

Homogenization theory for periodic potentials in the Schrödinger equation

LENNON Ó NÁRAIGH¹ AND DOIREANN O'KIELY^{1,2}

¹School of Mathematical Sciences, University College Dublin, Belfield, Dublin 4

² School of Physics, University College Dublin, Belfield, Dublin 4

Abstract

We use homogenization theory to derive asymptotic solutions of the Schrödinger equation for periodic potentials. This approach provides a rigorous framework in which the key concepts in solid-state physics naturally arise (Bloch waves, band gaps, effective mass, and group velocity). We solve the resulting spectral cell problem using numerical spectral methods, and validate our solution in an analytically-solvable case. Finally, we briefly discuss the convergence of our asymptotic approach and we prove that the ground-state $k = 0$ effective mass is never less than the ordinary inertial mass.

PACS numbers: 71.15.-m, 03.65.-w

1 Introduction

In quantum mechanics, study of the motion of a charged particle in a periodic potential leads to a definitive characterization of metals, insulators, and semi-conductors. Solving the Schrödinger equation for such a many-body system is difficult, and many approximation techniques exist to make the problem more tractable. At the most advanced level, these techniques can be used to predict the electronic properties of real, three-dimensional crystal structures. However, the same techniques are used as a pedagogical tool to develop intuition about the electronic properties of solids [1, 2]. In this article, we introduce homogenization theory as a perturbation method that can be used to accomplish both these goals. The focus is on an application to simple one-dimensional crystal structures, with a view to providing a rigorous unified theoretical framework in which the key concepts in solid state physics (Bloch waves, band gaps, dispersion relations, effective mass, and group velocity) naturally arise.

We first of all review several existing approaches that are used to develop a student's understanding of the electronic properties of matter. The *Kronig-Penny model* is a simple one-dimensional model in which a piecewise-constant, periodic potential is prescribed along the real line [3]. The Schrödinger equation is solved in a typical periodic cell, with appropriate matching conditions at the cell boundaries. This gives a solution parametrized by a wavenumber k , and a characteristic equation in terms of a 4×4 determinant, which is then reduced to a single root-finding

condition, the solution of which gives the energy E as a function of k – a *dispersion relation*. There exist ranges of energy for which the dispersion relation is satisfied by real values of k . These are the allowed *energy bands*; energies outside of these bands are forbidden, and are referred to as *band gaps*. By periodicity, it suffices to consider k -values in the range $[-\pi/\ell, \pi/\ell]$, where ℓ is the periodicity of the potential. The same model can also be used to introduce the notion of Bloch waves, as the eigenfunctions consist of a phase e^{ikx} , multiplied by an ℓ -periodic function that depends parametrically on k . Conceptually, this approach is simple, but the algebra associated with solution of the eigenvalue problem is involved, and is further obscured by the root-finding which must be performed either numerically or graphically.

There exist other approaches that can explain the structure of the electron dispersion relation in periodic potentials. The *nearly-free electron model* applies in the limiting case where the periodic potential is weak [1]. In this case, the electron wavefunction can be written as a sum of plane waves. The resulting dispersion relation differs from that of free electrons only near $k = \pm\pi/\ell$, where Bragg reflection causes the opening up of a band gap in the dispersion relation. The *tight-binding model* is built around on the opposite approximation wherein the periodic potential is strong, such that electrons are localized near lattice sites [4]. A limiting case consists of electrons that are localized to the extent that the electron wave function consists of a linear combination of atomic orbitals, where each orbital is centred on an individual lattice site. In this description, the overlap between orbitals causes the energy levels to spread out, thus producing ‘bands’ of energy, separated by forbidden regions.

A drawback of all of these approaches is their inability to explain the idea of *effective mass*. This is the notion that the inertia with which an electron resists changes to its motion (as a result of the imposition of a large-scale external potential) is not the ordinary mass, but is rather an effective mass, given by the curvature of the dispersion relation. This can be negative. Typically, effective mass is introduced by an analogy with Newtonian physics [1]. We therefore propose a different approach for the approximate solution of the Schrödinger equation for the periodic potential. This is based on a separation of scales, wherein the wavefunction is separated into a rapidly-varying component, associated with the periodic potential, and a slowly-varying component, associated with large-scale forces on the system (such as an external electric field). We will demonstrate that the small-scale component of the solution satisfies a Bloch-type *spectral cell problem*, which can be solved in a straightforward manner for arbitrary potentials using a very simple and accurate numerical method [5]. Additionally, we will show that the large-scale component solves an ‘averaged’ Schrödinger equation, where the mass is replaced by the ‘effective mass’. Thus, our approach gives a simple yet quantum mechanically self-consistent demonstration of the concepts of the band gap and effective mass.

Given a generic partial differential equation (PDE) with coefficients that vary on small length scales compared to the domain size, homogenization theory naturally presents itself as a tool for understanding the effects of the small-scale disturbances on the large-scale features of the solution [6]. Typically, the small scales are bundled up into ‘effective’ coefficients, and the model reduces to a more manageable equation involving only large-scale variables. This method has been applied successfully to

the linear convection-diffusion equation in fluid mechanics [7, 8, 9], and also to problems in porous-medium flow [10], and reaction-diffusion [11, 12]. The same approach has been applied to the Schrödinger equation, wherein the potential varies in a periodic fashion on the small scale ℓ , and on a larger, domain-size scale L [13, 14, 15, 16, 17], with $\varepsilon := \ell/L \ll 1$. The focus of [14, 15, 16] is not on physical applications, but rather on a rigorous proof of *convergence*, namely a determination of the criteria for the solution of the basic Schrödinger equation to converge to the solution of the homogenized problem, in the limit as $\varepsilon \rightarrow 0$. In [15, 16], the authors proved convergence results, based on the condition that the unhomogenized solution be initialized with appropriate initial data. This is in contrast to diffusion-type problems, where convergence is guaranteed, independent of the form of the initial data [6]. The formal asymptotics in [17] are in the spirit of the present work; however the calculations in [17] are limited to critical points in the electron dispersion relation (that is, wavenumbers for which the group velocity vanishes). Our work benefits from being embedded in the theoretical framework of [14, 15, 16], since the formal asymptotic analysis is thus extended to arbitrary wavenumbers. That our calculations are valid for arbitrary wavenumbers also justifies our development of a simple and accurate numerical technique to solve the Bloch spectral cell problem.

