wells in a supercell 9 units wide in \( z \). All the two-dimensional potentials in this section consist of two wells spaced 4 units apart with \( V_0 = -12 \), supercell 1 unit wide in \( y \), \( \alpha = 30 \), and \( \alpha_z = \alpha \left( \frac{w}{z} \right)^3 \), where \( w \) is the supercell width in \( z \). Fig. 3-8 shows that when the grid is too sparse in \( z \), erroneous peaks arise. As the number of grid points approaches the marginally sufficient number of 25, the consistent reflectivity curve takes shape. Fig. 3-9 shows the curves for 25 \( z \) grid points and higher, with all curves computed with more than 25 being extremely consistent. Figures 3-10 and 3-11 illustrate the convergence with \( y \) grid points. Once the general shape of the potential is accurately captured, the curve is very close to correct. Even those grids that do a poor job of capturing the shape, do not create large deviations from the correct curve, showing the relative insensitivity to the potential in this direction of the reflectivity curve, in this simple case.

Figures 3-12–3-14 illustrate the effect of the supercell’s width in the \( z \)-direction on the reflectivity curve. Figures 3-12 and 3-13 show that errors are created when the matching surface is taken in an area in which the potential has not flattened to 0, but that a matching surface just outside the wells, where the potential has just hit zero, seems to be sufficient in this case. The reflectivity curves calculated using supercells of widths 6.5 and 7, corresponding to the potentials in Fig. 3-13 (c) and (d), seem to fall mostly in line with one another. Fig. 3-14 shows that the use of all supercells with widths greater than 7 match extremely well with those computed using a supercell width of 7.

Finally, Fig. 3-15 displays the coincidence of reflectivity curves calculated for normal incidence.
Figure 3-8: Reflectivity from 2D system with insufficient FFT grids in z: Reflectivity curves for two layers of cubic Gaussian-like wells computed with FFT grids too sparse in the z-direction to accurately model the system. A 21-by-25 ($y \times z$) is nearly sufficient.
Figure 3-9: Reflectivity from 2D system with sufficient FFT grids in z: Reflectivity curves for two layers of cubic Gaussian-like wells computed with FFT grids sufficient to accurately model the system. This shows that a 21-by-25 ($y \times z$) is just shy of dense enough and that all denser grids are sufficient.
Figure 3-10: **Reflectivity from 2D system with insufficient FFT grids in** $y$: Reflectivity curves for two layers of cubic Gaussian-like wells computed with a range of FFT grids in the $y$-direction (‘in-plane’). An 11-by-25 ($y \times z$) is more than sufficient to accurately model the system.
Figure 3-11: **2D potentials - FFT grid dependence in $y$**: Potentials of systems with two layers of cubic Gaussian-like wells using a range of grids in the $y$-direction (‘in-plane’). The number of grid points in $y$ are: (a) 2, (b) 4, (c) 6, (d) 8, and (e) 21.
Figure 3-12: **Reflectivity from 2D system with insufficient supercell widths**: Reflectivity curves for a system of two layers of cubic Gaussian-like wells computed with different supercell widths in $z$ that are mostly too small to allow the potential to return to very close to zero on the supercell boundary. All computations used FFT grids of 21 points in $y$ and approximately 9 times the supercell width in $z$. 
Figure 3-13: 2D potentials - supercell width dependence: Potentials of systems of two layers of cubic Gaussian-like wells for various supercell widths in the $z$-direction. The width of each is (a) 5.5, (b) 6, (c) 6.5, (d) 7, and (e) 12.5. All computations used FFT grids of 21 points in $y$ and approximately 9 times the supercell width in $z$. 
Figure 3-14: Reflectivity from 2D system with sufficient supercell widths: Reflectivity curves for a system of two layers of cubic Gaussian-like wells computed with different supercell widths in $z$ that are all large enough to allow the potential to return to very close to zero on the supercell boundary. All computations used FFT grids of 21 points in $y$ and approximately 9 times the supercell width in $z$. 
scattering from three layers of two-dimensional arrays of three-dimensional (true, quadratic) Gaussian wells arranged in a honeycomb pattern using three different supercell sizes. Each well in the supercell contributes a term to the potential of the form:

\[ V(y, z) = -V_0 e^{-(\alpha_x |z-a|^2 + \alpha (|x-b|^2 + |y-c|^2))}, \]

(3.56)

The wells are 10 units deep, \( \alpha = 50 \), and \( \alpha_x = \alpha \left( \frac{w}{T_x} \right)^2 \), where \( w \) is the supercell width in \( z \) and \( T_x \) is the supercell width in \( x \).

All of these model results show that the supercell, Bloch wave matching algorithm, which matches only the \((0,0)\) Fourier coefficients is capable of consistently calculating electron reflectivities in the lowest energy range for multidimensional systems for which the higher-order Fourier coefficients are significant parts of the solutions in the slab. If we look at the full specular reflection range, up to \( 4\pi^2 \) when the width in \( y \) is 1, we see that there are some problems with the curve, however. In Fig. 3-16, there are narrow vertical collections of disordered reflectivities between 35 and \( 4\pi^2 \approx 39.48 \) for all supercell sizes. I discuss such issues, and others, in the following section and Chapter 6.

We have also briefly studied off-normal scattering from some two-dimensional systems. Fig. 3-17 shows a colormap of the general incidence reflectivity spectrum for a system that I refer to as the ‘perturbed square trough.’ This system is discussed in more detail in Sec. 6.4. It is a system with a potential that is a product of a one-dimensional square well in the \( z \)-direction and the identity in the \( y \)-direction, with small square bumps added to the well in a periodic fashion. The unit cell of the potential is shown in Fig. 6-3. The spectrum shows the reflectivity as a function of energy for 30 \( q_y \)-points (or \( k_y \)-points, which are the same for specular reflection) between the \( \Gamma \)-point and the edge of the first Brillouin zone. Note that this includes only results for one supercell, so there are some gaps. The fact that the data starts at an energy higher than zero for normal incidence is due to a gap from 0 to 0.8. We can see that the features (peaks and valleys) of the curve move in a
Figure 3-15: Reflectivity from 3D system: Reflectivity curves for three layers of Gaussian wells arranged in a honeycomb pattern using different supercells in the scattering direction, $z$. The FFT grids used were 11-by-11 in $x$ and $y$ and had a number of points in the $z$-direction approximately two times the supercell width in $z$. 
Figure 3-16: Reflectivity from 2D system with problem points: As shown in Fig. 3-14, reflectivity curves for a system of two layers of cubic Gaussian-like wells. This plot includes a larger energy range, large enough to include some problem points.
Figure 3-17: Reflectivity from 2D perturbed square trough: Reflectivity spectrum including off-normal incidence for a two-dimensional perturbed square trough potential. Note the parabolic shape of the peaks and valleys and the streaks of narrow features caused by localized solutions.

The reflectivity spectrum shows a parabolic manner with increasing $q_y$. This is because the potential is very nearly constant in the $y$-direction. Thus, the solutions are very nearly product solutions, of the form: $\psi(y, z) = e^{ik_y y} f_{SW}(z)$, where $f_{SW}(z)$ are solutions for the one-dimensional finite square well potential. The energy of a given solution is close to $E = k_y^2 + E_{SW}$, where $E_{SW}$ is the energy of the one-dimensional solution $f_{SW}$. Thus, the states are free-electron-like in $y$, and their energy dependence with respect to $k_y$ is almost parabolic. If the potential varied more in the $y$-direction, then the solutions might have a more complicated $y$-dependence, and features would not simply shift parabolically with $q_y$, as we will see in the case of reflection from real systems, in Ch. 4 and Ch. 5.
Finally, we note that there are many strange spots in the spectrum at higher energies. These are due to vertical features like those seen in Fig. 3-16. As discussed in detail in Sec. 6.4, these spots are due to solutions that are localized in the z-direction but extended in the y-direction. For these simple systems, they are easily predicted and explained. For real systems, similar features arise, but they are not as easily understood.

### 3.4 Limitations and Issues

While our supercell, Bloch wave matching algorithm gets a lot right, there are a few limitations and issues. There are some complications in making sure that the system of equations for matching solutions at the supercell boundaries is well-determined, and there are certain solutions that create problems for it. There are also some aspects of the energy-sorting algorithm for off-normal incidence that need to be refined to improve the accuracy of the reflectivity spectra. Only a brief overview of some these issues is given here to the extent required to discuss the results in Chapters 4 and 5. More details about all but the artificial band gaps are presented in Ch. 6.

#### 3.4.1 Artificial Band Gaps

As mentioned above, one of the most important steps in this matching procedure is to find the appropriate set of degenerate solutions that satisfy the surface Bragg condition that gives a well-determined system of equations upon matching. The system that we have found, Eq. 3.42, is only guaranteed to be exactly soluble then when $D = 2N_{_{G_1}}(E)$. Unfortunately, this is not always the case. There is not always the correct number of linearly independent solutions inside the supercell to give a well-determined system. We have already encountered the simplest example of this failure in the one-dimensional square well. In that system, the artificial periodicity enforced on the potential (or equivalently, the Bloch form enforced on solutions) creates energy gaps - energies for which no solutions can be found. This is true in higher-dimensional systems as well. The Bloch
condition being forced on the solution in the $z$-direction causes artificial energy gaps in the bands in the $k_z$-direction. However, this can be overcome for the most part by computing reflectivities for different supercell sizes, in higher dimensions as well as in one. While we do not have a proof, we have found that a small number of supercells is generally sufficient to fill in much of the energies, as illustrated in Fig. 3-3 (b).

### 3.4.2 Problem Solutions

There are some parts of our computed reflectivity curves that are surprising. Most are sharp features, the sharpest of which appear to be nonphysical. Some, however, appear as if they could be true features of the reflectivity, perhaps produced by resonances in the system. In looking at the wavefunctions of the solutions that created these features, we have found that the features are usually associated with solutions that decay in amplitude away from the slab, or localized (in $z$) solutions. (Localized typically refers to the state being square-integrable. Thus, localized in one direction means square-integrable in that direction in some sense - at each $(x,y)$ or the average of the amplitude squared, etc.) States that are truly localized should not be a part of the scattering problem, since they will not be recorded by the measurement device. Good numerical approximations to true localized states would be very small at the supercell boundaries, producing erroneous reflectivity coefficients. Of course, with the use of Fourier methods in the supercell geometry, it is not clear that the approximations of true localized solutions would be good. The issue of which states are physical and which are artifacts of the model is not completely settled. I discuss this in more detail in Ch. 6, and Gao et al. discuss it in [50]. For now, I simply explain that some solutions have been filtered out of our matching process, so that the results displayed include only reflectivities computed with a subset of the solutions calculated. We have tried a few different filters but the filter with the best combination of rationale and results is one based on ensuring that the solutions used are sufficiently close to plane waves in the area near the left supercell boundary.
Explicitly, we calculate the inner product of the supercell solutions with right-moving plane waves of the same energy to compute the measure $\sigma = \sqrt{|\sigma_1|^2 + |\sigma_2|^2}$ with

$$\sigma_{1,2} = \frac{1}{I} \int_0^I \phi_{k_{1,2}}(z) e^{iz\sqrt{E-|q_\parallel|^2}} dz.$$  \hfill (3.57)

Then, only solutions with $\sigma$ values greater than a given threshold are used in the matching algorithm.

In the following chapters, computed reflectivities are shown that have been filtered by a couple different methods. For FLG reflectivity curves at fixed values of the in-plane wave vector of the incident beam, $q_\parallel$, multiple sets of results with different filters are shown, to provide a feel for the features that are affected. See Figures 4-2, 4-3, 4-5, and 4-6. In two cases, the displayed results were determined using an entirely different filter: only keeping solutions for which the determinants of the matrices in Eq. 3.42 (after normalizing the rows) are greater than a threshold value. One is the normal incidence curve for FLG, to provide a comparison to the $\sigma$ filter. Another is the normal incidence curve for FLG on a nickel substrate (Fig. 4-10), which was calculated at a time when the determinant filter was our first choice and has not been re-run. Finally, the two-layer graphene and two-layer 2H-MoS$_2$ results that are inappropriately calculated assuming mirror symmetry and used for comparison to the correct results in Figures 4-7 and 5-8 are also filtered with the determinant filter for the same reason. The majority of results, including all of those for MoS$_2$, are filtered by removing solutions with $\sigma$ values less than a threshold, and the threshold is given in each figure caption.

### 3.4.3 Energy-Sort Errors and Limitations

The energy-sort algorithm for off-normal reflectivity calculation works pretty well in many situations, however, there are certain situations for which it does not perform ideally. As mentioned in Sec. 3.2.3, the identification of a good energy difference threshold for a given system is not a
well-defined process. It depends on the number of points in the \( k \)-path in the band calculation and the dispersion of the bands of the system. This dispersion is not guaranteed to be uniform across all bands. When there are bands with significantly greater dispersion than the typical bands that are not symmetric about the \( \Gamma \)-plane, the spacing of energies for all states in the band can be greater than the best energy threshold for other bands. In this case, entire bands or large parts of bands can be rejected from the calculation. The desire to include more points must be weighed against the accuracy loss from including pairs of solutions that are not very close in energy. There are also errors that can be made due to the shape of the bands and the fact that the algorithm consists of moving through all solutions in order of energy and accepting pairs if they meet the criterion without checking for the best matches. A few types of these errors and possibilities for correcting them are discussed in Sec. 6.5.
Chapter 4

Low-Energy Electron Reflectivity from Few-Layer Graphene Systems

The first real system that we study with our supercell, Bloch wave matching technique is few-layer graphene. Graphene has been one of the most-studied solid state systems over the past ten years, and few-layer graphene (FLG) systems have been investigated in the search for methods to control certain properties of graphene for use in technological applications. LEEM is well-suited for studying FLG due to the strong interaction of low-energy electrons with surfaces in general, and graphene layers in particular. The literature contains a number of studies of few-layer graphene systems on various substrates by LEEM-IV. We study primarily free-standing few-layer graphene, calculating the fraction of low-energy electrons reflected back from the FLG. Our supercell, Bloch wave matching technique incorporates realistic, self-consistent potentials for the graphene system and produces outstanding results at the very lowest energies (where muffin-tin methods fail) with no reliance on the optimization of parameters. With the straightforward and simply implemented algorithm, we produce reflectivity spectra in the specular energy regime for normal and off-normal incidence electron beams that agree quite well with experiments on FLG on a substrate, for systems of various numbers of layers of graphene. The free-standing FLG is modeled as a slab containing only a small number of layers of graphene, surrounded by vacuum on both sides. The self-consistent potential is computed for this system, and then the band structure is computed with a non-self-consistent
calculation of solutions of Kohn-Sham, single-particle Schrödinger Equation. The solutions are taken from this computation and used in the wave matching algorithm. We also study FLG on a Ni(111) substrate, modeling it as a small number of layers of graphene on top of 10 layers of Ni. While the results do show some features in common with experimental results, the finite size of the substrate creates features that make a true comparison difficult.

Below, I motivate the study of graphene, especially with LEEM-IV, then describe our results for systems of free-standing few-layer graphene.

4.1 Graphene Structure and Properties

Strictly speaking, graphene refers to a single sheet of graphite, a one-atom thick, atomically flat sheet of carbon atoms arranged in a honeycomb lattice. It is in this form that graphene has the most surprising properties: it is a zero-gap semiconductor with Fermi level crossing through the linear Dirac cone at the $K$-point of the band structure, giving rise to relativistic electron behavior [54]. However, the term graphene is also used in the case of a small number of graphene layers stacked on a substrate or suspended above a substrate (few-layer graphene). The different configurations of graphene can have modified properties. For instance, different ways of closing ribbons to form tubes can produce semiconducting carbon nanotubes with different band gaps and just different edge configurations in nanoribbons themselves can produce a band gap, tunable with the ribbon width. Layering (through mechanical placement or growth) few-layer graphene systems with different twist angles between the layers can also produce different band gaps [55], as can changing the twist angle between graphene and a hexagonal boron nitride substrate [56]. Few-layer graphene films are sometimes grown or placed on substrates for testing their possible applications in devices as, for instance, contacts or components of transistors. The study of these systems depends on the detailed characterization of aspects like the number of layers of graphene, the stacking sequence of layers, the orientation of layers with respect to one another and the substrate,
and the presence of other materials in the system, for instance the intercalation of hydrogen atoms between the substrate and graphene layers. Thus, it is important to have tools that allow for such identifications. Raman spectroscopy is a common technique for determining the layer number and stacking sequences in few-layer graphene systems, capable of distinguishing up to 5 layers of graphene [54] and AB from ABC stacked three- and four-layer systems [57]. Rayleigh scattering of photons can also be used in layer counting, up to 6 layers [54]. X-ray photo-emission spectroscopy and diffraction can provide structural information, like the relative orientation of graphene on its substrate, as well as chemical information, like the location of contaminant bonding [58]. LEEM-IV is an important tool in the characterization of FLG systems, capable of determining the numbers of layers in such systems, as well as stacking orders, in-situ with temporal resolution and with spatial resolutions far exceeding those of Raman and x-ray photoemission spectroscopies.

4.2 LEEM Studies of Graphene

LEEM-IV has been shown through experiment to be an especially robust method for unambiguously counting the number of layers of graphene grown on silicon carbide substrates. Hibino et al. first showed that LEEM-IV curves in the very low energy range, 0-10 eV, for few-layer graphene systems grown on the Si-terminated 6H-(0001) and 4H-(0001) and C-terminated 4H-(0001) faces of SiC exhibit oscillations that are correlated to the number of layers [59, 60]. Following on the work of Strocov et al. on very-low-energy electron diffraction (very similar to LEEM-IV) from graphite [39], Hibino et al. show a clear correspondence between reflectivity peaks for few-layer graphene systems and band gaps in the Γ–A band structure of bulk graphite, and conversely, between reflectivity oscillations and dispersive bands in the bulk graphite band structure. They also propose a tight-binding model to support the layer counting that they describe, including the identification of the the first carbon-rich atomic layer as a non-graphene-like buffer layer and the correspondence of $m$ reflectivity minima and $m$ graphene layers above the buffer layer. The
model also reproduces the locations of the oscillation minima. Locatelli et al. use a related phase accumulation model of quantum-well resonances to describe their use of LEEM-IV for layer counting of few-layer graphene on a SiO$_2$ and suspended few-layer graphene, both of which show an $m$ minima to $m$ layers relationship, for two or more layers, with no minima for a single layer [61]. Feenstra et al. repeated this experiment to find that, in fact, there is a curve with a single minima that is associated with two layers of graphene, and that $m$ layers corresponds to $m - 1$ minima. Reidl et al. use LEEM-IV, among other techniques, to study graphene on SiC with and without intercalated hydrogen and find that the number of minima in the reflectivity at a given point on the sample decreases by one after the desorption of hydrogen [62].

