Theory of Electronic and Optical Properties of Nanostructures

Prabath Hewageegana

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THEORY OF ELECTRONIC AND OPTICAL PROPERTIES OF
NANOSTRUCTURES

by

PRABATH S. HEWAGEEGANA

Under the Direction of Dr. Vadym Apalkov

ABSTRACT

“There is plenty of room at the bottom.” This bold and prophetic statement from Nobel laureate Richard Feynman back in 1950s at Cal Tech launched the Nano Age and predicted, quite accurately, the explosion in nanoscience and nanotechnology. Now this is a fast developing area in both science and technology. Many think this would bring the greatest technological revolution in the history of mankind.

To understand electronic and optical properties of nanostructures, the following problems have been studied. In particular, intensity of mid-infrared light transmitted through a metallic diffraction grating has been theoretically studied. It has been shown that for $s$-polarized light the enhancement of the transmitted light is much stronger than for $p$-polarized light. By tuning the parameters of the diffraction grating enhancement can be increased by a few orders of magnitude. The spatial distribution of the transmitted light is highly nonuniform with very sharp peaks, which have the spatial widths about 10 nm. Furthermore, under the ultra fast response in nanostruc-
tures, the following two related goals have been proved: (a) the two-photon coherent control allows one to dynamically control electron emission from randomly rough surfaces, which is localized within a few nanometers. (b) the photoelectron emission from metal nanostructures in the strong-field (quasistationary) regime allows coherent control with extremely high contrast, suitable for nanoelectronics applications.

To investigate the electron transport properties of two dimensional carbon called graphene, a localization of an electron in a graphene quantum dot with a sharp boundary has been considered. It has been found that if the parameters of the confinement potential satisfy a special condition then the electron can be strongly localized in such quantum dot. Also the energy spectra of an electron in a graphene quantum ring has been analyzed. Furthermore, it has been shown that in a double dot system some energy states becomes strongly localized with an infinite trapping time. Such states are achieved only at one value of the inter-dot separation. Also a periodic array of quantum dots in graphene have been considered. In this case the states with infinitely large trapping time are realized at all values of inter-dot separation smaller than some critical value.

INDEX WORDS: Nanoplasmonic, Nanooptics, Nanostructures, Surface plasmon polaritons, Localized surface plasmons, Nanoantennas, Ultra fast nanostructures, Graphene, Graphene quantum dots.
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PRABATH S. HEWAGEEGANA

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Georgia State University
December 2008
To Loving...

Wife Duleeka, Daughter Nihinsa

and

My Parents
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Chapter 1

Fundamentals of nanoplasmonics

1.1 Introduction

The study of optical phenomena related to the electromagnetic response of metals has been recently termed plasmonic or nanoplasmonic. Nanoplasmonics forms a major part of the fascinating field of nanooptics, which is a modern branch of optical science that explores how optical frequency radiation can be confined on the nanoscale, i.e., 1 – 100 nm (much smaller than the optical wavelength). Such nanolocalized fields are due to the interaction processes (oscillation of polarization charges) between electromagnetic radiation and conduction electrons at metallic interfaces or in small metallic nanostructures, leading to an enhanced optical near field of sub-wavelength dimension. Such oscillations on the nanoscale are called surface plasmons. I will introduce a qualitative description of surface plasmons and local fields
associated with them in next two Chapters.

History has shown that there are two main components of plasmonics: *surface plasmon polaritons* and *localized surface plasmons*. However, in the earlier literature, separation was made rarely between the surface plasmon polaritons [see Chapter 3] which are electromagnetic waves and localized surface plasmons which are purely electric, nanolocalized mechanical oscillations, which will be discussed in Chapter 2. However, now nanoplasmonics is much more developed field in both theoretical and experimental studies. Therefore, there is a necessity to distinguish between them. Throughout this work I will consistently call a mode surface plasmon polariton when it propagates along a system at distances longer than its wavelength. In contrast, a mode is called a localized surface plasmon when its coherent propagation at distances comparable to wavelength does not occur. In that case, the magnetic component of the field, though generally not zero, does not define its properties and can be neglected in the theory [see Sec. 1.2]. In addition to that, throughout this work I will use the term *surface plasmons* to represent both surface plasmon polaritons and localized surface plasmons at the same time.

The theoretical description of these surface waves was established around the turn of the 20th century. In particular, the form of radio waves propagating along the surface of a conductor was described by A. Sommerfeld in 1899 [1], and J. Zenneck in 1907 [2]. Also the observation of sudden intensity drop in spectra was observed by R. Wood back in 1902 [3]. However, that observation was not explained until mid-
century [4]. A couple of years later, loss phenomena associated with metallic surfaces were also recorded via the diffraction of electron beams at thin metallic foils [5]. Then it was linked with the original work on diffraction gratings in the optical domain [6]. By that time, the excitation of Sommerfeld’s surface waves with visible light using prism coupling had been achieved [7]. More importantly, a unified description of all these phenomena in the form of surface plasmon polaritons was established.

The beginning of the modern nanooptics was pioneered by H. Bethe and C. J. Bouwkamp [8, 11]. In H. Bethe’s pioneering work, he showed that if there is a small hole (radius $R$), much smaller than radiation wavelength $\lambda$, i.e., $R \ll \lambda$, in an ideal (with infinite conductivity) metal, there will be some tunneling of the electromagnetic radiation through this hole. The total amount of energy, $E_t$, pass through such a small hole is depend on $R$ as, $E_t \propto R^6$. This result demonstrates two characteristic features of nanooptics:

- the possibility to localize optical fields on the nanoscale
- the efficiency of the energy concentration is extremely small for $R \ll \lambda$.

The inefficiency of such a system can be explained by quantum mechanics. From the quantum mechanical point of view, the electromagnetic radiation passing through a small hole is due to tunneling of photons through a classically forbidden region. For the small hole the probability of such a tunneling is very small. Therefore, we need to find ways to improve the efficiency of the optical field concentration on the nanoscale.
The spatially-periodic structure of holes in a metal film has been considered as one of the solution, where coherent addition of amplitudes of fields from different holes causes giant enhancement of transmission [9, 10]. A negative side of such systems as concentrators of energy on nanoscale is that the total size of the system is still macro- or microscopic, while the ultimate goal of nanooptics is to operate exclusively on the nanoscale. Another effect that can dramatically improve the efficiency of the nanolocalization of energy is resonant enhancement.

1.2 Nanolocalization of energy

It is worth to discuss the possibility of concentrating optical energy on the nanoscale although it is widely known that it is impossible to focus electromagnetic wave energy in regions whose size is significantly less than a half wavelength. A Fabry-Perot resonator is a classical example which has a $\lambda/2$ length and ideally reflecting mirrors. Here, the electric field of the wave is zero at the mirrors and maximum in the center of the cavity. Meanwhile, the magnetic field is maximum at the mirrors and zero in the center. If one attempts to squeeze this wave by making the cavity shorter, this electromagnetic mode will disappear. The physical reason for this is that the exchange of energy between the electric and magnetic fields takes a quarter of wavelength in space. This is a relatively slow, long-range process (compared to a nanoscale), which is due to the large term, speed of light, $c$ in the Maxwell equations [see Eq. (1.2)]. Furthermore, this is the coupling term of the electric and magnetic components.
Therefore, now the question is, how it is possible to concentrate the electromagnetic energy on the nanoscale in nanooptics? The answer is very simple, it is impossible. The optical energy concentrated on the nanoscale by the means of nanoplasmonics is not electromagnetic but purely electric-oscillation energy. Magnetic fields may be present but in contrast to the electric fields they do not play a significant role in the energy concentration. The reason is the following: light is in a sense *one-handed* when interacting with atoms of conventional materials. Out of the two field components of light (electric and magnetic) only the electric *hand* efficiently probes the atoms of a material. Meanwhile, the magnetic component remains relatively unused, due to the fact that, the interaction of atoms with the magnetic field component of light is normally weak. In nanoplasmonics, the scale of energy concentrations is not limited by the $\lambda$ which is few orders of magnitude larger than the nanoscale. The scale of energy concentrations is only determined by the characteristic size of the metal plasmonic nanosystem. However, there are principal limitations related to the spatial dispersion and Landau damping [see Sec. 1.5].