For a student of physics, the formal asymptotics in the references [14, 15, 16] are of interest, because they naturally give rise to Bloch waves, band gaps, and the effective mass. However, these calculations are obscured by the focus on rigorous convergence proofs. Consequently, in the present paper, we perform the detailed but purely *formal* calculations necessary to derive these concepts. Because this paper is pedagogical in scope, a number of the more involved asymptotic calculations is described in detail in a companion document. These could also be used by an instructor as exercises in quantum-mechanical singular perturbation theory.

This paper is organized as follows. In Section 2 we non-dimensionalize the Schrödinger equation, to highlight the separation of scales inherent in the problem. In Section 3 we carry out the formal homogenization theory and introduce Bloch waves, the dispersion relation, and effective mass. The Bloch spectral cell problem is solved numerically in Section 4. An alternative homogenization theory for the ground state is given in Section 5, and issues of convergence are discussed briefly. Conclusions are presented in Section 6.

2 Non-dimensionalization of the Schrödinger equation

We begin with the one-dimensional time-dependent Schrödinger equation, on a domain $[0, L]$:

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x)\psi(x, t). \quad (1a)$$

The potential $V(x)$ is assumed to have the following form:

$$V(x) = V_0(x/\ell) + V_1(x/L, x/\ell). \quad (1b)$$

Here $V_0(x/\ell)$ corresponds to the potential experienced by the electron in a crystal as it interacts with the lattice sites, spaced ℓ apart. Thus, $V_0(x/\ell)$ is 1-periodic.

Similarly, $V_1(x/L, x/\ell)$ represents a large-scale external force imposed on the system, and varies both the small scale ℓ , and, independently, on the large scale L . The small-scale variation of V_1 is also assumed to be 1-periodic (this small-scale variation is included as a way of accounting for perturbations to the atomic potential induced by the external force; the potential $V_0(x/\ell)$ thus represents the unperturbed case). In this description, it is natural to impose the condition that ψ be periodic on the domain-scale L [3], and to assume further that $\varepsilon := \ell/L$ is small. Thus, we introduce a dimensionless variable $\tilde{x} = x/L$ and scales A_0 and A_1 for the potential energy terms, such that $V_0 = A_0 \tilde{V}_0(\tilde{x}/\varepsilon)$ and $V_1 = A_1 \tilde{V}_1(\tilde{x}, \tilde{x}/\varepsilon)$. Here \tilde{V}_0 and \tilde{V}_1 are non-dimensional potential functions. Multiplying across by $2mL^2/\hbar^2$, Equation (1a) becomes

$$i \frac{2mL^2}{\hbar} \frac{\partial \psi}{\partial t} = -\frac{\partial^2 \psi}{\partial \tilde{x}^2} + \frac{2mL^2 A_0}{\hbar^2} \tilde{V}_0 \psi + \frac{2mL^2 A_1}{\hbar^2} \tilde{V}_1 \psi. \quad (2)$$

Thus, a suitable time scale is given by $\tau = 2mL^2/\hbar$. Introducing $\tilde{t} := t/\tau$, Equation (7) becomes

$$i \frac{\partial \psi}{\partial \tilde{t}} = -\frac{\partial^2 \psi}{\partial \tilde{x}^2} + \left[\alpha \tilde{V}_0(\tilde{x}/\varepsilon) + \beta \tilde{V}_1(\tilde{x}, \tilde{x}/\varepsilon) \right] \psi, \quad (3)$$

where $\alpha := 2mL^2 A_0/\hbar^2$ and $\beta := 2mL^2 A_1/\hbar^2$ are dimensionless numbers. Following standard practice, we henceforth omit the tildes from the dimensionless parameters.

The parameters α and β are set by the problem under investigation; however, in a theoretical investigation, they can be adjusted to model desired physical effects. In this work, we expect the effects of the periodic potential to dominate in determining the character of the wave-function. This is typical in problems involving electron motion in crystals [1]. Consequently, we take $\alpha \gg \beta$. In fact, we take $\alpha = 1/\varepsilon^2$, and $\beta = 1$ (for a further discussion on this parameter choice, see Section 3). Thus, the final form of the non-dimensional Schrödinger equation reads

$$i \frac{\partial \psi_\varepsilon}{\partial \tilde{t}} = -\frac{\partial^2 \psi_\varepsilon}{\partial \tilde{x}^2} + \left[\frac{1}{\varepsilon^2} V_0(x/\varepsilon) + V_1(x, x/\varepsilon) \right] \psi_\varepsilon, \quad (4)$$

where the subscript on the wavefunction denotes a parametric dependence of the solution on ε .