As discussed in Sec. 2.3.5, recent first-principles studies of low-energy electron reflectivity from free-standing graphene have led to insights about these systems. A method involving slab DFT calculations and Bloch wave matching (very similar to ours) was used to argue for a clarification of some issues in the counting of layers of graphene on substrates for normal incidence electron beams [47]. Specifically, Feenstra et al. find (as we do, described below) that $m$ layers of free-standing graphene produce $m - 1$ reflectivity minima. They use this fact (and results for graphene on metals) to argue that $m$ layers of graphene on a substrate will have $m - 1$ reflectivity minima if the bottommost graphene-like layer is strongly bound to the substrate (as in the case of SiC) and $m$ reflectivity minima if the bottommost graphene-like layer is weakly bound (as in hydrogen-intercalated SiC). This group has also modeled FLG on metal substrates [49] and included some inelastic effects [50]. Another group has modified the augmented-plane-wave approach to scattering at interfaces [63] to apply it to the scattering of electrons from a single, free-standing graphene sheet and argue that the broad peak in the reflectivity of this system is due to a special resonance originating from the coupling of in-plane and out-of-plane behavior [64].
4.3 Supercell, Bloch Wave Matching: Few-Layer Graphene

Our Bloch wave matching method for computing the specular reflection of low-energy electrons consists of first calculating the ground state and associated self-consistent potential for the model of the slab sample, followed by performing a non-self-consistent band calculation using the self-consistent potential at a selection of \( k \)-points in the first Brillouin zone, as described in Ch. 3. We determine the vacuum energy by computing the average of the self-consistent potential over an area near the supercell boundary, in which it is approximately flat. (This is sometimes done numerically, and sometimes graphically.) Then, for each Bloch wave scattering state computed in the band structure calculation, the Bloch solution is matched to the incident, reflected, and transmitted plane waves with energy equal to that of the Bloch solution compared to the vacuum energy to determine the reflectivity. In the following, I describe the details of our DFT calculations for free-standing few-layer graphene systems and then present the results of the Bloch wave matching for normal and off-normal angles of incidence.

4.3.1 Model Structure and DFT Details for Few-Layer Graphene Systems

DFT calculations are performed using the open-source Quantum ESPRESSO software package [65]. The local density approximation, ultrasoft pseudopotentials, and Perdew-Zunger exchange-correlation are used in all calculations. Gaussian smearing of 0.001 Ry is employed. The plane wave cutoff energy, which determines the FFT grid, is 50 Ry; in fact, there are two cutoff energies: \( \text{ecutwfc} \) is 50 Ry and \( \text{ecutrho} \) is 200 Ry. These grids are on the order of \( 20 \times 20 \times 400 \). The ground state and the self-consistent potential are first calculated using a \( 14 \times 14 \times 1 \) Monkhorst-Pack grid. (This is the \( k \)-point grid used for numerical integrations involved in the self-consistency calculation including, for instance, the calculation of the charge density.) For free-standing FLG, we use the experimental lattice parameters of graphite, \( a_G = 2.46 \text{ Å} \) for the in-plane lattice constant and 3.36 Å for the spacing between graphene layers. The layers are stacked in the Bernal stacking, also
Figure 4-1: **Graphene in bernal and AB stacking (three layer)**: The first and third layers have been colored gray (light) and the second black (dark), but they all represent carbon atoms. The basis of the lattice can be chosen as two atoms connected by a bond. Then the A lattice point can be thought of as one gray atom and the one below it. These form a hexagonal lattice. The black atoms occupy the B lattice positions. The lower gray atoms occupy the A positions again. In ABC stacking, they would occupy the C positions. Atomic visualization created with XCrySDen [3].

known as AB stacking, as displayed for three layers in Fig. 4-1. The minimum distance from the surface layers of the slab to the supercell boundary is 8 Å. Unless specified otherwise, we compute solutions at 72 points along a path in the first Brillouin zone parallel to $A - \Gamma - A$. The 36 points in the positive half of the first Brillouin zone are equally spaced, and the space between the first point and the $\Gamma$-plane and the last and the Brillouin zone boundary is $\frac{1}{4}$ the spacing of the others. The points in the negative half are a mirror image. For general incidence scattering, we calculate for 59-$\mathbf{k}_\parallel$ points along the $M - \Gamma - K$ path, with 29 equally spaced points on each leg, stopping one point short of $M$ and $K$. All of the FLG spectra presented here are calculated using two different supercell sizes, sufficient to resolve the relevant features. The pairs of supercell widths used are the following multiples of $a_G$: (7, 8), (8, 9), (9, 10), (11, 12), (12, 13), (13, 14), (15, 16), and (16, 17) for 1–8 layers, respectively.
4.3.2 Normal Incidence Scattering from Few-Layer Graphene Systems

We first consider incident beams that are normal to the surface, i.e., $q_\parallel = k_\parallel = 0$. Fig. 4-2 (a) shows our calculated reflectivity versus electron beam energy for one to eight layers of graphene with a normally-incident beam. As previously discussed, energies are referenced to the average of the self-consistent potential in the vacuum regions, so the zero here is that average. The cutoff energy for the first-order diffraction at normal incidence is $E_c(0) = \frac{4}{3}(\frac{2\pi}{A_{0.656}})^2 = 2.428\text{Ry} = 33.03\text{eV}$, since the length of each of the six shortest reciprocal lattice vectors is $\sqrt{2} \frac{2\pi}{a}$ with $a = 4.656$ Bohr radii. The results in Fig. 4-2 were filtered using the $\sigma$ filter described in Sec. 3.4.2. Fig. 4-3 shows two other versions of the same spectra, computed with different filters. Fig. 4-3 (a) simply uses a stricter threshold with the same filter as Fig. 4-2. The results shown in Fig. 4-3 (b) were filtered using the determinant of a normalized version of the matching matrix from Eq. 3.42. For ease of process, all three of these results were computed using the energy-sort algorithm designed for off-normal scattering, described in Sec. 3.2.3. Due to the symmetry of the $k$-paths used and, thus, the guaranteed degeneracies, these results are identical to those computed with the algorithm designed for normal incidence. (For completeness, the energy match threshold is 0.0001 Ry, but a different threshold would not change the results.)

The first thing to notice is that for two or more layers, two sets of oscillations appear in the spectra, between 0 and 6 eV and between 14 and 21 eV. The oscillations in reflectivity for energies between 0 and 6 eV are in good agreement with the experimental LEEM spectra of FLG on various substrates, especially those observed in the measured LEEM spectra for FLG up to eight layers on SiC [60]. The actual positions of the peaks and valleys can vary with the substrate [49]. The number of oscillations is directly linked to the number of graphene layers, a fact often used to determine the number of graphene layers in experiments. Our results show that there are $m-1$ reflectivity minima in each region of oscillations for a free-standing $m$-layer system up to five layers. For systems with six through eight layers, there are $m-2$ minima in the lower energy region of oscillations for an
Figure 4-2: Normal incidence FLG reflectivity: (a) Reflectivity spectra for a beam normally-incident upon 1 to 8 layers of free-standing graphene, bottom to top. The calculated data points are shifted vertically in half integers for clarity. The lines are a guide to the eyes. The filtering for these spectra is $\sigma > 0.01$. (b) Band structure of bulk graphite along the hexagonal axis from $\Gamma$ to $A$. The Fermi level of the bulk graphite is aligned with the Fermi level of the 8-layer free-standing graphene.
Normal incidence FLG reflectivity with alternative filtering: (a) Reflectivity spectra for a beam normally-incident upon 1 to 8 layers of free-standing graphene, bottom to top, with a filtering threshold of $\sigma > 0.1$. (b) Band structure of bulk graphite along the hexagonal axis from $\Gamma$ to $A$. The Fermi level of the bulk graphite is aligned with the Fermi level of the 8-layer free-standing graphene. (c) Reflectivity spectra for a beam normally-incident upon 1 to 8 layers of free-standing graphene, bottom to top, with a filtering threshold of $\text{det}(M) > 0.3$, where $M$ is the matching matrix from Eq. 3.42. (d) Same as (b).
$n$-layer system. This is discussed in more detail below. Layer counting of graphene on SiC must be compared to free-standing graphene carefully, as there is a carbon buffer layer in systems of FLG on Si-terminated SiC that has the structure of graphene but different electronic properties. This layer must be included in the counting to match with results from free-standing graphene. There is a second set of oscillations in the 14–21 eV range, which is less pronounced in the experimental observations. For this higher energy range, only the first minimum corresponding to a bilayer is observed in experiments on FLG with two or more layers. This may be explained by the stronger damping in this energy range due to stronger inelastic scattering at higher energies [39, 66]. It is somewhat consistent with the fact that the typical electron inelastic mean-free path at 20 eV is about 10 Å [67]. Note that we have yet to include damping in our modeling. Hibino et al. also offer, as an explanation for the lack of oscillations in this region, the fact that the elastic scattering of electrons from a potential change is weaker at higher energies [60]. However, this should be accounted for in our model, which does not show any decrease in amplitude in the higher-energy set of oscillations.

When comparing our results to those calculated by Feenstra et al. [47], we see that the two results agree quite well, with a small difference in the energies at which the reflectivity minima occur on the order of less than 0.5 eV. This shift becomes a more crucial difference in the results for six layers of graphene, for which we find only four reflectivity minima in the lower energy oscillations while Feenstra et al. find five. In some sense, it appears as if a minimum in our curves has fallen below 0 eV. However, an attempt to calculate reflectivity using solutions below the vacuum energy did not produce a minimum at negative energy. These differences are likely due to the difference in the type of DFT calculations we have used. We have used an ultrasoft pseudopotential method, while Feenstra et al. use the projector-augmented wave method. While we do not see the lowest energy minimum, we do see a slight inflection point very close to 0 eV. This is quite similar to what is seen in experiments of Hibino et al. [59]. For seven and eight layers, we find five and six minima,
respectively, while the experiments also show at most an inflection point that could be counted as the lowest energy minimum. Between energies of 15 and 20 eV, our results display \( m - 1 \) minima for \( m \) layers of graphene for systems of one through eight layers, in agreement with Feenstra et al.

The results also show that for one layer of graphene, the reflectivity has a peak at 25 eV and a minimum around 30 eV. This minimum may be due to the quantum interference within a single layer. If so, the fact that FLG is a weakly-coupled layered system would explain why this minimum actually appears in all spectra. Nazarov et al. suggest that the peak and the minimum are caused by a resonant state in the single graphene layer near 25 eV that couples the in-plane and out-of-plane motion of the electron.

Looking at the band structure for bulk graphite in Fig. 4-2 (b), we see that the positions of the two sets of oscillations correspond well to the two dispersive bands in bulk graphite. For energies between these three major valleys, nearly complete reflection is found, even for just two layers. These significant levels of reflection can be correlated to the “energy gaps” in the bulk graphite band structure along \( \Gamma-A \) if certain nearly flat bands are ignored. Much of this has been established previously [59], however, we discuss it here in anticipation of our extension to general angles of incidence.

It is also interesting to compare our results to the computed and measured transmission for (semi-infinite) graphite in the work of Strocov et al. [39]. The computed transmission coefficient, with no damping parameter, is almost identically 0 for areas in the band gaps of bulk graphite and rises into smooth, broad peaks at the energies of the two lowest energy dispersive bands as well as for a few other bands at higher energies (which they identify through the computation of Bloch wave partial absorbed currents [43, 44]). It appears, after an energy shift, to be very nearly the complement (in the sense of \( 1 - Reflectivity \)) of our computed reflectivity for 8 layers of free-standing graphene if the oscillations were averaged. The main difference is in the height/depth of the peak/valley located near 30 eV in our curve. In their method, they are able to add an optical
potential to smooth and damp their calculated $\frac{dT}{dE}$ curve and compare to the $\frac{dT}{dE}$ collected from a target current spectroscopy experiment. The agreement is very good, including the reproduction of a slight peak shoulder caused by a narrow feature in the transmission curve similar to that seen in our reflectivity curves at 17.5 eV. The authors claim that this feature is caused by the ‘hybridization’ of a localized (in $z$) state with a delocalized one. We have found a similar hybridization of our supercell states for few-layer graphene, as will be discussed in Ch. 6. The fact that they contribute to the reflectivity in graphene calculated with a semi-infinite crystal method suggests that these are not artifacts of the supercell geometry, as suggested by Gao et al. [50].

### 4.3.3 General Incidence Scattering from Few-Layer Graphene Systems

We now consider the general situation, where the incident beam is not necessarily aligned with the surface normal. In the specular reflection regime, where no higher-order diffraction is present, the parallel component of the incoming wave vector, $q_\parallel$, is limited to the first Brillouin zone, i.e., $q_\parallel = k_\parallel$. The energy range of the electron beams is constrained between a lower limit, $\frac{\hbar^2 q_\parallel^2}{2m}$, and the upper cut-off, $E_c(q_\parallel)$, discussed in Sec. 3.2.1. Fig. 4-4 displays the calculated reflectivity spectra for systems of one, two, three, four, and five layers of free-standing graphene. They are shown in colormaps in the $q_\parallel$–$E$ space, along a path of $q_\parallel$ corresponding to $M$–$\Gamma$–$K$. The curve for a fixed incident angle is a parabola in these spectra, starting at $(\Gamma, 0)$ and increasing toward $M$ or $K$. The energy match threshold is 0.0001 Ry. The spectra are filtered such that $\sigma > 0.01$. After filtering, a linear interpolation over the calculated energy points is made for each $q_\parallel$ to calculate reflectivity on a uniform grid for plotting as a colormap.

Our calculations show that the spectra at small incidence angles (a few degrees or less) have features similar to the normal incidence spectra ($q_\parallel = \Gamma$) with small energy shifts. These include the layer-independent minimum at 30 eV and peak at 25 eV and the layer-dependent oscillations between 0–20 eV. At angles above this, we find the peak at 25 eV in the normal incidence curve.
Figure 4-4: **General incidence FLG reflectivity**: Reflectivity spectra shown as colormaps for (a) one, (b) two, (c) three, (d) four, and (e) five layers of free-standing graphene for incident beams with in-plane wave vectors along $M$–$\Gamma$–$K$. Yellow arrows in (a) highlight the splitting of the peak at 25 eV. The filtering for all spectra is $\sigma > 0.01$. 
splits into three peaks as $q_\parallel$ moves away from $\Gamma$. This three-way splitting is most clearly seen in the one-layer spectra; in Fig. 4-4 (a), the three peaks are marked with arrows. One peak shifts upward in energy, one persists near 25 eV, and the third shifts downward in energy to below 10 eV at $M$ and at a point between $\Gamma$ and $K$ about the same distance from $\Gamma$ as the distance from $\Gamma$ to $M$. In multilayer systems our results show, despite some difficulties with resolving sharp features, that the same three-way splitting of the 25 eV peak occurs [Fig. 4-4(b–d)]. However, the downward shifting peak merges with the emerging 10 eV peak about half way between $\Gamma$ and the in-plane zone boundary. Our spectrum for one layer of graphene agrees well with that in Nazarov et al. [64], except for the presence of a broad, low peak from 3-7 eV in their spectrum. It is unlikely that this is related to their use of an all-electron potential, as opposed to our use of pseudopotentials, since the results of Feenstra et al. [47] do not show the peak despite their use of all-electron potentials. (Our framework does not require the use of pseudopotentials, it was just the choice of Quantum ESPRESSO that led us to use pseudopotentials.) Nazarov et al. also makes use of supercell calculations in this paper, so the difference must be caused by the difference in matching procedures or the specific type of DFT. They use a variational matching approach and LAPW.

The layer-dependent oscillations in reflectivity seen in normal incidence spectra occur for a wide range of $q_\parallel$ in the general incidence reflection. For electron energies less than 10 eV, the oscillation peaks shift to higher energies as $q_\parallel$ moves away from $\Gamma$ and toward $M$ or $K$. The shifts to higher energy are somewhat parabolic, as was seen for the perturbed square trough in Fig. 3-17, suggesting that the electron states associated with these oscillations are free-electron-like in-plane. Indeed, Feenstra et al. have argued that the reflectivity minima coincide with the interlayer bands of graphite [47], which are known to be free-electron-like in-plane [68, 69]. The lowest energy reflectivity minimum is lost as $q_\parallel$ approaches $M$ and $K$, and the full set is lost once $q_\parallel$ is about 85% of the way to $K$. These results are qualitatively consistent with measurements of general incidence LEEM-IV curves for one and two layers of graphene (plus the carbon buffer layer) on SiC [70],
which show the lowest energy set of minima increasing in energy with a similar parabolic shape. These results are not yet published, so a careful comparison has not been possible. This group interprets their results as a partial mapping of the (two-dimensional) conduction band structure of few-layer graphene systems, equating the minima with the existence of the interlayer band, based on the discussions in [47]. Our general incidence results could aid in this interpretation, allowing for a direct connection between reflectivity features and electron wavefunctions.

The second set of layer-dependent oscillations between 14 and 21 eV exists for a smaller range of $q_\parallel$ than the first set; it is limited by the downward shifting peak originating from 25 eV discussed in the previous paragraph. Interestingly, a new set of layer-dependent oscillations emerges near the $K$-point. These oscillations appear in the energy range of 9–15 eV. There may be additional sets of layer-dependent oscillations at higher energies near both $M$- and $K$-points, but our results are clear in that region. Without including inelastic effects, it is difficult to predict how many of the spectral features in these regions will be experimentally observable. The one glimpse of general incidence data that I have seen [70] suggests that the intensity is too low in most of these regions of the spectra to resolve these features, but experimental techniques can often be improved.