It is time to get a quick snap shot of the very basics of nanooptics to see what optics at the scale of a few nanometers makes perfect sense and is not forbidden by nature. The propagation of light in free space is described by the dispersion relation $\omega = c k$ where, $k = \sqrt{k_x^2 + k_y^2 + k_z^2}$ is three dimensional wavevector, $\omega$ is the angular frequency of a photon and $c$ is speed of propagation in free space (speed of light).
According to the Heisenberg’s uncertainty relation:

\[ \Delta x \Delta p_x \geq \frac{\hbar}{2} \]  

(1.1)

where \( \Delta x \) is the uncertainty in the spatial position of a microscopic particle in the \( x \) direction, \( \Delta p_x \) is the uncertainty in the component of its momentum in the same direction and \( \hbar \) is the reduced plank constant. However, for photons, the momentum \( \Delta p \) can be written as \( \Delta p = h \Delta k \). Now, for photons the Heisenberg’s uncertainty relation (for the \( x \)-direction) can be rewritten as \( \Delta x \geq (2\Delta k_x)^{-1} \). Therefore, spatial confinement is inversely proportional to the magnitude of wavevector components in the respective spatial direction, here \( x \). The maximum possible \( k_x \) is the total length of the \( k \) (= \( 2\pi/\lambda \)). Therefore, \( \Delta x \geq \lambda/4\pi \) which is very similar to the well-known expression for the Rayleigh diffraction limit. This result immediately shows that the spatial confinement that can be achieved is only limited by the spread of \( k \) in a given direction.

The following mathematical trick (property) can be used to increase the spread of wavevector components. Starting with two arbitrary perpendicular directions in space, e.g. \( x \) and \( z \), one can increase one wavevector component to a value beyond the total wavevector, at the same time requiring the wavevector in the perpendicular direction to become purely imaginary. However, we can still fulfill the requirement for the total length of the wavevector \( k \) to be \( 2\pi/\lambda \). Let’s assume that we choose to increase the wavevector in the \( x \)-direction, at the same time the possible range of wavevectors in this direction is also increased. Therefore, the confinement of light is
no longer limited by $\Delta x \geq \lambda/4\pi$. However, to achieve this we have to sacrifice something, which in this case is confinement in the $z$-direction, resulting from the purely imaginary wavevector component in this direction that is necessary to compensate for the large wavevector component in the $x$-direction. With a purely imaginary wavevector component in the expression for a plane wave, we have $\exp(ikz)$ or mathematically equal expression $\exp(-|\kappa|z)$. Therefore, in one direction (positive $z$-direction) we have an exponentially decaying field, an evanescent wave, while in the opposite direction (negative $z$-direction) the field is exponentially increasing. However, exponentially increasing fields have no physical meaning, this immediately shows that this result does not make any sense for infinite free space! Instead of taking one medium, one can divide infinite free space into at least two half-spaces with different refractive indices. Now the exponentially decaying field in one half-space can exist without needing the exponentially increasing counterpart in the other half-space. Note that to fulfill the boundary conditions for the fields at the interface different solutions can be considered in each half-space. The conclusion of the above simple argument is the following: in the presence of an inhomogeneity in space, the Rayleigh limit for the confinement of light is no longer strictly valid, but in principle infinite confinement of light becomes, at least theoretically possible. This property is the basis of nanooptics.
1.3 Maxwell’s equations and electromagnetics of metal

The interaction of metals with electromagnetic radiation is mainly dominated by the free conduction electrons in the metal. According to the simple Drude model, the electrons oscillate $180^\circ$ out of phase relative to the excitation electric field. Therefore, metals possess a negative dielectric constant at optical frequencies. As we know from everyday experience, for frequencies up to the visible part of the spectrum metals are highly reflective, i.e., they do not allow electromagnetic radiation to penetrate. Therefore, metals are traditionally used as cladding layers for the construction of resonators and waveguides for electromagnetic radiation at far-infrared frequencies. At low frequencies, due to the lack of penetration into the metal, one can assume the perfect or good conductor approximation. However, at higher frequencies towards the near-infrared and visible part of the spectrum, field penetration increases significantly. Finally, at ultraviolet frequencies, metals acquire dielectric character and allow the propagation of electromagnetic waves, albeit with varying degrees of attenuation, depending on the details of the electronic band structure. Alkali metals such as sodium have an almost free-electron-like response and thus exhibit an ultraviolet transparency. For noble metals such as gold or silver on the other hand, transitions between electronic bands lead to strong absorption in this energy range.

The interaction between metals and electromagnetic fields can be firmly under-
stood from classical framework based on Maxwell’s equations. Even the metallic nanostructures, which have sizes on the order of a few nanometres, can be described without going into quantum mechanics, because the high density of free carriers results in minute spacings of the electron energy levels compared to thermal excitations of energy $k_B T$ at room temperature. However, there are some important quantum effects in nanoplasmonics for which quantum electrodynamics is essential. Among them, notable are spontaneous photon emission by nanosystems and surface plasmon amplification by stimulated emission of radiation [13].

Let’s start with Maxwell’s equations which are two equations that describe the mutual interaction of electric $E$ and magnetic $H$ fields,

\[
\nabla \times E = \frac{1}{c} \frac{\partial B}{\partial t} ,
\]

\[
\nabla \times E = \frac{1}{c} \frac{\partial D}{\partial t} + \frac{4\pi}{c} j_{\text{ext}} ,
\]

where $c$ is the speed of light in vacuum, and $j_{\text{ext}}$ is the current of external (with respect to the system) charges. As one can see from the form of this equation, the Gaussian system of units have been used. This system is predominantly used in the fundamental literature. The SI system that is mostly used in engineering literature because it contains an extra unit (Ampere) that leads to the appearance in the equations of unphysical constants: permittivity and permeability of the vacuum.

The two vectors, $B$ and $D$ are determined by the material composition of the system, field strengths, etc. These are the electric displacement $D$ and magnetic
induction $\mathbf{B}$. The physical field that determines the force, $\mathbf{F}$ that acts on a point charge is given by the Lorentz law

$$\mathbf{F} = e\mathbf{E} + \frac{e}{c} \mathbf{v} \times \mathbf{B},$$

(1.4)

where $e$ is the charge and $\mathbf{v}$ is its velocity. From this it is obvious that the physical magnetic field is actually $\mathbf{B}$, not $\mathbf{H}$. For the plasmonics, this distinction between $\mathbf{B}$ and $\mathbf{H}$ is actually not important because in the plasmonics of metal nanosystems in optical spectral region, the magnetic field and induction coincide for any practical purposes, in other words the magnetic permeability $\mu = 1$. However, the magnetic response at optical frequencies is the main subject of a newly developed area in nanooptics of so called left-handed systems or negative-index materials [14]. I will leave left-handed systems outside of the scope of this work. For more details about left-handed systems and applications see Chapter 9 in Ref.[14] and references therein.

The other pair of Maxwell equations are the divergence equations,

$$\nabla \cdot \mathbf{D} = 4\pi \rho_{\text{ext}},$$

(1.5)

$$\nabla \cdot \mathbf{B} = 0,$$

(1.6)

where $\rho_{\text{ext}}$ is the density of external (i.e., not belonging to the system) charges. Using Eq. (1.5) and Eq. (1.6) one can immediately obtain the continuity equation for the external current, $\mathbf{j}_{\text{ext}}$

$$\partial_t \rho_{\text{ext}} + \nabla \cdot \mathbf{j}_{\text{ext}} = 0$$

(1.7)
In general, the external charges and currents are not present in optics, therefore, I will drop them from the Maxwell equations for the purpose of this work. However, any charges and currents induced in bulk or at the interfaces by the fields are automatically taken into account by the Maxwell equations through the dielectric polarization and magnetic induction.

Assuming that fields are weak enough that $D$ and $B$ can be obtained by perturbation theory, one can obtain integral linear-response relations in terms of the corresponding fields (i.e., relations between $D$ and $E$, and $B$ and $H$)

$$D(r, t) = \int_{-\infty}^{\infty} dt' \int_V \varepsilon(r - r', t - t') E(r', t') \, dr'$$ (1.8)

$$B(r, t) = \int_{-\infty}^{\infty} dt' \int_V \mu(r - r', t - t') H(r', t') \, dr'$$ (1.9)

where $\varepsilon(r - r', t - t')$ (dielectric function) and $\mu(r - r', t - t')$ (magnetic permeability) denote the response functions in space and time. The displacement $D$ at time $t$ depends on the electric field at time $t'$ previous to $t$ (temporal dispersion or frequency dispersion). In addition to that, the displacement at point $r$ also depends on the values of the electric field at neighboring point $r'$ (spatial dispersion). A spatially dispersive medium is also called a *non-local* medium. This effect can be observed at interface between different media or in metallic objects with sizes comparable with the mean-free path of electrons. In most cases of interest, the effect of the spatial dispersion is very weak, therefore, we can assume that the materials of the system are isotropic. Otherwise, both $\varepsilon$ and $\mu$ would have been tensors, which would make no difficulty in principal but would make the formulas somewhat more complicated.
However temporal dispersion is a widely encountered phenomenon and it is important to take it into account accurately.