3 Homogenization theory

Solving Equation (4) is problematic, as the potentials V_0 and V_1 are quite general. Even a numerical solution is difficult, as the presence of the small parameter ε would require resolution of an extremely large range of length scales. However, the large-scale behaviour of a system with phenomena occurring at various length- and time-scales is well described by homogenization theory [6], wherein the partial differential equation that describes the system is regarded as having rapidly oscillating differential operators corresponding to the different scales of the phenomena. Taking the appropriate limit of infinite scale separation, the solution of the homogenized partial differential equation describes the large-scale behavior induced by the small-scale dynamics. We apply this theory to Equation (4), and propose a solution

that depends independently on the large and small scales. Thus, the wavefunction $\psi_\varepsilon(x, t)$, with its two slots and a parametric dependence on ε , is replaced by an equivalent function with four slots $\psi(x, y, t, T)$; now the dependence on ε enters through the definition of the different scales: (x, y) represent (respectively) the large and small spatial scales, while (t, T) represent the large and small temporal scales. Because the small spatial scales enter Equation (4) in the potentials $V_0(x/\varepsilon)$ and $V_1(x, x/\varepsilon)$, it is natural to identify $y = x/\varepsilon$; the small time scale T is fixed below. Spatial derivatives of the two-slot function ψ_ε and of the four-slot function ψ are thus related through the chain rule:

$$\frac{\partial \psi_\varepsilon(x)}{\partial x} = \left(\frac{\partial}{\partial x} + \frac{dy}{dx} \frac{\partial}{\partial y} \right) \psi(x, y) = \left(\frac{\partial}{\partial x} + \frac{1}{\varepsilon} \frac{\partial}{\partial y} \right) \psi(x, y). \quad (5)$$

One may think of this as a replacement in Equation (4), whereby $\partial/\partial x$ is replaced by $(\partial/\partial x) + \varepsilon^{-1}(\partial/\partial y)$. In the same manner, the derivative $\partial/\partial t$ in Equation (4) is replaced by

$$\frac{\partial}{\partial t} + \frac{dT}{dt} \frac{\partial}{\partial T}; \quad (6)$$

we also take $dT/dt = \varepsilon^{-2}$. Trial and error confirms this choice (for example, as an exercise, it can be shown using standard homogenization theory that the choice $\alpha = \varepsilon^{-1}$, $\beta = 0$ and $\partial/\partial t \rightarrow \partial/\partial t$, leads to a homogenized Schrödinger equation that predicts a simple shift in all the energy levels, relative to the case where all the potential-energy terms are zero, a result that is clearly at odds with the physically observed electron behaviour in a periodic potential). Also, this prescription for the small-scale temporal variations is found in the homogenization theory of linear advection-diffusion, where it accurately describes diffusion-dominated transport. Such diffusion-dominated transport gives rise to an effective or averaged diffusion equation, wherein the effects of flow are bundled up into an effective-diffusion coefficient. Because the Schrödinger equation possesses a similar structure, we are justified in using the same diffusive scaling scheme for the small-scale temporal variations here. Motivated by this discussion, we apply Equations (5)–(6) to the Schrödinger equation and obtain the following two-time, two-scale problem:

$$i \frac{\partial \psi}{\partial t} + \frac{i}{\varepsilon^2} \frac{\partial \psi}{\partial T} = - \left(\frac{\partial}{\partial x} + \frac{1}{\varepsilon} \frac{\partial}{\partial y} \right)^2 \psi + \left[\frac{1}{\varepsilon^2} V_0(y) + V_1(x, y) \right] \psi, \quad (7)$$

where now x, y are completely independent variables taking values in the interval $[0, 1]$.

Because the potentials V_0 and V_1 are y -periodic functions with period 1, the Hamiltonian in Equation (7) commutes with the unit translation operator in the y -variable. Consequently, simultaneous eigenfunctions of unit translation and energy exist. These are the Bloch functions [3], and consist of an exponential part e^{iky} , together with a part that is 1-periodic in y . Here k is the eigenvalue of unit translation, and is identified with the *crystal momentum*. Thus, we propose the following ansatz for Equation (7):

$$\psi(x, y, t, T) = e^{iky} \sum_{p=0}^{\infty} \varepsilon^p u_p(x, y, t, T), \quad (8)$$

where each function $u_p(x, y, t, T)$ is 1-periodic in the y variable. Substitution of Equation (8) into the basic Schrödinger equation (7) yields the following equation:

$$\begin{aligned} \sum_{p=0}^{\infty} \varepsilon^p \left(\frac{i}{\varepsilon^2} \frac{\partial u_p}{\partial T} + i \frac{\partial u_p}{\partial t} \right) &= \sum_{p=0}^{\infty} \varepsilon^p \left(\frac{k^2}{\varepsilon^2} u_p - \frac{2ik}{\varepsilon^2} \frac{\partial u_p}{\partial y} - \frac{2ik}{\varepsilon} \frac{\partial u_p}{\partial x} \right) \\ &- \sum_{p=0}^{\infty} \varepsilon^p \left(\frac{\partial^2 u_p}{\partial x^2} + \frac{2}{\varepsilon} \frac{\partial^2 u_p}{\partial x \partial y} + \frac{1}{\varepsilon^2} \frac{\partial^2 u_p}{\partial y^2} \right) + \sum_{p=0}^{\infty} \varepsilon^p \left[\frac{1}{\varepsilon^2} V_0(y) + V_1(x, y) \right] u_p. \end{aligned} \quad (9)$$

We proceed to solve Equation (9) order-by-order.

The contribution to Equation (9) at $O(\varepsilon^{-2})$ is

$$i \frac{\partial u_0}{\partial T} = - \left(\frac{\partial}{\partial y} + ik \right)^2 u_0 + V_0(y) u_0. \quad (10)$$

We can immediately separate the time and space dependence in u_0 . Indeed, we can separate u_0 fully in terms of a product of separate functions of T , y , and (x, t) , letting

$$u_0(x, y, t, T) = e^{-i\lambda T} f(y; k) \phi(x, t) \quad (11)$$

such that

$$\lambda f(y; k) = - \left(\frac{\partial}{\partial y} + ik \right)^2 f(y; k) + V_0(y) f(y; k) \quad (12)$$

(here, the semicolon between the variables in $f(y; k)$ denotes a function of y that depends parametrically on k). The eigenvalue problem (12) for $f(y; k)$ is the *spectral cell problem*. For simplicity, we assume that the eigenspaces of the spectral cell problem are one-dimensional (i.e. non-degenerate), such that the separation of variables in Equation (11) involves only one linearly-independent function $f(y; k)$. Because of Bloch's theorem (Equation (8)), periodic boundary conditions in the y -variable are placed on $f(y; k)$, with $y \in [0, 1]$ (this is also consistent with standard practice in homogenization theory [6]). Thus, the eigenfunctions/eigenvalue pair – denoted here by $(f(y; k), \lambda)$ – associated with Equation (12) are discrete, with label n , such that $\lambda \rightarrow \lambda_n$, and $f(y; k) \rightarrow f_n(y; k)$. In solid state physics, the functions $f_n(y; k)$ are called the *Bloch functions*. Equation (12) is self-adjoint; the eigenvalue λ is therefore identified with the energy, which depends parametrically on the crystal momentum k : $\lambda_n = \lambda_n(k)$. Thus, we have a *dispersion relation*, wherein the electron energy is related to the momentum.

