Dynamics of Electrons in Graded Semiconductors

Michael R. Geller
Department of Physics, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6
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I present a theory of electron dynamics in semiconductors with slowly varying composition. I show that the frequency-dependent conductivity, required for the description of transport and optical properties, can be obtained from a knowledge of the band structures and momentum matrix elements of homogeneous semiconductor alloys. New sum rules for the electronic oscillator strengths, which apply within a given energy band or between any two bands, are derived, and a general expression for the width of the intraband absorption peak is given. Finally, the low-frequency dynamics is discussed, and a correspondence with the semiclassical motion is established. [S0031-9007(96)02038-8]

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Bloch’s seminal analysis of the quantum mechanical motion of a particle in a periodic potential lies at the heart of the modern electron theory of solids and provides a basis—band theory—for the entire conceptual framework of the subject. The present work is motivated by the tremendous interest in the electronic properties of nanometer-scale semiconductor structures [1] and focuses on the quantum mechanics of electrons in nearly periodic potentials. The nearly periodic potentials arise either from uniform crystals in the presence of scalar potentials varying slowly on the scale (for example, from impurities or gates), or from compositionally graded crystals with or without applied potentials. In this Letter I shall present a summary of new results on the time-dependent properties of electrons in graded semiconductors. Details of the calculations will be presented elsewhere.

(I) Semiclassical dynamics.—I begin by discussing the semiclassical equations of motion for an electron in a graded semiconductor. Let \( \epsilon_n(k, c) \) denote the energy bands of a homogeneous alloy \( A_nB_1-c \), which I assume are known. I shall consider a graded crystal with a composition \( c(r) \) varying slowly on the scale of a characteristic lattice constant, in the presence of a slowly varying scalar potential \( U(r) \), and I shall for simplicity consider only noncomposite bands. The stationary states \( \psi_{n\alpha}(r) = \sum_i \Phi_{n\alpha i}^a \Phi(i-r) \) and energies \( \epsilon_{n\alpha} \) of an electron in a graded crystal may be obtained by solving an eigenvalue problem

\[
\sum_i H_{ii'}^{n} \Phi_{n'i}^a + U(1) \Phi_{n1}^a = \epsilon_{n\alpha} \Phi_{n1}^a
\]

with an effective Hamiltonian

\[
H_{ii'}^{n} = \frac{1}{\nu} \int_{BZ} d^3k \epsilon_n(k, c) \left( \frac{1+1}{2} \right) e^{i\mathbf{k}(\mathbf{l}-\mathbf{r})} \]

(2)

determined by the local band structure \( \epsilon_n(k, c(r)) \) of the graded crystal [2]. Here \( \alpha \) is an index labeling the different states associated with band \( n \), and \( \nu \) is the Brillouin zone volume. The generalized Wannier functions \( \alpha_n \) in a nearly periodic potential are labeled by a band index \( n \) and a lattice vector \( \mathbf{I} \) about which the function is localized. They have the same completeness, orthonormality, and band-diagonality properties as the standard Wannier functions for strictly periodic potentials [3]. The use of generalized Wannier functions makes it possible to construct the stationary states from a single band, and hence I label them by the pair of indices \( n \) and \( \alpha \). This is possible as long as \( c(r) \) and \( U(r) \) are slowly varying.

The classical effective Hamiltonian for an electron in band \( n \) is \( H = \epsilon_n(k, c(r)) + U(r) \). The semiclassical equations of motion, regarding \( \mathbf{r} \) and \( \hbar \mathbf{k} \) as conjugate variables, are \( \dot{\mathbf{r}} = \hbar^{-1} \partial \epsilon_n(k, c(r))/\partial \mathbf{k} \) and \( \dot{\hbar \mathbf{k}} = -\nabla U(r) - [\partial \epsilon_n(k, c(r))/\partial \mathbf{c}] \nabla c(r) \). The force includes a contribution from the composition gradient. The effective Hamiltonian (2) can be used to show that these semiclassical equations also govern the quantum mechanical motion of wave packets in a graded semiconductor. This constitutes a generalization of Ehrenfest’s theorem to the motion of electrons in slowly graded crystals.