As we discussed above the relations (1.8) and (1.9) are non-local both in space and time. However, one can use a mathematically equivalent description in the Fourier domain which is local,

\[
D(k, \omega) = \varepsilon(k, \omega)E(k, \omega), \quad B(k, \omega) = \mu(k, \omega)H(k, \omega).
\]

(1.10)

Here we have introduced the corresponding arguments in the Fourier domain which are wave vector \( k \) and frequency \( \omega \). Therefore, the Fourier transform of the electric field is defined as

\[
E(k, \omega) = \int E(k, \omega) \exp(i k \cdot r - i \omega t) dr dt
\]

(1.11)

and of course one can get similar expressions for other quantities.

### 1.4 Characteristic lengths

When the characteristic size of the particle becomes comparable to the characteristic scale of the system, the spatial dispersion becomes much more important. One example of such a scale is the lattice constant in metals which is on the order of the electron wavelength at the Fermi surface \( \lambda_F \sim 1\AA \). Another important scale in nanooptics is the Debye screening radius (or Thomas-Fermi screening radius)

\[
r_D = \sqrt{\frac{\varepsilon_k E_F}{6\pi ne^2}},
\]

(1.12)
where $\varepsilon_h$ is the background dielectric constant of the metal that is due to the core (valence) electrons and ion motion (phonons), $n$ is the concentration of electrons in c.g.s units and $E_F$ is the electron Fermi energy.

$$E_F = \frac{\hbar^2 k_F^2}{2m^*},$$  \hspace{1cm} (1.13)

where $k_F = \sqrt[3]{3\pi^2 n}$ is the electron wavevector at the Fermi surface and $m^*$ is electron effective mass in the metal. Using the Bohr radius, $a_B = \varepsilon_h \hbar^2 / m^* e^2$ and $k_F$, one can rewrite Eq. (1.12) for most metals, including noble metals, as

$$r_D \simeq 2.9 \times 10^5 (n^{-1/6}) \lesssim 1\text{Å}.$$  \hspace{1cm} (1.14)

The correlation length, $l_c$: that an electron at the Fermi surface travels during a period of the optical radiation, is another important scale for optical interactions in a metal system, which is on the order of $\approx v_F / \omega$, where $v_F$ is the electron speed at the Fermi surface; for metals $v_F \sim 10^8$ cm/s, and $\omega \sim 10^{15}$ s$^{-1}$ is the optical frequency. This yields an estimate $l_c \sim 1$ nm which is the largest spatial scale compared with the other two scales. Therefore, when a characteristic size $a$ of the nanosystem becomes small, it may become comparable to $l_c$ which will make important the nonlocality in the optical responses of the electron system [15].
1.5 Nonlocal dielectric constant and Landau damping

The well known Lindhard formula [16] is one of the closed solutions in the theory of the Fermi system that explicitly gives the nonlocal dielectric response $\varepsilon(k, \omega)$.

$$\varepsilon(k, \omega) = \varepsilon_h + \frac{3\varepsilon_h \omega_p^2}{k^2 v_F^2} \left[ 1 - \frac{\omega}{2kv_F} \ln \left( \frac{\omega + kv_F}{\omega - kv_F} \right) \right], \quad (1.15)$$

where $\omega_p$ is the plasma frequency which is defined as

$$\omega_p = \sqrt{\frac{4\pi ne^2}{\varepsilon_h m^*}}. \quad (1.16)$$

The complex function in Eq. (1.15), $\ln \left( \frac{\omega + kv_F}{\omega - kv_F} \right)$ is defined as $\ln \left( \frac{\omega + kv_F}{\omega - kv_F} \right) = \ln \left| \frac{\omega + kv_F}{\omega - kv_F} \right| - i\pi$ for $\left( \frac{\omega + kv_F}{\omega - kv_F} \right) < 0$. Note that $\varepsilon(k, \omega)$ has a non-zero imaginary part, which describes optical losses, only when $\omega < kv_F$.

These optical losses can be connected to the excitation by a field of incoherent electron-hole pairs. This phenomenon is called Landau damping, which is described by Eq. (1.15). The Landau damping actually is dephasing, where coherent field oscillations are transformed into incoherent electron hole pairs, but the total energy of the system is not changed. Landau damping is fulfilled when the size of the system is comparable to or less than the correlation length, $l_c$, then the condition $\omega < kv_F$ is satisfied. Then Eq. (1.15) has an imaginary part,

$$\text{Im}[\varepsilon(k, \omega)] = \frac{3\pi \varepsilon_h \omega_p^2 \omega}{2(kv_F)^3}. \quad (1.17)$$
which has the same order of magnitude as $\text{Re}[\varepsilon(k, \omega)]$. This effect (Landau damping) is not a small effect even at its onset. As explicitly demonstrated in Eq. (1.17) it is obvious that the relaxation and losses in the electron system come only with a strong spatial dispersion (dependence on $k$). The Landau damping and the spatial dispersion are highly important for the nanoplasmonics, because they are the most pronounced for low-frequencies. In particular, it is in the small-size range of parameters where the nanoplasmonic effects are the strongest and most interesting. Even though these phenomena are very important for nano-optics, it is very difficult to take them into account because the expression for the dielectric response is relatively complex in the $k$ space [see Eq. (1.15)]. Note that the boundary conditions at the surfaces of the nanostructure are to be imposed in the real $r$ space.

### 1.6 Local dielectric constant

The total dielectric constant of a metal is given by the sum of a contribution from the free electrons of the metal and a contribution from the interband transitions. The contribution from the free electrons is given by the Drude free electron model [see Eq. (1.21)].
1.6.1 Drude-Sommerfeld theory

Here we assume that particles are non-interacting and the background dielectric constant is $\varepsilon_h$. For large systems where system size $\gg l_c$, one can obtain the Drude-Sommerfeld model for the free-electron gas. Therefore, the equation of motion of such a particle (electron) is [23]

$$m^* \partial_t^2 \mathbf{r} + m^* \Gamma \partial_t \mathbf{r} = e \mathbf{E}_0 e^{-i \omega t}$$

where $e$ and $m^*$ are the charge and the effective mass of the free electrons, $\mathbf{E}_0$ and $\omega$ are the amplitude and the frequency of the applied electric field and $\Gamma$ is the relaxation constant (damping constant) of the electron motion. Note that the equation of motion contains no restoring force since free electrons are considered. The damping term, $\Gamma$, is very small compared to the frequency of the excitation field in plasmonic region, i.e., $\Gamma \ll \omega$.

The presence of an electric field leads to a dipole moment $\mathbf{d}$ according to $\mathbf{d} = e \mathbf{r}$. The cumulative effect of all individual dipole moments of all free electrons results in a macroscopic polarization per unit volume $\mathbf{P} = n \mathbf{d} = n e \mathbf{r}$, where $n$ is the number of electrons per unit volume. Seeking a solution as $\mathbf{r}(t) = \mathbf{r}_0 e^{-i \omega t}$, from Eq. (1.18) one can write $\mathbf{P}$ as

$$\mathbf{P} = -\frac{e^2 n}{m^*} \frac{1}{\omega(\omega + i \Gamma)} \mathbf{E}_0.$$  

Using well known expression

$$\mathbf{D} = \mathbf{E}_0 + 4\pi \mathbf{P} = \varepsilon(\omega) \mathbf{E}_0,$$  

(1.20)
we can obtain the classical Drude formula

$$\varepsilon_{\text{Drude}}(\omega) = \varepsilon_h - \frac{\varepsilon_h \omega_p^2}{\omega(\omega + i\Gamma)} = \left[\varepsilon_h - \frac{\varepsilon_h \omega_p^2}{(\omega^2 + \Gamma^2)}\right] + i \left[\frac{\varepsilon_h \omega_p^2 \Gamma}{\omega(\omega^2 + \Gamma^2)}\right], \quad (1.21)$$

where $\omega_p = \sqrt{\frac{4\pi n e^2}{m^*}}$ is the volume plasma frequency. Because of its simplicity, this classical Drude formula is commonly used in theoretical computations. Therefore, it is very important to understand its limitations in describing the experimental data for metals, especially noble metals. On the other hand silver is known to possess the lowest dielectric losses in the visible and near-infrared (near-ir) spectral area and has the best pronounced plasmonic behavior. Therefore above model can be used to describe the behavior of the dielectric constant of the silver metal. A comparison is