In addition to the spectra shown in Fig. 4-4, we have also calculated the general incidence spectra for three layers of graphene in the ABC stacking. The results do not differ noticeably from those for the Bernal stacking.

There are narrow dispersive features present in these spectra. The small filter threshold that we have used has left many of these features in. (As can be seen in Figs. 4-5 and 4-6, a higher threshold would remove some of them, e.g., those between 5 and 15 eV.) Also, some narrow features are broadened by the linear interpolation when they appear in an artificial band gap. As discussed in Ch. 6, these may be caused by resonant states and, thus, may be physical effects that would be difficult to resolve experimentally. Alternatively, they may be due to the presence of solutions unfit for matching that are not being properly filtered out. Nazarov et al. appear to find some of
these in their (monolayer) spectrum as well, but they do not discuss them [64]. One such feature also appears in the calculated off-normal transmission spectra of semi-infinite graphite in [39]. In this work, the authors claim that this feature is faintly noticeable in their experimental off-normal VLEED spectra. This is more evidence to suggest that these features are not artifacts of the supercell geometry.

Figures 4-5 and 4-6 show one-dimensional cuts in the general incidence spectra at fixed values of $q_\parallel$, one between the $\Gamma$-point and $M$ and one between $\Gamma$ and $K$. In the reciprocal lattice basis, 
\[ \{b_1 = \frac{2\pi}{a}(1, \frac{1}{\sqrt{3}}), b_2 = \frac{2\pi}{a}(0, \frac{2}{\sqrt{3}})\} \], the two $q_\parallel$ for which results are displayed are $(0, 0.05)$ and $(0.05556, 0.05556)$. These plots show that there are quite a few sharp features that are not filtered out at off-normal incidence, which produce the streaks in the full general incidence spectra. Filtering at off-normal incidence is more complicated than at normal incidence. For instance, the four very flat and nearly degenerate bands at normal incidence around 4 eV, whose supercell FLG relatives are easy to filter out, splits into two pairs of flat nearly degenerate bands in the off-normal bulk graphite band structure. It appears that the supercell FLG bands associated with one of the pairs is easier to filter than the other. These one-dimensional off-normal spectra can also display that the energy-sorting algorithm has made some mistakes in pairing solutions. In the spectra for two and four layers of FLG in Fig. 4-5, there are points where the calculated reflectivity is greater than one and regions where the reflectivity curve is clearly erroneous, e.g., between 25 and 30 eV in the four-layer curve. This only occurs for even numbers of layers because the systems with odd numbers of layers are mirror symmetric, guaranteeing the exact degeneracy of a pair of computed solutions, since solutions are computed on a symmetric path in the Brillouin zone and the mirror symmetry implies that solutions with $k_z$ and $-k_z$ are degenerate. There is also apparently a symmetry in all systems that implies the degeneracy of solutions with $k_\parallel$ and $-k_\parallel$ for $k_\parallel$ between $\Gamma$ and $K$, as the curves for those points do not have any matching issues. Note that the colormaps for the general incidence spectra (throughout this dissertation) have been ‘capped’ at reflectivity of one, meaning
that all computed reflectivities above one are set to one for the purposes of plotting. All of these issues are discussed in more detail in Ch. 6.

While the energy-sorting algorithm is not perfect in finding matching pairs, it significantly improves results over the incorrect assumption that solutions with $k_z$ and $-k_z$ are degenerate. Fig. 4-7 allows for the comparison of the general incidence spectra for two-layer FLG computed with this assumption and with the use of energy sorting. For $q_\parallel$ between $\Gamma$ and $M$, especially far from $\Gamma$, the energy-sort algorithm corrects many miscalculated reflectivities, many of which are simply plotted as the maximum plotted value, one, when in fact they are greater than one. As mentioned above, a symmetry in the system ensures that solutions with $k_z$ and $-k_z$ are degenerate for $k_\parallel$ between $\Gamma$ and $K$, thus the results for the two methods agree on that side. However, for $k_\parallel$ between $\Gamma$ and $M$,
Figure 4-6: **Off-normal incidence FLG reflectivity between $K$ and $\Gamma$:** (a) Reflectivity spectra for incident beams with $\mathbf{q}_|| = 0.05556\mathbf{b}_1 + 0.05556\mathbf{b}_2$ reflecting from 1 to 5 layers of free-standing graphene, bottom to top. The calculated data points are shifted vertically in integers for clarity. The filtering for these spectra is $\sigma > 0.01$. (b) Band structure of bulk graphite along a $k$-path parallel to $\Gamma$ to $A$ with $\mathbf{k}_|| = 0.05556\mathbf{b}_1 + 0.05556\mathbf{b}_2$. The Fermi level of the bulk graphite is aligned with the Fermi level of the 5-layer free-standing graphene. (c) Same as (a) with filtering $\sigma > 0.1$. (d) Same as (b).
Figure 4-7: **Comparison of two methods for computing off-normal reflectivity for two-layer graphene:** (a) general incidence reflectivity spectra for two-layer graphene computed using the incorrect assumption that solutions with wave vectors with $z$-components $k_z$ and $-k_z$ are degenerate. These spectra have been filtered using the determinant of the matching matrix, Eq. 3.42, with threshold value 0.15. (b) general incidence reflectivity spectra for two-layer graphene computed using the energy-sort method to find degenerate pairs of solutions. These spectra are filtered with $\sigma > 0.1$ because this matches the filtering in (a) better than $\sigma > 0.01$.

This degeneracy does not hold and energy sorting is needed to find the correct degenerate pairs.

As an extension of what has been found for normal incidence scattering from FLG discussed in Sec. 4.3.2, we find correspondences between reflectivity peaks and ‘energy gaps,’ and between layer-dependent oscillations and dispersive bands for the general incidence spectra. Fig. 4-8 shows the band edges of certain dispersive bands in the bulk graphite band structure. To find these band edges, we look at band structures along cuts through the first Brillouin zone parallel to $\Gamma$–$A$ at fixed values of $k_\parallel$. In the normal incidence band structure ($k_\parallel=0$), we identify the dispersive bands whose edges correspond to reflectivity maxima and then follow those bands as $k_\parallel$ changes. Note that we also include a marginally dispersive band just below 25 eV. There is no visible reflectivity minimum at this energy range in the normal incidence spectra shown in Fig. 4-2. However, for $q_\parallel$ slightly away from the $\Gamma$-point the 25-eV peak splits, and this split clearly coincides with this particular band. A comparison to Fig. 4-4 reveals that these gaps coincide with peaks in the calculated reflectivity spectra, with the degree to which they coincide increasing with the number of layers of graphene.
Figure 4-8: **Band edges of certain dispersive bands in bulk graphite:** Each connected trace of solid points shows the position of the band edge of a bulk graphite band, along a cut parallel to $\Gamma-A$, as a function of $k_\parallel$. Each band edge is only recorded when the connection to the band at $\Gamma$ is clear. Cross-hatching marks the regions of ‘energy gaps.’ The dashed lines denote the energy limits for specular reflection only.
However, the match is still fairly good even for one layer of graphene, indicating the quasi-two-dimensional nature of graphite’s electronic structure. The band edges that may correspond to the highest-energy peaks shown in the reflectivity spectra (Fig. 4-4) are too difficult to identify consistently. Thus, they are not included in Fig. 4-8.

4.3.4 Normal Incidence Scattering from Few-Layer Graphene on Nickel Substrate

The FLG-Ni system admits a $1 \times 1$ interface lattice structure [71, 72, 73] because the lattice constant of graphene is shorter than the (experimental) in-plane lattice constant of Ni(111) by only 1%. For the first layer of graphene, the two carbon atoms in a unit cell are located above the Ni atoms in the first and the third layers, as shown in Fig. 4-9 (a). For Bernal stacking, the second layer of graphene has two possible placements. We use the model given in [72], as shown in Fig. 4-9 (b). We calculate the spacing between Ni and graphene to be $\sim 2.05$ Å. Relaxation produces little change in the spacing between Ni layers from the value in the bulk. The spacing between the graphene layers in a bilayer system is 3.18 Å. For 3 layers of graphene on Ni, the spacings are 3.27 and 3.17 Å from top to bottom. Dipole corrections [74] are added to the Ni side of the vacuum region to account for the asymmetry of the FLG-Ni systems. We choose the vacuum potential on the FLG side to be zero. The potential near the Ni surface is higher by approximately 1.9, 1.5, and 1.3 eV for one, two, and three layers of graphene, respectively. The pairs of supercell widths used for systems of graphene on Ni are the following multiples of the in-plane lattice constant, $a_{Ni} = 2.42$ Å: (18, 20), (19, 20), (20, 23), and (21, 22) for 0–3 layers of graphene, respectively. For consistency between different supercell sizes, the ground-state calculation for each system in the larger supercell is performed with the structure determined for that system through a relaxation in the smaller supercell.

Figure 4-10 shows the calculated, normal incidence reflectivity spectra for slabs consisting of 10
Figure 4-9: **FLG on Ni(111) structure:** Models of graphene on Ni(111) used in DFT calculations. (a) Top view along the surface normal direction of single-layer graphene on Ni. The hexagons of the graphene layer are centered on the Ni atoms (B sites) in the second layer. (b) Side view of 2 layers of graphene on Ni with the hexagons of the top graphene layer centered on the Ni atoms (A sites) in the first layer. Nickel atoms are colored and sized for visual contrast. Atomic visualization created with XCrySDen [3].

layers of Ni covered by 0–3 layers of graphene. These spectra were computed using the algorithm for normal incidence, described in Sec. 3.2.2. They have been filtered using the determinant of the matching matrix from Eq. 3.42, with different threshold values used for different energy ranges. This filtering removes more sharp features than the σ method does.

For the bare Ni surface, there are two apparent peaks between 20–30 eV, consistent with experimental observations [72]. The valley below 20 eV corresponds well to a dispersive band in bulk Ni. The reflectivity in the valley oscillates in a fashion similar to that of the free-standing FLG results. The number of oscillations is related to the number of layers in the Ni slab. Our results are quite consistent with the results calculated for a semi-infinite Ni surface [75]. For the system covered by one layer of graphene, the reflection curve does not have significant features, except for the oscillations due to the finite slab of Ni. For two and three layers, the two valleys in the reflectivity spectra stand out quite clearly, and the amplitudes of the finite-slab oscillations reduce significantly.
for energies between the valleys. This is likely due to the high reflectivity of FLG in these energy ranges. The number of oscillations in each valley is tied to the number of graphene layers, in the same way as for free-standing FLG. It also appears that the valleys are shifted to higher energies as compared to free-standing FLG. These results are in fair agreement with experimental IV curves for FLG on Ni(111) [76], which show the minima at higher energies than experimental curves for FLG on SiC.

While the study of graphene on a substrate has produced results somewhat comparable to experiment, it seems that the finite size of the substrate model, and the associated oscillations, makes it difficult to clearly interpret the calculated reflectivities. For the study of few-layer systems on substrates a modification of the method is likely the best approach. For instance, Srivastava et al. have demonstrated that the finite-size oscillations can be eliminated by matching the wave functions at the center of a symmetric slab to the bulk wave functions [49]. There are no fundamental difficulties with modifying our method in the same way to handle substrates.
Figure 4-10: **Normal incidence FLG on Ni(111) reflectivity**: (a) Reflectivity spectra for a beam normally-incident upon 0–3 layers of graphene on 10 layers of Ni, bottom to top. The calculated data points are shifted vertically in integers for clarity. The solid lines are a guide to the eyes. The free-standing FLG results with the same number of graphene layers are shown in dotted lines for comparison. The dotted lines have been shifted in energy by the dipole correction. (b) Band structure of bulk Ni along (111) from $\Gamma$ to $L$. The Fermi level of bulk Ni is aligned with the Fermi level of the 10-layer Ni slab.
Chapter 5

Low-Energy Electron Reflectivity from Few-Layer Molybdenum Disulfide Systems

5.1 MoS\textsubscript{2} Structure and Properties

Transition metal dichalcogenides (TMDs) form a large class of materials whose members’ electronic and optical properties can depend sensitively on the detailed structure of bulk and few-layer systems [77]. Numerous recent (and past) investigations of molybdenum disulfide have shown it to be a prime example of this correspondence between structure and function, leading to great excitement over its potential applications in energy, electronics, sensing, and other industries through the tuning of its properties by manipulating its structure. Before giving examples of the relationship between structure and properties, we must explore the different forms that MoS\textsubscript{2} can take. Bulk MoS\textsubscript{2} has three polymorphs: 1T, 2H, and 3R, the first being a metal and the latter two semiconductors [78, 79, 80, 81]. In fact, as shown in Fig. 5-1, there are two types of one layer of MoS\textsubscript{2}, 1H and 1T. In the 1H structure, the sulfur atoms are directly above one another. From the top, it is clear that the molybdenum atoms form one hexagonal lattice and the sulfur each form another. Together they form a honeycomb lattice, like graphene, with, say, molybdenum at the A site, sulfur at the B
site, and nothing at the C site. In the 1T structure, the sulfur are not directly above one another. As shown in the top view, each layer within the layer still forms a hexagonal lattice, but there is no clear honeycomb structure. If again the molybdenum atoms are at the A sites, then one layer of sulfur is at the B site and the other at the C site.

A few different multilayer systems are possible. 1T-MoS$_2$ stacks with one layer directly on top of another with no shift or rotation. When 1H layers stack, however, there are different possibilities. Fig. 5-2 shows two possibilities for three layers of 1H-MoS$_2$. In 2H-MoS$_2$, the molybdenum atoms alternate between the A and B sites (and the sulfur alternate between B and A). In the 3R structure, the molybdenum atoms cycle through the A, B, and C sites as the layers increase (as do the sulfur atoms, starting with B). The bulk versions of 2H and 3R structures of course simply repeat these patterns infinitely, and multilayered systems other than trilayer are just truncations of these.

The types of properties determined by these different structures are best illustrated by a few examples. Valley-dependent spin polarization has been found in bulk 3R-MoS$_2$, made possible by its lack of inversion symmetry [81]. It has also been found in 1H-MoS$_2$, which is similarly noncentrosymmetric [82, 83]. Inversion symmetry also affects the optical properties of few-layer 2H structures: second-harmonic generation is only possible in systems with odd numbers of layers, i.e., those which are noncentrosymmetric [84]. It has also been suggested to play a part in piezoelectricity [85]. The metallic 1T phase has been used to improve contacts on MoS$_2$ transistors [86]. Finally, it is well-known that MoS$_2$ goes from having an indirect bandgap in multilayers to a direct bandgap in a single layer.

Just as is the case for graphene, this wide variety of structures and properties for MoS$_2$, and other TMDs[77], makes it crucial to have tools for identifying the phase, number, and stacking sequences of these materials. The differences in optical responses allow for some optical determinations of structure, like second-harmonic generation [84]. X-ray photoemission spectroscopy can be used for differentiating the 1T phase from the 1H phase, while Raman spectroscopy has been used for layer
Figure 5-1: **One-layer MoS$_2$ polymorphs**: (a) Side view and (b) top view of 1H-MoS$_2$. (c) Side view and (d) top view of 1T-MoS$_2$. Molybdenum atoms are larger and purple, while the sulfur atoms are smaller and yellow. Atomic visualization created with XCrySDen [3].
Figure 5-2: Three-layer MoS$_2$ polymorphs: (a) Stacking of the 2H-MoS$_2$ structure. (b) Stacking of the 3R-MoS$_2$ structure. Note that in both structures, each layer is a 1H-MoS$_2$ layer. Molybdenum atoms are larger and purple, while the sulfur atoms are smaller and yellow. Atomic visualization created with XCrySDen [3].
counting and phase determination in some TMDs [77].

Here I present our results for normal and off-normal incidence reflectivity from few-layer MoS$_2$ systems. At present, these are predictions because there are no published results with which to compare. However, they suggest that low-energy electron microscopy, specifically LEEM-IV, could be used as a tool for determining the number of layers in such systems, as well as the phase and stacking structure, again with the advantages that it can be performed *in-situ* with temporal resolution and with spatial resolutions far exceeding those of Raman and x-ray photoemission spectroscopies.

### 5.2 LEEM Studies of MoS$_2$

There has been much less work on studying few-layer MoS$_2$ systems with LEEM than there has been for graphene, but the literature is growing, and we are aware of one unpublished LEEM-IV measurement, associated with the LEEM imaging and µLEED investigation of few-layer MoS$_2$ described in [87]. There has been some experimental and theoretical work on LEED from bulk crystals of MoS$_2$ and other TMDs. Van Hove *et al.* analyzed LEED data to study the structure near the surface of bulk MoS$_2$. They found that there is no change in lateral arrangement, a 5% contraction of the top interplanar spacing, within the top layer, and a 3% contraction of the Van der Waals gap between the top two layers [88, 89]. LEED reflectivities from bulk MoS$_2$ in the specular regime were calculated using a scattering matrix approach in 1984 [90]. Modern theoretical studies of LEEM reflectivity from transitional metal dichalcogenides have been carried out by Krasovskii with others on bulk NbSe$_2$, TiS$_2$, TiTe$_2$, and VSe$_2$ [40, 41, 42]. Van Hove’s surface structure determination for bulk MoS$_2$ is the closest thing we have found to calculations of IV curves for few-layer TMDs.
5.3 Supercell, Bloch Wave Matching: Few-Layer MoS$_2$

In the following sections, I first describe the details of the models we study and our DFT calculations on them. Then, I show applications of the method to normal incidence scattering from free-standing MoS$_2$ systems. Our results predict layer-dependent oscillations and phase- and stacking-dependent features that would make LEEM-IV a very valuable tool in the monitoring and study of few-layer MoS$_2$ systems. Finally, I present the full LEEM reflectivity results for free-standing 1T-, 2H-, and 3R-MoS$_2$ with general incidence angles.

