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Applied Quantum Mechanics
Chapter 8

8 Time-dependent perturbation

8.1 Introduction

Engineers who design transistors, lasers and other semiconductor components want to understand and control the cause of resistance to current flow so that they may better optimize device performance. A detailed microscopic understanding of electron motion from one part of a semiconductor to another requires the explicit calculation of electron scattering probability. One would like to know how to predict electron scattering from one state to another. In this chapter we will see how to do this using powerful quantum-mechanical techniques.

In addition to understanding electron motion in a semiconductor we also want to understand how to make devices that emit or absorb light. In Chapter 6 it was shown that a superposition of two harmonic oscillator eigenstates could give rise to dipole radiation and emission of a photon. The creation of a photon was only possible if a superposition state existed between a correct pair of eigenstates. This leads directly to the concept of rules determining pairs of eigenstates which can give rise to photon emission. Such selection rules are a useful tool to help us understand the emission and absorption of light by matter. However, the real challenge is to use what we know to make practical devices which operate using emission and absorption of photons. This usually requires imposing some control over atomic-scale physical processes which, of course, can only be understood using quantum mechanics.

Our study begins by considering electronic transitions due to an abrupt time-dependent change in potential. Following this, we will derive important results from first-order time-dependent perturbation theory which we will use to calculate excitation of a charged particle in a harmonic potential due to a transient electric field pulse. We will then go on to derive Fermi's golden rule. As an example, we will use Fermi's golden rule to calculate the elastic scattering rate from ionized impurities for electrons in the conduction band of n -type GaAs. Such calculations are of practical importance for the design of high-performance transistors and laser diodes. Our study will result in a number of predictions, such as the temperature dependence of conductivity and the fact that we must take into account the response of many mobile electrons to the presence of a scattering site. We will also learn that, by controlling the position of scattering sites on an atomic scale, the probability of elastic scattering can be dramatically altered.

As a basic starting point, and by way of example, we would like to know how to cause an electronic transition to take place from, say, a ground state to an excited state in a quantum mechanical system. The key idea is application of a time-dependent potential to change the distribution of occupied states. In principle, the change in potential could take

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place smoothly or abruptly in time. To explore the influence of a time-varying potential in a quantum system, we consider an abrupt change in potential first.

8.1.1 An abrupt change in potential

Let us start with a familiar system. A particle of mass m is in a one-dimensional rectangular potential well in such a way that $V(x) = 0$ for $0 < x < L$ and $V(x) = \infty$ elsewhere. The energy eigenvalues are $E_n = \hbar^2 k_n^2 / 2m$, and the eigenfunctions are $\psi_n = \sqrt{2/L} \sin(k_n x)$, where $k_n = n\pi/L$ for $n = 1, 2, 3, \dots$. The energy levels and wave functions are illustrated in Fig. 8.1

We assume that the particle is initially prepared in the ground state ψ_1 with eigenenergy E_1 . Then, at some time, say $t = 0$, the potential is very rapidly changed in such a way that the original wave function remains the same but $V(x) = 0$ for $0 < x < 2L$ and $V(x) = \infty$ elsewhere. This situation is illustrated in Fig. 8.2. One would like to know what effect such a change in potential has on the expectation value of particle energy and the probability that the particle is in an excited state of the system at time $t > 0$.

We start by finding the expectation value of particle energy after the potential well is abruptly increased in width. We know that the energy of the particle $\langle E \rangle = E_1$ for $t < 0$. Since the wave function after the change in potential ψ is the same as the original

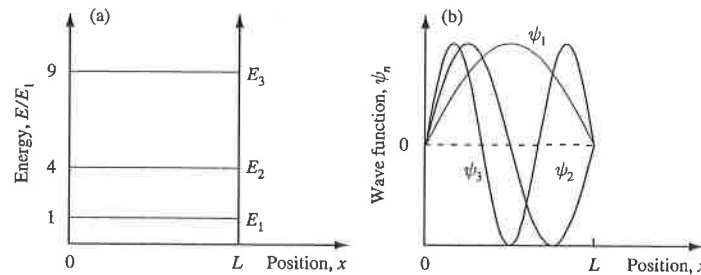


Fig. 8.1 (a) Sketch of a one-dimensional rectangular potential well with infinite barrier energy showing the energy eigenvalues E_1 , E_2 , and E_3 . (b) Sketch of the eigenfunctions ψ_1 , ψ_2 , and ψ_3 for the potential shown in (a).

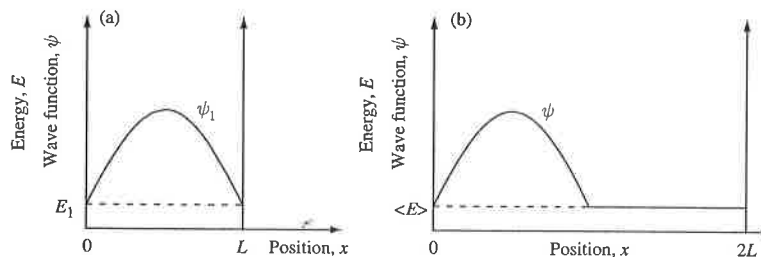


Fig. 8.2 (a) Sketch of a one-dimensional rectangular potential well with infinite barrier energy showing the lowest-energy eigenvalue E_1 and its associated ground-state wave function ψ_1 . (b) The potential barrier at position L is suddenly moved to position $2L$, resulting in a new wave function ψ . The energy expectation value of the new state is $\langle E \rangle = E_1$.

wave function ψ_1 but with the addition of a constant zero value for $L < x < 2L$, one might anticipate that the expectation value in energy is $\langle E \rangle = E_1$ for time $t \geq 0$. It is important to check that the kink in the wave function at position $x = L$ does not contribute $\Delta \langle E \rangle = -\hbar^2 \psi(x=L) \Delta \psi / 2m$ to the energy (see Section 3.1.1 in Chapter 3). Clearly, since $\psi(x=L) = 0$, the kink does not make a contribution, and so it is safe to conclude that $\langle E \rangle = E_1$ after the change in potential.

When time $t \geq 0$, the new state ψ is not an eigenfunction of the system. The *new* eigenfunctions of a rectangular potential well of width $2L$ with infinite barrier energy are $\psi_m = \sqrt{1/L} \sin(k_m x)$, where $k_m = m\pi/2L$ and the index $m = 1, 2, 3, \dots$

Since the state ψ is not an eigenfunction, it may be expressed as a sum of the new eigenfunctions, so that

$$\psi = \sum_m a_m \psi_m \quad (8.1)$$

The coefficients a_m are found by multiplying both sides by ψ_m^* and integrating over all space. This overlap integral gives the coefficients

$$a_m = \int \psi_m^* \psi dx \quad (8.2)$$

The effect of the overlap integral is to project out the components of the new eigenstates that contribute to the wave function ψ . The value of $|a_m|^2$ is the probability of finding the particle in the eigenstate ψ_m .

To illustrate how to find the contribution of the new eigenstates to the wave function ψ , we calculate the probability that the particle is in the new ground state $\psi_{m=1}$ when $t \geq 0$. The probability is given by the square of the overlap integral, a_m :

$$a_1 = \langle \psi_{m=1} | \psi \rangle = \int_{x=0}^{x=L} \sqrt{\frac{1}{L}} \sin\left(\frac{\pi x'}{2L}\right) \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x'}{L}\right) dx' \quad (8.3)$$

Using $2 \sin(x) \sin(y) = \cos(x-y) - \cos(x+y)$ we write

$$a_1 = \frac{\sqrt{2}}{L} \int_{x=0}^{x=L} \left(\frac{1}{2} \cos\left(\frac{\pi x'}{2L}\right) - \frac{1}{2} \cos\left(\frac{3\pi x'}{2L}\right) \right) dx' \quad (8.4)$$

$$a_1 = \frac{\sqrt{2}}{L} \left[\frac{1}{2} \frac{2L}{\pi} \sin\left(\frac{\pi x'}{2L}\right) - \frac{1}{2} \frac{2L}{3\pi} \sin\left(\frac{3\pi x'}{2L}\right) \right]_0^L \quad (8.5)$$

$$a_1 = \frac{\sqrt{2}}{L} \left(\frac{L}{\pi} + \frac{L}{3\pi} \right) = \frac{4\sqrt{2}}{3\pi} \quad (8.6)$$

Hence, the probability of finding the particle in the new ground state of the system is

$$|a_1|^2 = \frac{32}{9\pi^2} = 0.36025 \quad (8.7)$$

The idea that the potential can be modified so rapidly that the wave function does not change may seem a little extreme. However, it is possible to think of systems in which

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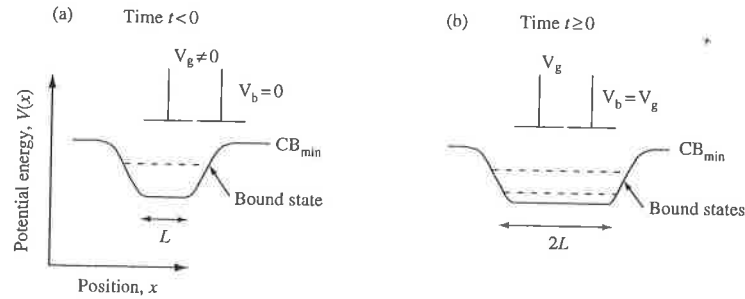


Fig. 8.3 Illustration showing use of gate electrode to control potential seen by an electron in the conduction band of a semiconductor heterostructure. In (a) the potential well is of width L , and in (b) the width is increased to approximately $2L$ by application of a gate electrode potential $V_g = V_b$. The line labeled CB_{\min} is the energy of the conduction-band minimum as a function of position in the device.

such an approach is possible. Figure 8.3 illustrates a system in which voltage applied to a gated semiconductor heterostructure potential well is used to control well width, L .

In this section, we have only considered a potential that changed instantaneously. In other words, the potential energy changed much faster than the particle's response time. Classically, this means that the potential barrier moved faster than the velocity of a particle with energy E .

If the potential barrier moves at a velocity that is comparable to the velocity of a particle with energy E , then our previous approach is not suitable. A different method that goes beyond the abrupt or sudden approximation is needed.

8.1.2 Time-dependent change in potential

Consider a quantum-mechanical system described by Hamiltonian H_0 and for which we know the solutions to the time-independent Schrödinger equation. That is,

$$\hat{H}_0|n\rangle = E_n|n\rangle \quad (8.8)$$

are known. The time-independent eigenvalues are $E_n = \hbar\omega_n$, and the orthonormal eigenfunctions are $|n\rangle$. The eigenfunction $|n\rangle$ evolves in time according to

$$|n, t\rangle = |n\rangle e^{-i\omega_n t} = \phi_n(x) e^{-i\omega_n t} \quad (8.9)$$

and satisfies

$$i\hbar \frac{\partial}{\partial t} |n\rangle e^{-i\omega_n t} = \hat{H}_0 |n\rangle e^{-i\omega_n t} \quad (8.10)$$

To introduce the basic idea, at time $t = 0$ we apply a time-dependent change in potential $\hat{W}(t)$ the effect of which is to create a new Hamiltonian:

$$\hat{H} = \hat{H}_0 + \hat{W}(t) \quad (8.11)$$

and state $\psi(t)$, which evolves in time according to

$$i\hbar \frac{\partial}{\partial t} \psi(t) = (\hat{H}_0 + \hat{W}(t)) \psi(t) \quad (8.12)$$

The time-dependent change in potential energy $\hat{W}(t)$ might, for example, be a step function or an oscillatory function.

We seek solutions to the time-dependent Schrödinger equation, which includes the change in potential (Eq. (8.12)), in the form of a sum over the *known* eigenstates of the unperturbed system,

$$\psi(t) = \sum_n a_n(t) |n\rangle e^{-i\omega_n t} \quad (8.13)$$

where $a_n(t)$ are time-dependent coefficients.

Substituting Eq. (8.13) into Eq. (8.12) gives

$$i\hbar \frac{d}{dt} \sum_n a_n(t) |n\rangle e^{-i\omega_n t} = (\hat{H}_0 + \hat{W}(t)) \sum_n a_n(t) |n\rangle e^{-i\omega_n t} \quad (8.14)$$

Using the product rule for differentiation ($(fg)' = (f'g + fg')$), one may rewrite the left-hand side as

$$i\hbar \sum_n \left(\left(\frac{\partial}{\partial t} a_n(t) \right) |n\rangle e^{-i\omega_n t} + a_n(t) \left(\frac{\partial}{\partial t} |n\rangle e^{-i\omega_n t} \right) \right) = (\hat{H}_0 + \hat{W}(t)) \sum_n a_n(t) |n\rangle e^{-i\omega_n t} \quad (8.15)$$

Making use of Eq. (8.10), we notice that the terms

$$i\hbar \sum_n a_n(t) \frac{\partial}{\partial t} |n\rangle e^{-i\omega_n t} = \sum_n a_n(t) \hat{H}_0 |n\rangle e^{-i\omega_n t} \quad (8.16)$$

may be removed from Eq. (8.15) to leave

$$i\hbar \sum_n |n\rangle e^{-i\omega_n t} \frac{\partial}{\partial t} a_n(t) = \sum_n a_n(t) \hat{W}(t) |n\rangle e^{-i\omega_n t} \quad (8.17)$$

Multiplying both sides by $\langle m|$ and using the orthonormal relationship $\langle m|n\rangle = \delta_{mn}$ gives

$$i\hbar \frac{d}{dt} a_m(t) = \sum_n a_n(t) \langle m|\hat{W}(t)|n\rangle e^{i\omega_{mn}t} \quad (8.18)$$

However, since

$$\int \phi_m^*(x) e^{i\omega_{mn}t} \hat{W} \phi_n(x) e^{-i\omega_n t} dx = W_{mn} e^{i\omega_{mn}t} \quad (8.19)$$

where $\hbar\omega_{mn} = E_m - E_n$ and W_{mn} is defined as the matrix element $\int \phi_m^*(x) \hat{W} \phi_n(x) dx$, we may write

$$i\hbar \frac{d}{dt} a_m(t) = \sum_n a_n(t) W_{mn} e^{i\omega_{mn}t} \quad (8.20)$$

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The intrinsic time-dependence of each state can be factored out by introducing different time-dependent coefficients so that $c_n(t) = a_n(t)e^{i\omega_{mn}t}$. This is called the *interaction picture* in contrast to the a -coefficient formalism that is the *Schrödinger picture*.

The probability that the system can be found in a stationary state $|n\rangle$ after the perturbation is turned off at time t is

$$P_n(t) = |a_n(t)|^2 = |c_n(t)|^2 \quad (8.21)$$

It is important to recognize that Eq. (8.20) is an *exact* result. However, the right-hand side contains the time-dependent coefficients we want to find. At first sight, not a great deal of progress seems to have been made. To make a little more headway, it helps to be quite specific.

Suppose the system is initially in the ground state $|0\rangle$. Then, for times such that $t < 0$ one has $a_n(t < 0) = c_n(t < 0) = \delta_{n,0}$. We now assume that there is a constant step change in potential $W(t)$ that is turned on at time $t = 0$ for duration τ so that $\hat{W}(t) \neq 0$, $\partial\hat{W}(t)/\partial t = 0$, and $\hat{W}(t) = 0$ for $0 > t > \tau$. Figure 8.4 is an illustration of this time-dependent potential.

We are now in a position to make some qualitative statements about the time evolution of the system subject to the time-dependent potential, $\hat{W}(t)$.