We make the replacement $\partial/\partial T \rightarrow -i\lambda$ throughout Equation (9). Thus, the contribution at $O(\varepsilon^{-1})$ now reads

$$\lambda_n u_1 = - \left(\frac{\partial}{\partial y} + ik \right)^2 u_1 + V_0(y) u_1 - 2ik f_n \frac{\partial \phi}{\partial x} - 2 \frac{\partial f_n}{\partial y} \frac{\partial \phi}{\partial x}. \quad (13)$$

This also has a separable solution $u_1 = g(y; k)(\partial\phi/\partial x)$, such that

$$\lambda_n g(y; k) = - \left(\frac{\partial}{\partial y} + ik \right)^2 g(y; k) + V_0(y) g(y; k) - 2ik f_n - 2 \frac{\partial f_n}{\partial y} \quad (14)$$

(later on in this section, we comment about the solvability condition for this equation). Similarly, at $O(1)$, we have

$$\begin{aligned} \lambda_n u_2 + i \frac{\partial g}{\partial t} f_n(y; k) &= -f_n(y; k) \frac{\partial^2 \phi}{\partial x^2} + V_1(x, y) f_n(y; k) \phi - \left(\frac{\partial}{\partial y} + ik \right)^2 u_2 \\ &\quad + V_0(y) u_2 - 2ik f_n(y; k) \frac{\partial^2 \phi}{\partial x^2} - 2 \frac{\partial f_n}{\partial y} \frac{\partial^2 \phi}{\partial x^2}. \end{aligned} \quad (15)$$

Again, we make the separation assumption $v_2 = h(y; k)(\partial^2 \phi / \partial x^2)$ and obtain

$$\begin{aligned} \lambda_n h(y; k) \frac{\partial^2 \phi}{\partial x^2} + i \frac{\partial \phi}{\partial t} f_n(y; k) &= V_1(x, y) f_n(y; k) \phi \\ - \frac{\partial^2 \phi}{\partial x^2} \left[f_n(y; k) + 2ik f_n(y; k) + 2 \frac{\partial f_n}{\partial y} \right] &+ \frac{\partial^2 \phi}{\partial x^2} \left[- \left(\frac{\partial}{\partial y} + ik \right)^2 h(y; k) + V_0(y) h(y; k) \right]. \end{aligned} \quad (16)$$

Equations (14) and (16) have a remarkably simple solution, which we now derive.

Case 1. At critical points in the dispersion relation: A critical point of a generic function of a single variable is a point for which the derivative vanishes. We examine the properties of the Bloch spectral cell problem evaluated at such a point k_n , with $(d\lambda_n/dk)_{k_n} = 0$. More precisely, we differentiate the Bloch spectral cell problem (12) once *with respect to* k and evaluate the result at k_n . The derivative of Equation (12) with respect to k and evaluated at k_n is

$$\lambda_n \frac{\partial f_n}{\partial k} = - \left(\frac{\partial}{\partial y} + ik \right)^2 \frac{\partial f_n}{\partial k} - 2i \left(\frac{\partial}{\partial y} + ik \right) f_n + V_0(y) \frac{\partial f_n}{\partial k}. \quad (17)$$

Comparison between Equation (14) and Equation (17) immediately shows that

$$g(y; k) = -i \frac{\partial f}{\partial k} \Big|_{k_n}, \quad u_1 = -i \frac{\partial \phi}{\partial x} \frac{\partial f}{\partial k} \Big|_{k_n}. \quad (18)$$

It is clear from this construction that Equation (14) has a solution. However, by multiplying Eq. (14) by f_n^* , integrating the resulting product with respect to y , and employing the self-adjoint property of the operator $\lambda_n + (\partial_y + ik)^2 - V_0(y)$, it is also clear that

$$\int_0^1 \left(ik |f_n|^2 + f_n^* \frac{\partial f_n}{\partial y} \right) dy = 0. \quad (19)$$

Equation (19) is therefore a further property of the solution at critical points in the dispersion relation. Equally, it can be regarded as the consistency criterion in order for Equation (14) to have a solution. This consistency condition constrained the calculations in [17] to be valid only at the critical points of the dispersion relation. In this work, this restriction is lifted in Case 2 (below).