5.3.1 DFT Details for Few-Layer MoS$_2$ Systems

DFT calculations are performed using the open-source QUANTUM ESPRESSO software package. [65] A relaxation of the bulk 2H structure with a $16 \times 16 \times 6$ Monkhorst-Pack grid produces an in-plane lattice constant, $a = 3.1$ Å, close to the experimentally accepted 3.16 Å[91]. For each slab system, all ground states and self-consistent potentials are calculated using a $16 \times 16 \times 1$ Monkhorst-Pack grid. Relaxations of the vertical coordinates produce relaxed layer spacings (Mo–Mo) of: 5.98 Å for 2H bilayer, 5.85 Å for 1T bilayer, 6.02 Å for 2H trilayer, 5.83 Å for 1T trilayer, and 6.00 and 5.99 Å for 3R trilayer, all smaller than but within 5% of experimental values [91]. The general incidence spectra presented here are calculated using two different supercell sizes, sufficient to resolve the relevant features and to check consistency between different supercells, while the normal incidence spectra use 2–4 supercell widths, as necessary to clarify certain features in Figs. 5-3 (a), 5-4 (a), and 5-5 (a). The minimum distance from the surface layers of the slab to the supercell boundary is 14 Å. For consistency between different supercell sizes, the ground-state calculation for each system in a larger supercell is performed with the structure determined for that system in the smallest supercell. We perform the non-self-consistent band structure calculations on 72 $k$-points along paths parallel to $A$–$\Gamma$–$A$ in the Brillouin zone, at fixed $k_\parallel$ values. The $k$-points are symmetric with respect to $\Gamma$ and equally spaced from $\Gamma$ to $A$. For general incidence
scattering, we calculate 59 $k_\parallel$-points along the $M$–$\Gamma$–$K$ path. The local density approximation, ultrasoft pseudopotentials, and Perdew-Zunger exchange-correlation are used in all calculations. The plane wave cutoff energy is 60 Ry; in fact, there are two cutoff energies: $ecutwfc$ is 60 Ry and $ecutrho$ is 240 Ry. $1T$-MoS$_2$ and the trilayer $2H$ and $3R$ systems are run with Gaussian smearing with a degauss value of 0.001 Ry (to obtain a Fermi energy with which to align the bulk MoS$_2$ band structure). The pairs of supercell widths used are the following multiples of $a$: (10,12), (12,14), and (14,16) for 1–3 layers, respectively. In addition, for normal incidence results for the $2H$ and $3R$ trilayer systems, an extra two supercell widths are used: 17,18 times $a$. Also, for the normal incidence results for $1T$ systems, one extra supercell is used for each system: 14, 16, and 18 times $a$ for 1–3 layers, respectively. All MoS$_2$ results are filtered with $\sigma > 0.01$.

5.3.2 Normal Incidence Scattering from Few-Layer MoS$_2$ Systems

We first consider incident beams that are normal to the surface, i.e., $q_\parallel = k_\parallel = 0$. Fig. 5-3 (a) shows our calculated reflectivity versus electron beam energy for one to three layers of $2H$-MoS$_2$ with a normally-incidence beam. The zero energy is referenced to the self-consistent potential in the vacuum regions (vacuum level). The cutoff energy $E_c(0)$ for the first-order diffraction at normal incidence is about 20.6 eV. The results show that even for one layer of MoS$_2$, the reflectivity has significant features at low energies, in contrast to free-standing graphene [59]. The minimum at 7.5 eV is clearly a one-layer manifestation of a layer-dependent property, coinciding with two and three minima in the two- and three-layer spectra. Between 4 and 5 eV, a layer-dependent feature emerges beginning in the two-layer spectrum as a single minimum, becoming two minima in the three-layer spectrum. These features should make LEEM-IV a powerful tool for unambiguous layer counting in few-layer $2H$-MoS$_2$ systems, as it has been for few-layer graphene systems. There are also very narrow layer-dependent features between 3 and 4 eV, however, they have somewhat smaller $\sigma$ values than other states and thus have some chance of being unphysical or unobservable.
Figure 5-3: 2H-MoS2 layer dependence: (a) Reflectivity spectra for a beam normally-incident upon 1 to 3 layers of free-standing 2H-MoS2, bottom to top. The calculated data points are shifted vertically in integers for clarity. (b) Band structure of bulk 2H-MoS2 along the hexagonal axis from Γ to A. The Fermi level of the bulk MoS2 is aligned with the Fermi level of the trilayer free-standing MoS2. The filtering is ς > 0.01.
Figure 5-4: **1T-MoS\textsubscript{2} layer dependence**: (a) Reflectivity spectra for a beam normally-incident upon 1 to 3 layers of free-standing 1T-MoS\textsubscript{2}, bottom to top. The calculated data points are shifted vertically in integers for clarity. (b) Band structure of bulk 1T-MoS\textsubscript{2} along the hexagonal axis from \( \Gamma \) to \( A \). The Fermi level of the bulk MoS\textsubscript{2} is aligned with the Fermi level of the trilayer free-standing MoS\textsubscript{2}. The filtering is \( \sigma > 0.01 \).
Figure 5-5: MoS$_2$ stacking dependence: (a) Reflectivity spectra for a beam normally-incident upon 3 layers of free-standing MoS$_2$, in the 3R (red) and 2H (black) configurations. The calculated data points are shifted vertically in integers for clarity. Lines are simply a guide to the eye. (b) Band structure of bulk 3R-MoS$_2$ along the hexagonal axis from Γ to A. (c) Band structure of bulk 2H-MoS$_2$ along the hexagonal axis from Γ to A. In each band structure, the Fermi level of the bulk MoS$_2$ is aligned with the Fermi level of the free-standing MoS$_2$. The filtering is $\sigma > 0.01$. 
We also see from Fig. 5-3 (b) (and Fig. 5-5 (b) and (c)) that for 2H-MoS$_2$, band gaps in the bulk band structure normal to layer planes tend to correspond to reflectivity peaks, and dispersive bands correspond to layer-dependent oscillations as found in graphene [60]. A preliminary comparison with unpublished, experimental LEEM-IV curves for free-standing and supported 1H- and 2H-MoS$_2$ (taken from experiments described in Yeh et al. [87]) shows that while some calculated features are present in the experiment, many are not or are muted due to effects not included in our calculations, like temperature and inelastic collisions.

Fig. 5-4 shows that LEEM-IV should also easily distinguish the 1T phase from the 2H phase of MoS$_2$. In one, two, and three layer 1T-MoS$_2$, there are two clear regions of low reflectivity between 1.5 and 3.5 eV, while all 2H systems show complete reflection through that energy range. This energy range may allow for determining layer number in 1T systems, with a significantly higher peak between the two minima for bilayer compared to monolayer and additional minima in the trilayer spectrum. Higher energy ranges display much clearer layer dependence. The spectra at energies above 12.5 eV show an increase in the number of minima with each additional layer; from 6.5 eV to 9.5 eV, it appears to do the same, however, the presence of flat bands in the supercell band structure make it less clear. As seen in Fig. 5-4 (b), the correspondence between bulk band structure and reflectivity is not as clear for 1T-MoS$_2$. In fact, a nearly degenerate pair of strongly dispersive bands exist through much of the broad reflectivity peak from 9 to 12.5 eV.

Fig. 5-5 shows our calculated reflectivity spectra for the 2H and 3R stackings of trilayer MoS$_2$. There are only small differences in the spectra below 10 eV, although a calculation of the 2H structure with 3R layer spacing confirms that the difference is due to more than just differences in layer spacings. There are significant differences at higher energies, including additional small peaks between 10 and 15 eV for the 2H structure and a more pronounced, wider peak in the 3R structure between 15 and 18 eV. The latter feature could allow for the use of LEEM-IV as a method for distinguishing stacking structure in MoS$_2$ systems, depending on the intensity of the signal in this
energy range for MoS\(_2\). This is in contrast to our calculations on three-layer graphene systems which show no stacking-dependence for Bernal versus ABC systems.

### 5.3.3 General Incidence Scattering from Few-Layer MoS\(_2\) Systems

We now consider the general situation, where the incident beam is not necessarily aligned with the surface normal. In the specular reflection regime, where no higher-order diffraction is present, the parallel component of the incoming wave vector, \(q_\parallel\), is limited to the first Brillouin zone, i.e., \(q_\parallel = k_\parallel\). The energy range of the electron beams is constrained between a lower limit, \(\hbar^2|q_\parallel|^2/2m\), which is simply the energy of the lowest energy beam with in-plane wave vector \(q_\parallel\), and the upper cut-off, \(E_c(q_\parallel)\), discussed in Sec. 3.2.1. Fig. 5-6 shows the general incidence reflectivity spectra for monolayers of 1T- and 1H-MoS\(_2\). Fig. 5-7 displays the calculated reflectivity spectra for systems of two and three layers of free-standing 2H-MoS\(_2\) and for three layers of free-standing 1T-MoS\(_2\). All spectra are shown in colormaps in the \(q_\parallel–E\) space, along a path of \(q_\parallel\) corresponding to \(M–\Gamma–K\). A linear interpolation of calculated energy points is made for each \(q_\parallel\). These spectra exhibit very complex features, presumably due to the complex band structure of MoS\(_2\). The broad valley containing two minima and one peak at low energies in the normal incidence spectrum of 1T-MoS\(_2\) moves up in energy parabolically away from \(\Gamma\) but also narrows until it becomes a very sharp feature (in Fig. 5-6 (a)). The two minima between 6.5 and 8.5 eV in the normal incidence spectrum behave very differently away from \(\Gamma\). The broader valley around 7 eV persists only a short way toward \(M\) and \(K\), remaining near 7 eV. The narrow valley slightly above 8 eV follows a drastically curved path away from \(\Gamma\), broadening significantly as it moves toward \(M\). Finally, there are features at 5, 9, and 12.5 eV in the general incidence 1T-MoS\(_2\) spectrum that appear only away from the \(\Gamma\)-point, meaning that even slightly off-normal LEEM-IV curves may appear very different from normal incidence spectra. The 2H-MoS\(_2\) monolayer spectrum (Fig. 5-6 (b)) contains mostly narrow features at energies below 7.5 eV, with two broad valleys around \(\Gamma\) appearing at energies above 11...
Figure 5-6: One-layer MoS$_2$ general incidence reflectivity spectra: Displayed as colormaps for (a) one layer of 1T-MoS2 and (b) one layer of 1H-MoS2 for incident beams with in-plane wave vectors along $M$–$\Gamma$–$K$. Filtering is $\sigma > 0.01$. 
Figure 5-7: Multilayer MoS\textsubscript{2} general incidence reflectivity spectra: Displayed as colormaps for (a) two layers and (b) three layers in 2H stacking and (c) three layers in 3R stacking of free-standing MoS\textsubscript{2} for incident beams with in-plane wave vectors along $M$–$\Gamma$–$K$. Filtering is $\sigma > 0.01$. 
Figure 5-8: **Comparison of two methods for computing off-normal reflectivity for twolayer 2H-MoS$_2$:** (a) general incidence reflectivity spectra for two-layer 2H-MoS$_2$ computed using the incorrect assumption that solutions with wave vectors with $z$-components $k_z$ and $-k_z$ are degenerate. These spectra have been filtered using the determinant of the matching matrix, Eq. 3.42, with threshold value 0.3. (b) general incidence reflectivity spectra for two-layer 2H-MoS$_2$ computed using the energy-sort method to find degenerate pairs of solutions. These spectra are filtered with $\sigma > 0.1$ because this matches the filtering in (a) better than $\sigma > 0.01$.

eV and a few other large valleys from 3–11 eV far from $\Gamma$. Looking at the monolayer and multilayer 2H-MoS$_2$, we find that the layer-dependent features around 4-6 eV and 7-9 eV persist away from $\Gamma$, but possibly not more than a quarter of the way to the Brillouin zone edge in either direction. These features have very little dispersion in-plane, suggesting that they do not arise from states that are free-electron-like in-plane, as suggested for the lowest-energy, layer-dependent features in few-layer graphene systems [47, 68, 69]. There is a resonance-like feature that meets with the lowest-energy layer-dependent feature in the 7-9 eV range but decreases in energy away from $\Gamma$, which would change the correspondence between reflection minima and layer number for slightly off-normal incidence IV measurements. There is a sharp reflectivity valley below 4 eV that is consistent across all the systems modeled and highly dispersive in-plane. The stacking dependence of the features between 14 and 18 eV is even more evident in the general incidence spectra. We are hopeful that just moderate signal strength in this range will allow for differentiation between the 2H and 3R structures.
As shown in Sec. 4.3.3, the energy-sort algorithm significantly improves results over the incorrect assumption that solutions with $k_z$ and $-k_z$ are degenerate for two-layer graphene. The improvement is even more pronounced in the case of two-layer 2H-MoS$_2$. Fig. 5-8 allows for the comparison of the general incidence spectra for two-layer 2H-MoS$_2$ computed with this assumption and with the use of energy sorting. For $q_\parallel$ between $\Gamma$ and $M$, the energy-sort algorithm corrects many miscalculated reflectivities, many of which are simply plotted as the maximum plotted value, one, when in fact they are greater than one.
Chapter 6

Limitations and Issues

In this chapter, I provide significantly more details on some of the issues and limitations in our supercell, Bloch wave matching approach that have been alluded to in previous chapters. I point out two physical effects that have not been included in our method. I provide a short discussion of the problem with extending our method to higher-order diffraction due to the difficulty in finding the correct number of solutions for the matching in the supercell geometry. I mention some of the issues that could be generated by a matching procedure that only matches a limited number of in-plane Fourier components. Then, I turn to two more serious issues. First, I provide an in-depth discussion of some solutions that produce unexpected features in our reflectivity curves that may be unphysical. I discuss the localized or somewhat localized natures of many of these solutions and the possibilities that some are caused by errors in approximating exponential solutions and that some are resonant-like states that do exist in physical systems. Finally, I demonstrate some of the downfalls of the energy-sorting approach to finding degenerate pairs of solutions for matching in the case of off-normal, specular reflection for systems without mirror symmetries.

6.1 Physical Effects Not Yet Included

There are two main physical effects that we have not yet tried to include in our framework for calculating low-energy electron diffraction intensities: inelastic collisions and temperature effects. Our calculation models elastically scattered electrons exclusively; the electrons lose no energy to
the system and emerge from the system at the same energy. In real scattering some electrons undergo inelastic scattering and emerge at a lower energy. LEEM and LEED devices are designed to detect only elastically scattered electrons, and so inelastic scattering will decrease the recorded intensity. Typically, the inelastic scattering increases with electron energy producing a decrease in recorded intensity as a function of energy. Gao et al. have developed a method to include this in their supercell, Bloch wave matching method [50].

Our calculation also does not include any temperature effects, essentially modeling scattering from a sample at absolute zero. Higher temperatures manifest as vibrations of the atoms in the crystal lattice and can cause decreases in peak heights due to imperfect constructive interference from a system of atoms displaced from their perfect crystal positions.

6.2 Determined Matching Systems for Higher-Order Diffraction

Our calculations are currently limited to energies in the specular reflection only regime. The general matching framework discussed in Ch. 3 is valid for first-order and higher-order diffraction, but finding the correct number of solutions to produce a determined matching system becomes problematic at higher energies. The use of a supercell limits the solutions that can be used in the matching to those in the real band structure. From investigating model systems and real systems, we have found that the required number of solutions to produce a determined matching system is often not present in the supercell band structure. Thus, to calculate higher-order diffraction intensities with this method, significant modifications of the algorithms are expected.

For the complex band structure methods, the danger of an under- or over-determined system is not a concern due to the inclusion of evanescent waves. After computing the complex band structure, one can include enough evanescent solutions both inside and outside the crystal in addition to the propagating Bloch solutions for the system to be fully determined. For Pendry and early methods, the number of Fourier components to include was chosen, then the number of evanes-
cent waves to include, both inside and outside the crystal, was chosen so that the total number of solutions on either side of the surface matched the number of Fourier coefficients. Following Krasovskii’s notation \[38\], the solution in the vacuum is given by the incoming wave and a set of reflected waves and evanescent waves of temporarily arbitrary size:

\[
\Phi(\mathbf{r}_\parallel, z) = e^{i\mathbf{q}_\parallel \cdot \mathbf{r}_\parallel} e^{i\mathbf{q}_\perp z} + \sum_s a_s e^{i(\mathbf{q}_\parallel + \mathbf{G}_s) \cdot \mathbf{r}_\parallel - q_s^z z},
\] (6.1)

and the solution inside the crystal can be written as a linear combination of \( N_{\text{sol}} \) (temporarily arbitrary) Bloch waves with energy \( E \) and Bloch wave vector (in-plane) \( \mathbf{k}_\parallel = \mathbf{q}_\parallel + \mathbf{G}_s^* \) in the first Brillouin zone:

\[
\Phi(\mathbf{r}_\parallel, z) = \sum_n t_n \psi_n (E, \mathbf{k}_\parallel; \mathbf{r}_\parallel, z). \] (6.2)

A finite Fourier approximation to a Bloch solution can be written in the Laue representation:

\[
\psi(\mathbf{r}_\parallel, z) = e^{i\mathbf{k}_\parallel \cdot \mathbf{r}_\parallel} \sum_{s=0}^{N_F-1} f_{sn}(z) e^{i\mathbf{G}_s^* \cdot \mathbf{r}_\parallel}. \] (6.3)

Thus, there is a finite set of plane waves making up each \( \psi_n \) (the same set since they all have the same \( \mathbf{k}_\parallel \)) and the only requirement on \( N_F \) is that it is large enough to include Fourier components for all reflected waves. When matching the values of \( \Phi \) at \( z = 0 \), the wave vectors of the set of reflected and evanescent waves outside the crystal must be the same as those of the Fourier components making up the \( \psi_n \). Thus, there will be \( N_F \) unknowns, \( a_s \), in the solution in the vacuum. And there will be two equations for matching the values and the normal derivatives for each Fourier component term. So there will be \( 2N_F \) equations. Thus, if enough evanescent states inside the crystal are chosen so that \( N_{\text{sol}} = N_F \), there will be the same number of unknowns as equations and the system will be soluble.