Before application of $\hat{W}(t)$: Time-independent, stationary-state solutions satisfy $\hat{H}_0|n\rangle = E_n|n\rangle$. The probability of finding the state, in this case $|0\rangle$, is assumed to be unity.

During application of $\hat{W}(t)$: The state of the system evolves according to

$$\psi(t) = \sum_n a_n(t)|n\rangle e^{-iE_n t/\hbar} \quad (8.22)$$

The time-dependent change in potential causes *transitions between eigenstates* of the initial system (*off-diagonal* matrix elements) and can *shift energy levels* of the initial eigenstates (*diagonal* matrix elements).

After application of $\hat{W}(t)$: Stationary-state solutions satisfy $\hat{H}_0|n\rangle = E_n|n\rangle$. Any time after $\hat{W}(t)$ is turned off at time $t = \tau$ there is a probability of finding the state in any of the known initial time-independent stationary solutions. The final state of the system may be a *superposition* of these eigenstates

$$\psi(t) = \sum_n a_n(t)|n\rangle e^{-iE_n t/\hbar} \quad (8.23)$$

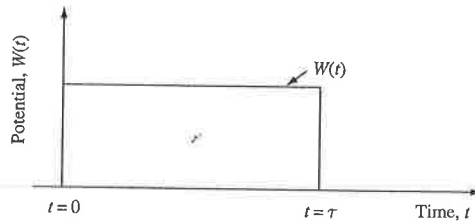


Fig. 8.4 Plot of the time-dependent potential $W(t)$ discussed in the text.

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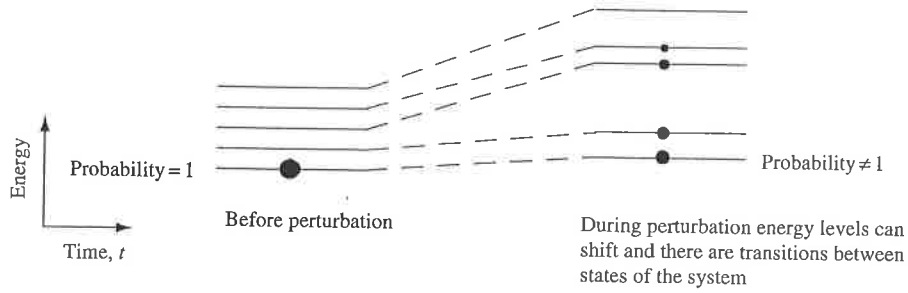


Fig. 8.5 Illustration of energy level shifts and changes in population of energy levels during perturbation.

For the above example, one may visualize the perturbation as changing the population of eigenstates and shifting energy eigenvalues. This is illustrated in Fig. 8.5.

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While Eq. (8.20) is an *exact* result, we often need to make approximations if we wish to calculate actual probabilities. One way to proceed is to assume $a_n(t \leq 0) = 1$ for the eigenstate $|n\rangle$ and $a_m(t \leq 0) = 0$ for $m \neq n$ and then approximate the value of $a_n(t > 0) = 1$ by $a_n(t = 0)$. Such an approximation is called first-order perturbation theory. Typically, this approach is valid when the time-dependent change in potential $\hat{W}(t)$ is small and thus may be considered a perturbation to the initial system described by the Hamiltonian \hat{H}_0 .

Consider the case in which the system is in an eigenstate $|n\rangle$ of \hat{H}_0 at $t \leq 0$, so $a_n(t = 0) = 1$ and $a_m(t = 0) = 0$ for $m \neq n$. There is now only one term on the right-hand side of Eq. (8.20) which, for $m \neq n$ and $t > 0$, becomes

$$i\hbar \frac{d}{dt} a_m(t) = W_{mn} e^{i\omega_{mn}t} \quad (8.24)$$

since all coefficients $a_m(t = 0) = 0$ except for $a_n(t = 0) = 1$. This means that the matrix element W_{mn} couples $|n\rangle$ to $|m\rangle$ and creates the coefficient $a_m(t)$ for times $t > 0$ and $m \neq n$.

To find how $a_m(t)$ evolves in time from $t = 0$, Eq. (8.24) is rewritten as an integral

$$a_m(t) = \frac{1}{i\hbar} \int_{t'=0}^{t'=t} W_{mn} e^{i\omega_{mn}t'} dt' \quad (8.25)$$

We assume that the state with eigenenergy E_n is not degenerate, so that the perturbed wave function can be expressed as a sum of unperturbed states weighted by coefficients $a_k(t)$

$$\psi(x, t) = \sum_k a_k(t) e^{-i\omega_k t} \phi_k(x) \quad (8.26)$$

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If $|a_m|^2 \ll 1$, then we may assume that the coefficient $a_n(t) = 1$. In this case, Eq. (8.26) may be written as

$$\psi(x, t) = \phi_n(x)e^{-i\omega_n t} + \sum_{m \neq n} \frac{1}{i\hbar} \int_{t'=0}^{t'=t} W_{mn} e^{i\omega_{mn} t'} dt' e^{-i\omega_m t} \phi_m(x) \quad (8.27)$$

One should note that there is an obvious problem with normalization of the scattered state given by Eq. (8.27). Clearly, in a complete theory correction for the normalization error must be performed self-consistently.

In a pictorial way, depicted in Fig. 8.6 one may visualize the scattering event using arrows to indicate initial and final states. The lengths of the arrows are a measure of $|a_m|^2$. The initial state is $|n\rangle$ with $|a_n|^2 = 1$ for time $t \leq 0$. After the scattering event, a number of states are excited in such a way that $|a_m|^2 \neq 0$ for $m \neq n$. However, because we have assumed that the perturbation is weak, the final states are dominated by the state $|n\rangle$ with $|a_n|^2 = 1$. The final states after scattering by a weak perturbation have probability $|a_m|^2 \geq 0$, which may be found using

$$a_m(t) = \frac{1}{i\hbar} \int_{t'=0}^{t'=t} W_{mn} e^{i\omega_{mn} t'} dt' \quad (8.28)$$

where t is the time the perturbation is applied and W_{mn} is the matrix element for scattering out of the initial state $|n\rangle$. The assumption that the perturbation is weak means that the probability of scattering out of the initial state is small. This means that $|a_m|^2 \ll 1$.

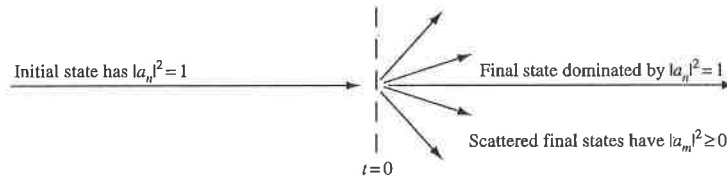


Fig. 8.6 Illustration of initial state with probability amplitude $|a_n|^2 = 1$ and final state at time $t = 0$ being either the same state or a scattered state with probability amplitude $|a_m|^2 \geq 0$. The arrows represent the k -state direction or the direction of motion of the particle. The length of the lines is related to the probability amplitude.

8.2.1 Charged particle in a harmonic potential

To illustrate an application of first-order time-dependent perturbation theory we consider a particle of mass m_0 and charge e moving in a one-dimensional harmonic potential. The potential might have been created by the electronic structure of a molecule. Our aim is to use what we have learned so far to control the state of the electron in the molecule. The way we are going to proceed is to apply a macroscopic external pulse of electric field that has a Gaussian time dependence. While use of a macroscopic field to manipulate an atomic-scale entity may seem a little crude, it is in fact quite a powerful way to control single electrons.

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We begin by assuming that the charged particle is initially (at time $t = -\infty$) in the ground state of the one-dimensional harmonic potential $V(x)$ of the molecule. As already mentioned, we have decided to control the state of the charged particle by applying a pulse of electric field $\mathbf{E}(t) = -\mathbf{E}_0 e^{-t^2/\tau^2}$, where \mathbf{E}_0 and τ are constants. $|\mathbf{E}_0|$ is the maximum strength of the applied electric field and $2\tau\sqrt{\ln(2)}$ is the full-width-half-maximum (FWHM) of the electric field pulse. The potential seen by the particle with charge e is $\hat{W}(t) = e|\mathbf{E}(t)|x$. To demonstrate our ability to control the electron state, we are interested in finding the value of τ that gives the *maximum* probability of the system being in an excited state a long time after application of the pulse.

Starting from the exact result, Eq. (8.20),

$$i\hbar \frac{d}{dt} a_m(t) = \sum_n a_n(t) W_{mn} e^{i\omega_{mn}t} \quad (8.29)$$

we approximate $a_n(t)$ by its initial value $a_n(t = -\infty)$. So, if the system is initially in an eigenstate $|n\rangle$ of the Hamiltonian \hat{H}_0 , then $a_n(t = -\infty) = 1$ and $a_m(t = -\infty) = 0$ for $m \neq n$. There is now only one term on the right-hand side of the equation and we can write

$$i\hbar \frac{d}{dt} a_m(t) = a_n(t) W_{mn} e^{i\omega_{mn}t} = W_{mn} e^{i\omega_{mn}t} \quad (8.30)$$

Since we approximate $a_n(t)$ by its initial value, we have set $a_n(t) = 1$. Integration gives

$$a_m(t) = \frac{1}{i\hbar} \int_{t=-\infty}^{t=\infty} W_{mn} e^{i\omega_{mn}t'} dt' \quad (8.31)$$

The charged particle starts in the ground state $|n = 0\rangle$ of the harmonic potential. The probability of the system being in an excited state after the electrical pulse has gone ($t \rightarrow \infty$) is given by the sum

$$P_{t \rightarrow \infty} = \left| \sum_{m \neq n} a_m(t = \infty) \right|^2 \quad (8.32)$$

If each final state $|m\rangle$ is an independent parallel channel for the scattering process, then we may write

$$P_{t \rightarrow \infty} = \sum_{m \neq n} |a_m(t = \infty)|^2 \quad (8.33)$$

The matrix element for transitions from the ground-state of the harmonic oscillator in the presence of a uniform electric field is

$$W_{m,n=0} = e|\mathbf{E}_0| e^{-t^2/\tau^2} \langle m|x|n=0\rangle \quad (8.34)$$

The only matrix element that contributes to the sum for the probability P is the ground state to the first excited state. This is separated in energy by the energy spacing of the harmonic oscillator which is just $\hbar\omega = \hbar\sqrt{\kappa/m_0}$. Substituting Eq. (6.11) into Eq. (8.34) gives matrix element

$$W_{10} = e|\mathbf{E}_0| e^{-t^2/\tau^2} \left(\frac{\hbar}{2m_0\omega} \right)^{1/2} \langle 1|(\hat{b} + \hat{b}^\dagger)|0\rangle = e|\mathbf{E}_0| e^{-t^2/\tau^2} \left(\frac{\hbar}{2m_0\omega} \right)^{1/2} \quad (8.35)$$

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Hence, the probability after the electrical pulse has gone ($t \rightarrow \infty$) is

$$P_{t \rightarrow \infty} = \frac{1}{\hbar^2} \left| \int_{t=-\infty}^{t=\infty} W_{10} e^{i\omega_{10}t'} dt' \right|^2 = \left(\frac{\hbar}{2m_0\omega} \right) \frac{e^2 |\mathbf{E}_0|^2}{\hbar^2} \left| \int_{t=-\infty}^{t=\infty} e^{-t'^2/\tau^2} e^{i\omega t'} dt' \right|^2 \quad (8.36)$$

where we note that the frequency $\omega_{mn} = \omega_{10} = \omega$. Completing the square in the exponent in such a way that $-(t'/\tau - i\omega\tau/2)^2 - \omega^2\tau^2/4$, one may write

$$P_{t \rightarrow \infty} = \left(\frac{e^2 |\mathbf{E}_0|^2}{2m_0\hbar\omega} \right) e^{-\omega^2\tau^2/2} \left| \int_{t=-\infty}^{t=\infty} e^{-(t'/\tau - i\omega\tau/2)^2} dt' \right|^2 \quad (8.37)$$

Fortunately, the integral is standard, with the solution¹

$$\int_{t=-\infty}^{t=\infty} e^{-(t'/\tau - i\omega\tau/2)^2} dt' = \tau\sqrt{\pi} \quad (8.38)$$

Hence, Eq. (8.36) may be written

$$P_{t \rightarrow \infty} = \left(\frac{\pi e^2 |\mathbf{E}_0|^2}{2m_0\hbar\omega} \right) \tau^2 e^{-\omega^2\tau^2/2} \quad (8.39)$$

The physics of how the transition is induced is illustrated in Fig. 8.7. The electric field pulse exerts a force on the charged particle through a change in the potential energy. We know from Chapter 6 that at any given instant at which the electric field has value $|\mathbf{E}_0|$ the parabolic harmonic potential energy is shifted in position by $x_0 = e|\mathbf{E}_0|/\kappa$ and reduced in energy by $\Delta E = -e^2|\mathbf{E}_0|^2/2\kappa$. Transitions from the ground state are induced by this change in potential energy.

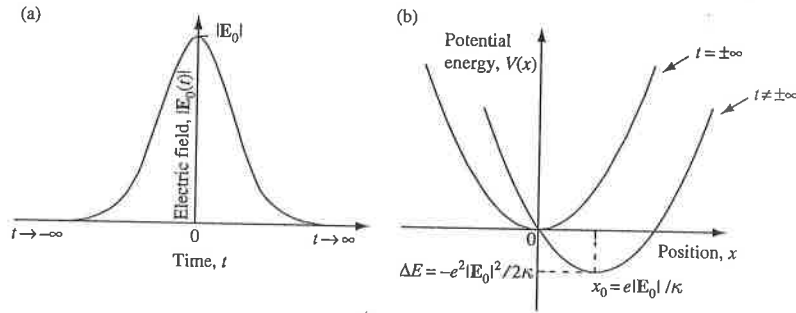


Fig. 8.7 (a) Electric field pulse is Gaussian in shape and centered at time $t = 0$. (b) The harmonic oscillator potential evolves in time.

1. To see this, change variables to $y = t'/\tau - i\omega\tau/2$ so $dy = dt'/\tau$. The integral becomes $\int_{-\infty}^{\infty} e^{-y^2} \tau dy = \tau\sqrt{\pi}$.

The maximum transition probability occurs when the derivative of the probability function with respect to the variable τ is zero (one may check that this is a maximum by taking the second derivative):

$$0 = \frac{d}{d\tau} P_{t \rightarrow \infty} = 2\tau e^{-\omega^2 \tau^2 / 2} - \frac{2\omega^2 \tau}{2} \tau^2 e^{-\omega^2 \tau^2 / 2} = 2\tau - \omega^2 \tau^3 \quad (8.40)$$

Hence, the maximum transition probability occurs when the value of τ is

$$\tau = \frac{\sqrt{2}}{\omega} \quad (8.41)$$

Suppose $\omega = 10^{12} \text{ rad s}^{-1}$. Then, according to Eq. (8.41), the maximum transition probability occurs for $\tau = 1.4 \text{ ps}$, corresponding to an electric field pulse with a FWHM of 2.3 ps.