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**Figure 1.1:** Real part (a) and imaginary part (b) of dielectric permittivity for silver as function of excitation frequency $\hbar \omega$. The dashed curves represent a fit to Drude formula Eq. (1.21) with parameters $\hbar \omega_p = 9.24 \text{ eV}$, $\hbar \Gamma = 0.02 \text{ eV}$ and $\varepsilon_h = 1$. The solid curves display the experimental data from [17].
shown in Fig. 1.1 of both the experimental data [17] and a theoretical fit to these data. A relatively close relationship between the Drude formula and the experimental data for Re[ε(ω)] can be seen from the Fig. 1.1(a). Here the real part of the dielectric constant is negative. One obvious consequence of this behavior is the fact that light can penetrate a metal only to a very small extent since the negative dielectric constant leads to a strong imaginary part of the refractive index $n = \sqrt{\epsilon}$. In contrast to the Re[ε(ω)], the general agreement with Im[ε(ω)] is much worse. A quantitative agreement takes place only between 1 and 2 eV. The strong disagreement can be seen around $\hbar \omega \geq 3.5$ eV, and this is due to the electron transitions from the $d$-band to the conduction $sp$-band. These almost localized $d$ electrons do contribute to the optical absorption in the blue and near-ultraviolet (near-uv) spectral region. However, they do not participate in the plasmonic oscillations. The cause of the strong deviation from the Drude behavior in the red to near-ir spectral region seen in Fig. 1.1 is not quite clear (the frequency still appears too high for the phonons to contribute significantly). A possible cause may be the Landau damping due to electron scattering from grain boundaries in the metal. Note that the condition of the Landau damping $a \lesssim l_c = v_F/\omega$ is easier to fulfill in the red to near-ir region than for higher frequencies. Because the dielectric losses described by Im[ε(ω)] play a decisive role in the optical enhancement processes by metal plasmonic nanostructures, the Drude formula cannot be used, even for silver, for quantitative theories except, perhaps for a narrow spectral range $1 - 2$ eV.
1.6.2 Interband transitions

In real metals, besides the contribution of the free electrons, one must consider the contribution from interband transitions. For the noble metals such as silver and gold, the influence of interband transitions in the visible range has been considered. For silver and gold, the interband transitions are $4d \rightarrow 5sp$ and $5d \rightarrow 6sp$, respectively, and the free electrons are in the $5s$ and $6s$ states, respectively [18]. The dielectric constant, $\varepsilon(\omega)$ of a real metal is given by the sum of the contribution for the free electron, $\varepsilon_{\text{Drude}}(\omega)$ (Eq. (1.21)) and the contribution of the interband transitions, $\varepsilon_{ib}(\omega)$,

$$\varepsilon(\omega) = \varepsilon_{\text{Drude}}(\omega) + \varepsilon_{ib}(\omega).$$

(1.22)

Although the Eq. (1.21) gives quite accurate results for the optical properties of metals in the infrared regime, it has to be corrected in the visible range by the response of bound electrons. Bound electrons in metals exist, in lower-lying shells of the metal atoms. Using the same method for the free electrons, one can get the equation of motion for a bound electron as [18]

$$\tilde{m}^* \partial_t^2 \mathbf{r} + \tilde{m}^* \tilde{\Gamma} \partial_t \mathbf{r} + \beta \mathbf{r} = e E_0 e^{-i\omega t}.$$

(1.23)

Here, $\tilde{m}^*$ is the effective mass of the bound electrons, which is in general different from the $m^*$, $\tilde{\Gamma}$ is the damping constant describing mainly radiative damping in the case of bound electrons, and $\beta$ is the spring constant of the potential that keeps the electron in place. Using the same steps as before one can get the contribution of
bound electrons to the dielectric function

\[ \varepsilon_{ib}(\omega) = \varepsilon_h + \frac{\varepsilon_h \omega_p^2}{(\omega_0^2 - \omega^2) - i\Gamma \omega}. \]  

(1.24)

Here \( \omega_p = \sqrt{\frac{4\pi n e^2}{m^*}} \) and \( n \) is the density of the bound electrons. \( \omega_p \) is introduced in analogy to the plasma frequency in the Drude-Sommerfeld model, however, obviously here with a different physical meaning and \( \omega_0 = \sqrt{\beta/m^*} \). Finally, we can rewrite Eq. (1.24) to separate the real and imaginary parts

\[ \varepsilon_{ib}(\omega) = \left[ \varepsilon_h + \frac{\varepsilon_h \omega_p^2 (\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + \Gamma^2 \omega^2} \right] + i \left[ \frac{\varepsilon_h \Gamma \omega_p^2 \omega}{(\omega_0^2 - \omega^2)^2 + \Gamma^2 \omega^2} \right] \equiv \text{Re}[\varepsilon_{ib}(\omega)] + i \text{Im}[\varepsilon_{ib}(\omega)] \]  

(1.25)

Finally we have the both contributions to the dielectric constant, namely, the effect of the free electrons through Eq. (1.21) and the effect of interband transitions through Eq. (1.25),

\[ \varepsilon(\omega) = \left[ 2\varepsilon_h - \frac{\varepsilon_h \omega_p^2}{(\omega^2 + \Gamma^2)} + \frac{\varepsilon_h \omega_p^2 (\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + \Gamma^2 \omega^2} \right] + i \left[ \frac{\varepsilon_h \omega_p^2 \Gamma}{\omega(\omega^2 + \Gamma^2)} + \frac{\varepsilon_h \Gamma \omega_p^2 \omega}{(\omega_0^2 - \omega^2)^2 + \Gamma^2 \omega^2} \right]. \]  

(1.26)

1.6.3 Size effects

The dielectric constant discussed in previous section is related to bulk metals. Now the question is, how can we relate this when the dimension of the metal is decreased, i.e., nanoparticles, where the dielectric constant deviates from that for the bulk metal. When the size of the particle becomes smaller than the mean free path of the free electrons, the electrons collide with the boundary of the particle. There
have been many attempts to include this effect by adding the rate of the collisions with the surface of the nanoparticle [19, 20] to obtain the damping constant. If this effect is included, the damping constant is given by [28]

\[ \Gamma + A \frac{v_f}{a} \]  

where \( a \) is the radius of the particle, and \( A \) is a dimensionless constant. The value of \( A \) depends on the particle shape and is usually around unity.

![Figure 1.2: (color) Real part (a) and imaginary part (b) of dielectric permittivity for silver as a function of excitation frequency \( \hbar \omega \) for different radii as indicated in colors. Here, the size effect has been considered and \( \varepsilon_a = 1 \) and \( A=1 \).](image)

The real part and imaginary part of the dielectric constant for silver is shown in Fig. 1.2. It is illustrated as a function of excitation frequency \( \hbar \omega \) for different radii including the size effect. The experimental data from [17] has been used for the dielectric constant of the silver. Note that, here the dielectric constant of the ambient is 1 and \( A=1 \). As one can see there is no significant change in \( \text{Re}[\varepsilon(\omega)] \), however, it is
a different story for $\text{Im}[\varepsilon(\omega)]$. For the frequency, $\hbar \omega < 2 \text{ eV} \text{ Im}[\varepsilon(\omega)]$ is significantly increasing with the decreasing $a$.

However, as the size of a nanosystem decreases, the effects of the spatial dispersion (dependence on $k$) become more important (as we already know from the above-discussed Lindhart formula in Sec.1.5). For small nanosystems ($a \sim 1 \text{ nm}$), the enhancement of the losses (temporal dispersion) always comes together with a strong spatial dispersion. Again this can be explicitly illustrated by the phenomenon of Landau damping [see Eq. (1.15) and its discussion].
Chapter 2

Plasmon modes in metal nanoparticles: Particle plasmons

2.1 Plasmon resonance of small metal particles

Here I introduce the fundamental excitation of localized surface plasmons in nanoparticles: known as particle plasmons. Instead of localized surface plasmons the term particle plasmon has been used for plasmons in nanoparticles. In nanooptics we are interested in establishing field confinement in two or even three dimensions. Therefore, it is useful to analyze theoretically the electromagnetic modes associated with small particles called nanoparticles. We will see in the Chapter 3 that surface plasmon polaritons are propagating, dispersive electromagnetic waves coupled to the electron plasma of a conductor at a dielectric interface and the electromagnetic field
is strongly localized in one dimension, i.e., normal to the interface. Localized surface plasmons on the other hand are non-propagating excitations of the conduction electrons of metallic nanostructures coupled to the electromagnetic field. We will see that these modes arise naturally from the scattering problem of a small, sub-wavelength metal nanoparticle in an oscillating electromagnetic field. The curved surface of the particle exerts an effective restoring force on the driven electrons, so that a resonance can arise, leading to field amplification both inside and in the near-field zone outside the particle. This resonance is called the localized surface plasmon or in case of small particle it is called particle plasmon.

Gold and silver particles with diameters on the nanometer scale show very bright colors both in transmitted and reflected light. These resonantly enhanced absorption and scattering falls into the visible region of the electromagnetic spectrum. These
Figure 2.2: (color) Ancient Roman Lycurgus cup (4th century AD, now at the British Museum in London). The colors originates from metal nanoparticles embedded in the glass. The Lycurgus cup illuminated by a light source from behind [panel (a)]. Light absorption by the embedded gold or silver nanoparticles leads to a red color of the transmitted light whereas scattering by the particles yields greenish colors [panel (b)]. From [22].