In the more recent methods, a variational approach is used, so that the number of evanescent waves to be included is also a choice, in addition to the choice of how many Fourier components of
solutions to keep. This choice of the number of evanescent waves to include can be guided by only including them only up to the point that the ‘quality’ of the trial wavefunctions is comparable to the quality of the Bloch solutions from the band structure calculation [46, 38].

The evanescent solutions in the case of the supercell are physically irrelevant, as they would be solutions that decay from one side of the supercell through the slab to the other side of the supercell. Thus, we must stick with the real band structure and solve for diffraction intensities only when we have the correct number of solutions. For the specular reflection regime, this is usually sufficient. For higher-order diffraction, it appears to be inadequate typically, and another approach must be sought. Perhaps, a least squares fit or the use of multiple supercell solutions together could be investigated.

6.3 Limited Fourier Component Matching

It is important to note that our method uses only those Fourier components of the Bloch solutions in the supercell corresponding to the same in-plane reciprocal lattice vectors as those that define the diffracted and reflected waves. Thus, for instance, in the specular reflection regime, only the $\mathbf{G}_\parallel = (0,0)$ component is involved in the matching. This simplifies the matching greatly, however, it does mean that if any of the supercell wavefunctions have higher-order character near the supercell boundary, those components are ignored in the matching procedure. Thus, in order to claim that our method is matching the vacuum solutions to the complete wavefunctions in the supercell, we must have that solutions are transformed almost completely into the free electron beams near the supercell boundary. This would imply that all higher-order Fourier components decay to negligible levels near the supercell boundary. It does not appear that this is the case for the states that we use. While the higher-order Fourier components are typically three to four orders of magnitude smaller than the $(0,0)$ component at the supercell boundary, they have not decayed to the level of numerical error. Also, in comparing the values of the components for solutions in supercells of
drastically different sizes (12 and 24 times the in-plane lattice parameter for five-layer FLG), it
does not appear to be the case that the values at the boundary are dropping exponentially with the
distance from the slab to the boundary. This may be a result of attempting to find exponentially
decaying solutions with Bloch boundary conditions (and Fourier expansions). It is possible that
the $(0,0)$ component, which does not decay, is accurately computed and that the reflectivity is as
well, but perhaps it should be investigated in more detail to see if the errors in the higher-order
terms affect the accuracy of the $(0,0)$ term.

6.4 Handling Non-Scattering and Resonance-Like States

Our algorithm relies on having a propagating state calculated from the supercell band structure to
match to the incoming and reflected plane waves. This means that the Bloch wave solution in the
supercell should become almost entirely plane-wave-like near the boundary of the supercell. In one
dimension, the only solutions that will be plane-wave like towards $\pm\infty$ are scattering states, those
with positive energy. The states with negative energy are bound states, and are square-integrable
over $\mathbb{R}$. However, in higher dimensions, wavefunctions can be localized in 1 to $n-1$ dimensions
and extended in the remaining directions and still be scattering states. (Localized in a given
dimension means that the function decays to zero in the positive and negative directions of that
dimension fast enough that the function is square-integrable over any Cartesian product of finite,
closed intervals in the other dimensions and $\mathbb{R}$ in the given direction.) Thus, in a three-dimensional
scattering problem, it is possible to have a solution which is localized in the scattering direction
($z$) but extended in the plane of the crystal surface. What is not immediately obvious is if and
how such solutions show up in the supercell band structure and how to treat them in the matching
algorithm. While the semi-infinite setup allows for infinitely many evanescent solutions [37], the
supercell geometry does not (at least not within the supercell). In the complex band structure of
a semi-infinite crystal, there are infinitely many evanescent solutions that decay into the crystal
Figure 6-1: **The square trough potential**: A square well potential in the scattering \((z)\) direction and constant in the ‘in-plane’ \((y)\) direction.

at any energy. In the semi-infinite vacuum, there are infinitely many evanescent states that decay into the vacuum at any energy. For the real band structure of the supercell that contains vacuum and a slab of the crystal, it is only at certain energies that one finds states with decaying nature towards the center of the crystal or towards the boundary. The solutions that decay towards the center of the crystal are not our concern, for if they connect to a state that propagates into the vacuum, this solution is simply a state of the slab (or an approximation of the scattering state for the semi-infinite crystal system) that reflects most of the incident electrons, and our matching algorithm finds this result. The concern consists of Bloch wave solutions of the supercell that decay toward the boundary.

It is instructive to consider model systems to aid in the understanding of these states. It is
simple to understand their nature for a separable system that I refer to as the two-dimensional square trough. Fig. 6-1 shows an illustration of the potential of this system. The potential is constant in the $y$-direction and a square well in the $z$-direction. The solutions to such a system are separable, of the form: $\psi(y, z) = e^{ik_y y} f_{SW}(z)$, where $f_{SW}(z)$ are solutions for the one-dimensional finite square well potential. The energy of a given solution is $E = k_y^2 + E_{SW}$, where $E_{SW}$ is the energy of the one-dimensional solution $f_{SW}$. Consider an electron beam approaching this system from the left in $z$ with some fixed energy, $E$, and wave vector, $q_y$. Now in the true square trough, the solution can be anything with the form $\psi(y, z) = e^{ik_y y} f_{SW}(z)$ with energy $E$. However, in anticipation of adding a weak potential with periodicity $a$ and reciprocal lattice $\{g\} = \{2n\pi/a\}_{n \in \mathbb{Z}}$, we consider only solutions with $k_y = q_y + g$ (Bragg condition for surfaces). Then the solutions with the lowest energies above $q_y^2$ will be products of $e^{iq_y y}$ and scattering states of the 1D square well, $f_{SW}^s(z)$. However, before the onset of the first-order diffraction limit at $E_c = (q_y + g)^2$, there will be a discrete set of solutions that are products of $e^{i(q_y + g)y}$ and bound states of the 1D square well, $f_{SW}^b(z)$, with energies $E = (q_y + g)^2 - E_{SW}^b$ (if we let energies of the 1D bound states be $-E_{SW}^b < 0$). At normal incidence, there will be a pair of degenerate solutions $e^{\pm ig_y y} f_{SW}^b(z)$ for each bound state. All of these solutions decay exponentially in the positive and negative $z$ directions. Each of these solutions will exist at the same energy as a solution of the form $e^{iq_y y} f_{SW}^s(z)$ (as well as its complex conjugate for normal incidence). This is too many solutions at one energy for the specular reflection calculation. For off-normal incidence, it is possible that the artificial band gaps in supercell calculations would mean that there are not too many solutions; for normal incidence, there always are. Regardless, however, the actual implementation of the algorithm that we use takes each solution at a given $k_z$ and energy and uses it and its complex conjugate to perform the matching and compute a reflectivity. Thus, a reflectivity is actually computed for each of these solutions. Fig. 6-2 (a) shows a computed reflectivity curve for the square trough. We see three narrow, vertical areas of reflectivities between 25 and 40 energy units. These are caused
by supercell approximations to the product solutions: $e^{\pm i\gamma} f_{SW}^0(z)$. In supercell calculations, the discrete set of bound states actually becomes a set of bands of localized solutions with very slight energy dispersion, which is why they appear in the reflectivity curves as almost vertical lines. The reflectivities for these bands seem to have no order, due to the fact that the $(0,0)$ component of the solution is very small. The matrix in the matching equation (Eq. 3.42) is essentially singular and the solution of the system will be dominated by error.

When we introduce a small periodic perturbation to the square trough, we end up with a system with a potential like that in Fig. 6-3, which I refer to as the perturbed square trough. In this case, the degeneracy of the product solutions for normal incidence is removed and the two degenerate bands split into two bands whose energy separation I was able to predict with a perturbative calculation. Fig. 6-2 (b) shows the reflectivities of two of these bands with energies labeled. We do not completely understand the reflectivities of these bands yet. For smaller supercells, some of the bands (usually the higher energy one of each pair) have reflectivities with some order, as shown in Fig. 6-2 (c), while other bands (usually the lower energy one in each pair) appear random. This seems to be due to the fact that these solutions consist primarily of Fourier components other than $(0,0)$, which decay to zero as functions of $z$ as $z$ approaches the supercell boundaries, but some have small but significant $(0,0)$ components that are a consistent order of magnitude throughout the supercell. Others have negligible $(0,0)$ components throughout the supercell. With larger supercells, these bands become less dispersive, and it is difficult to tell if their reflectivities are ordered or random. It also appears to be the case that the $(0,0)$ component decreases (relative to other components) as the supercell increases.

For off-normal scattering from the square trough and the perturbed square trough, these localized states are even more difficult to characterize, but they do illustrate something understandable and reminiscent of the streaking in the general incidence spectra of FLG and MoS$_2$. Fig. 6-4 (a) and (c) show the computed general incidence reflectivity spectra for two perturbed square trough
Figure 6-2: **Reflectivity spectra for square trough and perturbed square trough including localized solutions**: (a) The reflectivity curve for the square trough is the same as the curve for the 1D square well, except for the narrow features associated with localized solutions. (b) The reflectivity curve for the weakly perturbed square trough is very similar to that of the square trough, except that each narrow feature has split into two. (c) Zooming in on one of the narrow features in the perturbed square trough reflectivity curve, we see an orderly, but very narrow curve.
Figure 6-3: Perturbed square trough potential: A square well potential in the scattering \((z)\) direction and a small square bump in the ‘in-plane’ \((y)\) direction. The bump is exaggerated in this figure for demonstration purposes.
systems with different well widths, and one can see in them some streaks caused by the computed reflectivities of localized states. Fig. 6-4 (b) and (d) show the locations (in red) of all the localized solutions of the associated (unperturbed) square trough systems, whose energies are given by $E = (q_y + g)^2 - E_{SW}^b$, as mentioned above. In computing these energies, $E_{SW}^b$ values are taken from the one-dimensional square well bound state energies from one-dimensional supercell calculations with large supercells and the relevant $g$ is $2\pi$ since the unit cell is 1 unit wide in $y$. For generic $q_y$, there is no degeneracy for the perturbation to break; there is one localized perturbed square trough solution very close in energy to each square trough solution. Thus, localized solutions for the perturbed square trough should be very close to the red lines in the figure. Generally, we can see that the streaking occurs at the locations of the localized states, as expected. Fig. 6-4 (a) and (b) correspond to the system discussed in Sec. 3.3 with a wide well. They nicely display the free-electron-like nature of the major features. However, the correspondence between streaks in the reflectivity spectrum for the perturbed square trough and the localized solutions for the square trough, while suggestive, is not clear. 6-4 (c) and (d) correspond to the system discussed in this section above with a narrower, shallower well. They display clearly the coincidence of streaking in the reflectivity spectrum and the locations of localized solutions of the square trough.

The actual reflectivities of the bands of localized solutions as functions of energy appear random for the square trough away from normal incidence. For the perturbed square trough, they appear to be ordered - all of them, not just some as was the case for normal incidence. Thus, in these simple systems, we can understand the origin of these localized (decaying) states, but their reflectivities are not simple. I discuss these systems because it is somewhat easier to understand their localized states than those of realistic systems and yet they display some of the characteristics that the localized solutions of realistic systems (computed in a supercell) do.

Reflectivity features like those occurring in the perturbed square trough also appear in our calculated reflectivity spectra of FLG and MoS$_2$. To identify and potentially remove these solutions,
Figure 6-4: **Streaking in general incidence reflectivity of perturbed square trough**: (a) General-incidence reflectivity for a perturbed square trough with a well 6 units wide and 15 units deep, displaying a large number of narrow features due to localized solutions. (b) The positions of localized solutions in a square trough of the same dimensions as in (a). (c) General-incidence reflectivity for a perturbed square trough with a well 2 units wide and 5 units deep, displaying just a few narrow features due to localized solutions. (d) The positions of localized solutions in a square trough of the same dimensions as in (c). All systems were 1 unit wide in $y$, had bumps 0.25 units wide and 0.25 units high, and were computed with FFT grids with 31 points in $y$ and 51 points in $z$. In (b) and (d), the outer lines simply mark the specular reflection limits, not the position of localized solutions.
we need some way to characterize them. There are at least three different types of problematic solutions in the specular reflection regime for normal incidence scattering (at least for few-layer graphene, the system we studied most carefully). The easiest type to identify and explain actually have many properties that could be used to algorithmically remove them. They:

- are quadruply degenerate at normal incidence, i.e, the band itself is doubly degenerate and then the band is symmetric about \( \Gamma \),

- create reflectivities that appear random (likely caused by round-off error) and are at times greater than one; other solutions have reflectivities between zero and one,

- possess a higher level of symmetry than others,

- have the smallest \((0,0)\) Fourier components, which are of the same order of magnitude throughout the whole supercell, on the order of \(10^{-12} - 10^{-8}\) smaller than the the higher-order components in the slab (the largest Fourier components for these solutions), and

- have higher-order Fourier coefficients of the same or greater order of magnitude compared to the \((0,0)\) coefficient throughout the supercell.

The second type look similar to those of the first type when viewing their amplitudes graphically - they decay towards the boundary. However, their \((0,0)\) Fourier components are only on the order of \(10^{-1} - 10^{-2}\) smaller than the largest Fourier component throughout the supercell. The \((0,0)\) Fourier component is dominant near the supercell boundary for these solutions. They do not have additional degeneracies or symmetries and their reflectivities always fall between zero and one. Both of these types have some features in common with the perturbed square trough problem solutions. Finally, the last type of problematic solution is the most difficult to deal with. These solutions occur when, in the supercell band structure for a fixed width, there are bands which cross one another. In fact, they occur when bands of solutions of the second type cross bands of propagating solutions. Typically, the former is a fairly flat band and the latter dispersive. The dispersive bands
of propagating solutions appear at differing energies for different supercell sizes. Thus, the supercell width determines when these types of band crossings will occur. Now, in fact, these bands exhibit anti-crossing, in which the bands are distorted near the points at which crossings would occur in a way that prevents the crossing; bands bend away from one another. Gao et al. \cite{50} discuss this in the context of their work, which is very similar to ours, with the main difference with respect to the current issue being that they typically work with much larger supercells than we do. An example of this is given for five-layer graphene in Fig. 6-6. When this occurs, the mostly localized solutions on distorted bands can obtain more plane wave character (in $z$) in the vacuum than those solutions on the undistorted portion of the band.

Early on in the development of this method, we recognized that localization of solutions was the main issue causing our matching algorithm to produce reflectivity curves that seemed unrealistic. We attempted a number of methods to remove these problematic solutions from our reflectivity curves, including computing the integrated magnitude of the wavefunctions over a portion of the vacuum region, comparing magnitudes of $(0, 0)$ and first-order Fourier coefficients, and computing the determinant of the matching matrix, Eq. 3.42. These methods all had some success, but the third type of solution, occurring at band crossings, always produced problems for us. Finally, when the group at Carnegie Mellon published their results on the supercell, Bloch wave matching of few-layer graphene with the description of a filter for removing problem solutions in the supplemental material \cite{47}, we decided to try this measure to see how well it worked with our computations. Their idea is that the supercell states that can describe scattering electrons should have plane wave character in the vacuum region. Thus, they employ a measure that computes the inner product of the supercell solutions with right-moving plane waves of the same energy. In fact, they use standing wave-like combinations of the $(0, 0)$ Fourier components of computed supercell solutions, $\phi_\pm(z) = \phi_{k_1}(z) \pm \phi_{k_2}(z)$, with $\phi_{k_j}(z) = e^{i k_j \cdot r} c_{k_j}(0, z)$ as in Eq. 3.42. Each is projected onto the
plane wave (over a finite interval) and the two are added quadratically\(^1\): \(\sigma^{SW} = \sqrt{|\sigma_+|^2 + |\sigma_-|^2}\) with
\[
\sigma_\pm = \frac{1}{I} \int_0^I \frac{\phi_{k_1}(z) \pm \phi_{k_2}(z)}{\sqrt{2}} e^{iz\sqrt{E - |q|_2}} dz. \tag{6.4}
\]

For the Carnegie Mellon group, \(I\) is chosen far enough from the slab that the potential has leveled out to the vacuum potential. For our calculations, we have ensured this by choosing \(I\) to be \(\frac{1}{6}\) of the distance from the supercell boundary to the slab. (In fact, it may be best to choose \(I\) to be at a fixed distance from the slab, so that all of the increased vacuum space in a larger supercell would be added onto \(I\).) In the case of off-normal incidence scattering, this definition is adjusted simply enough:
\[
\sigma_\pm = \frac{1}{I} \int_0^I \frac{\phi_{k_1}(z) \pm \phi_{k_2}(z)}{\sqrt{2}} e^{iz\sqrt{E - |q|_2}} dz. \tag{6.5}
\]

Despite the fact that the beams now have \(k_\parallel \neq 0\), solutions are forced to have the correct in-plane nature by computing Bloch solutions with fixed \(k_\parallel = q_\parallel\). Thus, the only behavior that needs to be checked is the \((0,0)\) component as a function of \(z\), for specular reflection. The Carnegie Mellon group chooses these standing wave combinations presumably because they are the functions that they use in their matching algorithm, however, it is simpler to define \(\sigma\) using the two wavefunctions directly, in place of the standing wave combinations: \(\sigma^{WF} = \sqrt{|\sigma_1|^2 + |\sigma_2|^2}\) with
\[
\sigma_{1,2} = \frac{1}{I} \int_0^I \phi_{k_{1,2}}(z) e^{iz\sqrt{E - |q|_2}} dz. \tag{6.6}
\]

These two definitions are in fact equivalent. If we define, for convenience,
\[
\eta = \int_0^I \phi_{k_1}(z) e^{iz\sqrt{E - |q|_2}} dz \tag{6.7}
\]