In the same manner, double differentiation of the spectral cell problem with respect to k and subsequent evaluation at k_n yields

$$\lambda_n \frac{\partial^2 f_n}{\partial k^2} + f_n \frac{d^2 \lambda_n}{dk^2} = V_0(y) \frac{\partial^2 f_n}{\partial k^2} - \left(\frac{\partial}{\partial y} + ik \right)^2 \frac{\partial^2 f_n}{\partial k^2} - 4i \left(\frac{\partial}{\partial y} + ik \right) \frac{\partial f_n}{\partial k} + 2f_n. \quad (20)$$

Comparison between Equation (16) and Equation (20) implies that

$$h(y; k) = -\frac{1}{2} \frac{\partial^2 f_n}{\partial k^2} \Big|_{k_n}, \quad u_2 = -\frac{1}{2} \frac{\partial^2 \phi}{\partial x^2} \frac{\partial^2 f_n}{\partial k^2} \Big|_{k_n}, \quad (21)$$

provided the following consistency criterion is satisfied:

$$i f_n(y; k) \frac{\partial \phi}{\partial t} = -f_n(y; k) \frac{1}{2} \left(\frac{d^2 \lambda_n}{dk^2} \right)_{k_n} \frac{\partial^2 \phi}{\partial x^2} + f_n(y; k) V_1(x; y) \phi. \quad (22)$$

Finally, multiply both sides of Equation (22) by $f_n^*(y; k)$, use the fact that the Bloch wave functions have unit norm, and integrate with respect to y to obtain

$$i \frac{\partial \phi}{\partial t} = -\frac{1}{2} \left(\frac{d^2 \lambda_n}{dk^2} \right)_{k_n} \frac{\partial^2 \phi}{\partial x^2} + V_{1,\text{eff}}(x) \phi(x), \quad (23a)$$

where

$$V_{1,\text{eff}}(x) = \int_0^1 dy |f_n(y; k_n)|^2 V_1(x, y). \quad (23b)$$

Equations (23) comprise the non-dimensional effective Schrödinger equation for the behaviour of the electron, averaged over the macroscopic extent of the crystal. The small-scale behaviour of the electron is determined entirely by the Bloch spectral cell problem (12), and the response of the electron to the large-scale force V_1 is through the averaged Schrödinger equation (23a). On the macroscopic scale, the inertia with which the electron resists changes in its acceleration is not the ordinary mass, but rather an *effective mass*, identified through the prefactor of the operator $\partial^2/\partial x^2$ in Equation (23a).

We now determine the effective mass in dimensional terms. Upon re-dimensionalizing Equation (23a), the dimensional prefactor in front of $\partial^2/\partial x^2$ becomes $(\hbar^2/2m)(1/2)(d^2 \tilde{\lambda}/d\tilde{k}^2)$. Here, the tildes have been momentarily restored to denote dimensionless quantities, with $\tilde{\lambda} = E\tau/\hbar$ and $\tilde{k} = kL$, where E is the dimensional eigenvalue of energy. In this way, the dimensional prefactor becomes

$$\frac{\hbar^2}{4m} \frac{d^2 \tilde{\lambda}}{d\tilde{k}^2} = \frac{\hbar^2}{4m} \frac{\tau}{\hbar L^2} \frac{d^2 E}{dk^2} = \frac{1}{2} \frac{d^2 E}{dk^2},$$

and it is therefore natural to identify

$$m_{\text{eff}} := \left(\frac{1}{\hbar^2} \frac{d^2 E}{dk^2} \right)^{-1} \quad (24)$$

as the (dimensional) effective mass. The corresponding non-dimensional effective mass is simply

$$\widetilde{m}_{\text{eff}} = \left(\frac{1}{2} \frac{d^2 \tilde{\lambda}}{d\tilde{k}^2} \right)^{-1}. \quad (25)$$

Case 2. At general k -values: It is a straightforward (albeit lengthy) calculation to make the replacement

$$\tilde{\phi}(x, t) = \phi\left(x - \frac{1}{\varepsilon} \frac{d\lambda}{dk} t, t\right), \quad (26)$$

and to demonstrate that the lowest-order (in powers of ε) solution to Equation (7) at a general k -value (i.e. one not necessarily equal to k_n) is $\psi \sim e^{-i\lambda_n T} f_n(y, k) \tilde{\phi}(x, t)$. This calculation is discussed in the companion document. Note that there is no violation in the separation-of-scales function in the replacement (26). The solution $\phi(\cdot, \cdot)$ is a function of two slots, determined by the large-scale balance equation (23a). Once $\phi(\cdot, \cdot)$ is determined in this way, it is immaterial which variables are entered into these slots.

4 Numerical methods and results

The determination of the energy levels of the periodic system, and hence the effective response of the system to large-scale forcing, relies on accurate solution of Equation (12). In this section, we develop a numerical technique for this purpose. Because Equation (12) is posed on a periodic domain, it is appropriate to expand a trial solution in terms of the following basis functions [18]:

$$f(y) \approx \sum_{p=-N}^N a_p e^{i2\pi p y}, \quad (27a)$$

where a_p are $2N + 1$ complex numbers to be determined. Here N is the order of the truncation; we expect Equation (27a) to be exact as $N \rightarrow \infty$. We substitute this solution into the spectral cell problem and obtain

$$\lambda \sum_{p=-N}^N a_p e^{2\pi i p y} = \sum_{p=-N}^N [(2\pi p + k)^2 a_p + V_0(y) a_p] e^{2\pi i p y}. \quad (27b)$$

We evaluate the result at the collocation points $y_q = q/(2N+2)$, for $q = 1, 2, \dots, 2N+1$. The result is a generalized eigenvalue problem

$$L\mathbf{a} = \lambda M\mathbf{a}, \quad \mathbf{a} = (a_{-N}, \dots, a_N)^T, \quad (27c)$$

where

$$L_{pq} = [(2\pi q + k)^2 + V_0(y_p)] e^{2\pi i q y_p}, \quad M_{pq} = e^{2\pi i q y_p}. \quad (27d)$$

This is the so-called numerical *spectral method* [5]. This method is superior to other methods for a number of compelling reasons [19]: it computes the spectrum of eigenvalues, rather than a single eigenvalue (as in the ‘shooting’ method [20]); the approximate, numerical solution converges exponentially fast to the true solution as N is increased [18] (finite-difference methods converge only algebraically in N [19]). Its implementation is also very simple: we have programmed the algorithm (27) in 20 lines in MATLAB (see the companion document for a sample code).