Bright colors of noble metal such as gold and silver, have fascinated people for many centuries. However, for long time it was not clear what causes these colors. Today it is known that they are due to gold nanoparticles embedded in the glass for example [see Figs. 2.1, 2.2]. One example of a historical application is the staining of church windows [21] in the Middle Ages [see Fig. 2.1] or the beautiful Lycurgus cup [see Fig. 2.2] manufactured in Roman times, which is now at the British Museum in London [22].
2.2 Particle plasmon oscillations: Simple semi-classical model

To understand the mechanism of resonant excitation of a collective oscillation of the conduction band electrons in the nanoparticles, consider the plasmon modes in metal nanoparticles. The metal nanosphere is subjected to an excitation field of an external wave with wave vector $k$. [see a schematic in Fig. 2.3].

![Diagram of metal nanosphere](image)

Figure 2.3: Schematic of metal nanosphere subjected to electric field of an external electromagnetic wave.

Using the following simple semi-classical model, one can qualitatively understand many properties of particle plasmons. Since the skin depth of electromagnetic waves in metals is on the order of the diameter of the nanoparticle (the skin depth at optical frequencies is ~30nm for gold and silver), the excitation light is able to penetrate the particle. The field inside the particle shifts the conduction electron with respect to...
the fixed positive lattice ions, and electrons build up a negative charge on one side of the surface and the lattice ions build positive charge on the opposite side [see Fig. 2.3]. This shift is greatly exaggerated in the figure, for realistic fields it is much smaller. There is another way of analyzing the uniformly polarized nanosphere, which nicely describes the idea of a bound charge [23, 24]. What we have, actually, is two spheres of charge: a positive sphere and a negative sphere. In the absence of the polarization the charges of electrons and lattice overlap in the bulk of the nanosphere that stays electrically neutral. But when the material is uniformly polarized (as shown in Fig. 2.3), all the positive charges shift slightly toward the $-z$ direction, and all the negative charges move slightly toward the $+z$ direction. Now the two spheres no longer overlap perfectly: at the surface there are crescents of uncompensated negatively charged electron and positively charged lattice charges. The reason is called surface, the charges whose density $-\nabla P$ are all at the surface [23, 24] while the dielectric polarization $P$ is uniform within the volume of the metal nanosphere.

The attraction between these uncompensated surface charges generates restoring force between the electrons and lattice ions along with the mass of the electron forms a mechanical oscillator, which is a particle plasmon or localized surface plasmon. In general this force depends on the separation of the surface charges, i.e., particle size, and the polarizability. More importantly the restoring force is directly related to the resonance frequency of the system. The alternating surface charges form an oscillating dipole, which radiates electromagnetic waves. This simple semi-classical
model for particle plasmons can be considered as optical antenna [25]. At the same
time that system leads to another effect which is the dipole field in the surrounding
medium. This dipole electric field is the local plasmonic field. This plasmonic field
is localized in the region on the scale of the radius of the nanosphere which is much
smaller than the excitation wavelength.

2.3 Particle plasmons in a metal nanosphere

In order to keep the analysis simple and more attractive, the discussion will be
limited to the quasi-static approximation which neglects retardation: I assumed that
all points of an object respond simultaneously to an excitation field. This is a very
good approximation if the characteristic size of the object is much smaller than the
excitation wavelength. As we discussed in Chapter 1, fields at the nanoscale are
governed by quasistatic equations, therefore, the Earnshow theorem is applicable:
fields and any of their components ($x, y, or z$) can have a local or global extremum
(minimum or maximum) only at the surfaces or interfaces. In this approximation the
Helmholtz equation reduces to the Laplace equation which is much easier to solve. In
general the electric field of an oscillating dipole is given by [26],

$$ E(r, t) = \frac{1}{4\pi\varepsilon_a} \left[ k^2 (\hat{r} \times d) \times \frac{e^{ikr}}{r} + [3\hat{r}(\hat{r} \cdot d) - d] \left( \frac{1}{r^3} - \frac{ik}{r^2} \right) e^{ikr} \right] e^{i\omega t} \quad (2.1) $$
where, $\mathbf{d}$ is the dipole moment, in the near field zone ($kr \ll 1$). Equation (2.1) can be approximated to [26]

$$
\mathbf{E}(\mathbf{r}, t) = \frac{1}{4\pi \varepsilon_a} [3\mathbf{r}(\mathbf{r}.\mathbf{d}) - \mathbf{d}] \frac{e^{i\omega t}}{r^3}.
$$

Equation (2.2)

In other words, this is exactly the electrostatic field of a point dipole. This has only time oscillating term, $e^{i\omega t}$, that is why, it is termed *quasi-static*. In the quasi-static limit potential, $\phi$, has to satisfy the following equations.

$$
\mathbf{E} = -\nabla \phi, \quad \nabla^2 \phi = 0.
$$

Let us consider a nanosphere with radius $a$ centered at the origin. The sphere is illuminated by a $z$-polarized plane wave. The geometry is shown in Fig. 2.4.

express the Laplace equation (2.3) in spherical coordinates $(r, \theta, \varphi)$ as [23]

$$
\frac{1}{r^2 \sin \theta} \left[ \sin \theta \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin \theta \sin \varphi} \frac{\partial^2}{\partial \varphi^2} \right] \phi(r, \theta, \varphi) = 0.
$$

Figure 2.4: The metal nanosphere with dielectric permittivity $\varepsilon_m(\omega)$ is illuminated by $z$-polarized plane wave. The dielectric constant of embedding medium is $\varepsilon_a$. 

express the Laplace equation (2.3) in spherical coordinates $(r, \theta, \varphi)$ as [23]
The solutions are of the form [23]

\[ \phi(r, \theta, \varphi) = \sum_{\ell,m} A_{\ell,m} \phi_{\ell,m}(r, \theta, \varphi). \]  

(2.5)

Here, the \( A_{\ell,m} \) are constant to be determined from the boundary conditions and the \( \phi_{\ell,m} \) are of the form [23]

\[
\begin{align*}
\phi_{\ell,m} &= \begin{cases} 
 r^\ell & \text{if } \ell \geq 0 \\
 r^{-\ell-1} & \text{if } \ell < 0
\end{cases} \\
&= \begin{cases} 
 P_{\ell}^m(\cos \theta) & \text{if } \ell \geq 0 \\
 Q_{\ell}^m(\cos \theta) & \text{if } \ell < 0
\end{cases} \\
&= \begin{cases} 
 e^{im\varphi} & \text{if } \ell \geq 0 \\
 e^{-im\varphi} & \text{if } \ell < 0
\end{cases}
\end{align*}
\]

(2.6)

where the \( P_{\ell}^m(\cos \theta) \) are the Legendre polynomials and the \( Q_{\ell}^m(\cos \theta) \) are the Legendre polynomials of second kind [23]. Using the proper boundary conditions and the continuity of the tangential electric fields and the normal components of the displacement vector at the surface of the sphere imply that

\[
\begin{align*}
\left[ \frac{\partial \phi_{in}}{\partial \theta} \right]_{r=a} &= \left[ \frac{\partial \phi_{out}}{\partial \theta} \right]_{r=a} \\
\varepsilon_m \left[ \frac{\partial \phi_{in}}{\partial \theta} \right]_{r=a} &= \varepsilon_a \left[ \frac{\partial \phi_{out}}{\partial \theta} \right]_{r=a}
\end{align*}
\]

(2.7)

(2.8)

where \( \phi_{in} \) is the potential inside the sphere and \( \phi_{out} \) is the total potential, i.e., potential of the incoming field, \( \phi_0 \), and the scattered fields, \( \phi_{scatter} \), (\( \phi_{out} = \phi_{scatter} + \phi_0 \)). For the incoming electric field, it has been assumed that the homogeneous \( z \)-polarized plane wave and potential is \( \phi_0 = -E_0 z = -E_0 \frac{3a}{\varepsilon_m + 2\varepsilon_a} r \cos \theta \). Finally the solutions are [23, 24]

\[
\begin{align*}
\phi_{in} &= -E_0 \frac{3\varepsilon_a}{\varepsilon_m + 2\varepsilon_a} r \cos \theta \\
\phi_{out} &= -E_0 r \cos \theta + E_0 \frac{\varepsilon_m - \varepsilon_a}{\varepsilon_m + 2\varepsilon_a} a^3 \cos \theta \frac{1}{r^2}
\end{align*}
\]

(2.9)