\(^1\)In fact, there is a factor of \(\sqrt{2}\) difference between this definition that we have used and the one given in \([47]\). Perhaps this is due to a wavefunction normalization issue, or something else, but with the definition above, we have found \(\sigma\) values very similar to those reported in \([50]\) for the same system.
and
\[
\rho = \int_0^I \phi_{k_2}(z) e^{iz\sqrt{E-|q||^2}} dz, \tag{6.8}
\]
then
\[
(\sigma^{WF})^2 = \frac{1}{I^2} (|\eta|^2 + |\rho|^2). \tag{6.9}
\]
And
\[
\sigma_\pm = \frac{1}{\sqrt{2I}} (\eta \pm \rho). \tag{6.10}
\]
Thus,
\[
(\sigma^{SW})^2 = \frac{1}{2I^2} (|\eta + \rho|^2 + |\eta - \rho|^2) \tag{6.11}
\]
\[
= \frac{1}{2I^2} \left( \text{Re}(\eta + \rho)^2 + \text{Im}(\eta + \rho)^2 + \text{Re}(\eta - \rho)^2 + \text{Im}(\eta - \rho)^2 \right) \tag{6.12}
\]
\[
(\sigma^{SW})^2 = \frac{1}{2I^2} \left( 2 \text{Re}(\eta)^2 + 2 \text{Re}(\rho)^2 + 2 \text{Im}(\eta)^2 + 2 \text{Im}(\rho)^2 \right) = \frac{1}{I^2} (|\eta|^2 + |\rho|^2). \tag{6.13}
\]
Thus,
\[
(\sigma^{SW})^2 = (\sigma^{WF})^2. \tag{6.14}
\]

The idea behind this \(\sigma\) measure is that for large vacuum regions this integral will be close to one for a well approximated propagating state. This is because the wavefunctions are normalized, and when the vacuum regions are large, the weight of the wavefunction inside the slab is overwhelmed by that outside, and thus the amplitude in the vacuum region of the plane wave-like (or standing wave-like) solutions in the vacuum will approach one. Then, the value of \(\sigma\) will approach one, as well, since the two propagating solutions in the vacuum at a given energy should essentially ‘contain’ one right propagating wave and one left propagating wave (more precisely, each is a vector of norm close to one in the span of the functions, \(\{e^{i\sqrt{E-|q||^2}}, e^{i\sqrt{E-|q||^2}}\}\)). One of these will contribute something close to one in \(\sigma\), while the other will contribute the integral of a fairly
highly oscillatory function, which is bounded, divided by the length of the domain of integration, $I$. Thus, as the vacuum region grows, $\sigma$ approaches one. As a simple illustration of this, imagine that the two propagating solutions in the vacuum are in fact exactly linear combinations of left- and right-moving plane waves with wave vectors matching that of the incoming beam, $q_z$ (which our solutions should approximate in the vacuum region):

$$\phi_{k_{1,2}}(z) = A_{1,2}e^{i q_z z} + B_{1,2}e^{-i q_z z}.$$  

(6.15)

Then,

$$\sigma_{1,2} = \frac{1}{I} \int_0^I \phi_{k_{1,2}}(z) e^{i q_z z} dz$$  

(6.16)

$$= \frac{1}{I} \int_0^I (A_{1,2}e^{i q_z z} + B_{1,2}e^{-i q_z z}) e^{i q_z z} dz$$  

(6.17)

$$= \frac{1}{I} \int_0^I (A_{1,2} e^{i 2q_z z} + B_{1,2}) dz$$  

(6.18)

$$= B_{1,2} + \frac{A_{1,2}}{i 2 q_z I} (e^{i q_z I} - 1)$$  

(6.19)

For normal incidence, $\phi_{k_1} = \phi_{k_2}^*$, thus $A_2 = B_1^*$. And, since the wavefunctions are normalized, $|A_2|^2 + |B_2|^2 \approx 1$. Thus,

$$|B_1|^2 + |B_2|^2 = |B_1^*|^2 + |B_2|^2 = |A_2|^2 + |B_2|^2 \approx 1.$$  

(6.20)

Thus, for a given $q_z$, as $I \to \infty$, $\sigma = \sqrt{|\sigma_1|^2 + |\sigma_2|^2} \to |B_1|^2 + |B_2|^2 \approx 1$. For low energies, $q_z$ is small, thus for the fixed $I$ that we use, this limit is not approached. This can be seen in the $\sigma$ values for the lowest energy solutions, as shown in Fig. 6-5; they are not very close to one, sometimes well above it. For off-normal incidence, when there is a mirror plane parallel to the slab surface, a similar argument, using the relationship between the two solutions derived in Sec. 3.2.3, gives the same conclusion. However, for general materials, we do not have a proof that $|B_1|^2 + |B_2|^2 \approx 1$ in
the limit. We have not seen large differences in $\sigma$ values between symmetric and mirror-symmetric systems, however. Perhaps, current conservation ensures that $|B_1|^2 + |B_2|^2 \approx 1$.

Fig. 6-5 (c) shows the $\sigma$ values for solutions of a five-layer, free-standing graphene system in supercells of three different sizes, 12, 13, and 24 times the graphene in-plane lattice parameter, $a_G$. Fig. 6-5 (b) shows the unfiltered, normal incidence reflectivity curves for this system in all three supercells and (c) shows the supercell band structure for the supercell of size 12 times $a_G$. The band structure shows two colors: the green are solutions with certain additional symmetries, as calculated by the QUANTUM ESPRESSO band structure calculation’s ‘lsym’ option. They coincide with solutions of the first type, which also show the smallest $\sigma$ values.

The $\sigma$-filtering method filters only about as much as some of our other methods. It removes the first type of problem solutions easily, since they have $\sigma$ values very small, separated by orders of magnitude, compared to all the other solutions. The second type can be removed with the proper setting of the filter threshold. This can be seen in Figs. 4-2 and 4-3, which do not show the bands at 3.9 eV and the latter of which filters out most of the flat bands between 5 and 10 eV. The band crossings at 17.5 eV are not filtered well at all. The Carnegie Mellon group describes in more detail how they employ this measure and additional manual filtering to handle the band crossings in [50]. As Gao et al. explain, to remove all ‘spurious’ states from consideration, a more detailed filtering around band crossings and anti-crossings is necessary, which can be quite difficult for some systems. As seen in Figs. 5-3 (b), 5-4 (b), and 5-5 (b), the band structure of bulk MoS$_2$ does not contain clear flat bands, like those in bulk graphite, making this detailed filtering difficult.

The use of the $\sigma$-measure for off-normal incidence is even less clear. We find that the separation by orders of magnitude of the $\sigma$-measure for the first type of problem solution from those of all other solutions does not occur for $k_\parallel$ along the path from $\Gamma$ to $K$. In addition, for $k_\parallel$ along the path from $\Gamma$ to $K$, the lowest energy problem solutions near 3.9 eV, which are of the first type, split into two bands. One of these remains of the first type, while the other is of the second type.
Figure 6-5: **Types of problem solutions for five-layer graphene**: (a) The supercell band structure for a 5-layer FLG system with a supercell 5 times as wide as the graphene lattice constant, $a_G$. Green bands represent those with additional symmetries. (b) The unfiltered, normal incidence reflectivity curves for 5-layer FLG systems, computed with supercells 12 (red diamond), 13 (blue cross), and 24 (black circles) times $a_G$. (c) The computed $\sigma$ values for the same systems (and markers) as in (b). The different types of problem solutions discussed above are labeled.
Figure 6-6: **Type III problem solutions for five-layer graphene**: (a) Supercell band structure for system with supercell width 12 times $a_G$. (b) Unfiltered reflectivity for 5-layer FLG systems, computed with supercells 12 (red diamond), 13 (blue cross), and 24 (black circles) times $a_G$. (c) The computed $\sigma$ values for the same systems (and markers) as in (b). Note that some curves were shifted slightly to get these features to coincide well in this region of the curves.
This second type is unfiltered in the general incidence spectra of FLG with $\mathbf{q}_\parallel$ along the path from $\Gamma$ to $M$ (Fig. 4-5). It is also unfiltered for $\mathbf{q}_\parallel$ along the path from $\Gamma$ to $K$. This creates the streak seen in the general incidence colormap spectra, which also shows up in another group’s calculations of LEED from monolayer graphene [64] and in calculations and experimental data for LEED from graphite [39]. It is in this last paper, recall, that calculations and experimental results both show a feature similar to those caused by the band crossings at 17.5 eV.

Thus, while the $\sigma$-measure is a fairly cleanly motivated and useful measure, it is still unclear exactly how to identify supercell solutions that should be removed from the matching algorithm. If this method is to be applied for widespread use, this must be further investigated.

### 6.5 Errors in Energy-Sort Pairings

It was mentioned in Sec. 4.3.3 that there are some off-normal reflectivities that are calculated incorrectly due to incorrect pairing of degenerate solutions in the energy-sorting algorithm. In fact, many of these errors produce calculated reflectivities greater than one. This led us to cap reflectivities displayed in colormaps at one, so that the scale was reasonable for other points. There are a few different situations in which errors are made. One type occurs when, near a minimum of the band structure, the two lowest energy solutions are on the same side of the minimum. Then, the algorithm uses them as a degenerate pair despite the fact that it might have been a more accurate pairing for the lowest energy solution to be discarded and the next in energy of either side to be taken. Fig. 6-7 displays an example of this type of error. It shows that in this case, the more appropriate pairings are eventually reverted to because the energy difference between the inappropriate pairing grows too large. It also shows that the error in the value of reflectivity is significant but does not change the fundamental nature of the curve (especially if one zooms out). Another type of error can have much more impact on the shape of the curve. Fig. 6-8 shows an example where a band is steeper for one range of $k_z$ than for another, making the density of $k$-points...
Figure 6-7: **Energy-sort matching errors I:** (a) Narrow sliver of reflectivity curve for a beam with \( k_\parallel = 0.1b_2 \) (one-fifth of the way from \( \Gamma \) to \( M \)) incident upon three layers of MoS\(_2\) in the 3R stacking that displays erroneous results. (b) Small piece of the band structure of three layers of 3R-MoS\(_2\) along a \( k \)-path parallel to \( \Gamma \)-\( A \) with \( k_\parallel = 0.1b_2 \). Ovals indicate pairs of solutions found via the energy-sorting algorithm with an energy difference threshold of 0.0001 Ry. The \( x \)-axis gives the number of the \( k_\parallel \)-point in the path of 72 points between the bottom and top of the Brillouin zone. The \( \Gamma \)-plane is between the 36th and 37th points.

with respect to energy smaller. In this case, the difference is enough that in the more dense range there are sometimes two \( k \)-points between two \( k \)-points in the other range in energy. In some cases, then, two such solutions are taken as the matching pair, whereas other times two solutions far from one another in \( k_\parallel \) are taken (the correct pairing). As shown, the reflectivity curve then alternates between two different curves, producing what appear to be two curves in the same energy range.

Now, both of these examples can be addressed by requiring that solutions with simultaneous \( k_\parallel \) values not be allowed as matching pairs. Fig. 6-9 shows the improvement in the reflectivity curve from Fig. 6-7 discussed above, when pairs of solutions with consecutive \( k_\parallel \) values are rejected. The
Figure 6-8: **Energy-sort matching errors II**: (a) Narrow sliver of reflectivity curve for a beam with $k_{\parallel} = 0.1b_2$ (one-fifth of the way from Γ to M) incident upon three layers of MoS$_2$ in the 3R stacking that displays erroneous results. Red points and green crosses correspond to reflectivities computed with the pairs circled in red (solid) and green (dotted) ovals in (b). (b) Small piece of the band structure of three layers of 3R-MoS$_2$ along a $k$-path parallel to Γ–A with $k_{\parallel} = 0.1b_2$. Ovals indicate pairs of solutions found via the energy-sorting algorithm with an energy difference threshold of 0.0001 Ry. The $x$-axis gives the number of the $k_z$-point in the path of 72 points between the bottom and top of the Brillouin zone. The Γ-plane is between the 36th and 37th points.
lowest energy solution is skipped and the pairings are improved. Of course, this approach will not always fix the second type of problem discussed above. If the band in one section is especially dense compared to another section, rejecting consecutive points would still not be enough to ensure proper pairings. There is another issue with this attempt to correct the inappropriate pairings. When the points calculated are approximately symmetric about a minimum, solutions with consecutive \( k_z \) actually form the correct pairing. However, the restriction to non-consecutive \( k_z \) means that one of the pair will be discarded and the other will be paired with a less appropriate solution. Fig. 6-10 shows such a band structure and the difference between the reflectivity curve computed with and without the restriction against consecutive \( k_z \). This piece of the reflectivity curve for three layers of 3R stacked MoS\(_2\) displays a few interesting properties regarding the difficulties with the energy sort, actually. First, the significant vertical offset between the two curves is caused by exactly the issue mentioned above. It appears that the method that allows consecutive \( k_z \) has found the correct pairs for the lowest three energies. The method that rejects consecutive \( k_z \) has rejected the lowest energy pair despite the fact that they are on opposite sides of a minimum and are, thus, the appropriate pair. Second, the two reflectivity curves both show a jump in the reflectivity after the first few points. This occurs when the pairings change from involving two points within the first six points in the \( k \)-path to involving one point from the left side of the \( k \)-path (with negative \( k_z \)) and one point on the right side (with positive \( k_z \)). A similar jump is seen at the high energy end of this piece of the curve, where the \( k_z \) of solution pairs are taken from near a maximum in the band. It is not clear why this should cause such jumps. It is likely related to the distortion of the reflectivity curve when solutions are taken from points on the bands too close to points at which there is only one solution, which for normal incidence scattering are \( \Gamma \) and the Brillouin zone boundary, as discussed in Sec. 3.2.1. These results beg the question of what is too close to such points, as many \( k \)-points are affected. This should be further investigated, as it raises a question about the matching technique itself for off-normal incidence. Finally, the curve calculated without
Figure 6-9: **Energy-sort matching errors III**: (a) Narrow sliver of reflectivity curve for three layers of MoS$_2$ in the 3R stacking that displays erroneous results. Red crosses and blue points correspond to reflectivities computed with the pairs circled in red (solid) and blue (dotted) ovals in (b). (b) Small piece of the band structure of three layers of 3R-MoS$_2$. Ovals indicate pairs of solutions found via the energy-sorting algorithm with an energy difference threshold of 0.0001 Ry. The x-axis gives the number of the $k_z$-point in the path of 72 points between the bottom and top of the Brillouin zone. The Γ-plane is between the 36th and 37th points.

rejecting consecutive $k_z$ has a cusp in the middle of the region shown. The point that appears to be missing was calculated to have reflectivity of over 3, a clear error. The pair of solutions used to calculate this are on the same side of a wide peak, similar to the situation in Fig. 6-8. In this case, the change in pairings from energies below this consecutive pair to energies above this pair causes the curvature of the curve to change substantially.

Clearly, a better solution is desirable. The ideal solution would actually be to use a DFT solution technique that solves the ‘inverse band structure’ problem for the supercell, finding solutions with given $k_z$ for given energy and in-plane wave vector, $k_{\parallel}$. If sticking to the standard band structure
Figure 6-10: **Energy-sort matching errors IV**: (a) Narrow sliver of reflectivity curve for three layers of MoS$_2$ in the 3R stacking that displays erroneous results. Red crosses and blue points correspond to reflectivities computed with the pairs circled in red (solid) and blue (dotted) ovals in (b). (b) Small piece of the band structure of three layers of 3R-MoS$_2$. Ovals indicate pairs of solutions found via the energy-sorting algorithm with an energy difference threshold of 0.0001 Ry. The $x$-axis gives the number of the $k_z$-point in the path of 72 points between the bottom and top of the Brillouin zone. The $\Gamma$-plane is between the 36th and 37th points.
approach is preferred, perhaps the best approach would be to perform a preliminary band structure calculation with a limited, but sufficient $k_z$ grid. Then one could interpolate to find other $k_z$-points at approximately the same energies as the originals, on which to run a subsequent band structure calculation. Alternatively, specific energies could be chosen and pairs of $k_z$ determined from the interpolation, and those could be used for another band structure calculation. This would have to be performed for each $k_{||}$, adding significantly to the total computation time for a general incidence spectra. Finally, perhaps a perturbative approach could work to find corrections to the wavefunctions at a given energy or $k_z$ that would better approximate those at a nearby energy or $k_z$.

It possible that an analysis of each band and a set of instructions for handling different cases, e.g., symmetric vs asymmetric $k_z$ distribution about minima, would be a more efficient and adequate solution. Or perhaps an optimization of the pairings, rather than simply sorting and linearly proceeding through the energies, could be a successful approach.
I have described a theoretical and computation framework for calculating the reflectivity of low-energy electrons from crystalline surfaces, along with an implementation of the framework that incorporates realistic potentials determined by density functional theory. I have presented the results of applications of the method to model systems in one, two, and three dimensions and to realistic systems of free-standing, few-layer graphene and MoS$_2$.

I have demonstrated that the general framework for matching Bloch wave solutions of any single particle, time-independent Schrödinger Equation in the supercell geometry allows, in theory, for the calculation of reflectivity and diffraction intensity curves from a free-standing crystal slab, using only a small number of diffracted beams and a small number of Fourier components of the solutions in the real band structure of the supercell system at each energy. In practice, the process is simplest for the lowest energies in which only the specularly reflected beam emerges from the crystal, and for this situation I have described detailed algorithms for calculating the reflectivity intensities for beams with normal and off-normal incidence. The applications to specular reflection from model systems shows that the method behaves as expected with respect to FFT grid density and changes to supercell size. They support the hope that this method can be a simple and efficient approach to calculating LEED and LEEM-IV curves in the lowest energy range that improve upon many other methods. However, already in these model systems, hints of difficulties are present in the form of narrow and sometimes disordered features due to the existence of states that are localized normal...
to the surface at scattering energies.