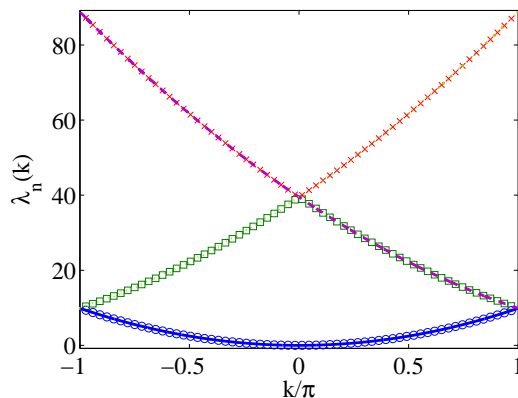


Figure 1: Dispersion relation for the case with zero periodic potential: comparison between the numerical solver (symbols) and the formula and the formula $\lambda_n(k) = (k - 2n\pi)^2$, where $n \in \mathbb{Z}$ (lines). Circles: ground state, numerical method; Squares and crosses: first and second excited states respectively. Solid line: $n = 0$; Dashed line: $n = 1$; Dotted line: $n = -1$. The resolution of the numerical calculation is $N = 20$.

We have validated the correctness of our numerical code by using it to solve the eigenvalue problem (12) with $V_0 = 0$, for which the eigenvalues are known to be $\lambda_n(k) = (k - 2n\pi)^2$, where $n \in \mathbb{Z}$ (Fig. 1). Sample results for the model one-dimensional potential $V_0(y) = A \sin(2\pi y)$ are shown in Figure 2. The numerical method converges with $N = 20$ and yields a non-trivial subset of the complete spectrum of eigenvalues. For each k -value, there is a spectrum of allowed λ -values. These are called the *bands*. The bands with the three smallest λ -values are shown. A clear gap exists between the two lowest-energy bands at $k = \pm\pi$. This is precisely the *band gap* concept in electronic physics. The gap narrows as the amplitude A decreases. In the limit as $A \rightarrow 0$, the free-electron model is recovered, and the band gap shrinks to zero. The band gap between higher λ -levels is smaller than that for the lowest two bands but is never zero. Again, this makes sense physically: as the electron's kinetic energy increases, the effect of the periodic potential is smaller, and the electron behaves more and more like a 'free' electron, for which the band gap is zero. Qualitatively, our plot of the dispersion relation obtained using the dispersion relation agrees with those obtained using the 'nearly-free' and 'tight binding' models found in textbooks [1]. The group velocity and the effective mass are also shown in Figure 2. The group velocity $d\lambda/dk$ is determined by central differencing, and the effective mass is computed in the same way. The effective mass is infinite at the turning points of the group velocity.

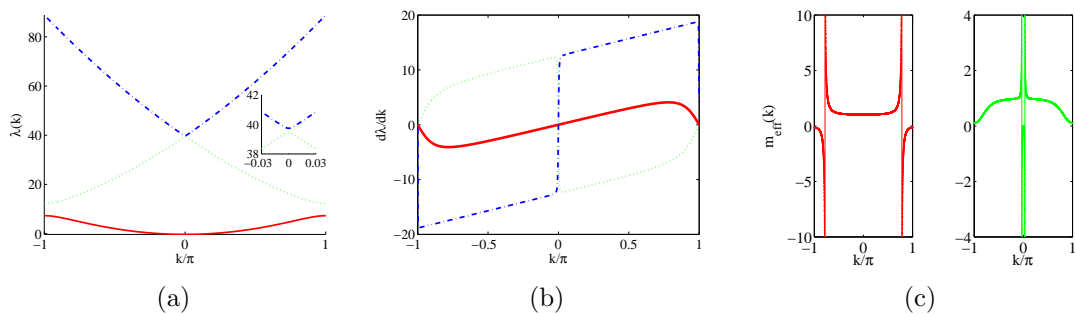


Figure 2: Dispersion relation (a), group velocity (b), and effective-mass diagram (c) for the model potential $V_0 = 5 \sin(2\pi y)$. An inset is shown in (a) to indicate the band gap between the second and third energy bands. In (c) the effective mass for the first and second bands is shown on separate scales. The effective mass is infinite at points where the curvature of the dispersion relation vanishes.

5 Some further mathematical aspects of homogenization theory

5.1 Alternative characterization of the ground state

We present an alternative factorization of the Schrödinger equation, valid for the ground state at $k = 0$. The purpose of this section is twofold. It first serves as a simple and elegant application of several standard mathematical methods studied at undergraduate level (first-order separable ordinary differential equations (ODEs), and the Cauchy–Schwartz inequality). Secondly, this approach yields a proof of the relation

$$m_{\text{eff}}(n = 0, k = 0) \geq m,$$

where m is the ordinary inertial mass and $n = 0$ denotes the ground state.

We start with the following ‘factorization’ for the $k = 0$ ground state wavefunction:

$$v_\varepsilon(x, t) := e^{i\lambda t/\varepsilon^2} \frac{\psi_\varepsilon(x, t)}{f_0(x/\varepsilon; k = 0)}. \quad (28)$$

Here $\psi_\varepsilon(x, t)$ satisfies the full (unhomogenized) Schrödinger equation (4) and $f_0(x/\varepsilon; k = 0)$ satisfies the spectral cell problem (12) in the ground state. Physically, we can think of ‘dividing out’ the small scales in the problem, such that $v_\varepsilon(x, t)$ contains only large-scale variations. Mathematically, the division in Equation (28) by the ground-state wavefunction is legitimate because this is never zero [15]. It is now straightforward to demonstrate that $v_\varepsilon(x, t)$ in Equation (28) satisfies the following equation:

$$i\mu(x/\varepsilon) \frac{\partial v_\varepsilon}{\partial t} = -\frac{\partial}{\partial x} \left(\mu(x/\varepsilon) \frac{\partial v_\varepsilon}{\partial x} \right) + V_1(x, x/\varepsilon) \mu(x/\varepsilon) v_\varepsilon(x, t), \quad (29)$$

with $\mu(x/\varepsilon) = |f_0(x/\varepsilon; k = 0)|^2 > 0$. We now perform a standard homogenization calculation on Equation (29), writing $v_\varepsilon(x, t) \rightarrow v(x, y, t) = v_0(x, y, t) + \varepsilon v_1(x, y, t) +$