The value of the maximum transition probability is found by substituting Eq. (8.41) into Eq. (8.39). This gives

$$P_{\max} = \left(\frac{\pi e^2 |\mathbf{E}_0|^2}{m_0 \hbar \omega^3} \right) e^{-1} \quad (8.42)$$

There is an obvious difficulty with this result, since when $\omega \rightarrow 0$ or $|\mathbf{E}_0| \rightarrow \infty$ the maximum transition probability $P_{\max} > 1$. According to Eq. (8.42) $P_{\max} = 1$, when $\omega = (\pi e^2 |\mathbf{E}_0|^2 e^{-1} / m_0 \hbar)^{1/3}$

The resolution of this inconsistency is that the perturbation theory we are using only applies when the time-dependent change in potential $W(t)$ is small. The assumption that the perturbation is weak means that the probability of scattering out of the initial state $|n\rangle$ is small, so that $|a_m|^2 \ll 1$. This condition is simply $P_{\max} \ll 1$, which constrains the value of ω and $|\mathbf{E}_0|$ so that

$$\left(\frac{\pi e^2 |\mathbf{E}_0|^2 \hbar^2}{m_0} \right) e^{-1} \ll \hbar^3 \omega^3 \quad (8.43)$$

For the case we are considering, with $\omega = 10^{12} \text{ rad s}^{-1}$, this results in $|\mathbf{E}_0| \ll 5.7 \times 10^4 \text{ V m}^{-1}$. Clearly, the lesson to be learned here is that, while perturbation theory can be used to calculate transition rates, it is always important to identify and understand limitations of the calculation.

8.3 Fermi's golden rule

We already know from our previous work that a perturbing potential $\hat{W}(t)$ can bring about transitions between eigenstates of the unperturbed Hamiltonian. If the system is initially prepared in state $|n\rangle$ and $\hat{W}(t) = 0$ for $t \leq 0$, then up to time $t = 0$ the system remains in state $|n\rangle$ with energy $E_n = \hbar \omega_n$. For times $t > 0$, we allow $\hat{W}(t) \neq 0$. Hence, when $t > 0$ it is possible that the system is in a different state $|m\rangle$ with energy $E_m = \hbar \omega_m$.

To calculate the transition probability we start with Eq. (8.25)

$$a_m(t) = \frac{1}{i\hbar} \int_{t'=0}^{t'=t} W_{mn} e^{i\omega_{mn} t'} dt' \quad (8.44)$$

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If the perturbation $\hat{W}(t > 0) \neq 0$ does not depend on time $\left(\frac{\partial}{\partial t} \hat{W}(t > 0) = 0\right)$ then the probability of scattering out of state $|n\rangle$ into state $|m\rangle$ as a function of time is

$$P_n(t) = |a_m(t)|^2 = \frac{1}{\hbar^2} \left| \int_{t'=0}^{t'=t} W_{mn} e^{i\omega_{mn}t'} dt' \right|^2 = \frac{|W_{mn}|^2}{\hbar^2} \left| \frac{e^{i\omega_{mn}t} - 1}{\omega_{mn}} \right|^2 \quad (8.45)$$

where $\hbar\omega_{mn} = E_m - E_n$ and $W_{mn} = \langle m | \hat{W} | n \rangle$. Since

$$|e^{ix} - 1|^2 = 4 \sin^2(x/2) \quad (8.46)$$

Eq. (8.45) may be written

$$P_n(t) = \frac{|W_{mn}|^2}{\hbar^2} \frac{\sin^2((\omega_{mn}t)/2)}{(\omega_{mn}/2)^2} \quad (8.47)$$

We now take the long time limit so that $t \rightarrow \infty$ and make use of the relationship

$$\frac{\sin^2(xt)}{\pi t x^2} \Big|_{t \rightarrow \infty} = \delta(x) \quad (8.48)$$

so that

$$P_n(t) = \frac{|W_{mn}|^2}{\hbar^2} \pi t \delta(\omega_{mn}/2) \quad (8.49)$$

Making use of the fact

$$\delta(ax) = \delta(x)/|a| \quad (8.50)$$

if we set $x = \omega_{mn}/2$ and $a = 2\hbar$, then $\delta(\omega_{mn}/2) = 2\hbar\delta(\hbar\omega_{mn})$ and

$$P_n(t) = \frac{2\pi t}{\hbar} |W_{mn}|^2 \delta(\hbar\omega_{mn}) = \frac{2\pi t}{\hbar} |W_{mn}|^2 \delta(E_m - E_n) \quad (8.51)$$

We notice that the probability of a transition is *linearly* proportional to time. The reason for this is embedded in the approximations we have used to obtain this result. Also note that the delta function $\delta(E_m - E_n)$ in Eq. (8.51) ensures energy conservation. For a constant perturbation \hat{W} in the long time limit the energy of the final state must be the same as the energy of the initial state. This is, therefore, an example of elastic scattering, in which the incident particle in state $|n\rangle$ neither gains nor loses energy from the perturbation as it scatters into state $|m\rangle$.

If, rather than a discrete final state $|m\rangle$, there is a continuum of final states described by a density of states $D(E_m)$ in the energy interval E_m to $E_m + dE_m$ then the transition probability is given by

$$P_n(t) = \frac{2\pi t}{\hbar} |W_{mn}|^2 \int D(E) \delta(E_m - E_n) dE \quad (8.52)$$

where it is assumed that each scattering process is an independent parallel *channel* and the matrix element squared $|W_{mn}|^2$ varies slowly over the energy interval of interest.

8.3 FERMI'S GOLDEN RULE

The *transition rate* is the time derivative of the probability $P_n(t)$

$$\frac{d}{dt}P_n(t) = \frac{2\pi}{\hbar}|W_{mn}|^2 D(E) \quad (8.53)$$

Recognizing $dP_n(t)/dt$ as the inverse probability lifetime τ_n of the state $|n\rangle$, we can write Fermi's golden rule:

$$\boxed{\frac{1}{\tau_n} = \frac{2\pi}{\hbar}|W_{mn}|^2 D(E)\delta(E_m - E_n)} \quad (8.54)$$

in which the inverse lifetime $1/\tau_n$ of the initial state $|n\rangle$ only depends upon the matrix element squared coupling the initial state to any scattered state $|m\rangle$ multiplied by the final density of scattered states $D(E)$. The delta function in Eq. (8.54) ensures energy conservation.

In the case where the perturbation is harmonic in time so that, for example,

$$\hat{W}(t > 0) = (\hat{b}e^{i\omega t} + \hat{b}^\dagger e^{-i\omega t}) \quad (8.55)$$

then the transition rate for scattering out of state $|n\rangle$ into state $|m\rangle$ in the $t \rightarrow \infty$ limit is (see Problem 8.9)

$$\frac{1}{\tau_n} = \frac{2\pi}{\hbar} \left| \langle m|\hat{b}|n\rangle \right|^2 \delta(E_m - E_n + \hbar\omega) + \frac{2\pi}{\hbar} \left| \langle m|\hat{b}^\dagger|n\rangle \right|^2 \delta(E_m - E_n - \hbar\omega) \quad (8.56)$$

Again, the delta functions ensure energy conservation. For the delta function $\delta(E_m - E_n + \hbar\omega)$ the final energy is $E_m = E_n - \hbar\omega$ indicating that the system was initially in an excited state and, after the perturbation, emitted a quanta of energy $\hbar\omega$. This process is called stimulated emission and is, for example, important when describing the operation of a laser diode. For the delta function $\delta(E_m - E_n - \hbar\omega)$ the final energy is $E_m = E_n + \hbar\omega$ indicating that the system absorbed a quanta of energy $\hbar\omega$.

If, rather than a discrete final state $|m\rangle$, there is a continuum of final states described by a density of states $D(E_m)$ then Fermi's golden rule for the stimulated emission rate is given by

$$\frac{1}{\tau_n^{\text{emi}}} = \frac{2\pi}{\hbar} \left| \langle m|\hat{b}|n\rangle \right|^2 D(E)\delta(E_m - E_n + \hbar\omega) \quad (8.57)$$

and the absorption rate is

$$\frac{1}{\tau_n^{\text{abs}}} = \frac{2\pi}{\hbar} \left| \langle m|\hat{b}^\dagger|n\rangle \right|^2 D(E)\delta(E_m - E_n - \hbar\omega) \quad (8.58)$$

Notice that because the perturbation \hat{W} is Hermitian (see Eq. (5.13)), the matrix elements in Eq. (8.56) and Eq. (8.57) are related via

$$\langle m|\hat{b}|n\rangle = \langle n|\hat{b}^\dagger|m\rangle^* \quad (8.59)$$

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so that

$$\left| \langle m | \hat{b} | n \rangle \right|^2 = \left| \langle m | \hat{b}^\dagger | n \rangle \right|^2 \quad (8.60)$$

It follows from Eq. (8.60) that Eq. (8.57) and Eq. (8.58) satisfy

$$\tau_n^{\text{emi}} D(E_m = E_n - \hbar\omega) = \tau_n^{\text{abs}} D(E_m = E_n + \hbar\omega) \quad (8.61)$$

which is known as the principle of detailed balance.

The derivation of Fermi's golden rule involved a number of approximations that can limit its validity in some applications. For example, use of the $t \rightarrow \infty$ limit implies that the collision is completed. Hence, one should check to make sure that the perturbing potential is small, so that collisions do not overlap in space or time. It is also assumed that the probability of scattering out of the initial state $|n\rangle$ is so small that $|a_n|^2 = 1$ and conservation of the number of particles can be ignored. Also, *if*, as will often happen, we use a plane wave initial state characterized by wave vector \mathbf{k} and a final plane wave state characterized by wave vector \mathbf{k}' , then the actual *collision is localized in real space*, so that the use of Fourier components is justifiable. All of these assumptions can be violated in modern semiconductor devices and other situations in which scattering can be quite strong and nonlocal effects can become important. So, we need to proceed with caution.

In Section 8.4 we will use Fermi's golden rule to calculate the average distance (the mean free path) an electron travels before scattering in an n -type semiconductor with ionized substitutional impurity concentration n . The microscopic model we develop will allow us to estimate the electrical mobility and electrical conductivity of the material.

In Section 8.5, Fermi's golden rule will be used to calculate the probability of inducing stimulated optical transitions between electronic states. Stimulated emission of light is a key ingredient determining the operation of lasers.

8.4 Elastic scattering from ionized impurities

Establishing a method to control electrical conductivity in semiconductors is essential for many practical device applications. The performance of transistors and lasers depends critically upon flow of current through specific regions of a semiconductor. An important way to control the electrical conductivity of a semiconductor is by a technique called substitutional *doping*.

Substitutional doping involves introducing a small number of impurity atoms into the semiconductor crystal. Each impurity atom replaces an atom on a lattice site of the original semiconductor crystal. In the example, we will be considering a density n of Si donor impurity atoms that occupy Ga sites in a GaAs crystal. At each impurity site, three of the four chemically active Si electrons are used to replace Ga valence electrons. At low temperatures, the remaining Si electron is bound by the positive charge of the Si donor impurity ion. In a GaAs crystal, this extra electron has an effective electron mass of $m_e^* = 0.07 m_0$ and is in a hydrogenic s -like electronic state (Table 2.1). The coulomb potential seen by the electron is screened by the presence of the semiconductor dielectric which is characterized by dielectric permittivity ϵ . The screened coulomb potential and

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the low effective electron mass in the conduction band of GaAs increases the Bohr radius (Eq. (2.69)) characterizing a hydrogenic state from

$$a_B = \frac{4\pi\epsilon_0\hbar^2}{m_0e^2} = 0.0529 \text{ nm} \quad (8.62)$$

to an effective Bohr radius given by

$$a_B^* = \frac{4\pi\epsilon_0\epsilon_{r0}\hbar^2}{m_e^*e^2} = a_B \frac{\epsilon_{r0}}{m_e^*} = 10 \text{ nm} \quad (8.63)$$

where the use of the low-frequency relative dielectric (permittivity) constant, ϵ_{r0} , implies that we are considering low-frequency processes.

In addition, the hydrogenic binding energy is reduced from its value of a Rydberg in atomic hydrogen (see Section 2.2.3.2)

$$Ry = \frac{m_0}{2} \frac{e^4}{(4\pi\epsilon_0)^2\hbar^2} = 13.6058 \text{ eV} \quad (8.64)$$

to a new value (an effective Rydberg constant, Ry^*), which is given by

$$\begin{aligned} Ry^* &= E_{CB_{\min}} - E_{\text{donor}} = \frac{m_e^*}{2} \frac{e^4}{(4\pi\epsilon)^2\hbar^2} = Ry \left(\frac{m_e^*/m_0}{\epsilon_{r0}^2} \right) \\ &= 13.6 \frac{0.07}{(13.2)^2} = 5.5 \text{ meV} \end{aligned} \quad (8.65)$$

From Eq. (8.65) one concludes that the donor electron is only loosely bound to the donor ion in GaAs. The reasons for this are the small effective electron mass and the value of the low frequency relative permittivity ϵ_{r0} in the semiconductor.

At finite temperatures, lattice vibrations or interaction with freely moving electrons can easily excite the donor electron from its bound state into unbound states in the conduction band. This ionization process is shown schematically in Fig. 8.8(a).

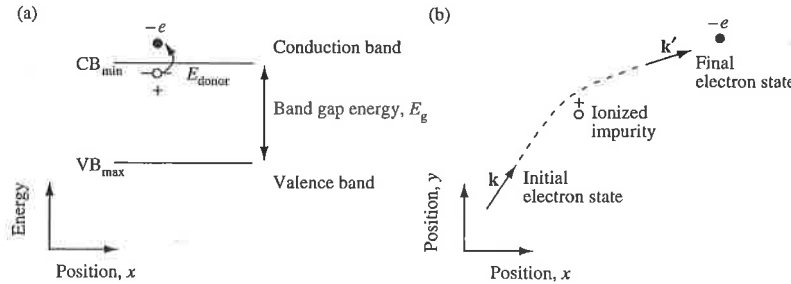


Fig. 8.8 (a) Conduction band minimum (CB_{\min}) and valence band maximum (VB_{\max}) of a semiconductor with band gap energy E_g . The energy level of a donor impurity is shown. When an electron is excited from the donor level into the conduction band, a positively charged ion core is left at the donor site. This is called an ionized impurity. (b) An electron moving in the conduction band in initial state k can be elastically scattered into final state k' by the coulomb potential of an ionized impurity. The sketch is supposed to represent the trajectory of the wave vector associated with the electron.

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For temperatures for which $k_B T > |E_{CB_{\min}} - E_{\text{donor}}|$ and low impurity concentrations, the loosely bound donor electron has a high probability of being excited into the conduction band, leaving behind a positive Si^+ ion core. For high-impurity concentrations in which there is a significant overlap between donor wave functions, electrons can also move freely through the conduction band. In either case, the coulomb potential due to the positive ion core acts as a scattering potential for electrons moving in the conduction band. If we introduce a density n of Si impurities into the semiconductor to increase the number of electrons, we also increase the number of ionized impurity sites in the crystal that can scatter these electrons.

In the remainder of this section we are going to consider the interesting question of why it is possible to increase the conductivity of a semiconductor by increasing the number of electrons in the conduction band through substitutional impurity doping. It is, after all, not yet obvious that such a strategy would work, as we have to consider the role of electron scattering from the increased number of ionized impurity sites.

Anticipating our solution, we will assume that electrons in the conduction band can be described by well-defined $|\mathbf{k}\rangle$ states that scatter into final states $|\mathbf{k}'\rangle$, transferring momentum \mathbf{q} in such a way that $\mathbf{k} = \mathbf{k}' + \mathbf{q}$.² This is illustrated in Fig. 8.8(b), where an electron moving past an ionized impurity is scattered from an initial state $|\mathbf{k}\rangle$ to a final state $|\mathbf{k}'\rangle$. We expect to deal with a dilute number of impurity sites, weak scattering, and a plane-wave description for initial and final states. On average, the distance between scattering events is l_k . This distance, called the *mean free path*, is assumed to be longer than the electron wavelength. We also assume no energy transfer, so that we are in the elastic scattering limit.