Applications to realistic systems demonstrate that the use of the method with Bloch wave solutions from density functional theory can produce revealing and physically accurate reflectivity curves for some systems at the lowest energies. While the method should work best for free-standing samples, it actually models the reflection of electrons at 0-12 eV from few-layer systems of graphene on 6H-SiC(0001) quite accurately, despite the fact it does not account for the substrate. In this setting, it is a useful method for confirming and aiding the understanding of the relationship between layer number and reflectivity in FLG systems. The layer- and structure-dependent features in our calculated reflectivity curves for MoS$_2$ suggest that the method may be useful in understanding the relationship between reflectivity and structure in other systems as well. The calculated reflectivity spectra for general angles of incidence produced by our method should aid in the mapping of some conduction bands in few-layer systems, especially FLG for which there are layer-dependent oscillations close to the Fermi level. The varied and intricate features in the general incidence spectra for both FLG and MoS$_2$ suggest that general incidence LEEM-IV can provide a wealth of data for distinguishing structures in the specular reflectivity regime. On the other hand, the uncertainty in nature of numerous calculated narrow features and the quick drop off in intensity of recorded IV curves with energy mean that what seems like a large amount of information may be largely inaccessible.

I believe that our supercell, Bloch wave method could be useful in the study and calculation of some of the many layered systems certain to be studied over the next few years, especially for studying LEEM-IV curves as a complement to higher energy $\mu$LEED data. However, its success and more widespread use will depend upon some improvements to the method. Most importantly, the nature of the problem solutions discussed in Sec. 6.4 needs to be better understood, so that a confident and systematic filtering can be performed. The first step toward this would be a thorough investigation of the claim in Gao et al. that all three types of problem solutions are spurious and
some claims about the $\sigma$ values and magnitudes of the wavefunctions for these solutions [50]. These claims should be tested for wavefunctions for off-normal scattering, as well. Also, the study of many layered heterostructures would likely require higher-order diffraction given that they are likely to have large unit cells, and therefore a lower energy onset of diffracted beams, $E_c(q_\parallel)$. This would require overcoming the insufficient number of solutions for solving the matching system for high-order diffraction in the supercell, for which no clear path exists. FLG reflectivities suggest that inelastic effects may be important for accurate curves above 10 eV. It is not yet clear if temperature effects will be important for energies below 30 eV.
APPENDICES
A.1 Schrödinger Equation and Time-Dependence

The general Schrödinger Equation is:

$$H \Psi = i \frac{\partial}{\partial t} \Psi$$  \hspace{1cm} (A.1)

where $\Psi$ is a vector in an appropriate Hilbert space and $H$ is a Hermitian operator on that space. Note that we will always be working in atomic (specifically Rydberg) units, i.e., $\hbar$ and $2m$ have been set to one, so that the unit of length is the Bohr radius, $a_0 = 0.52918$ Å, and the unit of energy is Rydberg, $R_y = 13.60569$ eV. $m$ is the mass of the electron.

If the Hamiltonian has no explicit time dependence, the equation is separable and the time evolution is simply given by $\Psi(r, t) = \psi(r)e^{-iEt}$, where $\psi(r)$ solves the time-independent Schrödinger equation (TISE):

$$H \psi = E \psi$$  \hspace{1cm} (A.2)

In all discussions of scattering problems examined here, the assumption will be that we can treat the Hamiltonian as time-independent so that we will be working with the TISE.

Now solid state systems consist of an arrangement of atoms, meaning an arrangement of nuclei and electrons. The Hamiltonian for such a system contains kinetic energy terms for all nuclei and electrons in the system plus potential energy terms for the interactions between of all these particles. However, we will be working in the Born-Oppenheimer approximation, which involves taking the nuclei mass to infinity so that kinetic energy terms associated with them vanish, or assuming that the nuclei are fixed and that the electrons are moving around them. More subtly, the approximation is the assumption that electronic and nuclei degrees of freedom can be separated, so that nuclei positions are not arguments of the state of the system but rather parameters. This is justified by the fact that the enormous ratios of nuclear masses to the electron mass imply that electrons respond almost instantaneously to changes in positions of the nuclei. Under this assumption, a solid state system is described by the wavefunction $\psi(r_1, \ldots, r_N)$ for N electrons solving the following TISE:

$$- \sum_{i=1}^{N} \nabla_i^2 \psi + \frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|} \psi + V_{\text{ext}}(r_1, \ldots, r_N) \psi = E \psi$$  \hspace{1cm} (A.3)

where $V_{\text{ext}}$ describes the interaction between the electrons and the nuclei.
A.2 Independent Particle Approximation

We shall begin working under the independent-particle approximation, i.e., that the complicated many-body problem involving huge numbers of interacting electrons in a solid can be accurately modeled by the problem of non-interacting electrons in an effective potential that accounts for all interactions between electrons (including some enforcement of the Pauli Exclusion Principle required by identical particle considerations). This means that Eq. A.3 becomes:

\[-\nabla^2 \psi(r) + V_{\text{eff}}(r) \psi(r) = E \psi(r)\] (A.4)

and instead of solving for one function, \( \psi(r_1, \ldots, r_N) \), of \( 3N \) variables, we solve for \( N \) functions of three variables. One justification for this approach is provided by the Kohn-Sham formulation of density functional theory as described in Sec. A.5, which employs an iterative method for determining a ‘self-consistent’ effective potential by solving a Schrödinger Equation with an approximate effective potential and using that solution to determine a better approximate effective potential. (See A.5 or [92], Chapters 6-9 for more details.) In this dissertation, it will generally be assumed that an effective potential (either the self-consistent one or an intermediate guess) is given, and that the present goal is to solve the Schrödinger Equation with this fixed potential.

The importance of the independent particle picture cannot be overstated. An overwhelming majority of treatments of solid state physics is dependent upon this assumption. The categorization of solids into insulators, metals, and semiconductors based on band gaps is based on the band structure picture of solids in the independent particle picture. Most of the discussion in this dissertation is based on band structure. It should be noted that there are entire classes of materials, often referred to as strongly correlated electron systems, in which the independent particle picture fails and the many-body wavefunction must be handled more directly.

A.3 Free Electron Gas

The simplest approximate problem to investigate is one in which the cumulative effects of atomic nuclei and core and valence electrons is modeled by a uniform, constant potential. This model is called the free electron gas and is best suited for describing metals. The Schrödinger Equation in this case is simply

\[-\nabla^2 + V_{\text{eff}} \psi(r) = E \psi(r)\] (A.5)

where \( V_{\text{eff}} \) is constant. The solutions to this differential equation are plane waves: \( \psi(r) = Ae^{ikr} \), where the wave vector \( k \) can take on any value in \( \mathbb{R}^d \) \( (d = 1, 2, 3 \) as the problem dictates). If the energy scale is shifted so that the potential is zero, then the eigenenergies are just the kinetic energies of the plane wave electrons:

\[ E_k = k^2. \] (A.6)

The free electron gas model arises from assuming that \( N \) electrons inhabit a crystal of finite volume \( V \) and assuming periodic boundary conditions (the Born-von Karman assumption) which restricts the set of allowed wave vectors, which creates a discrete set of energy levels through Eq. A.6. Then one imagines the \( N \) electrons filling these levels in order of increasing kinetic energy. Taking the limit of a large (infinite) system of constant density, \( N/V \), provides a consistent framework in which a continuous energy band arises with a well-defined, non-trivial ‘density of states,’ i.e., the number of electron states in a given range of wave vectors or energies. Using this framework
Figure A-1: Examples of band structures: (a) The band structure of a free electron gas in the reduced zone scheme for an arbitrary period. In the extended zone scheme it would simply be a parabola. (b) The band structure of a periodic square well potential. (c) The band structure along the labeled path in reciprocal space of graphite.

and some statistical physics, one is able to derive or at least shed some light on various properties of metals, including the plasma energy, electronic heat capacity, and some simple results about magnetic susceptibility, electrical conductivity, and optical reflectivity.

A.4 Plane Waves: Electrons in Periodic Potential

In order to move beyond the free electron gas model, a non-constant potential is introduced. In the study of solids, it is nearly universally assumed (and experimentally confirmed) that the atoms that make up solids are periodically arranged in space. Thus, the potential produced by the atomic nuclei of a solid will be periodic. It will be shown that a single electron subject to a periodic potential has a wavefunction that yields a periodic charge distribution. Thus, it is reasonable to assume that any effective potential that approximates the effects on one electron of all electrons in the solid in other states will be periodic. Thus, the study of electrons in periodic potentials is crucial to the study of electrons in solids.

Therefore, assume an electron is subjected to a periodic effective potential, $V_{\text{eff}}(r)$. The wavefunction of such an electron is the solution of the Schrödinger Equation:

$$(-\nabla^2 + V_{\text{eff}}(r)) \psi_j(r) = E_j \psi_j(r) \quad (A.7)$$

If one assumes the Born-von Karman boundary conditions, i.e., that the wavefunction is periodic in each of the primitive vector directions on a macroscopic scale, then the wave function can be expanded in plane waves, i.e., in a Fourier series,

$$\psi_j(r) = \frac{1}{C} \sum_{\mathbf{q}} c_j(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{r}}, \quad (A.8)$$

where the sum is over all $\mathbf{q}$ in the reciprocal lattice to the lattice created when periodically extending the macroscopic crystal boundaries (as prescribed by the Born-von Karman boundary conditions).

Now, the potential is assumed to be periodic in the lattice of the crystal, and so it can be expanded in a Fourier series with a sum over only the reciprocal lattice vectors of the crystal, $\{ \mathbf{G}_m \}$. 

\[
V_{\text{eff}}(r) = \sum_m V_{\text{eff}}(G_m)e^{iG_m \cdot r}
\]

(A.9)

Thus, a priori, the expansion of the wavefunction contains terms with the same wave vectors as the expansion of the potential, but also many other wave vectors. However, substituting A.8 and A.9 into A.7, using the orthogonality of plane waves, and rewriting any wave vector \( \mathbf{q} \) as \( \mathbf{k} + \mathbf{G} \), where \( \mathbf{k} \) is in the first Brillouin zone and \( \mathbf{G} \) is the appropriate reciprocal lattice vector, one finds:

\[
\sum_{m'} \left[ |\mathbf{k} + \mathbf{G}_m|^2 \delta_{m,m'} + V_{\text{eff}}(G_m - G_{m'}) \right] c_{j,m'}(\mathbf{k}) = E_j(\mathbf{k}) c_{j,m}(\mathbf{k}),
\]

(A.10)

where \( c_j(\mathbf{q}) = c_j(\mathbf{k} + \mathbf{G}_m) = c_{j,m}(\mathbf{k}) \).

There are two important observations to be made here...

### A.4.1 Bloch’s Theorem

First, we now see that for each given wave vector \( \mathbf{k} \) in the first Brillouin zone, each eigenfunction associated with that wave vector involves only plane waves with eigenvectors of the form \( \mathbf{k} + \mathbf{G}_m \), where \( \mathbf{G}_m \) is a reciprocal lattice vector. This result is one statement of Bloch’s Theorem, i.e., that the wavefunction of a particle in a periodic potential can be written:

\[
\psi_j(r) = \frac{1}{C} \sum_{m'} c_{j,m'}(\mathbf{k})e^{i(\mathbf{k} + \mathbf{G}_{m'}) \cdot r}
\]

(A.11)

\[
= e^{i\mathbf{k} \cdot \mathbf{r}} \frac{1}{C} \sum_{m'} c_{j,m'}(\mathbf{k})e^{i\mathbf{G}_{m'} \cdot \mathbf{r}}
\]

(A.12)

\[
= e^{i\mathbf{k} \cdot \mathbf{r}} u_{j,\mathbf{k}}(\mathbf{r}),
\]

(A.13)

with \( u_{j,\mathbf{k}}(\mathbf{r}) \) periodic in the crystal lattice. If there is no degeneracy at a given energy, then all solutions at that energy are given by a constant multiple of this Bloch solution. In the case of a degeneracy, the Bloch solutions at that energy provide a basis for the solution space at that energy. Thus, there is a basis of solutions to the time-independent Schrödinger Equation consisting of functions in Bloch wave form.

### A.4.2 Electronic Band Structure

Secondly, one finds that because of this result, it is possible to determine a relationship between energy and the wave vector \( \mathbf{k} \) (often referred to as crystal momentum) by solving for the eigenenergies at a fixed value of \( \mathbf{k} \) or finding the values of \( \mathbf{k} \) that give rise to a fixed energy. It is this relationship that is referred to as the band structure of a solid due to the fact that in the limit of large structures, the allowed wave vectors become dense in \( \mathbb{R}^d \) and the discrete energy levels become a continuous band of energy levels. Numerically, computing the band structure is handled by viewing Eq. A.10 as a matrix eigenvalue problem (once the plane waves are restricted to a finite set) and using the determinantal or secular equation,

\[
\det[A(\mathbf{k}, V_{\text{eff}}) - E(\mathbf{k})I] = 0,
\]

(A.14)

to derive the relationship between \( \mathbf{k} \) and \( E_j \).

The simplest example of a band structure is that of the free electron gas discussed in Sec. A.3. In fact, Eq. A.6 describes the band structure, and of course a plot of energy versus wave vector
in this case would be a parabola. However, a constant potential is also a periodic function of any period. Thus, one could carry out the above analysis for a constant potential with an arbitrary period and find the band structure in terms of the first Brillouin zone of that lattice. This is shown in Fig. A-1 (a) and it can be seen as pieces of a parabola shifted horizontally so that they all fit in the first Brillouin zone. Fig. A-1 (b) shows a band structure for a square well ‘perturbation’ of the constant potential which demonstrates the opening of band gaps at the origin and at the Brillouin zone boundaries. Note that the well depth is 10, which is why the bands do not start until nearly 10. There is one bound state below 10, and all others are at energies above 10. Fig. A-1 (c) shows a real (3D) band structure for graphite, along a piecewise linear path in the 3D Brillouin zone.

**Complex Band Structure**

When discussing band structures for bulk crystals, it is typical to discuss only real band structures, meaning solutions of Eq. A.14 for real numbers $E$ and $k$. This way, all Bloch solutions have complex exponential Bloch factors and do not blow up in any directions. However, at crystal surfaces, real exponential Bloch factors, which decay into the crystal are allowed because in the direction in which they grow the potential ends (at the crystal surface). Thus, the solution for a semi-infinite crystal can involve a Bloch solution that grows exponentially up to the surface and then changes into another function which solves the Schrödinger Equation for whatever potential is on the outside of the crystal. This Bloch solution that grows in one direction and decays in the other has a Bloch wave vector with an imaginary component, $k_z$, such that $ik_z < 0$ if the crystal extends toward $\infty$ in $z$. These solutions that decay into the crystal are referred to as evanescent states. (In fact, there are also states outside the crystal that decay into the vacuum, which are also called evanescent states.) When these imaginary Bloch wave vectors are included in solutions to Eq. A.14, one creates the complex band structure of the semi-infinite crystal. In fact, it is sometimes easier to let both $E$ and $k$ be imaginary but in the end only states with real $E$ are physically relevant. The complex band structure plays a crucial role in studying electron scattering in the semi-infinite crystal geometry. It turns out that in a three-dimensional complex band structure, one can find infinitely many evanescent states, decaying into the crystal, at a given energy and with fixed $k_x$ and $k_y$ [37], a fact that is leveraged in semi-infinite methods for electron scattering.

**A.5 Density Functional Theory**

Our method makes use of density functional theory (DFT) to incorporate realistic scattering potentials, especially for directionally bonded materials. Using DFT also reduces the dependence on fitting parameters as compared to traditional methods.

DFT is a very widely-used approach to simplify the many-body Schrödinger Equation that describes the behavior of large numbers of electrons to make computational studies more tractable. In fact, it applies to any many-body quantum system of interacting particles in an external potential, $V(r)$, but we focus on interacting electrons in an external potential of atomic nuclei in the Born-Oppenheimer approximation, which is modeled by the TISE Eq. A.3. There are approaches to studying this many-body problem and solving for this wavefunction of $3N$ variables (e.g., Hartree-Fock, Configuration Interaction, Coupled-cluster), but many are very computationally intensive and can be prohibitive even for fairly small systems of under 100 atoms. DFT provides a means to transform the problem into a more tractable one. The foundation of (general) DFT is provided by two Theorems of Hohenberg and Kohn. The first states that $V_{ext}(r)$ and hence all properties of the many body system are determined by the ground state density, $\rho_0(r) = N \int dr_2 \cdots dr_N |\psi_0(r, r_2, \ldots, r_N)|^2$. The second Hohenberg-Kohn Theorem states that
there exists a functional for the energy that is written as a function of the density and whose form is universal (but still depends on $V_{\text{ext}}$) and that the minimization of this functional leads to the ground state energy and density. If this functional were known, then this would give a clear approach to finding the ground state (energy and density, at least). It is not known, and really will never be known, but it can be approximated. Thus, at this point, DFT has reduced the many-body problem of finding the Schrödinger Equation solution with $3N$ arguments to finding the minimizer of the energy functional, a function with 3 arguments (plus approximating the universal functional - perhaps the hardest part).

In fact, a large majority of DFT calculations are performed under the Kohn-Sham formulation. According to Marder, “Kohn and Sham retreated slightly from the hope of writing all material properties as functions of the electron density, and proposed using instead a set of N lowest energy single-electron wave functions, $\psi_l(r)$ as main ingredients.” This approach involves the ansatz that there exists an auxiliary, independent particle problem whose N lowest energy single-electron wave-functions, $\psi_l(r)$, give a density equal to the exact ground-state density via $n_0(r) = \sum_{l=1}^{N} |\psi_l(r)|^2$. The kinetic energies in the auxiliary system are given by the standard expression and the other piece of the Hamiltonian is written as an effective potential. Typically, this effective potential consists of the external potential, a simplified form of the Coulomb interaction between a given particle and all the others ($V_{\text{Hartree}}$), and the so-called ‘exchange-correlation’ potential ($V_{xc}$), which contains all of the many-body effects and is physically motivated by the exchange-correlation hole picture [93].

This method is put into practice through an iterative scheme. At an arbitrary step, the one-particle wave functions are solved for using any one of many methods, say a Fourier spectral method. Then these are used to determine the density and from that the ground state energy. This energy is compared to the previously computed energy to check for convergence (given a convergence threshold). If convergence has not been reached, the potential terms ($V_{\text{Hartree}}$ and $V_{xc}$) are computed from the density and the new Schrödinger Equation with this potential is solved.