$\varepsilon^2 v_2(x, y, t) + \dots$. The equation at $O(\varepsilon^{-2})$ reads

$$\frac{\partial^2 v_0}{\partial y^2} = 0, \quad (30)$$

with solution $v_0 = v_0(x, t)$. The equation at $O(\varepsilon^{-1})$ reads

$$\frac{\partial \mu}{\partial y} \frac{\partial v_1}{\partial y} + \mu \frac{\partial^2 v_1}{\partial y^2} = -\frac{\partial \mu}{\partial y} \frac{\partial v_0}{\partial x}. \quad (31)$$

A sequence of obvious steps reduces Equation (31) to a first-order separable ODE, the solution of which is $v_1(x, y) = g(y)(\partial v_0/\partial x)$, where $g(y)$ satisfies

$$\frac{\partial g}{\partial y} = -1 + \frac{\text{Const.}}{\mu} \quad (32)$$

(this is a different definition of g from that considered in Section 3). Because $g(y)$ is 1-periodic, the constant is determined, and Equation (32) becomes

$$\frac{\partial g}{\partial y} = -1 + \frac{1}{\mu(y) \int_0^1 \mu^{-1} dy}. \quad (33)$$

Finally, the equation at $O(1)$ reads

$$i\mu \frac{\partial v_0}{\partial t} = -\mu \frac{\partial^2 v_0}{\partial x^2} - \frac{\partial}{\partial x} \left(\mu \frac{\partial v_1}{\partial y} \right) + \mu V_1(x, y)v_0 - \frac{\partial}{\partial y} \left(\mu \frac{\partial v_2}{\partial y} \right) - \frac{\partial}{\partial y} \left(\mu \frac{\partial v_1}{\partial x} \right). \quad (34)$$

Integrating this equation over $y \in [0, 1]$ yields

$$i \frac{\partial v_0}{\partial t} = -\langle \mu \rangle \left(1 + \frac{\langle \mu f' \rangle}{\langle \mu \rangle} \right) \frac{\partial^2 v_0}{\partial x^2} + \langle \mu V_1(x, \cdot) \rangle v_0, \quad (35)$$

where $\langle \cdot \rangle = \int_0^1 (\cdot) dy$. Here, the factor in front of the derivative $\partial^2/\partial x^2$ gives the effective mass.

It is straightforward to show that effective mass in Equation (35) is positive. For brevity, call $A := \langle \mu f' \rangle / \langle \mu \rangle$. From Equation (33), we can re-write A as

$$A = \frac{1}{\langle \mu \rangle} \int_0^1 \mu(y) (-1 + \mu^{-1}(y) \langle \mu^{-1} \rangle^{-1}) dy.$$

But $\langle \mu \rangle = \int_0^1 |f_0(y; k=0)|^2 dy = 1$, hence $A = -1 + \langle \mu^{-1} \rangle^{-1}$. Thus, the dimensional effective mass is

$$m_{\text{eff}} := \frac{m}{1 + A} = m \langle \mu^{-1} \rangle. \quad (36)$$

Hence, the $k=0$ effective mass is always positive in the ground state. Moreover, an application of Hölder's inequality (a generalization of the familiar Cauchy–Schwartz inequality [21]) yields $\langle \mu^{-1} \rangle \geq \langle \mu \rangle^{-1} = 1$. Thus, the ground-state effective mass at $k=0$ always exceeds the ordinary (inertial) mass. This is in agreement with Figure 2 and with existing perturbation theories [17, 1].

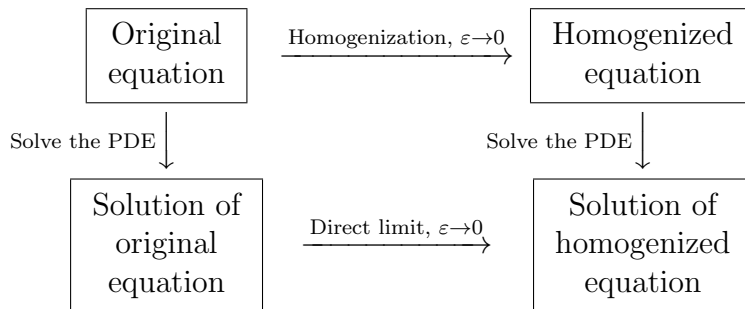


Figure 3: A commutative diagram showing convergence of the asymptotic expansions.

5.2 Convergence of the asymptotic expansions

Consider the solution $\psi_\varepsilon(x, t)$ to the unhomogenized Schrödinger equation (4). Referring to the perturbation ansatz (8), there is no *a priori* guarantee that the lowest-order solution $e^{iky}u_0(x, y, t, T)$ of the homogenized problem should coincide with $\psi_\varepsilon(x, t)$ in the limit as $\varepsilon \rightarrow 0$ (see Figure 3). Rather, a convergence theorem must be proved. The following result concerns critical points k_n , with $(d\lambda/dk)_{k_n} = 0$. In this case, for wavefunctions $\psi_\varepsilon(x, t)$ with initial data

$$\psi_\varepsilon(x, t = 0) = f_n(x/\varepsilon; k)e^{ikx/\varepsilon}u_\varepsilon(x, t = 0),$$

where $u_\varepsilon(x, t = 0)$ and its x -derivative are square-integrable, and with subsequent evolution

$$\psi_\varepsilon(x, t) = e^{-i\lambda t/\varepsilon^2} e^{ikx/\varepsilon}u_\varepsilon(x, t),$$

the solution $\psi_\varepsilon(x, t)$ converges to the homogenized problem

$$e^{iky}u_0(x, y, t, T) = e^{iky}e^{-i\lambda_n T} f_n(y; k)\phi(x, t)$$

in the sense that

$$\lim_{\varepsilon \rightarrow 0} \int_0^1 |u_\varepsilon(x, t) - f_n(x/\varepsilon; k)\phi(x, t)|^2 dx = 0. \quad (37)$$