A natural question concerns the justification for using time-dependent perturbation theory for an electron scattering from a static potential $v(\mathbf{r})$ that has no explicit time dependence. The answer to this question is that an expansion of a state function belonging to one time-independent Hamiltonian in the eigenfunctions of another time-independent Hamiltonian have time-dependent expansion coefficients. In our case, the incident particle is described by a plane-wave state far away from the scattering center. The final state is also described by a plane-wave state far away from the scattering center. However, near the scattering center the particle definitely cannot be described as a plane wave. As indicated in Problem 8.5, it is straightforward to show that in the limit of a static scattering potential the matrix element coupling initial and final states is related to the transition probability per unit time in the same way as Eq. (8.53) and hence Fermi's golden rule applies.

We will consider an electron that scatters from a state $\psi_{\mathbf{k}} = Ae^{i(\mathbf{k}\cdot\mathbf{r})} = |\mathbf{k}\rangle$ of energy $E(\mathbf{k})$ and a final state $|\mathbf{k}'\rangle$ with the same energy. Fermi's golden rule requires that we evaluate the matrix element $\langle \mathbf{k}' | v(\mathbf{r}) | \mathbf{k} \rangle$, where $v(\mathbf{r})$ is the spatially symmetric coulomb potential. Simple substitution of initial and final plane-wave states into this matrix element reveals that $\langle \mathbf{k}' | v(\mathbf{r}) | \mathbf{k} \rangle = v(\mathbf{q})$, where $v(\mathbf{q})$ is the Fourier transform of the coulomb potential in real space. It is clear then, that we would like to find an expression for the coulomb potential in momentum (wave vector) space.

2. It is convention to choose $\mathbf{k} = \mathbf{k}' + \mathbf{q}$ as opposed to $\mathbf{k} = \mathbf{k}' - \mathbf{q}$ to indicate that momentum \mathbf{q} is transferred from the incident particle. D. Pines and P. Nozières, *Theory of Quantum Liquids*, New York, Benjamin, 1966, p. 86.

8.4.1 The coulomb potential

The *bare* coulomb potential energy in real space between charge e and $-e$ separated by a distance r is

$$v(r) = \frac{-e^2}{4\pi\epsilon_0 r} \quad (8.66)$$

To obtain the potential energy in wave vector space, one may take the Fourier transform. The result for the bare coulomb potential (see Exercise 8.2) is

$$v(q) = \frac{-e^2}{\epsilon_0 q^2} \quad (8.67)$$

In a uniform dielectric such as an isotropic semiconductor characterized by relative dielectric (permittivity) function ϵ_r , the term ϵ_0 in Eq. (8.67) is replaced with $\epsilon = \epsilon_0 \epsilon_r$. In this case, ϵ is constant over real space, but the value of ϵ_r depends in general upon wave vector \mathbf{q} , so that $\epsilon = \epsilon(\mathbf{q}) = \epsilon_0 \epsilon_r(\mathbf{q})$. We expect such a dependence because many electrons can respond to the long-range electric field components of the real-space coulomb potential. This effect, called *screening*, reduces the coulomb potential for small values of \mathbf{q} . Because screening is embedded in ϵ one talks of a screened *dielectric response function*, $\epsilon(\mathbf{q})$. In general, the dielectric response should also have a frequency dependence, so that $\epsilon = \epsilon(\mathbf{q}, \omega)$. However, we ignore this at present. In the following, we simply replace a constant value of ϵ with $\epsilon(\mathbf{q})$. Later, we will find expressions for the functional form of $\epsilon(\mathbf{q})$.

We now have a coulomb potential energy in wave vector space

$$v(\mathbf{q}) = \frac{-e^2}{\epsilon(\mathbf{q}) q^2} \quad (8.68)$$

and in real space

$$v_q(r) = \frac{-e^2}{4\pi\epsilon_q r} \quad (8.69)$$

where we note that the subscript \mathbf{q} is used because $v(r)$ and ϵ depend upon the scattered wave vector.

The potential energy at position \mathbf{r} , due to ion charge at position \mathbf{R}_j , is

$$v_q(\mathbf{r} - \mathbf{R}_j) = \frac{-e^2}{4\pi\epsilon_q |\mathbf{r} - \mathbf{R}_j|} \quad (8.70)$$

which only depends upon the separation of charges.

To obtain $v(\mathbf{q})$, we take the Fourier transform

$$v(\mathbf{q}) = \int d^3 r v(\mathbf{r} - \mathbf{R}_j) e^{-i\mathbf{q} \cdot (\mathbf{r} - \mathbf{R}_j)} \quad (8.71)$$

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where the integral is over all space. Clearly, in a homogeneous medium, if we determine $v(\mathbf{q})$ at one position in space, then we have determined it for all space.

8.4.1.1 Elastic scattering of electrons by ionized impurities in GaAs

We wish to estimate the elastic scattering rate for electrons in GaAs doped to $n = 10^{18} \text{ cm}^{-3}$ due to the presence of ionized impurities. Suppose \mathbf{R}_j is the position of the j -th dopant atom in n -type GaAs and, as shown in Fig. 8.9, we are interested in an electron at position \mathbf{r} . The interaction potential in real space is the sum of the contributions from the n individual ions per cm^3 . Thus, the total potential is

$$V(\mathbf{r}) = \sum_{j=1}^n v(\mathbf{r} - \mathbf{R}_j) \quad (8.72)$$

In wave vector space we have a sum of Fourier transforms of $v(\mathbf{r} - \mathbf{R}_j)$

$$V(\mathbf{q}) = \sum_{j=1}^n \int d^3 r v(\mathbf{r} - \mathbf{R}_j) e^{-i\mathbf{q}\cdot\mathbf{r}} = \sum_{j=1}^n \int d^3 r v(\mathbf{r} - \mathbf{R}_j) e^{-i\mathbf{q}\cdot\mathbf{r}} e^{i\mathbf{q}\cdot\mathbf{R}_j} e^{-i\mathbf{q}\cdot\mathbf{R}_j} \quad (8.73)$$

$$V(\mathbf{q}) = \sum_{j=1}^n \int d^3 r v(\mathbf{r} - \mathbf{R}_j) e^{-i\mathbf{q}\cdot(\mathbf{r}-\mathbf{R}_j)} e^{-i\mathbf{q}\cdot\mathbf{R}_j} = v(\mathbf{q}) \sum_{j=1}^n e^{-i\mathbf{q}\cdot\mathbf{R}_j} \quad (8.74)$$

Hence, the total potential seen by the electron in the presence of n ionized impurities per unit volume is

$$\boxed{V(\mathbf{q}) = v(\mathbf{q}) \sum_{j=1}^n e^{-i\mathbf{q}\cdot\mathbf{R}_j}} \quad (8.75)$$

For elastic scattering, we consider transitions between a state $\psi_{\mathbf{k}} = A e^{i(\mathbf{k}\cdot\mathbf{r})} = |\mathbf{k}\rangle$ of energy $E(\mathbf{k})$ and a final state $|\mathbf{k}'\rangle$ with the same energy. Fermi's golden rule (the first term in the Born series) involves evaluating the matrix element $\langle \mathbf{k}' | v(r) | \mathbf{k} \rangle$. Since $|\mathbf{k}\rangle$ and $|\mathbf{k}'\rangle$ are plane-wave states of the form $e^{i\mathbf{k}\cdot\mathbf{r}}$ (we have assumed that $kl_k \gg 1$, so the mean free path l_k is many electron wavelengths long), we write

$$\langle \mathbf{k}' | v(r) | \mathbf{k} \rangle = \int d^3 r e^{-i\mathbf{k}'\cdot\mathbf{r}} v(r) e^{i\mathbf{k}\cdot\mathbf{r}} = \int d^3 r v(r) e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} = \int d^3 r v(r) e^{i\mathbf{q}\cdot\mathbf{r}} \quad (8.76)$$

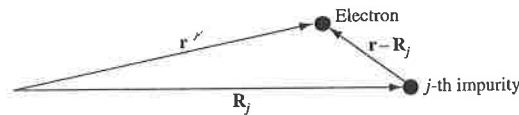


Fig. 8.9 Diagram illustrating the relative position $\mathbf{r} - \mathbf{R}_j$ of an electron at position \mathbf{r} and the j -th ionized impurity at position \mathbf{R}_j .

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Fig. 8.10 (a) Diagram illustrating initial wave vector \mathbf{k} , final wave vector \mathbf{k}' , and transferred momentum \mathbf{q} . To indicate that momentum is transferred from the incident particle we choose the convention $\mathbf{k} = \mathbf{k}' + \mathbf{q}$. (b) For elastic scattering, the scattered angle θ is related to q by $k \sin(\theta/2) = q/2$.

which, since $v(r)$ is symmetric, is just the Fourier transform of the coulomb potential in real space.

$$\langle \mathbf{k}' | v(r) | \mathbf{k} \rangle = \int d^3 r v(r) e^{-i\mathbf{q}\cdot\mathbf{r}} = v(\mathbf{q}) \quad (8.77)$$

In this expression $\mathbf{q} = \mathbf{k} - \mathbf{k}'$, since momentum conservation requires $\mathbf{k} = \mathbf{k}' + \mathbf{q}$. As illustrated in Fig. 8.10, the scattering angle θ for elastic scattering (no energy loss) is such that $k \sin(\theta/2) = q/2$

The probability of elastic scattering between the two states is

$$1/\tau'_{\mathbf{k}\mathbf{k}'} = \frac{2\pi}{\hbar} |v(\mathbf{q})|^2 \delta(E(\mathbf{k}) - E(\mathbf{k} - \mathbf{q})) \quad (8.78)$$

where the δ -function ensures that no energy is exchanged. The total scattering rate is a sum over all transitions, so that for a *single impurity*

$$1/\tau_{\text{el}} = \frac{2\pi}{\hbar} \int \frac{d^3 q}{(2\pi)^3} |v(\mathbf{q})|^2 \delta(E(\mathbf{k}) - E(\mathbf{k} - \mathbf{q})) \quad (8.79)$$

Elastic scattering from n impurities can now be calculated using

$$|V(\mathbf{q})|^2 = |v(\mathbf{q})|^2 \left| \sum_{j=1}^n e^{-i\mathbf{q}\cdot\mathbf{R}_j} \right|^2 = |v(\mathbf{q})|^2 s(\mathbf{q}) \quad (8.80)$$

where

$$s(\mathbf{q}) = \left| \sum_{j=1}^n e^{-i\mathbf{q}\cdot\mathbf{R}_j} \right|^2 \quad (8.81)$$

In this $s(\mathbf{q})$ is a *structure factor* that contains phase information on the scattered wave from site \mathbf{R}_j . For n large and random \mathbf{R}_j , the sum over n random phases is $n^{1/2}$, and so the sum squared is n . It follows that if there are n spatially *uncorrelated* scattering sites corresponding to random impurity positions, we expect $s(\mathbf{q}) = n$. To show that this is so see Exercise 8.3. For a large number of spatially random impurity positions, the matrix element squared given by Eq. (8.80) becomes

$$|V(\mathbf{q})|^2 = n |v(\mathbf{q})|^2 \quad (8.82)$$

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and the *total elastic scattering rate* from n impurities per unit volume is

$$1/\tau_{\text{el}} = \frac{2\pi}{\hbar} n \int \frac{d^3q}{(2\pi)^3} \left| \frac{e^2}{\varepsilon(\mathbf{q})q^2} \right|^2 \delta(E(\mathbf{k}) - E(\mathbf{k} - \mathbf{q})) \quad (8.83)$$

where the integral over d^3q is the final density of states.

Physically, each impurity is viewed as contributing independently, so that the scattering rate is n times the scattering rate from a *single impurity atom*. We can also see why increasing the impurity concentration n does not necessarily result in a linear increase in scattering rate $1/\tau_{\text{el}}$. The integral contains a matrix element squared $|e^2/\varepsilon(\mathbf{q})q^2|^2$, which can influence scattering rate. The $1/q^2$ term reflects the fact that ionized impurity coulomb scattering is weighted toward final states with small q transfer. This means that electrons moving in a given direction are mainly scattered by small angles without too much deviation from the forward direction. The dielectric function $\varepsilon(\mathbf{q})$ also has an influence on scattering rate, in part because of its \mathbf{q} dependence but also because the function depends upon carrier concentration, n .

8.4.1.2 Correlation effects due to spatial position of dopant atoms

Thus far, we have assumed that each substitutional dopant atom occupies a random crystal lattice site. However, the constraint that *substitutional impurity atoms in a crystal occupy crystal lattice sites* gives rise to a *correlation effect because double occupancy of a site is not allowed*. Suppose a fraction f of sites are occupied. In this case, we no longer have a truly random distribution, and, for small f , the scattering rate will be reduced by $s(\mathbf{q}) = n(1 - f)$. The factor $(1 - f)$ reflects the fact that not allowing double occupancy of a site is a correlation effect.

Other spatial correlation effects are possible and can, in principle, dramatically alter scattering rates.³

8.4.1.3 Calculating electron mean free path

We wish to calculate the mean-free-path of a conduction band electron in an isotropic semiconductor that has been doped with n randomly positioned impurities. We start from the expression for total elastic scattering rate of an electron mass m_e^* and charge e from a density of n random ionized impurities given by Eq. (8.83). Because the aim is to evaluate the total elastic scattering rate as a function of the incoming electron energy E , it is necessary to express the volume element d^3q in terms of energy $E = \hbar^2 k^2 / 2m_e^*$ and scattering angle θ . Since the material is isotropic, one may write $q = 2k \sin(\theta/2)$. It can be shown (Exercise 8.4) that

$$1/\tau_{\text{el}} = \frac{2\pi m_e^*}{\hbar^3 k^3} n \left(\frac{e^2}{4\pi\varepsilon_0} \right)^2 \int_{\eta=0}^{\eta=1} \frac{dn}{(\varepsilon_r(q))^2 \eta^3} \quad (8.84)$$

3. A. F. J. Levi, S. L. McCall, and P. M. Platzman, *Appl. Phys. Lett.* **54**, 940 (1989) and A. L. Efros, F. G. Pikus, and G. G. Samsonidze, *Phys. Rev.* **B41**, 8295 (1990).

or, as a function of energy,

$$1/\tau_{\text{el}}(E) = \frac{\pi}{(2m_e^*)^{1/2}n} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 E^{-3/2} \int_{\eta=0}^{\eta=1} \frac{d\eta}{(\epsilon_r(2k\eta))^2 \eta^3} \quad (8.85)$$

where $\eta = \sin(\theta/2)$, scattered wave vector $q = 2k\eta$, and dielectric function $\epsilon(q) = \epsilon_0\epsilon_r(q)$.

Before estimating the value of the integral given by Eq. (8.84), we calculate the pre-factor using parameters for GaAs with $n = 10^{18} \text{ cm}^{-3}$. In this case, the conduction band electron has effective electron mass $m_e^* = 0.07 m_0$ and Fermi wave vector in three dimensions $k_F = (3\pi^2 n)^{1/3} = 3 \times 10^6 \text{ cm}^{-1}$. The Fermi energy is $E_F = \hbar^2 k_F^2 / 2m_e^*$, and the wavelength associated with an electron at the Fermi energy is $\lambda_F = 2\pi/k_F = 20 \text{ nm}$ in this case.