(II) Dynamic conductivity.—The frequency-dependent conductivity tensor for an electron in a state \( \psi_{n\alpha} \) is given by

\[
\alpha_{ij}(\omega) = \frac{ie^2}{m(\omega + is)V} \left[ \left( \delta_{ij} - \frac{1}{m} \sum_{n'\alpha'} \left( \left< \psi_{n\alpha} | p_i | \psi_{n'\alpha'} \right> \left< \psi_{n'\alpha'} | p_j | \psi_{n\alpha} \right> \right) - \left< \psi_{n\alpha} | p_i | \psi_{n\alpha} \right> \right] \delta(\omega - \epsilon_{n\alpha} + \hbar \omega + is),
\]

(3)

where \( m \) is the electron mass, \( V \) is the volume of the crystal, and \( s \) is a positive infinitesimal. The real part is

\[
\alpha_{ij}(\omega) = \frac{\pi e^2 \hbar}{2mV} \sum_{n'\alpha'} \left[ f_{n\alpha, n'\alpha'} ^{ij} \left( \delta(\epsilon_{n'\alpha'} - \epsilon_{n\alpha} - \hbar \omega) + \delta(\epsilon_{n'\alpha'} - \epsilon_{n\alpha} + \hbar \omega) \right) + \frac{\pi e^2 \hbar}{mV} \sum_{n'\alpha'} \left( \left< \psi_{n\alpha} | p_i | \psi_{n'\alpha} \right> \right) \delta(\omega - \epsilon_{n\alpha} + \hbar \omega) \right],
\]

(4)

where \( f_{n\alpha, n'\alpha'} ^{ij} \) is a contribution from the composition gradient. The effective Hamiltonian (2) can be used to show that these semiclassical equations also govern the quantum mechanical motion of wave packets in a graded semiconductor. This constitutes a generalization of Ehrenfest’s theorem to the motion of electrons in slowly graded crystals.
where
\[
    f_{n,n',n''}^{ij} = \frac{2}{m} \frac{\text{Re}\langle \psi_{na} | p^i | \psi_{n'a} \rangle \langle \psi_{n'a} | p^j | \psi_{na} \rangle}{\varepsilon_{n'a} - \varepsilon_{na}}
\]

is the oscillator strength for an optical transition between states \(\psi_{na}\) and \(\psi_{n'a}\). The primed summation in (4) means that the \(n'\) \(n''\) term is to be excluded. Thus to calculate \(\sigma^{ij}(\omega)\) we need, in addition to the energies \(\varepsilon_{na}\) determined from (1), also the momentum matrix elements \(\langle \psi_{na} | p | \psi_{n'a} \rangle = \sum_n (\Phi_{n}^{a})^* \Phi_{n'}^{a'}(a_\alpha|p|a_{\alpha'}) \). Because the generalized Wannier functions are localized, the quantity \(\langle a_\alpha|p|a_{\alpha'} \rangle\) depends only on the composition of the alloy near \(\mathbf{I}\) and \(\mathbf{I}'\). Hence in a slowly graded crystal
\[
    \langle \psi_{na} | p | \psi_{n'a} \rangle = \frac{1}{\mathcal{V}} \sum_{\mathbf{k}} (\Phi_{n}^{a})^* \Phi_{n'}^{a'} \int d^3 k e^{i\mathbf{k}\cdot(\mathbf{r} - \mathbf{r}' )} \times \mathbf{p}_{\alpha\alpha'}(\mathbf{k}, c \left(\frac{1+1}{2}\right)),
\]

where \(\mathbf{p}_{\alpha\alpha'}(\mathbf{k}, c) \equiv \langle \varphi_{n\alpha}, c|p|\varphi_{n'\alpha'}\rangle\) are the usual Bloch function matrix elements for a homogeneous semiconductor with composition \(c\). Therefore, an evaluation of the dynamic conductivity does not require a knowledge of the generalized Wannier functions, which are difficult to calculate, but only of band structures \(\varepsilon_n(c)\) and momentum matrix elements \(\mathbf{p}_{\alpha\alpha'}(\mathbf{k}, c)\) of homogeneous alloys, which are obtainable from conventional electronic structure calculations or experiments.