(2.10)
and the electric field can be calculated from first equation in Eq. (2.3)

\[
E_{in} = E_0 \frac{3\varepsilon_a}{\varepsilon_m + 2\varepsilon_a}(\cos \theta \hat{r} - \sin \theta \hat{\theta}) = E_0 \frac{3\varepsilon_a}{\varepsilon_m + 2\varepsilon_a}\hat{x}; \text{ for } r \leq a
\]  

\[
E_{out} = E_0(\cos \theta \hat{r} - \sin \theta \hat{\theta}) + E_0 \frac{a^3}{r^3} \frac{\varepsilon_m - \varepsilon_a}{\varepsilon_m + 2\varepsilon_a}(2\cos \theta \hat{r} + \sin \theta \hat{\theta}); \text{ for } r > a.
\]  

The Eq. (2.11) describes the uniform electric field at point \( r \), where \( r \) is inside the nanosphere and outside it is a superposition of the uniform excitation field [first part of Eq. (2.12)] and dipolar local field [second part of Eq. (2.12)]. Following the above simple theory, the magnitude of the local optical electric field, \( |E| \), in the vicinity of a silver nanosphere of radius \( a = 10 \) nm is displayed in Fig. 2.5, where \( \varepsilon_a = 1 \). Here the local fields are represented by bright areas on a dark background. In panel (a) results are shown for a frequency of 1.51 eV, which is significantly off from the surface plasmon resonance. Note that the surface plasmon resonance frequency of a silver nanosphere in vacuum is 3.5 eV. As shown in panel (a) the maximum field enhancement in this case is obviously not very large, but still results in the local intensity enhancement which is proportional to \( |E|^2 \) by one order of magnitude. The electric field penetrates the metal very weakly due to its high dielectric permittivity at low frequency [see Fig. 1.1]. This field is concentrated to radii of order \( a \), with the maximum at the surface of the metal. The spatial distribution of the field is clearly elongated in the \( z \)-axis, which is the direction of the polarization.

The same plot for frequency of 3.37 eV is shown in Fig. 2.5(b), which is close to the surface plasmon resonance frequency. The maximum field enhancement in this case is not large, but still results in a local intensity enhancement by two orders of
Figure 2.5: Local electric field distributions around a silver nanosphere with a 10nm radius. The polarization of the excitation radiation is linear in the $z$ direction. Panels (a)-(d): For frequencies indicated, magnitudes $|E|$ of the local electric field, calculated from Eqs. (2.11) and (2.12), are displayed as density plots. The corresponding density scales are shown in the right hand side of the each panel.
magnitude. The spatial distribution of the field has the same elongated behavior in the direction of polarization. The panel (c) shows the same plot for a frequency of 3.5 eV which is the surface plasmon resonance frequency for a silver nanosphere in vacuum [17]. In this case the local intensity is enhanced by a factor of ≈ 400, which is due to the resonance of the excitation field with the surface plasmon oscillations of the conduction electrons. This high enhancement can be related to the high value of the resonance quality factor $Q$ for silver, which is defined as: $Q = \frac{-\text{Re}[\varepsilon]}{\text{Im}[\varepsilon]}$. One can clearly see that the field penetrates metal significantly which is an indication of breakdown of the qualitative behavior of the metal as an ideal conductor at the surface plasmon resonance frequency. At the surface plasmon frequency, the local fields are also localized, with a maximum at the surface; the localization radius is on the order of radius $a$ of the nanosphere. Now consider the case, for a frequency slightly higher than the surface plasmon resonance frequency. This situation is displayed in Fig. 2.5(d), and the picture is significantly different: the field is mostly concentrated in the metal. In contrast to the case of the plasmon resonance frequency, here it is enhanced by relatively small factor, i.e., a factor of ≈ 4, as expected.

Using the well known relation, the electric fields can be combined with optical polarizability, $\alpha(\omega)$ [24]. The excitation optical fields $E_0$ induce a dipole moment $d$ oscillating with optical frequency on the nanosphere ($a \ll \lambda$). Therefore,

$$d = \varepsilon_a \alpha(\omega) E_0, \quad \alpha(\omega) = a^3 \frac{\varepsilon_m(\omega) - \varepsilon_a}{\varepsilon_m(\omega) + 2\varepsilon_a}. \quad (2.13)$$

In applications the dispersion (frequency dependence) of the dielectric medium
surrounding the metal can be ignored and one can assume a constant \( \varepsilon_a \). However, the dielectric function of the metal is highly dispersive. Therefore the solution for the fields is characterized by the denominator \( \varepsilon_m + 2\varepsilon_a \). The \( \alpha(\omega) \) has maximum value when the real part of its denominator vanishes, which defines frequency \( \omega_{sp} \) of the surface plasmon resonance through an equation

\[
\text{Re } \varepsilon_m(\omega_{sp}) = -2\varepsilon_a. \tag{2.14}
\]

### 2.4 Scattering by a small metal sphere

The scattering problem for an arbitrary sphere has been solved exactly by Mie [27]. However, the quasi-static approximation is more appropriate if one wishes to obtain a clear physical insight. The scattering cross-section of the sphere is obtained by driving the total radiated power of the sphere’s dipole by the intensity of the excitation plane wave.

The time average of the energy flow can be expressed by the real part of the Poynting vector, \( \tilde{S} \) [23]

\[
\tilde{S} = \frac{1}{2} \text{Re} \left[ E_\theta \times H^*_\phi \hat{r} - E_r \times H^*_\theta \hat{\theta} \right]. \tag{2.15}
\]

Here \( \mathbf{H} \) is magnetic field and \( \mathbf{H}^* \) is the complex conjugate of \( \mathbf{H} \). Starting with Eq. (2.2) and using Eq. (2.13), the total radiation power, \( P \) can be written as [23]

\[
P = \int_0^{2\pi} \int_0^\pi |\tilde{S}| r^2 \sin \theta d\theta d\phi = \frac{\omega k^3 |d|^2}{12\pi \varepsilon_a} = \frac{\omega k^3 \varepsilon_a}{12\pi} |\alpha(\omega)|^2 E_0^2. \tag{2.16}
\]
Figure 2.6: (color) Scattering cross section, $\sigma_{sca}$, of a silver nanosphere in vacuum for different radii (as indicated). Here the $\sigma_{sca}$ is normalized by $a^6$.

From the Eq. (2.15), the energy density of the excitation field $\tilde{S}_0$ can be written as

$$\tilde{S}_0 = \frac{\omega \varepsilon_a}{2k} E_0^2.$$  \hspace{1cm} (2.17)

Therefore, the scattering cross-section $\sigma_{sca}$ is given by [18]

$$\sigma_{sca} = \frac{P}{\tilde{S}_0} = \frac{k^4}{6\pi} |\alpha(\omega)|^2,$$  \hspace{1cm} (2.18)

The power loss from the excitation field due to the presence of a particle is not only due to the scattering but also due to the absorption. Therefore, we need to take into account, the power that is dissipated inside the particle. The power dissipated by a point dipole can be expressed as $(\omega/2) \text{Im}[d \cdot \mathbf{E}_0]$ by the Poynting’s theorem [23]. Assuming $\varepsilon_a$ is real, then the absorption cross-section has the form
\[ \sigma_{abs} = k \text{Im}[\alpha(\omega)]. \] 

(2.19)

The spectra of the scattering cross section of silver spheres of various radii are shown in Fig. 2.6. The scattering cross section \( \sigma_{sca} \) has been normalized by \( a^6 \), because \( \sigma_{sca} \) is proportional to \( a^6 \). The maximum peak appearing around 3.5 eV is caused by the localized surface plasmon resonances. At this frequency the real part of the denominator of the polarizability is zero [see Eq. (2.14)]. Due to the high imaginary part of the dielectric constant of small spheres, low peak height can be seen for the small spheres. As expected, large particles have a low and broadened peak due to the retardation effect. The absorption cross section of silver spheres of various radii are shown in Fig. 2.7. The absorption cross section \( \sigma_{abs} \) has been normalized by the
volume of the sphere $V$ for the same reason as for the scattering. The figure is somewhat similar to the spectra of the scattering, but here the absorption is due to the interband transition, which we discussed in Chapter 1.

### 2.5 Beyond the quasi-static approximation

In this section I will briefly discuss the plasmon resonance of particles beyond the quasi-static regime. Here, the properties of polarizability will be discussed qualitatively. The plasmon resonance of particles beyond the quasi-static regime is described by two competing processes [28] [see Fig. 2.8]: a radiative decay process into photons shown in Fig. 2.8(a) (this process dominates for large particles), where the quasi-static approximation breaks down due to retardation effects. Radiative decay is caused by a direct radiative route of the coherent electron oscillation into photons [31], which is the main reason for the weakening in the strength of the dipole plasmon resonance as the particle volume increases [32]. The second process: non-radiative process is shown in Fig. 2.8(c). The non-radiative decay is a result of the creation of electron-hole pairs via either intraband excitations within the conduction band or interband transitions from lower-lying $d$-bands to the $sp$-conduction band (for noble metal nanoparticles), which is due to the Pauli exclusion principle: the electrons can only be excited into empty states in the conduction band. In other words, non-radiative decay is due to a dephasing of the oscillation of individual electrons.