Because we will be interested in relating the calculated elastic scattering rate to the measured low-temperature conductivity and mobility of the semiconductor, we need to estimate $1/\tau_{\text{el}}$ for an electron of energy $E = E_F$. This is because at low temperatures the motion of electrons with energy near the Fermi energy determines electrical conductivity.

The pre-factor of the integral given by Eq. (8.84) is

$$\frac{2\pi}{\hbar^3} n \frac{e^4 m_e^*}{(4\pi\epsilon_0)^2 k_F^3} = \frac{2\pi n c (m_e^*/m_0)}{3\pi^2 n} \frac{m_0 e^2}{4\pi\epsilon_0 \hbar^2} \frac{e^2}{4\pi\epsilon_0 \hbar c} = \frac{2c(m_e^*/m_0)}{3\pi a_B \alpha^{-1}} \quad (8.86)$$

Putting in the numbers, we have in SI-MKS units

$$\frac{2c(m_e^*/m_0)}{3\pi a_B \alpha^{-1}} = \frac{2 \times 3 \times 10^8 \times 0.07}{3\pi \times 0.53 \times 10^{-10} \times 137} = 6.14 \times 10^{14} \text{ s}^{-1} \quad (8.87)$$

Notice that when evaluating the pre-factor we used known *physical values* and *dimensionless units* as much as possible. This helps us to avoid mistakes and confusion.

To estimate the integral in Eq. (8.84), we assume that $\epsilon_r(q) \sim \epsilon_{r0} \sim 10$, and we approximate the integral as $1/\epsilon_{r0}^2 = 1/100$, so that

$$1/\tau_{\text{el}} \sim \frac{6.14 \times 10^{14}}{\epsilon_{r0}^2} = 6.14 \times 10^{12} \text{ s}^{-1} \quad (8.88)$$

The mean free path is the characteristic length l_k between electron scattering events. For elastic scattering at the Fermi energy in *n*-type GaAs, we have $l_{k_F} = v_F \tau_{\text{el}}$, where Fermi velocity $v_F = \hbar k_F / m_e^* = 5 \times 10^7 \text{ cm s}^{-1}$. Hence, $l_{k_F} = 5 \times 10^7 / 6 \times 10^{12} = 83 \text{ nm}$. We can compare this length with the average spacing between impurity sites, which is only 10 nm for an impurity concentration $n = 10^{18} \text{ cm}^{-3}$. Obviously, this impurity concentration is *not* the *dilute* limit that we had previously assumed, since the electron wavelength $\lambda_F = 2\pi/k_F = 20 \text{ nm}$ is similar to the average spacing between impurities. However, $l_{k_F} > \lambda_F$, so that $k_F l_{k_F} \gg 1$, justifying our assumption of weak scattering. One may also compare the average spacing between impurity sites, which is 10 nm (many times the GaAs lattice constant $L = 0.56533 \text{ nm}$), with the effective Bohr radius for a hydrogenic *n*-type impurity

$$a_B^* = \frac{4\pi\epsilon_0\epsilon_{r0}\hbar^2}{m_e^* e^2} \quad (8.89)$$

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which, using a value $\epsilon_{r,0} = 13.2$ for the *low-frequency* dielectric constant, gives $a_B^* = 10$ nm. Because a_B^* is comparable to the average spacing between impurity sites, there should be a significant overlap between donor electron wave functions giving rise to metallic behavior. More formally, one introduces a parameter r_s that is the radius of a sphere occupied, on average, by one electron, assuming a uniform electron density n , divided by the effective Bohr radius, a_B^* :

$$r_s = \left(\frac{3}{4\pi n} \right)^{1/3} \frac{1}{a_B^*} \quad (8.90)$$

For GaAs with an impurity concentration $n = 10^{18} \text{ cm}^{-3}$, this gives $r_s = 0.63$. Again, because $r_s < 1$, we expect metallic behavior. This is indeed the case, and we can use our calculation of mean free path to estimate the electrical mobility and conductivity.

8.4.1.4 Calculating mobility and conductivity

Electron mobility is defined as

$$\mu = e\tau_{el}^*/m_e^* \quad (8.91)$$

where $1/\tau_{el}^*$ is an appropriate elastic scattering rate and m_e^* is the effective electron mass. It is usual for mobility to be quoted in CGS units of $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. If we wish to calculate the mobility of electrons that are characterized on average by a Fermi wave vector k_F and a mean free path l_{k_F} , where we assume $\tau_{el}^* = \tau_{el}$, then the mobility is

$$\mu = e\tau_{el}/m_e^* = el_{k_F}/\hbar k_F \quad (8.92)$$

Conductivity is proportional to mobility and is defined as

$$\sigma = ne\mu = \frac{ne^2\tau_{el}^*}{m_e^*} \quad (8.93)$$

If we wish to calculate the conductivity of electrons which are characterized by a Fermi wave vector k_F and a mean-free-path l_{k_F} where we assume $\tau_{el}^* = \tau_{el}$, then the conductivity of the material is

$$\sigma = ne\mu = \frac{ne^2\tau_{el}}{m_e^*} = \frac{ne^2l_{k_F}}{\hbar k_F} \quad (8.94)$$

For our particular example we can put in numbers for mobility of GaAs doped to $n = 10^{18} \text{ cm}^{-3}$. Using CGS units and the value for τ_{el} in Eq. (8.88) gives

$$\begin{aligned} \mu_n = e\tau_{el}/m_e^* &= 1.6 \times 10^{-12} / 6 \times 10^{12} \times 0.07 \times 9.1 \times 10^{-28} \\ &= 4.1 \times 10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \end{aligned} \quad (8.95)$$

As shown in Fig. 8.11, the experimentally measured value of electron mobility in bulk *n*-type GaAs with carrier concentration $n = 10^{18} \text{ cm}^{-3}$ at temperature $T = 300 \text{ K}$ is $\mu_n = 2\text{--}3 \times 10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. At the lower temperature of $T = 77 \text{ K}$, the mobility is measured to

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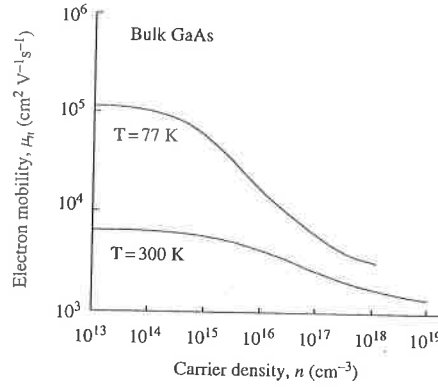


Fig. 8.11 Experimentally determined electron mobility of bulk n -type GaAs as a function of carrier density n on a logarithmic scale for the indicated temperatures, T .

be $\mu_n = 3-4 \times 10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. So the agreement between our very crude estimates and experiment is quite good.

As a next step to *improve* on our calculation of elastic scattering rate, $1/\tau_{el}$, we will consider how electron scattering from the static distribution of ionized impurities is modified due to the presence of mobile electron charge in the system. The coulomb potential of each ionized impurity is modified, or screened, by mobile charge carriers. Because the coulomb potential is modified, the total elastic scattering rate and its angular dependence will also change.

8.4.2 Linear screening of the coulomb potential

Previously we have assumed that a doped semiconductor has an ionized impurity distribution that is random. The static ionized charge distribution is $\rho_i(\mathbf{r})$, with net charge $Q_i = e \int d^3 r \rho_i(\mathbf{r})$. The total mobile charge attracted is exactly $-Q_i$. The mobile charge (which is considered a nearly free electron gas) is a *screening charge* and has its own distribution in space given by $\rho_s(\mathbf{r})$.

The screened potential energy from the static impurity charge and the mobile screening charge is exactly

$$V(r) = \int d^3 r' \frac{-e^2(\rho_i(\mathbf{r}') + \rho_s(\mathbf{r}'))}{4\pi\epsilon_0|\mathbf{r} - \mathbf{r}'|} \quad (8.96)$$

As shown schematically in Fig. 8.12, one may imagine a pile-up of electron charge density around the positive impurity ion. The mobile electron charge density *screens* the coulomb potential due to the impurity.

8.4.2.1 Calculating the screened potential in real space

To calculate the screened coulomb potential, let us begin by considering an isotropic three-dimensional free-electron gas with equilibrium time-averaged electron particle density n_0 . Suppose we now place a test charge (the impurity ion) into this electron gas. The test

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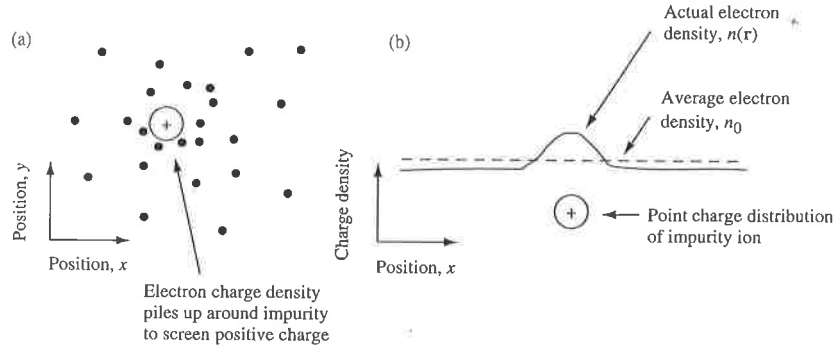


Fig. 8.12 (a) Illustration to represent the response of an electron gas to the presence of a positive charge distribution due to an impurity ion. On average, electrons spend more time in the vicinity of the impurity. (b) The average electron density is greater than average near the positively charged impurity ion. The impurity ion may be modeled as a point charge.

charge will try to create a coulomb potential $\phi_{\text{ex}}(r) = -e/4\pi\epsilon r$. However, the response of the electron gas to the presence of the test charge is to create a new electron particle density $n(r)$, which will create a new screened potential $\phi(r)$.

We make the simplifying assumption that the relationship between the energy of an electron at position \mathbf{r} and its wave vector is only modified from its free-electron value by the *local potential*, so that

$$E(k) = \frac{\hbar^2 k^2}{2m} - e\phi(r) \quad (8.97)$$

The assumption of a local potential can only be true for electrons localized in space and so described (semi-classically) as wave packets. However, the electron wave packets are spread out in real space by a characteristic distance (at least $1/k_F$ for a low-temperature degenerate electron gas). To ensure that use of a local potential is an accurate approximation, we must require that $\phi(r)$ vary slowly on the scale of the wave packet size.

The new screened potential may be written in the form

$$\phi(r) = \frac{1}{r} f(r) \quad (8.98)$$

where $f(r)$ is a function we will determine using Poisson's equation $\nabla^2 \phi = -\rho(r)/\epsilon$, which relates the *local* charge density to the *local* potential. The change in equilibrium charge density is

$$\rho(r) = -e(n(r) - n_0) \quad (8.99)$$

where the averaged electron particle density is

$$n_0 = \int \frac{d^3k}{(2\pi)^3} 2f_k = \int \frac{d^3k}{(2\pi)^3} 2 \frac{1}{e^{(E_k - \mu)/k_B T} + 1} \quad (8.100)$$

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and the local particle density at position r is

$$n(r) = \int \frac{d^3k}{(2\pi)^3} 2f_k = \int \frac{d^3k}{(2\pi)^3} 2 \frac{1}{e^{(E_k - e\phi(r) - \mu)/k_B T} + 1} \quad (8.101)$$

In the expressions for n_0 and $n(r)$, notice that f_k is the Fermi-Dirac distribution function (Eq. (7.50)) and that the factor 2 in the integral accounts for electron spin $\pm\hbar/2$. Eqs. (8.100) and (8.101) allow us to rewrite Eq. (8.99) as

$$\rho(r) = -e(n_0(\mu + e\phi(r)) - n_0(\mu)) \quad (8.102)$$

If the potential ϕ is small, then Eq. (8.102) may be expanded to first order to give

$$\rho(r) = -e \left(n_0(\mu) + \frac{\partial n_0}{\partial \mu} e\phi(r) - n_0(\mu) \right) = -e^2 \frac{\partial n_0}{\partial \mu} \phi(r) \quad (8.103)$$

which shows how the change in equilibrium charge density is related to the screened potential.

For an isotropic, *nondegenerate, three-dimensional electron gas at equilibrium*, the local change in number of carriers due to a local change in potential is given by a Boltzmann factor, so

$$n = n_0 e^{e\phi/k_B T} \quad (8.104)$$

and Poisson's equation becomes

$$\nabla^2 \phi(r) = \frac{-\rho(r)}{\epsilon} = \frac{e(n - n_0)}{\epsilon} = \frac{en_0}{\epsilon} (e^{e\phi/k_B T} - 1) \quad (8.105)$$

This is a *nonlinear* differential equation for $\phi(r)$. To simplify the equation, we assume that the test charge is small so that one may reasonably expect that the induced potential should also be small. If this is true, then the exponential can be expanded to give $e^{e\phi/k_B T} \sim 1 + e\phi/k_B T + \dots$, so that

$$\nabla^2 \phi(r) \approx \frac{e^2 n_0}{\epsilon k_B T} \phi(r) \quad (8.106)$$

which is a *linear* differential equation for $\phi(r)$. Substituting $\phi(r) = f(r)/r$ gives

$$\nabla^2 \phi(r) = \frac{e^2 n_0}{\epsilon k_B T} \frac{1}{r} f(r) \quad (8.107)$$

In spherical coordinates, the left-hand side of Poisson's equation can be written

$$\nabla^2 \phi(r) = \nabla^2 \left(\frac{1}{r} f(r) \right) = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \frac{1}{r} f(r) \right) \quad (8.108)$$

$$\nabla^2 \phi(r) = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \left(\frac{-1}{r^2} f(r) + \frac{1}{r} \frac{\partial f(r)}{\partial r} \right) \right) \quad (8.109)$$

$$\nabla^2 \phi(r) = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r \frac{\partial f(r)}{\partial r} - f(r) \right) = \frac{1}{r^2} \left(\frac{\partial f(r)}{\partial r} + r \frac{\partial^2 f(r)}{\partial r^2} - \frac{\partial f(r)}{\partial r} \right) = \frac{1}{r} \frac{\partial^2 f(r)}{\partial r^2} \quad (8.110)$$

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so that

$$\frac{\partial^2 f(r)}{\partial r^2} = \frac{e^2 n_0}{\epsilon k_B T} f(r) \quad (8.111)$$

Hence, the solution for $f(r)$ is proportional to $e^{-q_D r}$, where

$$q_D^2 = \frac{n_0 e^2}{\epsilon k_B T} \quad (8.112)$$

The value $1/q_D$ is called the Debye screening length. The Debye screening length applies to the *equilibrium, nondegenerate electron gas* and scales with carrier density as $\sqrt{1/n_0}$ and with thermal energy as $\sqrt{k_B T}$. In this case, our screened coulomb potential in real-space becomes

$$\phi(r) = \frac{1}{r} f(r) = \frac{-e}{4\pi\epsilon r} e^{-q_D r} \quad (8.113)$$

where $\epsilon = \epsilon_0 \epsilon_{r0}$.