(III) Sum rules.—I shall consider partial sums of oscillator strengths of the form \(\sum_{n'} f_{n,n',n''}^{ij} \). When \(n' \neq n\), this is the sum of interband oscillator strengths between \(\psi_{na}\) and all states \(\psi_{n'a}\) in band \(n'\), whereas, when \(n' = n\), it is the sum of all oscillator strengths between \(\psi_{na}\) and all other states in the same band. In terms of the projection operator \(P_n = \sum_{\alpha} |\psi_{na}\rangle \langle \psi_{na}|\), I find
\[
    \sum_{n',n''} f_{n,n',n''}^{ij} = \frac{\langle \psi_{na} | x_i P_n p^j - p^j P_n x_i | \psi_{na} \rangle}{i\hbar}.
\]

It is clear from (7) that the partial sum depends only on the state \(\psi_{na}\) and on the properties of the crystal in the absence of applied fields. Note that \(\sum_{n',n''} f_{n,n',n''}^{ij} = \delta^{ij}\), as expected.

An intraband sum rule may be obtained from (7) with \(n' = n\),
\[
    \sum_{\alpha \neq \alpha'} f_{n,n,\alpha',\alpha}^{ij} = \frac{\langle \psi_{na} | [x_i^j, P_n^a] | \psi_{na} \rangle}{i\hbar},
\]

where \(O_n = P_n^2 P_n\) denotes a projected operator. This commutator can be evaluated in a Wannier function basis, leading to
\[
    \sum_{\alpha \neq \alpha'} f_{n,n,\alpha',\alpha}^{ij} = -\frac{m}{\hbar^2} \sum_{\alpha} (\Phi_{n}^{a})^* \delta_{\alpha \alpha'}(1 - 1') (1 - 1') \Phi_{n'}^{a'}. \tag{9}
\]

The sum of the oscillator strengths for transitions between a given state \(\psi_{na}\) and the other states in the same band is therefore proportional to the expectation value of the second moment of (2) in the state \(\Phi_{n}^{a}\).

The result (9) is valid for any state \(\psi_{na}\) in band \(n\). However, if the state is near in energy to a band edge, the sum rule simplifies to an expectation value of the local inverse effective mass tensor
\[
    \sum_{\alpha \neq \alpha'} f_{n,n,\alpha',\alpha}^{ij} = m \left(\frac{1}{m^* (\mathbf{r})}\right)^{ij} F_{n\alpha}, \tag{10}
\]

where \((F|O|F) = \int d^3 r \Phi^* OF\) is the ordinary envelope function expectation value.

The intraband sum rule leads immediately to a sum rule for the intraband contribution to \(\sigma^{ij}(\omega)\), namely
\[
    \int_{\text{intra}} d\omega \sigma^{ij}_\omega = -\frac{\pi e^2}{2V\hbar^2} \sum_{\alpha} (\Phi_{n}^{a})^* \mathcal{H}_{W} \times (1 - 1') (1 - 1') \Phi_{n'}^{a'}, \tag{11}
\]

where the integration is to be taken from zero to the largest intraband frequency.

Interband sum rules may also be obtained from (7) with \(n' \neq n\). Using a Wannier function basis, I find
\[
    \sum_{\alpha} f_{n,n',\alpha,\alpha}^{ij} = \sum_{\alpha} (\Phi_{n}^{a})^* \Phi_{n'}^{a'} \frac{1}{V} \int_{BZ} d^3 k \times \int_{\mathbf{a}_{\alpha}} \left(\frac{1+1}{2}\right) e^{i\mathbf{k}\cdot(\mathbf{r} - \mathbf{r}' )} \left(\frac{1+1}{2}\right) e^{i\mathbf{k}\cdot(\mathbf{r} - \mathbf{r}' )}, \tag{12}
\]

where \(f_{\alpha\alpha'}^{ij}(\mathbf{k}, c)\) is the conventional Bloch electron oscillator strength. For a state near in energy to a band edge, the interband sum rule reduces to
\[
    \sum_{\alpha} f_{n,n',\alpha,\alpha}^{ij} = (F_{n\alpha} | f_{n'n'}^{ij} [0, c|p]| F_{n''\alpha}), \tag{13}
\]

an extremely simple form indeed.