The first TM modes of Mie theory for the polarizability $\alpha_m$ of a sphere of volume
Figure 2.8: Schematic of radiative (a) and non-radiative (c) decay of localized surface plasmons in noble metal nanoparticles. The non-radiative decay occurs via excitation of electron-hole pairs either within the conduction band (intraband excitation) or between the d band and the sp conduction band (interband excitation).

\[ \alpha_m(\omega) = \frac{1 - \frac{\epsilon_m(\omega) + \epsilon_a}{10} x^2 + O(x^4)}{\frac{\epsilon_m(\omega)}{d(\epsilon_m(\omega) - \epsilon_a)} - \frac{(\epsilon_m(\omega) + \epsilon_a)x^2}{10} - i \frac{4\pi^2 \epsilon_a^{3/2}}{3} \frac{V}{\lambda^3} + O(x^4)} V, \]  

(2.20)

where \( x = \pi a/\lambda \) is the so called \textit{size parameter}, which combines the radius \( a \) with free-space wavelength \( \lambda \). In contrast to the simple quasi-static solution Eq. (2.13), this expression has couple of additional terms, where each term has a distinct physical meaning to it. The \( x^2 \) term in the numerator describes the effect of retardation of the exciting field over the volume of the sphere, leading to a shift in the plasmon resonance. A similar term in the denominator includes an energy shift of the resonance, due to the retardation of the depolarization field [30] inside the particle.
Chapter 3

Surface plasmon polaritons in nanostructured systems

3.1 Introduction

The aim in this Chapter is to present a discussion of the propagating part of the surface plasmon, which are called surface plasmon polaritons. Surface plasmon polaritons are electromagnetic waves propagating at and bound to surfaces and interfaces between two different media [12]. The electromagnetic fields of surface plasmon polaritons are typically localized to within a few wavelengths of a surface, in the sense that their amplitude is a maximum at the surface and decays exponentially away from it. Therefore, these waves are evanescent waves. These electromagnetic surface waves arise via coupling of the electromagnetic fields to oscillations of the conduc-
tor’s electron plasma. The specific properties of the surface polaritons depend on the characteristics of the material, normally as described by their dielectric function.

Robert Wood back in 1902 reported the observation of sudden drop of the light intensity, scattered from a metallic diffraction grating, from maximum to minimum which occurred within a very narrow range of wavelength [3]. Wood was unable to explain his own results and therefore named them singular anomalies. However, now one of these anomalies is known to correspond to the excitation of surface plasmon polaritons.

The coupling of light to these oscillations results in guided polariton modes that are confined and propagate along the interface [12]. The generation of surface plasmon polaritons by incident light is forbidden for translationally invariant interfaces due to a mismatch between the momentum of the incident light and that of the surface plasmon polaritons at the same frequency, since the surface plasmon polaritons have greater momentum than a free-space photon. The general approach to provide additional momentum and satisfy the momentum conservation law for the coupling of the incident light and the surface plasmon polaritons is to introduce some inhomogeneous structure at the interface. Such structures can be subwavelength defects (holes), or periodic corrugation, i.e., grating, on the metallic surface. Placing a grating on top of the plasmon waveguide can facilitate an additional wave vector which is equal to a multiple of the grating vector [12]. The generation of surface plasmon polaritons and coupling with light has been discussed in detail in Ref. [12]
An important application of surface plasmon polaritons is related to the enhancement of an electro-magnetic field near a metal-dielectric interface due to the generation of surface plasmon polaritons. Such enhancement opens up the possibility of manipulating the interaction strength between light and matter. One of the applications of surface plasmon polaritons is strong signal enhancement in surface-enhanced Raman spectroscopy [36, 37], where a molecule is placed near the metallic nanostructure. The enhancement of optical effects by generation of plasmon polaritons at the surface of small metallic objects was the topic of broad research not only in physics, but also in biology, chemistry, and material science. Recently, there has been a great deal of interest in studying the optical properties of semiconductor layered systems using grating couplers [38, 39, 40] with surface plasmon effects [55, 56]. Grating couplers are a widely used and promising tool in the semiconductor nano-systems to design optoelectronic devices [55, 56].

Taking the wave equation as a starting point, this chapter describes the fundamentals of surface plasmon polaritons both at a single, flat interface and in a metal/dielectric interface.

### 3.2 Mathematical description

In order to understand the physical properties of surface plasmon polaritons we can apply Maxwell’s equations, Eqs. (1.2)-(1.3) and (1.5)-(1.6) to the flat interface between a conductor and a dielectric. To present this discussion more clearly, it is
advantageous to cast the equations first in a general form applicable to the guiding of electromagnetic waves, the wave equation. Without the external charge and current densities [see Sec. 1.3], the curl equations Eq. (1.2) can be combined to yield [24]

\[ \nabla \times \nabla \times \mathbf{E} = -\frac{1}{c^2} \frac{\partial^2 \mathbf{D}}{\partial t^2} \quad (3.1) \]

Using the identities \( \nabla \times \nabla \times \mathbf{E} \equiv \nabla(\nabla \cdot \mathbf{E}) - \nabla^2 \mathbf{E}, \quad \nabla[\varepsilon(\mathbf{r})\mathbf{E}] \equiv \mathbf{E} \cdot \nabla \varepsilon(\mathbf{r}) + \varepsilon(\mathbf{r}) \nabla \cdot \mathbf{E} \)
and taking into account the absence of external charge and current densities, \( \nabla \cdot \mathbf{D} = 0 \)
one can rewrite the Eq. (3.1) as

\[ \nabla \left( -\frac{1}{\varepsilon(\mathbf{r})} \mathbf{E} \cdot \nabla \varepsilon(\mathbf{r}) \right) - \nabla^2 \mathbf{E} = -\varepsilon(\mathbf{r}) \frac{1}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2}. \quad (3.2) \]

It has been shown in Chapter 1 that the variation of the dielectric profile \( \varepsilon = \varepsilon(\mathbf{r}) \)
over distances on the order of one optical wavelength is negligible. Therefore the Eq. (3.2) can be simplified to the following equation,

\[ \nabla^2 \mathbf{E} - \frac{\varepsilon}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} = 0. \quad (3.3) \]

In the homogeneous environment one can solve the Eq. (3.3) separately and the obtained solutions have to be matched using appropriate boundary conditions. To obtain the description of confined propagating waves, we assume in all generality a harmonic time dependence \( \mathbf{E}(\mathbf{r}, t) = \mathbf{E}(\mathbf{r}) e^{-i\omega t} \) of the electric field. Then we have

Helmholtz equation [24],

\[ \nabla^2 \mathbf{E} + k_0^2 \varepsilon \mathbf{E} = 0, \quad (3.4) \]

where, \( k_0 = \omega/c \) is the wave vector of the propagating wave in vacuum.
Figure 3.1: The geometry, used to specify the propagation of surface polaritons at an interface.

Now it is time to define the propagation geometry. Consider the geometry shown in Fig. 3.1, where it has been assumed that there is a single interface at $z = 0$ separating two isotropic media. A one-dimensional problem has been considered for simplicity, i.e., $\varepsilon$ depends only on one spatial coordinate. Also the direction of the wave propagation is taken along the $y$-axis, and shows no spatial variation in the perpendicular, in-plane $x$-direction [see Fig. 3.1]; therefore $\varepsilon = \varepsilon(z)$. Then, the propagating waves, which travel along the interface, $z = 0$, can be described as [24]

$$
E(x, y, z) = E(z)e^{ik_y y}.
$$

(3.5)

The complex parameter $k_y$, is the propagation constant of the traveling waves. The following form of the wave equation can be obtained by combining the Eq. (3.4) and Eq. (3.5).

$$
\frac{\partial^2 E(z)}{\partial z^2} + (k_0^2\varepsilon - k_y^2)E = 0.
$$

(3.6)

One can get similar equation for the magnetic field $H$. Using the following properties: (1) harmonic time dependence; i.e., $\frac{\partial}{\partial t} = -i\omega$, (2) for propagation along the
\( y \)-direction; i.e., \( \frac{\partial}{\partial y} = ik_y \) and homogeneity in the \( x \)-direction, i.e., \( \frac{\partial}{\partial x} = 0 \), it can easily be shown that Eq. (3.6), allows two sets of self-consistent solutions with different polarization properties of the propagating waves. The first kind is the transverse magnetic (TM) electromagnetic mode solution, i.e., a mode where the magnetic field is perpendicular to the plane of propagation of the radiation field (also known as \textit{p-polarization}, here the \( p \) stands for parallel), where only the field components \( E_y, E_z \) and \( H_x \) are nonzero. The second kind is the transverse electric (TE) electromagnetic mode solution, i.e., a mode where the electric field is perpendicular to the plane of propagation of the radiation field (also known as \textit{s-polarization}, here the \( s \) stands for German word “senkrecht” meaning perpendicular), with only \( H_y, H_z \) and \( E_x \) being nonzero.