For a three-dimensional, *degenerate electron system* at low temperature we may obtain the Thomas–Fermi screening length by simply identifying the Fermi energy as the characteristic energy of the system $E_F = 3k_B T/2$. Substitution into our previous expression for q_D gives

$$q_{TF}^2 = \frac{3n_0 e^2}{2\epsilon E_F} \quad (8.114)$$

Since $E_F = \hbar^2 k_F^2 / 2m$ and $n_0 = k_F^3 / 3\pi^2$, this expression may be rewritten as

$$q_{TF}^2 = \frac{k_F m e^2}{\epsilon \pi^2 \hbar^2} \quad (8.115)$$

The low-temperature Thomas–Fermi screening length $1/q_{TF}$ scales with the characteristic Fermi wave number as $\sqrt{1/k_F}$. In this case, our screened-coulomb potential in real-space becomes

$$\phi(r) = \frac{-e}{4\pi\epsilon r} e^{-q_{TF} r} \quad (8.116)$$

8.4.2.2 Calculating the screened potential and dielectric function in wave vector space

For the coulomb potential energy we had for a single ion at position $\mathbf{R}_j = 0$

$$v_q(r) = \frac{-e^2}{4\pi\epsilon_0 \epsilon_{r0} r} \quad (8.117)$$

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This is a long-range interaction that will be screened by mobile electron charge. Suppose there is a characteristic screening length r_0 . Then we approximate the screened potential energy with a function similar to Eq. (8.113) or Eq. (8.116) so that

$$v_q(r) = \frac{-e^2}{4\pi\epsilon_0\epsilon_{r0}r} e^{-r/r_0} \quad (8.118)$$

This is a static potential energy with no time dependence. To find $v(q)$ for this static screened potential energy, one takes the Fourier transform:

$$v(q) = \int d^3r v(r) e^{-i\mathbf{q}\cdot\mathbf{r}} \quad (8.119)$$

Leaving the integration to Exercise 8.5, the solution is

$$v(q) = \frac{-e^2}{\epsilon_0\epsilon_{r0}(q^2 + 1/r_0^2)} \quad (8.120)$$

We now compare this with our previous expression in terms of a dielectric function

$$v(q) = \frac{-e^2}{\epsilon(q)q^2} = \frac{-e^2}{\epsilon_0\epsilon_{r0}q^2(1 + 1/q^2r_0^2)} \quad (8.121)$$

where r_0 is a characteristic screening length. It is apparent that the effect of screening is to modify the dielectric function in such a way that $\epsilon = \epsilon(q)$. For a degenerate electron gas in the low-temperature limit one may use the Thomas–Fermi screening length such that $1/r_0^2 = q_{TF}^2$. In this case,

$$\boxed{\epsilon(q) = \epsilon_0\epsilon_{r0} \left(1 + \frac{q_{TF}^2}{q^2} \right)} \quad (8.122)$$

This is the Thomas–Fermi dielectric function that, if valid for all q , describes a statically screened, real-space potential energy of the Yukawa type

$$\boxed{v_q(r) = \frac{-e^2}{4\pi\epsilon_0\epsilon_{r0}r} e^{-rq_{TF}}} \quad (8.123)$$

where

$$q_{TF}^2 = \frac{k_F m e^2}{\epsilon \pi^2 \hbar^2} = \frac{k_F m e^2}{\epsilon_0 \epsilon_{r0} \pi^2 \hbar^2} \quad (8.124)$$

is the Thomas–Fermi wave number. The inverse of the Thomas–Fermi wave number defines the length scale for screening.

To get a feel for the value of q_{TF} , consider the semiconductor GaAs with the impurity concentration $n = 10^{18} \text{ cm}^{-3}$ and a conduction band effective electron mass of $m_c^* = 0.07m_0$. In this situation, $q_{TF} = 2 \times 10^6 \text{ cm}^{-1}$. This may be compared with the Fermi wave vector, which has a value $k_F = (3\pi^2 n)^{1/3} = 3 \times 10^6 \text{ cm}^{-1}$. The fact that $1/q_{TF} = 5 \text{ nm}$ and $1/k_F = 3 \text{ nm}$ have comparable values is not unexpected, since they are both a measure

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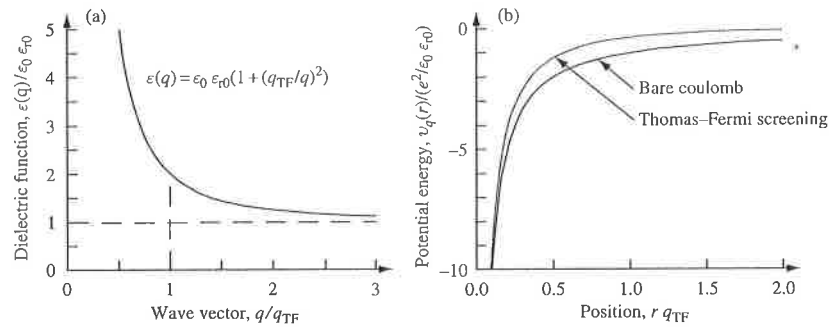


Fig. 8.13 (a) The Thomas–Fermi screened dielectric function as a function of q/q_{TF} and (b) the bare-coulomb and screened-coulomb potential as a function of position r/q_{TF} .

of highest spatial frequency that can be used by the electrons to screen the coulomb interaction.

In Fig. 8.13(a), The Thomas–Fermi dielectric function is plotted as a function of wave vector normalized to q_{TF} . In Fig. 8.13(b) the Thomas–Fermi statically screened real-space potential energy is shown, along with the bare-coulomb potential energy as a function of position, r .

Large values of r in the real-space potential correspond to long-wavelength excitations or equivalently small q scattering in wave vector space. At large values of r , there are many conduction electrons between the impurity and the test charge. Hence, many conduction band electrons can respond to and effectively screen the impurity potential. Short-wavelength or high-spatial-frequency components of the potential correspond to small values of r in the real space potential. In this case, there are few electrons that can respond to screen the impurity potential. High q scattering from a real-space potential involves the incident electron getting close to the ionized impurity. When this happens, there are fewer electrons available to screen the ion.

In general, the dielectric function will have a dynamic (or frequency-dependent) part, so $\epsilon = \epsilon(q, \omega)$. However, we ignore energy exchange processes (which change electron energy by $\hbar\omega$) as we consider elastic electron scattering only. There are other limitations to our model dielectric function. For example, our discussion of Debye and Thomas–Fermi screening adopted a semi-classical approximation that required the screened potential to vary slowly. This approximation is not valid in the limit of $r \rightarrow 0$ (or, equivalently, large q). Substitution of the Thomas–Fermi screened-coulomb potential into Poisson’s equation predicts a screened charge density proportional to $(q_{TF}^2 e^{-q_{TF} \cdot r})/r$, which diverges as $r \rightarrow 0$. This deficiency may be overcome by using a different model dielectric function that does not require the screened potential to vary slowly. In one such approach, called the random phase approximation (RPA), due to Lindhard⁴ one exploits the approximation that the induced charge density contributes linearly to the total potential. The Schrödinger equation is then used to calculate the electronic wave functions self-consistently in the presence of the new potential. However, for most calculations of practical interest (see Exercise 8.7), differences between the RPA and Thomas–Fermi results are relatively

4. J. Lindhard, *Kgl. Danske Videnskab. Selskab Mat.-Fys. Medd.* 28 no. 8 (1954).

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small, and so we will continue to use the Thomas–Fermi dielectric function to calculate elastic, ionized-impurity, electron scattering rates in semiconductors.

8.4.2.3 Using the Thomas–Fermi dielectric function to calculate elastic, ionized-impurity, electron scattering in GaAs

From Eq. (8.84) the elastic scattering rate is

$$1/\tau_{el} = \frac{2\pi m}{\hbar^3 k^3} n \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \int_{\eta=0}^{\eta=1} \frac{d\eta}{(\epsilon_r(q))^2 \eta^3} \quad (8.125)$$

where $\eta = \sin(\theta/2)$ and $q = 2k\eta$. For the Thomas–Fermi dielectric function we have a scattering rate that is given by the expression

$$1/\tau_{el} = \frac{2\pi m}{\hbar^3 k^3} n \left(\frac{e^2}{4\pi\epsilon_0\epsilon_{r0}} \right)^2 \int_{\eta=0}^{\eta=1} \frac{d\eta}{\left(1 + \frac{q_{TF}^2}{q^2} \right)^2 \eta^3} \quad (8.126)$$

Figure 8.14(a) shows results of using Eq. (8.126) to calculate the total elastic scattering rate in GaAs for the indicated values of n -type impurity concentration. The conduction band effective electron mass is taken to be $m_c^* = 0.07 m_0$, and the value of ϵ_{r0} is 13.2. The elastic scattering rate for an electron of energy $E = 200$ meV in GaAs with $n = 10^{17} \text{ cm}^{-3}$ is about $2 \times 10^{12} \text{ s}^{-1}$ corresponding to a scattering time of $\tau = 0.5$ ps.

Figure 8.14(b) shows the calculated elastic scattering rate as a function of scattered angle for an electron of energy $E = 100$ meV and $E = 300$ meV in the conduction band of GaAs with $n = 10^{17} \text{ cm}^{-3}$. It is clear that the coulomb potential favors small-angle scattering. This is particularly true when the electron has a large value of energy, E .

Figure 8.15 illustrates the difference in calculated elastic scattering rate as a function of scattered angle with and without Thomas–Fermi screening for the indicated electron energies in the conduction band of GaAs with $n = 10^{18} \text{ cm}^{-3}$.

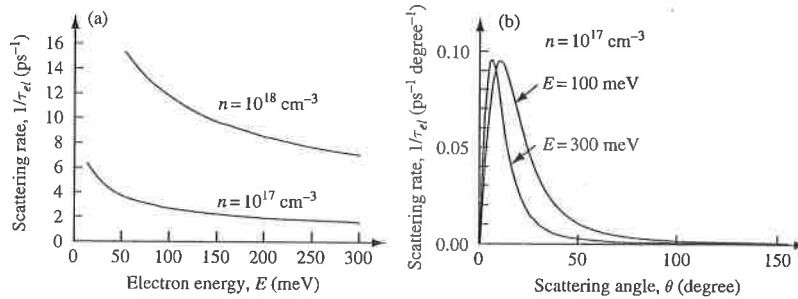


Fig. 8.14 (a) Calculated total elastic scattering rate for an electron of energy E in the conduction band of GaAs due to the presence of the indicated random ionized impurity density. The calculation uses the Thomas–Fermi dielectric function. (b) Elastic scattering rate as a function of scattered angle for an electron of energy $E = 100$ meV and $E = 300$ meV in the conduction band of GaAs with $n = 10^{17} \text{ cm}^{-3}$.

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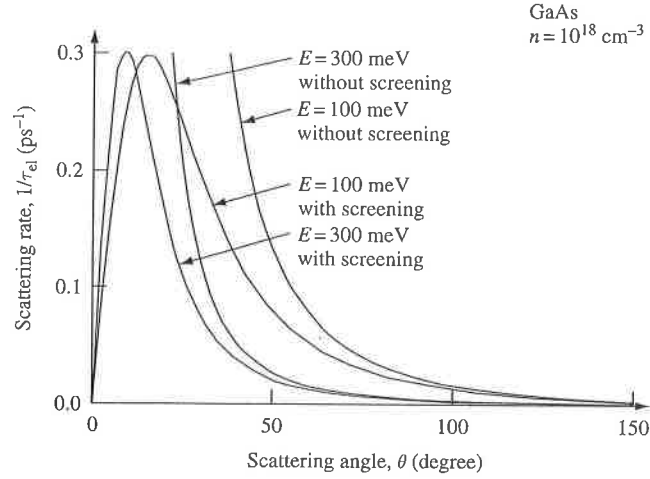


Fig. 8.15 Calculated total elastic scattering rate from random ionized impurities as a function of angle θ with and without Thomas–Fermi screening of the coulomb potential. The parameters used in the calculation are those for GaAs with n -type impurity concentration $n = 10^{18} \text{ cm}^{-3}$.

The effect of screening is to increase the dielectric constant for small scattered wave vector q , since

$$\varepsilon(q) = \varepsilon_0 \varepsilon_{r0} \left(1 + \frac{q_{\text{TF}}^2}{q^2} \right) \quad (8.127)$$

This reduces the value of the integral when q is small. Small q corresponds to small-angle scattering since $q = 2k \sin(\theta/2)$. It is small-angle scattering (or long-wavelength excitations) that are suppressed.

Figure 8.14(a) shows that a high-energy electron scatters less than an electron of low energy. This is typical behavior for coulomb scattering, the origin of which in this case can be traced back to the $E^{-3/2}$ term in Eq. (8.85). Using this energy dependence, it is straightforward to show that, when elastic scattering from ionized impurities dominates electron dynamics, our calculations predict that mobility has a $T^{3/2}$ temperature dependence (see Exercise 8.6). Typically, elastic scattering from ionized impurities is most significant at low temperatures, and so, as shown in Fig. 8.16, mobility increases with increasing temperature for $T < 50 \text{ K}$. However, at temperatures above $T = 50 \text{ K}$, *inelastic* scattering from lattice vibrations can dominate, causing a decrease in mobility with increasing temperature. In this book, we will not develop a microscopic theory of inelastic scattering.

8.4.2.4 Elastic electron scattering in the limit of small initial velocity

Recall that r_0 is a characteristic screening length that represents the range of action of the potential and that k is the magnitude of the initial wave vector. For a degenerate electron gas $1/r_0^2 = q_{\text{TF}}^2$, and for a nondegenerate electron gas $1/r_0^2 = q_0^2$. If we consider an

8.4 ELASTIC SCATTERING FROM IONIZED IMPURITIES

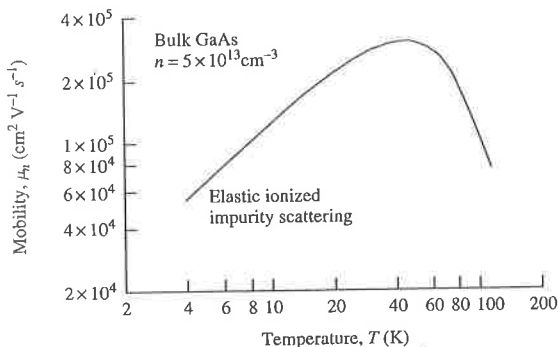


Fig. 8.16 Measured temperature dependence of mobility in bulk GaAs with an n -type impurity concentration of $n = 5 \times 10^{13} \text{ cm}^{-3}$. The axes use a logarithmic scale. At low temperatures, elastic ionized impurity scattering dominates mobility, and mobility increases with increasing temperature dependence. At temperatures above $T = 50 \text{ K}$, inelastic scattering from lattice vibrations dominates, causing a decrease in mobility with increasing temperature.

electron with small initial velocity, then $k \rightarrow 0$, and so $kr_0 \ll 1$. The scattering amplitude is proportional to

$$V(q) = \int d^3 r V(r) e^{-iq \cdot r} \quad (8.128)$$

In the limit $kr_0 \ll 1$, then $e^{-iq \cdot r} \sim 1$, since $q = 2k \sin(\theta/2)$ and $k \rightarrow 0$. Hence,

$$V(q)|_{k \rightarrow 0} = \int d^3 r V(r) = 4\pi \int dr V(r) r^2 \quad (8.129)$$

and we may conclude that the scattering is isotropic, independent of the incident velocity. This is illustrated in Fig. 8.17.

8.4.2.5 Elastic electron scattering in the limit of large initial velocity

For large velocity $k \rightarrow \infty$ and so $kr_0 \ll 1$. In this limit the scattering is anisotropic into a cone $\Delta\theta \sim 1/kr_0$. This is illustrated in Fig. 8.18. Outside of this cone, the term $e^{-iq \cdot r}$

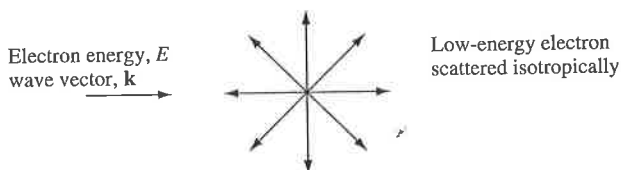


Fig. 8.17 Illustration showing slow-velocity electron of initial energy E and wave vector \mathbf{k} elastically scattered by the coulomb potential. Isotropic scattering means that the velocity of the scattered electron is independent of the initial velocity.