A.5.1 Pseudopotentials vs All-Electron Calculations

There are many different varieties of DFT that may differ in the form of the density functional or basis sets, among other things. For the purposes of this dissertation, it is important to differentiate between two types of plane wave methods: pseudopotential and all-electron methods. Both are methods for solving single-particle Schrödinger Equations and use plane waves as their basic basis set elements. Both methods differentiate between core and valence states. They transform the Schrödinger Equation such that the strong Coulomb potential and the effects of the core electrons become a smoother, weaker potential in a way that the wavefunctions of the valence states are the same as they are for the original potential away from the nucleus. (The trade-off is that the potential is now a non-linear operator and the eigenvalue problem becomes a generalized eigenvalue problem.) The solutions found for these valence states in pseudopotential methods are called pseudowavefunctions and only match the real Kohn-Sham wavefunctions in the region away from the nucleus. All-electron plane wave methods, like the projector augmented wave method, use the same potential operator as the pseudopotential but retain the all-electron core wavefunctions. Thus, in some sense, they more accurately capture the behavior near the nucleus [92].
APPENDIX B

DETAILS OF THE COMPUTATION PROCESS

In this appendix, I describe the process of calculating reflectivities using our method from calculating self-consistent potentials and band structures with Quantum ESPRESSO (QE) through performing the wavefunction matching at the supercell boundaries to combining reflectivity curves from different supercells and filtering and interpolating them. I provide at least the names of many of the routines and functions called to aid anyone attempting to perform these calculations on their own with access to my files. At the time of writing, the programs involved have not been bundled into a distribution.

B.1 Tasks Performed Once for Each System and Supercell

The calculations of the self-consistent potential and the vacuum energy only need to be performed once for each physical system with a given supercell width.

B.1.1 DFT Self-Consistency Calculation

Example input filename: ‘3LGraphene.scf_c10.in’

The first step in the process of calculating a reflectivity spectrum using our supercell, Bloch wave method is to run a self-consistent field calculation with the pw.x program in Quantum ESPRESSO to determine the self-consistent ground state potential of the slab-in-supercell system. The input file includes the atomic positions of the atoms in the system. The type of calculation can be set to ‘scf’ to compute the ground state potential for the given atomic coordinates or ‘relax’ to find the ground state atomic configuration through iterative calculations of the ground state potential with adjustments to the atomic positions made at each iteration based on the computed forces on the atoms. Either way, the final ‘scf’ calculation will produce the ground state potential that will be used in the band structure calculations that compute the wavefunctions used in the matching algorithms.

B.1.2 Determination of Vacuum Energy


In order to determine the vacuum energy for the calculated potentials, we use the pp.x and average.x programs in Quantum ESPRESSO to find the average value of the potential near the supercell boundary. The post-processing program pp.x is run with the setting ‘plot_num=1’ to designate that the values of the three-dimensional ground state potential be written to file. Then, average.x averages the potential over the in-plane directions to produce the average ground state potential as a function of $z$. Typically, I then manually inspect the plot of this average to determine the approximate value near the supercell boundary ($z = 0$) to within approximately 0.0005 Ry. I have also written a Matlab function to average this average potential over a set of gridpoints near...
the boundary (example: ‘Vacuum_energy_Free_FLG.m’). However, typically, to get results from different supercells to line up with one another best, the exact value of the vacuum energy needs to be adjusted slightly anyway.

B.2 Tasks Performed for Each Value of the In-plane Wave vector, $k_\parallel$

For normal incidence, the procedures in this section need to be completed just once. For any calculation involving off-normal incidence beams, these procedures must be completed once for each value of the in-plane wave vector of the Bloch solutions, $k_\parallel$. Generally, I have created a bash control script to loop through $k_\parallel$ values, running through all of the steps in this section in each loop iteration (e.g., ‘Free_FLG_Off_Normal_Energy_Sort_Feenstra_00_Amp-3L_c_plotbands_MATLAB_bg_cmp1_Unix_job_queue.sh’). Because the storage of the eigenvector files is large, the scripts are currently set up to rewrite all of the QE output for each $k_\parallel$.

B.2.1 Band Calculation

Example Input Filename: ‘3LGraphene.bands_Off_N_kpar_0.1_0.1_c10.in’

To calculate the scattering wavefunctions inside the supercell for each $k_\parallel$, we run a band structure calculation with the pw.x program in QUANTUM ESPRESSO. The input file sets the calculation types as ‘bands’, which means that the calculation is non-self-consistent (the potential is fixed, not recalculated from the solutions) and that any number of solutions can be calculated for each point in a specified path of points through reciprocal space ($k$-point path). The number of solutions must be set high enough for solutions of all desired energies to be calculated. (This cannot be known for certain in advance. It is sometimes best to run a band structure calculation at one value of $k_\parallel$, say (0,0), with a large number of bands to see for how many bands all calculations should be set to run.) The specified $k$-point path should have $k_\parallel$ fixed, and $k_z$ should range over the first Brillouin zone, avoiding the boundaries (and usually 0). It should be sufficiently dense to produce a satisfactory energy-sort matching.

B.2.2 Conversion of Binary QUANTUM ESPRESSO Files

We are working with an external program, QUANTUM ESPRESSO, and using quantities that are not a standard output of the program. The closest thing one can get using the standard post-processing program, pp.x, to the Kohn-Sham wavefunction is the contribution from one electron state to the overall charge density, which is essentially the squared amplitude of the wavefunction. This is not enough. Thus, we need to access the wavefunctions themselves from the binary output files produced by QE. When pw.x is run in parallel with the option ‘wf_collect = .true.’, it produces an eigenvector file for each point in the $k_z$-path, placed in the folder created for each $k_z$-point. In order to convert these files to a readable form, we use the QE input/output ‘iotk’ programs. We also must convert the ‘gkvectors.dat’ files which contain information about the ordering of

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1In the regime of specular reflection only, $k_\parallel$ is equal to the in-plane wave vector of the incident beam, $q_\parallel$, so the repetitions of this process are determined by the desired incident beam spectra. For higher energies, in which case $q_\parallel$ can be outside the first Brillouin zone and higher-order diffracted beams are possible, the repetitions would be tied to the necessary $k_\parallel$ values in the first Brillouin zone, but at each step in the process, more reflectivity values would be computed.

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the Fourier coefficients in the wavefunction files. I have written a bash script, `iotk_convert.sh`, which calls iotk functions to convert these two files for each point in the $k_z$-path. Note that it is important here to differentiate between eigenvectors and wavefunctions. The eigenvectors are solutions of the Schrödinger Equation in reciprocal space, which are really the periodic parts of the wavefunctions. Each is stored in the QE output files as the Fourier coefficients of the periodic part of the wavefunction. The wavefunctions include the exponential factor with the associated Bloch wave vector, $e^{i k \cdot r}$. In my code, generally, the eigenvectors are stored and the exponential factor is included in calculations that involve the full wavefunctions.

Note: One could potentially make the code more efficient by learning more about the binary file formats and directly accessing the data from the binary files, skipping this conversion.

B.2.3 Main MATLAB Functions

Example Filename: `FLG_3L_c10_Off_N_E_Sort_Feen_func_of_k_par_2_thresh.m` with inputs: $k_1$, $k_2$, Flat band thresh, Energy diff thresh, Vac frac.

This function is actually a mix of inputs and a control script. Many input variables are set in it, and then it calls the script described immediately below to analyze data and perform the matching. Values in this file must be changed for each system and supercell, including the number of points in the FFT grid, the plane wave energy cut offs, the lattice parameter and reciprocal lattice vectors, the number of layers in the system, the width of the supercell in terms of the lattice parameter, and the vacuum energy in Rydberg. This function then creates the filename for the reflectivity curve output and the path in which the QE output folder is found. (In other words, the contents of this function must be made to match the QE output folder.) This function then calls a script, which accesses all of the variables set in this function, to extract the necessary data from QE output files and perform the matching. $k_1$ and $k_2$ are the components of the in-plane wave vector of the incident beam in the reciprocal lattice basis, $b_1$ and $b_2$. Often, I set up multiple instances to run simultaneously for various values of the filtering thresholds ($E_{\text{diff\_thresh}}$, Flat band thresh) and/or the fraction of vacuum on one side of the slab to integrate over in the calculation of $\sigma$ (Vac frac).

Example Script Filename: `Refl_curve_script_Off_N_E_Sort_Feenstra_00_Amp_2_thresh.m`

This script performs the bulk of the matching process. It reads in the $k_z$-path, the energies, eigenvectors, and eigenvector component indices. It then uses this information to remove flat bands, perform matching with pairs of wavefunctions of the ‘same’ energy, and compute and record various details of the wavefunctions. This script is broken up into the following steps, with the function calls in each step listed.

**Compute Vacuum Size**

Function call: `get_atomic_pos_robust.m`

In some versions of this script, I have added an initial step which retrieves the number of atoms and atomic positions from the ‘data-file.xml’ and uses them to compute the width of the vacuum on one side of the slab for later use in the calculation of $\sigma$. This calculation assumes that the slab is centered.

**Read in k_path and Energies**

Function calls: `get_k_path_robust.m`, `Read_eigenval.m`
These functions extract the \( k \)-path from ‘data-file.xml’ within QE output folder and energies from ‘eigenval.xml’ within \( k \)-point folders in QE output folder and convert them to Rydberg. In this step, the reading of eigenvalues is first done for just the first \( k \)-point, extracting all energies. Then it is determined how many bands have energies above the vacuum energy to determine ‘pos_energy_states’. (This is assumed to be the same for all \( k \灵气点). If the lowest energy band crosses the vacuum energy, then this could be missing one positive energy state for some \( k \)-points or including one negative energy state for some \( k \)-points.) Then, the energies are read for each \( k \)-point, shifted by the vacuum energy, recorded (in ‘Energy_index’ matrix), and sorted. Finally, the upper and lower energy bounds for the given \( k_\parallel \) are calculated for use in constraining the energy pair search.

**Identify Flat Bands**

This section of the function identifies sets of wavefunctions with energies within a given flat band threshold and removes (flat) bands which have 90% of their points contained, pairwise, within this threshold. (It was decided that this filter was unnecessary. Most recent runs have set the threshold to 0, negating this filter, but the option remains to use it if it is deemed appropriate.)

**Find Energy Pairs**

This section of the function finds pairs of wavefunctions with energies that differ by less than \( E_{\text{diff thresh}} \) and that are within the lower and upper energy bounds for the specular reflection regime. It records energy, band number, and \( k \)-slot for the two wavefunctions in the pair in the matrix Energy_pairs.

**Read in Eigenvectors**

Function calls: ‘get_num_PWVs.m’, ‘Read_gk_vectors.m’, ‘Fill_eigenvectors_par_Off_N_G_par_zero.m’, ‘Retrieve_eigenvector_norms_par.m’

The coefficients of the eigenvectors are not stored according to a uniform grid but by the energy of the associated plane wave basis element (including the Bloch wave vector), \(|\mathbf{k}+\mathbf{G}|^2\), and coefficients are only included up to an energy cutoff: ecutwfc for the wavefunction and ecutrho for the charge density and the potential. Thus, it is necessary to know how many plane wave components are used and in which order the associated coefficients are stored. These functions extract this structure of the eigenvector datafiles, by finding the number of components recorded (num_PWVs) and the indices of components. Then, they read the coefficients of the \((0,0)\) component (the coefficients in the \( z \)-direction) of the eigenvector into a matrix and compute the norm of the entire eigenvector. This norm is then used to normalize the coefficients of the \((0,0)\) component.

Note: One could potentially improve the efficiency of the code by using the coefficients as stored, rather than reading them into a full matrix the size of the FFT grid, perhaps by making use of the FFT modules in QE (e.g., ‘fft_scalar.f90’).

**Process Energy Pairs**

The following four steps are performed within a loop over the pairs of (sufficiently) degenerate solutions that have been identified.
IFFT

The $(0,0)$ component of the eigenvector is inverse Fourier transformed (in one dimension) to give it as a function of $z$. (This vector is multiplied by the number of FFT grid points in the $z$-direction to normalize properly.)

Max Amp Sq

The maximum of the squared amplitude of the $(0,0)$ component of the wavefunction (in real space) is recorded. Previously, this was used as a filter to remove states which did not have significant weight in the $(0,0)$ component, in neither the vacuum nor the slab.

$\sigma$ Measure

The computation of the $\sigma$ measure involves the $(0,0)$ components of the two wavefunctions of an energy pair (as given by *Energy_pairs*). These components are multiplied by their respective Bloch factors ($e^{ik_0z}$) then added (subtracted) and divided by $\sqrt{2}$ to create $\phi_+(z)$ ($\phi_-(z)$). Then, each of these is integrated against a plane wave with wave vector equal to $\kappa_0 = \sqrt{E - |k|}^2$. Thus,

$$\sigma_\pm = \frac{\sqrt{A} \cdot \text{sprclwz}}{\text{Vac}_\text{param} \cdot \sqrt{V}} \int_0^{\text{Vac}_\text{param}} \phi_\pm(z) e^{i\kappa_0z} dz.$$ 

Then, $\sigma$ is computed as $\sigma = \sqrt{\sigma_+^2 + \sigma_-^2}$. *sprclwz* is the supercell width. $A$ is the area of the in-plane unit cell. *Vac_param* is the length of the vacuum over which the integration is performed. It is calculated as a fraction of the vacuum on one side of the slab by multiplying *Vac_frac*, typically 1/6, by the calculated vacuum width. (In Chapters 3 and 6, *Vac_param* is written as $I$.)

The above calculation of $\sigma$ differs in two ways from the descriptions in Chapters 3 and 6, however, due to the history of the development of the code and for consistency sake, the above is what has been calculated in most runs performed up to now and what currently remains in the code. The first difference is that the above uses the standing-wave-like combinations of the $(0,0)$ components of the wavefunctions, $\phi_\pm$, as opposed to the components of the wavefunctions themselves, $\phi_{1,2}$. As shown in Ch. 6, these are equivalent, but for completeness I point out that $\phi_\pm$ are currently used in the code. Secondly, there is an issue of a factor of $\sqrt{2}$. If the prefactor multiplying the integral is simplified, the $\sqrt{A(sprclwz)}$ and the $\sqrt{V}$ cancel, leaving simply $\frac{1}{\sqrt{2}}$. In Chapters 3 and 6, the $\sqrt{2}$ is not included. The code currently computes with the factor $\frac{1}{\sqrt{2I}}$, however, the filtering has been adjusted (in relation to the quoted threshold values) so that the quoted filter thresholds match a calculation of $\sigma$ using the prefactor $\frac{1}{I}$.

Matching

Function call: ‘SingleBeamMatching_Off_N_Energy_Pair_det_M_index.m’

This function performs the matching of plane waves to supercell, Bloch wave solutions for each pair of (sufficiently) degenerate solutions. The energy used to determine the wave vector of the plane wave is the lower energy of the two solutions in the pair.
B.2.4 Write Output to File

All reflectivity data, including the energy converted to eV (of the lower energy solution in the pair), is written to the output file, with my Matlab ‘Write Matrix to File.m’ function. The format of the output file is:

<table>
<thead>
<tr>
<th>Column</th>
<th>Data</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Energy</td>
<td>eV</td>
</tr>
<tr>
<td>2</td>
<td>Refl</td>
<td>fraction of incoming intensity</td>
</tr>
<tr>
<td>3</td>
<td>det_M</td>
<td>none</td>
</tr>
<tr>
<td>4</td>
<td>det_M_norm</td>
<td>none</td>
</tr>
<tr>
<td>5</td>
<td>kz_slot_1</td>
<td>none</td>
</tr>
<tr>
<td>6</td>
<td>energy_band_1</td>
<td>none</td>
</tr>
<tr>
<td>7</td>
<td>kz_slot_2</td>
<td>none</td>
</tr>
<tr>
<td>8</td>
<td>energy_band_2</td>
<td>none</td>
</tr>
<tr>
<td>9</td>
<td>amp_sq_00_comp_max_1</td>
<td>none</td>
</tr>
<tr>
<td>10</td>
<td>amp_sq_00_comp_max_2</td>
<td>none</td>
</tr>
<tr>
<td>11</td>
<td>PW_Proj_measure (σ)</td>
<td>none</td>
</tr>
<tr>
<td>12</td>
<td>eigenvec_norm_1</td>
<td>none</td>
</tr>
<tr>
<td>13</td>
<td>eigenvec_norm_2</td>
<td>none</td>
</tr>
</tbody>
</table>

B.3 Combining, Filtering, Interpolating

Control script: ‘Plot_FLG_CMap_Off_N_Energy_Sort_2_thresh_Feenstra_MGK_Comb_2SC.m.’

Once all matching is done, I use a separate Matlab script to combine data from different supercell runs, filter the data according to some column in the reflectivity data files (usually the σ measure), interpolate the data along a fixed \( k_\parallel \), and plot a colormap of the general incidence reflectivity spectra.

B.3.1 Combining Supercells

Function call: ‘Combine_Off_N_E_Sort_2_thresh_Feenstra_NSĆ_func.m’
The data from any number of matching output files are combined and sorted by energy.

B.3.2 Filtering

Function call: ‘Filter_script_Energy_Sort_2_thresh_Feenstra_NSĆ_spec_func.m’
The data for energy points (energy pairs of wavefunctions) for which σ is greater than some threshold are removed. Then, the columns other than energy and reflection are removed.

B.3.3 Interpolating

Function call: ‘OneD_Interp_NSĆ_Off_N_E_Sort_2_thresh_Feenstra_spec_func.m’
A one-dimensional interpolation is performed on the combined and filtered data for each \( k_\parallel \), using any interpolation style that Matlab allows (given as an argument set in the control script), typically, linear. Then this data for all \( k_\parallel \) is written to a single file.
B.3.4 Plotting

Function call: ‘Plot_Off_N_E_Sort_2_thresh_Feenstra_CMap_interp1_func.m’
Matlab colormap plotting function, imagesc, is used to create a colormap, with limits set to 0 and 1. (This can be changed within this function, if desired, to see reflectivities that have been calculated to be larger than one.)
Bibliography