(IV) Principle of spectroscopic stability for a graded semiconductor.—I shall briefly discuss the physical origin of the new sum rules. For this purpose I study the stability of double sums of oscillator strengths of the form \(S_{n\alpha'} = \sum_{\alpha} \sum_{\alpha'} f_{n,n',\alpha,\alpha'}^{ij} \) in the presence of perturbations. Double sums of this type are commonplace in the theory of atomic spectra, where they characterize the total optical absorption strength between two multiplets \(n\) and \(n'\), the individual degenerate or nearly degenerate states in each multiplet being labeled by \(\alpha\) and \(\alpha'\), respectively. The invariance of the total absorption strength between two multiplets, under arbitrary unitary transformations among the degenerate or nearly degenerate states in each multiplet, is known as the principle of spectroscopic stability [4]. In the atomic physics context, these unitary transformations usually arise from the application of a weak electric or magnetic field. This principle is not immediately applicable to our double sum, however, because \(S_{n\alpha'}^{ij}\) describes the total absorption strength between bands of states which are not nearly degenerate.
I have proved a stronger version of the stability principle by showing that $S_{nn'}^{ij} = \text{Tr}_{k} \langle x^{i'} F_{n'}^{i'} - p^{i'} F_{n}^{i'} \rangle / (\hbar i)$, where the partial trace acts in the subspace spanned by band $n$. The invariance of $S_{nn'}^{ij}$ under arbitrary unitary transformations within the band $n$ and independently within the band $n'$ is now evident. In particular, $S_{nn'}^{ij}$ will be invariant under the action of slowly varying perturbations. Because $S_{nn'}^{ij}$ is conserved in going from a periodic potential to a nearly periodic one, the optical spectrum of the latter is related to that of the former by an intraband redistribution of the transition strengths. This fact implies the existence of general sum rules for the oscillator strengths of an electron in a graded semiconductor, as demonstrated above.

(V) Width of the Drude peak.—The intraband optical absorption spectrum of an electron of momentum $\mathbf{k}$ in a uniform crystal with composition $c$ is

$$\sigma_{1}^{ij}(\omega) = \frac{\pi e^2}{h^2 V} \frac{\partial^2 \epsilon_{n}(\mathbf{k}, c)}{\partial k_i \partial k_j} \delta(\omega).$$

(14)

In the presence of an applied potential $U(\mathbf{r})$ or a composition gradient or both, the width of this Drude peak is broadened and its integrated strength (11) changes. Here I shall present a general expression for the width $\delta \omega$, defined by

$$\delta \omega^2 = \int \frac{d \omega \omega^2 \sigma_{1}^{ij}}{d \omega \sigma_{1}^{ij}},$$

(15)

where $\sigma_{1}^{ij}$ is the real part of the conductivity for a state $\phi_{na}$, and the integrations are to include intraband contributions only. The denominator of (15) is determined by the intraband sum rule (11), whereas for the numerator I find

$$\int d \omega \omega^2 \sigma_{1}^{ij} = -\frac{\pi e^2}{m^2 h^2 V} \sum_{W} (\Phi_{nW}^{\ast})^2 [H, P^{i'}]_{W} \Phi_{nW}^{j},$$

(16)

where $H_{W} = \mathcal{H}_{W} + U(\mathbf{l}) \delta_{W}$ and $P_{W}^{i'} = (m/\hbar V) \times \int d^3k \partial \epsilon_{n}(\mathbf{k}, c(1+i)) / \partial k_{i} e^{\mathbf{k} \cdot (l - r)}$. The width depends only on the state $\Phi_{nW}^{j}$ and can be computed directly from (16) once $\Phi_{nW}^{j}$ is known. In the effective mass regime (16) simplifies to

$$\int d \omega \omega^2 \sigma_{1}^{ij} = \frac{\pi e^2}{V} \langle F_{na} \left| \left( \frac{1}{m^2} \right)^{ik} \right| F_{na} \rangle \times \nabla_{x} \nabla_{r} [\mathcal{E}(\mathbf{r}) + U(\mathbf{r})] F_{na},$$

(17)

where $\mathcal{E}(\mathbf{r}) = \epsilon_{n}(0, c(r))$ is the energy of the local band minimum.