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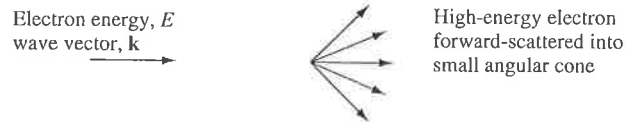


Fig. 8.18 Illustration showing high-velocity electron of initial energy E and wave vector \mathbf{k} elastically scattered by the coulomb potential. Forward-scattering means that the velocity of the scattered electron deviates little from the initial velocity of the electron. Electrons are forward-scattered into a small angular cone.

oscillates rapidly, and the integral of this with the slowly varying $V(r)$ is almost zero. Hence, in the limit $kr_0 \ll 1$.

$$V(q)|_{k \rightarrow \infty} = 4\pi \int_{r=0}^{r=r_0} dr V(r) e^{-iq \cdot r} r^2 \quad (8.130)$$

8.5 Photon emission due to electronic transitions

To understand and control the emission of photons from atoms or solids, we need to extend our knowledge to include something about the density of optical modes, light intensity, the background energy density in thermal equilibrium, Fermi's golden rule for optical transitions, the occupation factor for thermally distributed photons, and the Einstein \mathcal{A} and \mathcal{B} coefficients. In the next few pages, we explore these items by example. After completing this section, we will have the knowledge needed to consider the basic ingredients of a laser.

8.5.1 Density of optical modes in three-dimensions

For electromagnetic plane waves characterized by wave vector \mathbf{k} , the density of optical states in three-dimensions is

$$D_3^{\text{opt}}(k)dk = 2 \times 4\pi k^2 \frac{dk}{(2\pi)^3} = \frac{k^2}{\pi^2} dk \quad (8.131)$$

where the factor 2 is from the two orthogonal polarizations. This is the density of modes per unit volume in k -space. However, in a homogeneous nondispersive medium with refractive index n_r , the wave vector $k = n_r \omega / c$ and $dk = n_r d\omega / c$. Hence,

$$D_3^{\text{opt}}(\omega)d\omega = 2 \times 4\pi k^2 \frac{dk}{(2\pi)^3} \frac{d\omega}{(2\pi)^3} = 2 \times 4\pi \frac{\omega^2 n_r^3}{c^3} \frac{d\omega}{(2\pi)^3} \quad (8.132)$$

$$D_3^{\text{opt}}(\omega)d\omega = \frac{\omega^2 n_r^3}{\pi^2 c^3} d\omega \quad (8.133)$$

is the mode density. We will use this density of optical modes to calculate the background photon energy density at thermal equilibrium.

Notice that the density of optical modes in a medium with refractive index $n_r > 1$ is larger than that of free space, where $n_r = 1$. The underlying reason for this is that light travels more slowly in the medium.

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8.5.2 Light intensity

The Poynting vector $\mathbf{S} = \mathbf{E} \times \mathbf{H}$ (Eq. (1.114)) can be used to determine the energy flux density of a sinusoidally varying electromagnetic field. The magnitude of *average* power flux is given by

$$|\mathbf{S}_{\text{av}}| = \frac{1}{2} |\mathbf{E} \times \mathbf{H}| = \frac{1}{2} |\mathbf{E}_0| |\mathbf{H}_0| = \frac{1}{2} |\mathbf{E}_0| \frac{\omega \epsilon_0}{k} |\mathbf{E}_0| = \frac{1}{2} c \epsilon_0 |\mathbf{E}_0|^2 \quad (8.134)$$

where the factor 1/2 comes from taking the average. This is the average light intensity of a sinusoidally oscillating electromagnetic field in free space. It follows that the energy density for photons per unit frequency interval in free space is

$$U(\omega) = \frac{1}{2} \epsilon_0 |\mathbf{E}_0|^2 \quad (8.135)$$

8.5.3 Background photon energy density at thermal equilibrium

The average value of radiation energy density at frequency ω is given by the product of the density of states, the occupation factor, and the energy per photon:

$$U(\omega) = D_3^{\text{opt}}(\omega) g(\omega) \hbar \omega \quad (8.136)$$

We have already calculated $D_3^{\text{opt}}(\omega)$, and the occupation factor for a system in thermal equilibrium is given by the Bose-Einstein distribution function $g(\omega)$, so

$$U(\omega) = \frac{\omega^2}{\pi^2 c^3} \frac{1}{e^{\hbar \omega / k_B T} - 1} \hbar \omega = \frac{\hbar \omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar \omega / k_B T} - 1} \quad (8.137)$$

Here $U(\omega)$ is the background radiative photon energy per unit volume per unit frequency at thermal equilibrium. In an isotropic homogeneous medium with refractive index n_r , Eq. (8.137) is modified to

$$U(\omega) = \frac{\hbar \omega^3 n_r^3}{\pi^2 c^3} \frac{1}{e^{\hbar \omega / k_B T} - 1} \quad (8.138)$$

The background radiative photon energy per unit volume per unit frequency at thermal equilibrium in a dielectric medium with $n_r > 1$ is always greater than in free space, because the density of optical modes is greater (Eq. (8.133)).

8.5.4 Fermi's golden rule for stimulated optical transitions

When deriving Fermi's golden rule we had (Eq. (8.25))

$$a_m(t) = \frac{1}{i\hbar} \int_{t'=0}^{t'=t} W_{mn} e^{i\omega_{mn}t'} dt' \quad (8.139)$$

where $\omega_{mn} = \omega_m - \omega_n$. The simplest interaction between an atomic dipole and the oscillating electric field of a photon is by way of the dipole matrix element

$$W_{mn} = \mathbf{d}_{mn} \cdot \mathbf{E} = e r_{mn} |\mathbf{E}_0| \cos(\omega t) \quad (8.140)$$

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where

$$d_{mn} = e \langle m | \hat{\mathbf{r}} | n \rangle = e r_{mn} \quad (8.141)$$

is the dipole and

$$\mathbf{E} = \mathbf{E}_0 \cos(\omega t) = \frac{\mathbf{E}_0}{2} (e^{i\omega t} + e^{-i\omega t}) \quad (8.142)$$

is the oscillating electric field.

We wish to use Fermi's golden rule to calculate the transition rate between two states of an atomic system due to the presence of a sinusoidally oscillating electric field. For convenience, we consider an electric field in the z direction so that the dipole matrix element between state $|n\rangle$ and $|m\rangle$ changes from r_{mn} to z_{mn} . Equation (8.139) may now be written

$$a_m(t) = \frac{1}{i\hbar} \frac{e|\mathbf{E}_0|}{2} z_{mn} \int_{t'=0}^{t'=t} (e^{i\omega t'} + e^{-i\omega t'}) e^{i\omega_{mn} t'} dt' \quad (8.143)$$

$$a_m(t) = \frac{1}{\hbar} \frac{e|\mathbf{E}_0|}{2} z_{mn} \left(\frac{e^{i(\omega+\omega_{mn})t} - 1}{\omega + \omega_{mn}} + \frac{e^{-i(\omega-\omega_{mn})t} - 1}{\omega - \omega_{mn}} \right) \quad (8.144)$$

Since $\omega + \omega_{mn} \gg \omega - \omega_{mn}$ for ω near ω_{mn} , the first term can be set to zero:

$$a_m(t) \sim \frac{1}{\hbar} \frac{e|\mathbf{E}_0|}{2} z_{mn} \left(\frac{e^{-i(\omega-\omega_{mn})t} - 1}{\omega - \omega_{mn}} \right) \quad (8.145)$$

With this approximation,

$$a_m(t) = \frac{1}{\hbar} \frac{e|\mathbf{E}_0|}{2} z_{mn} \frac{e^{-i(\omega-\omega_{mn})t/2}}{\omega - \omega_{mn}} (e^{-i(\omega-\omega_{mn})t/2} - e^{i(\omega-\omega_{mn})t/2}) \quad (8.146)$$

$$a_m(t) = \frac{1}{\hbar} e|\mathbf{E}_0| z_{mn} \frac{e^{-i(\omega-\omega_{mn})t/2}}{\omega - \omega_{mn}} \sin((\omega - \omega_{mn})t/2) \quad (8.147)$$

Hence, the probability for a transition is

$$|a_m(t)|^2 = \left(\frac{e|\mathbf{E}_0|}{\hbar} \right)^2 |z_{mn}|^2 \frac{\sin^2((\omega - \omega_{mn})t/2)}{(\omega - \omega_{mn})^2} \quad (8.148)$$

The probability of a transition to the continuum or over the complete line shape is found by integrating over all frequency ω , so that

$$|a_m(t)|^2 = \left(\frac{e|\mathbf{E}_0|}{\hbar} \right)^2 |z_{mn}|^2 \int_{-\infty}^{\infty} \frac{\sin^2((\omega - \omega_{mn})t/2)}{(\omega - \omega_{mn})^2} d\omega \quad (8.149)$$

But

$$\int_{-\infty}^{\infty} \frac{\sin^2(ax)}{x^2} dx = a\pi \quad (8.150)$$

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So, we change variables such that $a = t/2$ and $x = (\omega - \omega_{mn})$, and our expression thus becomes

$$|a_m(t)|^2 = \left(\frac{e|\mathbf{E}_0|}{\hbar} \right)^2 |z_{mn}|^2 \frac{\pi t}{2} = \frac{\pi e^2}{\epsilon_0 \hbar^2} |z_{mn}|^2 U(\omega) t \quad (8.151)$$

where we used Eq. (8.135) to eliminate $|\mathbf{E}_0|^2$. For an isotropic energy density $U(\omega)$, averaging over the three directions of polarization, and differentiating with respect to time, gives the transition rate

$$\frac{d}{dt} |a_m(t)|^2 = \frac{\pi e^2}{3\epsilon_0 \hbar^2} |r_{mn}|^2 U(\omega) = \mathcal{B} U(\omega) \quad (8.152)$$

The factor $1/3$ comes from the average over polarization, and $\mathcal{B}U(\omega)$ is called the stimulated emission rate. The probability per unit time that an atom in state $|n\rangle$ makes a transition to any possible state $|m\rangle$ stimulated by electromagnetic radiation is

$$\mathcal{B}_{mn} U(\omega) = \frac{\pi e^2}{3\epsilon_0 \hbar^2} |\langle m | \hat{\mathbf{r}} | n \rangle|^2 U(\omega) \quad (8.153)$$

8.5.5 The Einstein \mathcal{A} and \mathcal{B} coefficients

We already know that electromagnetic radiation can stimulate transitions between electronic states. In addition to stimulated transitions, spontaneous transitions from a high-energy state to a lower-energy state are also possible. The existence of spontaneous emission from an excited state is *required* as a mechanism to drive the system back to thermal equilibrium. Einstein was able to show that, for a system in *thermal equilibrium*, stimulated and spontaneous transition rates are related to each other.⁵

Consider a two-energy-level atom system illustrated in Fig. 8.19 in which optical transitions take place between states $|1\rangle$ and $|2\rangle$. There are N_1 atoms in state $|1\rangle$ and N_2 atoms in state $|2\rangle$. The total stimulated transition rate is proportional to Eq. (8.153) multiplied by the number of occupied initial states. Under conditions of thermal equilibrium, the net rate of transition from $|2\rangle$ to $|1\rangle$ must equal that from $|1\rangle$ to $|2\rangle$, so that

$$N_2(\mathcal{B}_{21}U(\omega) + \mathcal{A}) = N_1\mathcal{B}_{12}U(\omega) \quad (8.154)$$

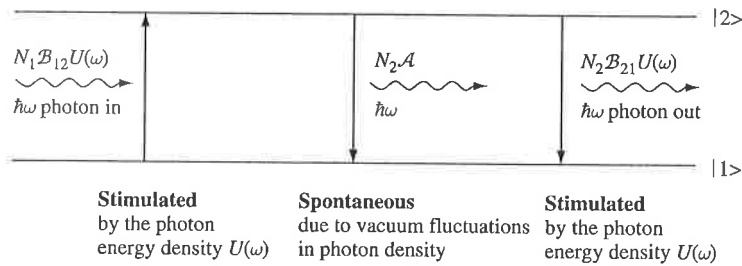


Fig. 8.19 Energy level diagram of a two-level atom system in which N_1 atoms are in state $|1\rangle$ and N_2 atoms are in state $|2\rangle$.

5. A. Einstein, *Phys. Z.* **18**, 121 (1917).

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where we have introduced a spontaneous transition rate \mathcal{A} . Spontaneous transitions occur from $|2\rangle$ to $|1\rangle$ due to vacuum fluctuations in photon density.

In thermal equilibrium, the ratio of occupation of levels is given by a Boltzmann factor, so we may write

$$\frac{\mathcal{B}_{21}}{\mathcal{B}_{12}} + \frac{\mathcal{A}}{\mathcal{B}_{12}U(\omega)} = \frac{N_1}{N_2} = e^{\hbar\omega/k_B T} \quad (8.155)$$

The Boltzmann factor is the ratio of the number of atoms, N_1/N_2 . Substituting our expression for electromagnetic energy density $U(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar\omega/k_B T} - 1}$ for black-body radiation gives

$$\frac{\mathcal{B}_{21}}{\mathcal{B}_{12}} + \frac{\mathcal{A}}{\mathcal{B}_{12}} \frac{\pi^2 c^3}{\hbar\omega^3} (e^{\hbar\omega/k_B T} - 1) = e^{\hbar\omega/k_B T} \quad (8.156)$$

Separating out the temperature dependent and temperature independent terms, we have

$$\frac{\mathcal{A}}{\mathcal{B}_{12}} \frac{\pi^2 c^3}{\hbar\omega^3} = 1 \quad (8.157)$$

and

$$\frac{\mathcal{B}_{21}}{\mathcal{B}_{12}} = 1 \quad (8.158)$$

Hence, we obtain the *Einstein relations*

$$\boxed{\begin{aligned} \mathcal{A} &= \frac{\hbar\omega^3}{\pi^2 c^3} \mathcal{B}_{12} \\ \mathcal{B}_{12} &= \mathcal{B}_{21} \end{aligned}} \quad (8.159)$$

The stimulated and spontaneous transition probability are related to each other. Using Eq. (8.153), we have

$$\mathcal{B} = \frac{\pi e^2}{3\varepsilon_0 \hbar^2} |\langle j|\hat{\mathbf{r}}|k\rangle|^2 \quad (8.160)$$

and it follows that the spontaneous emission rate $1/\tau_{\text{sp}} = \mathcal{A}$ is just

$$\mathcal{A} = \frac{e^2 \omega^3}{3\pi\varepsilon_0 \hbar c^3} |\langle j|\hat{\mathbf{r}}|k\rangle|^2 \quad (8.161)$$

It can be shown (see Exercise 8.9) that since the time dependence of spontaneous light emission intensity from a number of excited atoms is $I(t) = I(t=0)e^{-\mathcal{A}t} = I(t=0)e^{-t/\tau_{\text{sp}}}$, the associated spectral line has a Lorentzian line shape with full-width-half-maximum $1/\tau_{\text{sp}} = \mathcal{A}$ measured in units of rad s^{-1} .