We will not prove Equation (37) here as it is clear from our results that the solution to the homogenized equation is physically correct. For a Schrödinger-type equation, to prove that the convergence result in Figure 3, one must first prove that the functions $u_\varepsilon(x, t)$ and $\varepsilon \nabla_x u_\varepsilon$ are bounded in the appropriate norm. This guarantees that there exists a function to which $u_\varepsilon(x, t)$ converges as $\varepsilon \rightarrow 0$. Then it remains to show that $u_\varepsilon(x, t)$ agrees with $f_n(y; k)\phi(x, t)$ in the sense of Equation (37), in the limit as $\varepsilon \rightarrow 0$. Convergence is proved for a Schrödinger-type equation in the references [15, 16], where the result is further extended to general k -values (i.e. $k \in [-\pi, \pi]$ not necessarily equal to k_n).

6 Conclusions and didactic considerations

We have shown how homogenization theory can be applied to solve the Schrödinger equation with a periodic potential, thus characterizing the behaviour of an electron

in a crystal structure. We have derived an “effective mass theorem,” which gives the expression for the effective mass found in textbooks [1, 4] by first considering the special case $d\lambda/dk = 0$ and then extending the result to all values of k via a simple change of variables. We have computed the resulting dispersion relation by applying the numerical spectral method to the so-called *Bloch problem*, which is the lowest-order equation obtained from the homogenization theory. Our results are confirmed by agreement in cases where the analytical solutions are known: the free-electron case, and the nearly-free model for small-amplitude potentials, in which band gaps open at the Brillouin-zone boundaries. Our results also agree qualitatively with the tight-binding model for large-amplitude potentials, in the sense that the bands move further apart as the potential increased.

This approach would be useful in a learning environment because it is a first-principles approach that relies only on some basic notions in perturbation theory. Although the derivations are rather involved, they require only elementary multi-variable calculus. Additionally, the concept of effective mass is introduced without any *ad hoc* assumptions. The approach also provides a self-contained description of semiconductor band gaps and electron group velocity. Moreover, the techniques – both analytical and numerical – can be generalized in a straightforward manner to solve real solid state physics problems (as opposed to model one-dimensional ones), thus providing a bridge from classroom study to research-level problems.

Acknowledgements

We thank E. Sokell and R. Smith for helpful conversations.

References

- [1] C. Kittel. *Introduction to Solid State Physics*. Wiley, New York, seventh edition, 1996.
- [2] C. Cohen-Tannoudji, B. Diu, and F. Laloë. *Quantum Mechanics*. Wiley, New York, 1977.
- [3] R. L. Liboff. *Introductory Quantum Mechanics*. Addison-Wesley, Reading, MA., second edition, 1992.
- [4] N. D. Mermin N. W. Ashcroft. *Solid State Physics*. Harcourt Brace, Fort Worth; London, 1976.
- [5] L. N. Trefethen. *Spectral Methods in MATLAB*. SIAM, Philadelphia, 2000.
- [6] G. Pavliotis and A. M. Stuart. *Multiscale Methods*. Springer, Berlin, 2008.
- [7] D. W. McLaughlin, G. C. Papanicolaou, and O. R. Pironneau. Convection of microstructure and related problems. *SIAM J. Appl. Math.*, 45:780, 1985.
- [8] P. McCarty and W. Horsthemke. Effective diffusion coefficient for steady two-dimensional convective flow. *Phys. Rev. A*, 37:2112, 1988.

- [9] S. Rosencrans. Taylor dispersion in curved channels. *SIAM J. Appl. Math.*, 57:1216, 1997.
- [10] R. Mauri. Dispersion, convection, and reaction in porous media. *Phys. Fluids A*, 3:743, 1990.
- [11] G. C. Papanicolaou. *Diffusion in random media*, in *Surveys in Applied Mathematics*, page 205. Plenum Press, 1995.
- [12] L. Ó Náraigh and K. Kamhawi. Multiscale methods and modelling for chemical reactions on oscillating surfaces. *IMA Journal of Applied Mathematics*, 2011.
- [13] A. Bensoussan, J.-L. Lions, and G. Papanicolaou. *Asymptotic Analysis for Periodic Structures*. North-Holland, Amsterdam, 1978.
- [14] F. Poupaud and C. Ringhofer. Semi-classical limits in a crystal with exterior potentials and effective mass theorems. *Communications in Partial Differential Equations*, 21:1897–1918, 1996.
- [15] G. Allaire and A. Piatnitski. Homogenization of the Schrödinger equation and effective mass theorems. *Commun. Math. Phys.*, 258:1, 2005.
- [16] G. Allaire. Periodic homogenization and effective mass theorems for the Schrödinger equation. In *Quantum Transport*, Lecture Notes in Mathematics. Springer, 2008.
- [17] F. B. Pedersen. Simple derivation of the effective-mass equation using a multiple scale technique. *Eur. J. Phys.*, 18:43, 1997.
- [18] J. Boyd. *Chebyshev and Fourier Spectral Methods*. Dover, New York, second edition, 2001.
- [19] P. A. M. Boomkamp, B. J. Boersma, R. H. M. Miesen, and G. V. Beijnon. A Chebyshev collocation method for solving two-phase flow stability problems. *Journal of Computational Physics*, 132:191, 1997.
- [20] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery. *Numerical recipes in C*, 1992.
- [21] L. C. Evans. *Partial Differential Equations*. AMS, Providence RI, 1998.