(VI) Low-frequency dynamics.—Consider an electron in a state of energy $\epsilon_{na}$ near a band edge. At frequencies much less than the characteristic energy gap $\hbar \omega$ to the nearest state in the same band with appreciable oscillator strength, the conductivity is purely imaginary and is given by

$$\sigma^{ij}(\omega) = -i \frac{e^2 \omega}{V \omega^2} \left( F_{na} \left| \left( \frac{1}{m^2} \right)^{ij} \right| F_{na} \right).$$

(18)

Typically $\hbar \omega$ will be equal to the level spacing near $\epsilon_{na}$.

The low-frequency conductivity (18) can also be obtained from the semiclassical equation of motion $m^2(d^2 z/dt^2) + \frac{1}{2}(dm^2/dz)(dz/dt)^2 + d\mathcal{E}/dz = eE(\tau)$, where $m^2(z)$ is the position-dependent effective mass and $E(\tau) = E_{0} e^{-i\omega \tau}$ is the applied electric field. To find the response of the electron to the driving field I write $z(\tau) = z_{0}(\tau) + z_{1}(\tau)$, where $z_{0}$ is the semiclassical trajectory in the absence of the driving field with initial conditions corresponding to a solution with energy $\epsilon$. Expanding about the unperturbed motion and using the fact that $m^2(z)$ is slowly varying leads to

$$m^2(z_{0}) \frac{d^2 z_{1}}{dt^2} + \frac{dm^2(z_{0})}{dz} \frac{dz_{0}}{dt} \frac{dz_{1}}{dt} + \mathcal{E}''(z_{0}) z_{1} = eE(\tau).$$

(19)

Note that the coefficients of this linearized equation of motion are time dependent. The low-frequency response is determined by the solution of (19) with the driving frequency $\omega$ much smaller than the frequency of the unperturbed motion at energy $\epsilon$. This means that the electron completes many closed orbits during a single driving cycle. Because the motion is generally anharmonic, the response of the electron will contain a low frequency component at $\omega$ as well as higher harmonics. I shall determine the low-frequency component by averaging the rapidly varying coefficients over a period $T$ of the unperturbed motion. Thus

$$\langle m^2(z_{0}) \rangle \frac{d^2 z_{1}}{dt^2} + \left( \frac{dm^2(z_{0})}{dz} \right) \frac{dz_{0}}{dt} \frac{dz_{1}}{dt} + \mathcal{E}_{\omega}''(z_{0}) z_{1} = eE(\tau),$$

(20)

where $\langle f(\tau) \rangle = T^{-1} \int_{0}^{T} dt f(\tau)$. Therefore, the low-frequency response is that of a damped harmonic oscillator $\tilde{x} + \dot{\tilde{x}}/\tau + \Omega^2 \tilde{x} = eE(\tau)$, where $\tau = \langle m^2(z_{0}) \rangle / \langle (dm^2/dz) z_{0} \rangle$ and $\Omega^2 = \langle \mathcal{E}_{\omega}''(z_{0}) \rangle / (m^2)$. Both $\tau$ and $\Omega$ depend on the energy $\epsilon$ of the unperturbed orbit. Assuming $\omega \ll \Omega$ and $\omega \ll \tau^{-1}$, the low-frequency conductivity at this energy is

$$\sigma^{zz}(\omega) = -i \frac{e^2 \omega}{V \Omega^2 (m^2)},$$

(21)

in close correspondence with (18).