If light emission occurs in an isotropic, homogeneous medium characterized by refractive index $n_r > 1$, then the density of optical modes contributing to $U(\omega)$ is given by Eq. (8.138) and Eq. (8.161) is modified to

$$\mathcal{A} = \frac{e^2 \omega^3 n_r^3}{3\pi\varepsilon_0 \hbar c^3} |\langle j|\hat{\mathbf{r}}|k\rangle|^2 \quad (8.162)$$

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8.5.5.1 Estimation of the spontaneous emission coefficient \mathcal{A} for the hydrogen $|2p\rangle \rightarrow |1s\rangle$ transition

As a first application of quantum-mechanical spontaneous emission, consider a hydrogen atom. If a hydrogen atom in free space is in an excited state with $n = 2$, then quantum mechanics predicts the atom will relax to the $n = 1$ ground state by spontaneous emission of a photon. This physical process limits the excited-state lifetime on average to a time characterized by the spontaneous emission lifetime $\tau_{\text{sp}} = 1/\mathcal{A}$. To estimate this value, we start with our expression for the spontaneous emission coefficient given by Eq. (8.161). For the $k = 2$ to $j = 1$ transition the emission wavelength is $\lambda_{\text{photon}} = 122 \text{ nm}$ (Eq. (2.74)), and we calculate optical frequency using $ck = \omega = c2\pi/\lambda_{\text{photon}}$. The dipole matrix element can be estimated as $\langle 1s|\hat{\mathbf{r}}|2p\rangle \sim a_{\text{B}} = 0.053 \text{ nm}$, where a_{B} is the Bohr radius of the electron in a hydrogen atom (Eq. (2.69)). Putting in the numbers gives

$$\mathcal{A} = \frac{(2\pi)^3}{\lambda_{\text{photon}}^3} \frac{e^2}{3\pi\epsilon_0\hbar} a_{\text{B}}^2 = 1.12 \times 10^9 \text{ s}^{-1} = \frac{1}{\tau_{\text{sp}}} \quad (8.163)$$

Hence, an estimate for the spontaneous emission time is $\tau_{\text{sp}} = 0.89 \text{ ns}$. A more detailed calculation gives $|\langle 1s|\hat{\mathbf{r}}|2p\rangle|^2 = \frac{1}{3} \left(\frac{32}{27}\right)^3 a_{\text{B}}^2$ for the $|2p\rangle \rightarrow |1s\rangle$ transition in hydrogen, so that $\tau_{\text{sp}} = 1.6 \text{ ns}$.

The electromagnetic wave produced by the transition takes energy from the excited state and converts it to electromagnetic energy. Typically, the electromagnetic field intensity decays as $e^{-t/\tau_{\text{sp}}}$, so that the *length* of a photon when $\tau_{\text{sp}} \sim 1 \text{ ns}$ is about 0.3 m .

As the electron makes its transition, the superposition of the $|2p\rangle$ and $|1s\rangle$ states causes the hydrogen electron probability density cloud to oscillate at difference energy $\hbar\omega = \Delta E = E_2 - E_1 = 10.2 \text{ eV}$. The oscillation in expectation value of electron position creates a dipole moment, and electromagnetic radiation is emitted at wavelength $\lambda_{\text{photon}} = 2\pi c/\omega = 0.122 \mu\text{m}$, carrying away angular momentum of magnitude $\pm\hbar$ (quantum number ± 1).

8.5.5.2 Dipole selection rules for optical transitions

The dipole matrix element $d_{jk} = e\langle j|\hat{\mathbf{r}}|k\rangle$ (Eq. (8.141)) gives rise to a set of rules for optical transitions at frequency ω between initial eigenstate $|k\rangle$ and final eigenstate $|j\rangle$. Dipole radiation requires a parity difference (even-to-odd or odd-to-even) between initial and final states to ensure oscillation in the mean position of charge. Without oscillation in the mean position of charge, there can be no dipole radiation. Clearly, the dipole matrix element $\langle \text{even}(\text{odd})|r|\text{odd}(\text{even})\rangle \neq 0$, whereas $\langle \text{even}(\text{odd})|r|\text{even}(\text{odd})\rangle = 0$ from symmetry. Hence, for quantum numbers that sequentially alternate between odd and even parity we expect $\langle j|r|k\rangle \neq 0$ for $j - k = \text{odd}$. This type of condition is often called a dipole selection rule. Other rules also apply. For example, energy conservation requires that the separation in energy between initial and final states is the energy of the photon, $\hbar\omega$.

To illustrate a practical application of these ideas, we will now use dipole selection rules to calculate the spontaneous emission lifetime for an excited state of an electron in a one-dimensional, infinite, rectangular potential well.

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8.5.5.3 Spontaneous emission lifetime of an electron in a one-dimensional, rectangular potential well with infinite barrier energy.

As part of the design of a laser, we wish to calculate the spontaneous emission lifetime of the first excited state for an electron confined to a one-dimensional, infinite, rectangular potential well of width $L = 12.3$ nm. Figure 8.20(a) is a sketch of a one-dimensional, rectangular potential well with infinite barrier energy showing energy eigenvalues E_1 , E_2 , and E_3 . Figure 8.20(b) sketches the first three energy eigenfunctions ψ_1 , ψ_2 , and ψ_3 for the potential shown in Figure 8.20(a). In general, the eigenstates are $|j\rangle = A \sin(\pi j x/L)$, where j is a nonzero positive integer. Normalization requires $\langle j|j\rangle = 1$ giving $A = \sqrt{2/L}$. For j odd $|j\rangle$ is of even parity, and for j even $|j\rangle$ is of odd parity.

To help find a quick solution, we note that the de Broglie wavelength λ_e of an electron measured in nm is related to the electron energy E measured in eV through the relation

$$\lambda_e(\text{nm}) = \frac{1.23}{(E(\text{eV}))^{1/2}} \quad (8.164)$$

and that the wavelength of a photon λ_{photon} measured in μm is related to its energy E measured in eV through

$$\lambda_{\text{photon}}(\mu\text{m}) = \frac{1.24}{E(\text{eV})} \quad (8.165)$$

The electron wavelength of the ground state in this potential is $2L = 24.6$ nm, and the wavelength of the first excited state is $L = 12.3$ nm. This gives energy

$$E_1 = \left(\frac{1.23}{2L}\right)^2 = \left(\frac{1}{20}\right)^2 = 2.5 \text{ meV} \quad (8.166)$$

$$E_2 = \left(\frac{1.23}{L}\right)^2 = \left(\frac{1}{10}\right)^2 = 10 \text{ meV} \quad (8.167)$$

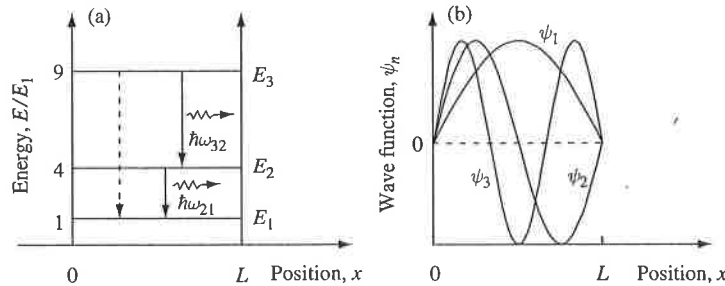


Fig. 8.20 (a) Sketch of a one-dimensional, rectangular potential well with infinite barrier energy showing the energy eigenvalues E_1 , E_2 , and E_3 . Spontaneous emission of a photon can occur between two states when a dipole matrix element exists between the two states. This is the case for $\psi_2 \rightarrow \psi_1$ and $\psi_3 \rightarrow \psi_2$. No dipole radiation can occur between the second excited state ψ_3 and the ground state ψ_1 , because the dipole matrix element is zero between states of the same parity. (b) Sketch of the energy eigenfunctions ψ_1 , ψ_2 , and ψ_3 for the potential shown in (a).

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Hence, the wavelength of the emitted photon is just

$$\lambda_{\text{photon}} = \frac{1.24}{E_2 - E_1} \mu\text{m} = \frac{1.24}{7.5 \times 10^{-3}} \mu\text{m} = 165.3 \mu\text{m} \quad (8.168)$$

We now calculate the dipole matrix element x_{jk} between two electron states $|j\rangle$ and $|k\rangle$.

$$x_{jk} = \langle j|x|k\rangle = \frac{2}{L} \int_0^L x \sin(j\pi x/L) \sin(k\pi x/L) dx \quad (8.169)$$

$$x_{jk} = \frac{2}{L} \int_0^L x (\cos((j-k)\pi x/L) - \cos((j+k)\pi x/L)) dx \quad (8.170)$$

where we used the fact that $2 \sin(x) \sin(y) = \cos(x-y) - \cos(x+y)$. Solving the integral by parts and introducing the integer parameter m , we have

$$\begin{aligned} \int_0^L x \cos(m\pi x/L) dx &= \left[\frac{L}{m\pi} x \sin\left(\frac{m\pi x}{L}\right) \right]_0^L - \frac{L}{m\pi} \int_0^L \sin\left(\frac{m\pi x}{L}\right) dx \\ &= \left[\left(\frac{L}{m\pi}\right)^2 \cos\left(\frac{m\pi x}{L}\right) \right]_0^L \end{aligned} \quad (8.171)$$

For even values of m , this gives

$$\int_0^L x \cos(m\pi x/L) dx = 0 \quad (8.172)$$

and for odd values of m

$$\int_0^L x \cos(m\pi x/L) dx = \frac{-2L^2}{m^2\pi^2} \quad (8.173)$$

When $m = 0$, the integral is

$$\int_0^L x \cos(m\pi x/L) dx = \frac{L^2}{2} \quad (8.174)$$

Since j and k are integers, m is even if $|j\rangle$ and $|k\rangle$ have the same parity, m is odd if $|j\rangle$ and $|k\rangle$ are of different parity, and $m = 0$ if $j = k$.

In the situation we are considering, the state functions with odd integer values are of even parity and the state functions with even integer values are of odd parity. Hence, we may conclude the dipole matrix element

$$x_{jk} = 0 \quad (8.175)$$

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for $|j\rangle$ and $|k\rangle$ of the same parity,

$$x_{jk} = \frac{-1}{L} \frac{2L^2}{\pi^2} \left(\frac{1}{(j-k)^2} - \frac{1}{(j+k)^2} \right) = \frac{-2L}{\pi^2} \left(\frac{(j+k)^2 - (j-k)^2}{(j-k)^2(j+k)^2} \right) \quad (8.176)$$

$$= \frac{-2L}{\pi^2} \frac{4jk}{(j^2 - k^2)^2}$$

for $|j\rangle$ and $|k\rangle$ of different parity, and

$$x_{jk} = \frac{1}{L} \frac{2L^2}{\pi^2} = \frac{L}{2} \quad (8.177)$$

for $j = k$. As shown in Fig. 8.20(a), electron transitions involving dipole radiation of light are allowed from the first excited state to the ground state ($\psi_2 \rightarrow \psi_1$) and from the second excited state to the first excited state ($\psi_3 \rightarrow \psi_2$). However, dipole radiation from the second excited state to the ground state ($\psi_3 \rightarrow \psi_1$) does not occur, because the dipole matrix element is zero between states of the same parity.

For the transition between the first excited-state $|k = 2\rangle$ and the ground state $|j = 1\rangle$, the states $|k\rangle$ and $|j\rangle$ are of different parity and so, using Eq. (8.176), we have dipole matrix element

$$x_{12} = \frac{-16L}{9\pi^2} \quad (8.178)$$

The Einstein spontaneous emission rate given by Eq. (8.161) can be rewritten for light of wavelength λ_{photon} with units of length in nm as

$$\mathcal{A} = \frac{7.235 \times 10^{17}}{\lambda_{\text{photon}}^3} |\langle j|r|k\rangle|^2 \quad (8.179)$$

Hence, the spontaneous emission lifetime for the transition between $|2\rangle$ and $|1\rangle$ is given by

$$\tau_{\text{sp}} = \frac{1}{\mathcal{A}} = \frac{\lambda_{\text{photon}}^3}{7.235 \times 10^{17}} \frac{1}{|x_{12}|^2} = \frac{(1.65 \times 10^5)^3}{7.235 \times 10^{17}} \frac{81\pi^4}{256 \times (12.3)^2} \quad (8.180)$$

$$= 1.26 \times 10^{-3} \text{ s}$$

The frequency spectral line width is just $\mathcal{A} = 1/\tau_{\text{sp}}$ measured in units of rad s^{-1} .

Our results would be modified if we were to consider the same transition for an electron in the conduction band of GaAs confined by a one-dimensional quantum well potential of the same width L . In this case, the conduction band electron has a low effective electron mass of $m_e^* = 0.07m_0$, the effect of which is to increase the separation in electron energy levels by a factor of 14.3 and shorten the emission wavelength to $11.5 \mu\text{m}$ compared with our calculation for a bare electron. For emission wavelengths near $10 \mu\text{m}$, the bulk refractive index for GaAs is $n_r \sim 3.3$. The combination of reduced emission wavelength and the presence of a medium with refractive index n_r changes the spontaneous emission

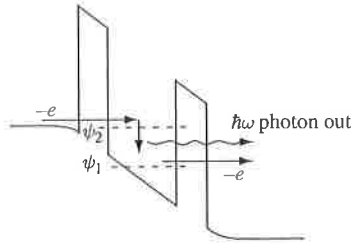


Fig. 8.21 Schematic cross-section of a GaAs/AlGaAs conduction band profile with electron tunnel injection into ψ_2 states and optical transition to ψ_1 states.

lifetime in Eq. (8.180) so that the spontaneous emission lifetime in the conduction band of a GaAs rectangular potential well of width $L = 12.3 \text{ nm}$ for wavelength $\lambda_{\text{photon}} = 11.5 \mu\text{m}$ is $\tau_{\text{sp}} = 1.2 \times 10^{-8} \text{ s}$.

The design of a device that has efficient conversion of excited electron states to photons requires injection of electrons into ψ_2 states. One way to achieve this is to use tunnel injection. Figure 8.21 shows a cross-section of a GaAs/AlGaAs conduction band profile with just such a tunnel injector. These ideas have been pursued to create a semiconductor laser with emission at wavelength in the $10 \mu\text{m}$ range.⁶

8.6 Example exercises

Exercise 8.1

(a) A particle of mass m is in a one-dimensional, rectangular potential well for which $V(x) = 0$ for $0 < x < L$ and $V(x) = \infty$ elsewhere. The particle is initially prepared in the ground state ψ_1 with eigenenergy E_1 . Then, at time $t = 0$, the potential is very rapidly changed so that the original wave function remains the same but $V(x) = 0$ for $0 < x < 2L$ and $V(x) = \infty$ elsewhere. Find the probability that the particle is in the first, second, third, and fourth excited state of the system when $t \geq 0$.

(b) Consider the same situation as (a) but for the case in which at time $t = 0$ the potential is very rapidly changed so that the original wave function remains the same but $V(x) = 0$ for $0 < x < \gamma L$, where $1 < \gamma < 5$, and $V(x) = \infty$ elsewhere. Write a computer program that plots the probability of finding the particle in the ground, first, second, third and fourth excited states of the system as a function of the parameter γ .

Exercise 8.2

The coulomb potential energy in real space between charges e and $-e$ is

$$V(r) = \frac{-e^2}{4\pi\epsilon_0\epsilon_r r}$$

6. For an introduction to the quantum cascade laser, see J. Faist, F. Capasso, D.L. Sivco, C. Sirtori, A.L. Hutchinson, and A. Y. Cho, *Science* **264**, 553 (1994).