(VII) Absorption spectrum in a quantum well.—As an application of my results I shall calculate the optical absorption spectrum of an electron in a slowly graded Al$_{x}$Ga$_{1-x}$As parabolic quantum well [5]. In particular, I will examine the effects of the position-dependent band structure on the intraband oscillator strengths and selection rules. The eigenstates of interest here are
near in energy to the minimum of the local conduction band and hence may be described by the effective mass Hamiltonian \[ H = -\frac{1}{2}\hbar^2 \nabla^2 (1/m^*(z)) \nabla_j + \mathcal{E}(r) \]. Here \( \mathcal{E}(r) = \frac{1}{2}m^*\hbar^2 z^2 \), where \( m^* \) is the electron effective mass in GaAs, and \( \hbar\omega_0 \) is the energy level spacing at the bottom of the well. The laser field is assumed to be polarized in the \( z \) direction. The effective mass for an electron at the \( \Gamma \) point of Al\(_x\)Ga\(_{1-x}\)As is known to be well-described by a linear interpolation between the effective mass of GaAs and the \( \Gamma \)-point effective mass of AlAs. The position-dependent effective mass in the quantum well may be written as \( m^*(z) = m^*[1 + \eta(z/\ell)^2] \), where \( \ell^2 = \hbar/m^*\omega_0 \), and where \( \eta \) is a dimensionless quantity characterizing the relative change in the effective mass over a length \( \ell \). In an Al\(_x\)Ga\(_{1-x}\)As parabolic quantum well with \( \hbar\omega_0 = 1 \text{ meV} \), it can be shown that \( \eta \ll 1 \). Thus the effective-mass gradient may be treated perturbatively. To this end I write \( H = H^0 + H^1 \), where \( H^1 = \eta\hbar\omega_0 (\frac{1}{2}\partial_z^2 + z\partial_z) \). The energies and normalized envelope functions of \( H^0 \) are given by \( E_{jk}^0 = (j + \frac{1}{2})\hbar\omega_0 + \hbar^2 k^2/2m^* \) and \( F_{jk}^0(r) = (2j!\pi^{1/2}\ell L^2)^{-1/2}e^{i\mathbf{k}\cdot\mathbf{r}}e^{-(1/2)\eta(z/\ell)^2}H_j(z/\ell) \), where \( \mathbf{k} \) is a wave vector in the plane of the quantum well, the \( H_j \) are Hermite polynomials, and where I have used periodic boundary conditions in the \( x \) and \( y \) directions. The envelope functions determine the actual eigenfunctions of the electron in the \( n \)th band through \( \psi_{njk} = \sum F_{jk}(r)\partial_{\alpha} \). I shall calculate the \( zz \) components of the intraband oscillator strengths \( f_{jk,j'k'} = 2m(\epsilon_{jk} - \epsilon_{j'k'}) \times |\langle \psi_{njk}\psi_{njk'} \rangle|^2/\hbar^2 \) to first order in \( \eta \). To this order the perturbed eigenvalues are \( \epsilon_{jk} = \epsilon_{jk}^0 - \frac{1}{3}\eta(j^2 + j + \frac{1}{2})\hbar\omega_0 \). The nonvanishing intraband oscillator strengths to order \( \eta \) are \( f_{jk,j+1,k} = (m/m^*)[j + 1 - \eta(j^2 + j + \frac{1}{2})] \) and \( f_{jk,j-1,k} = (m/m^*)[-j + \eta(j^2 + j + \frac{1}{2})] \). The selection rules \( j \to j \pm 1 \) are therefore unchanged to first order in the effective mass gradient. However, the oscillator strengths are indeed modified, and the optical absorption frequencies \( \epsilon_{j+1,k} - \epsilon_{j,k} = [1 - \eta(j + \frac{1}{2})]\hbar\omega_0 \) are decreased. The sum of the intraband oscillator strengths is \( (m/m^*)[1 - \eta(j + \frac{1}{2})] \), which is in agreement with (10) to order \( \eta \).

It is known that deviations from perfect parabolic confinement and the existence of a position-dependent effective mass both modify the optical absorption spectrum of an ideal parabolic quantum well by changing the level spacing and oscillator strengths. Is it possible to separate the effects of these two perturbations, which are always present in real quantum wells? The above analysis shows that the integrated intraband absorption strength depends on the presence of the position-dependent effective mass only, and is therefore a direct probe of this subtle band-structure effect.

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