Finally, for the TM modes the system of governing equations can be written as

\[
\frac{\partial^2 H_x(z)}{\partial z^2} + (k_0^2 \varepsilon - k_y^2) H_x = 0, \tag{3.7}
\]

\[
E_z = -\frac{k_y}{\varepsilon \omega} H_x, \tag{3.8}
\]

\[
E_y = -\frac{1}{\varepsilon \omega} \frac{\partial H_x}{\partial z}. \tag{3.9}
\]

Similarly, for TE modes

\[
\frac{\partial^2 E_x(z)}{\partial z^2} + (k_0^2 \varepsilon - k_y^2) E_x = 0, \tag{3.10}
\]

\[
H_z = \frac{k_y}{\omega} E_x, \tag{3.11}
\]

\[
H_y = i \frac{1}{\omega} \frac{\partial E_x}{\partial z}. \tag{3.12}
\]
Now we have enough mathematical background to start the discussion of the properties of surface plasmon polaritons at a metal-dielectric interface.

### 3.3 Surface plasmon polaritons at a metal-dielectric interface

The necessary conditions for the existence of surface plasmon polaritons at the plane interface of two \((m\)-metal and \(d\)-dielectric\) semi-infinite isotropic media are that one of the two media separated by such an interface should have a negative dielectric permittivity, \(\text{Re}[\varepsilon] < 0\) [see Sec.3.3.1], and the other should have a positive dielectric permittivity, \(\varepsilon\). As we discussed in Chapter 1, in a wide spectral region from near-ultraviolet to mid-infrared [17], the real part of the dielectric permittivity of metals including noble metals such as silver, gold, etc., is negative, \(\text{Re}[\varepsilon] < 0\). Therefore, materials with \(\text{Re}[\varepsilon] < 0\) can be treated as metals.

#### 3.3.1 Equations and solutions

In this Chapter, it has been assumed that the magnetic permeability \(\mu = 1\) and that the dielectric function is independent of the wave vector, \(k\), i.e., the absence of spatial dispersion effects. This is true for many materials. The directions of coordinate axes are chosen as in Fig. 3.2, the \(z\)-axis is perpendicular to the media interface and \(z = 0\), corresponds to the interface; the \(y\)-axis is directed along surface
plasmon polaritons propagation, and the $x$-axis lies in the interface plane. Consider an interface between two media with dielectric permittivities $\varepsilon_m$ (for metal) and $\varepsilon_d$ (for dielectric). In each half-space only a single $p$-polarized wave will be considered, because we are looking for homogeneous solutions that decay exponentially with distance from the interface. Therefore, the solutions of Maxwell's equations near the surface have the form [24]:

\begin{align}
H_x(z) &= A_d \exp(ik_y y - \kappa_d z) \quad , \quad z > 0, \quad (3.13) \\
H_x(z) &= A_m \exp(ik_y y + \kappa_m z) \quad , \quad z < 0, \quad (3.14)
\end{align}

where $\kappa_m$ and $\kappa_d$ are evanescent exponents for the metal and dielectric media, respectively, $k_y$ is the wave vector component along the direction of propagation. Such a field satisfies Maxwell's equations together with the boundary conditions for $p$-polarization

---

Figure 3.2: (a) Interface between metal and dielectric media with dielectric functions $\varepsilon_m$ and $\varepsilon_d$. The interface is defined by $z = 0$ in a Cartesian coordinate system, and (b) shows the penetration into each medium (skin depth). A complete discussion of skin depth will be given at the end of this chapter.
(TM modes). The field with s-polarization (TE modes) at the two media interface with \( \mu = 1 \) cannot satisfy the boundary conditions at any field wave vector (for more details see the end of this section). Therefore, in the surface plasmon polariton field, the magnetic field is perpendicular to the \( yz \)-plane \( \mathbf{H} = H_x \) and the electric field vector lies in the \( yz \) plane.

From the boundary conditions of the continuity of the tangential components of fields \( H_x \) and \( E_y \) at the interface, it follows that the wave vector \( k \) and amplitudes below and above the interface are correspondingly equal. Taking this into account, setting \( \varepsilon = \varepsilon_m \) in Eq. (3.9) for the medium \( z < 0 \) and \( \varepsilon = \varepsilon_d \) for the medium \( z > 0 \), the following two equations can be obtained.

\[
A_d = A_m, \quad (3.15)
\]

\[
\frac{\kappa_d}{\varepsilon_d} = -\frac{\kappa_m}{\varepsilon_m}. \quad (3.16)
\]

Substituting these into the wave equations, Eq. (3.7), one can get the following equations relating the wave vector \( k \) and evanescent exponent \( \kappa \) for each medium,

\[
\kappa_d^2 = k_y^2 - \varepsilon_d \kappa_0^2, \quad (3.17)
\]

\[
\kappa_m^2 = k_y^2 - \varepsilon_m \kappa_0^2, \quad (3.18)
\]

where the sign is chosen in such a way that \( \text{Re}[\kappa_d] > 0 \) and \( \text{Re}[\kappa_m] > 0 \) since in the system under consideration, the wave is decaying as it moves away from the surface.

Equations (3.16),(3.17) and (3.18) form a system of three equations for the three
unknown constituents of the wave vector $k_y$, $\kappa_d$, and $\kappa_m$,

$$k_y = k_0 \sqrt{\frac{\varepsilon_d \varepsilon_m}{\varepsilon_d + \varepsilon_m}},$$  \hspace{1cm} (3.19)

$$\kappa_d = k_0 \sqrt{-\frac{\varepsilon_d^2}{\varepsilon_d + \varepsilon_m}},$$  \hspace{1cm} (3.20)

$$\kappa_m = k_0 \sqrt{-\frac{\varepsilon_m^2}{\varepsilon_d + \varepsilon_m}}.$$  \hspace{1cm} (3.21)

Having derived Eqs. (3.19)-(3.21) we are in a position to discuss the conditions for an interface mode to exist. We are interested in interface waves, which are well localized at the interface, and propagate along the interface. This requires real values for the coefficient, $k_y$. This can be achieved if the sum and the product of the dielectric functions in the Eq. (3.19) are either both positive [see Eq. (3.22)] or both negative [see Eq. (3.23)].

$$\varepsilon_d + \varepsilon_m > 0, \quad \varepsilon_d \varepsilon_m > 0.$$  \hspace{1cm} (3.22)

$$\varepsilon_d + \varepsilon_m < 0, \quad \varepsilon_d \varepsilon_m < 0.$$  \hspace{1cm} (3.23)

Both $\varepsilon_d$ and $\varepsilon_m$ are almost real in absence of damping, i.e., with no losses. In order to obtain a bound solution for well-defined surface plasmon polariton modes, the normal components of the wave vectors have to be considered as purely imaginary in both media given rise to exponentially decaying solutions. By looking at Eqs. (3.20)-(3.21) this can be fulfilled if the summations in the denominator of Eqs. (3.20)-(3.21) are negative, i.e.,

$$\varepsilon_d + \varepsilon_m < 0.$$  \hspace{1cm} (3.24)
From Eqs. (3.22)-(3.24) we can conclude that the conditions for an interface mode to exist are the two inequalities in the Eq. (3.23), which means that at least one of the dielectric functions must be negative with an absolute value exceeding that of the other. As we discussed in Chapter 1, metals, especially noble metals such as silver and gold, have a large negative real part [see Fig. 1.1(a)] of the dielectric constant along with small imaginary part [see Fig. 1.1(b)]. Therefore, metals, in particular, noble metals are perfect candidates for the good plasmonic behavior. Thus, the well-defined surface plasmon polariton modes exist at the interface between a good metal and a good dielectric.

In the case of small dielectric losses in either or both of the two materials, the above conditions can be used without any corrections, but should specify the corresponding real parts. Finally, we can summarize that the conditions for good plasmonic behavior are:

\[
\text{Re}[\varepsilon_d] + \text{Re}[\varepsilon_m] < 0, \quad \text{Re}[\varepsilon_d] \cdot \text{Re}[\varepsilon_m] < 0, \quad (3.25)
\]

\[
\text{Im}[\varepsilon_d] \ll |\text{Re}[\varepsilon_d]| < 0, \quad \text{Im}[\varepsilon_m] \ll |\text{Re}[\varepsilon_m]| < 0. \quad (3.26)
\]

Before discussing the properties of the dispersion relation (3.19) in more details, now I will briefly analyze the possibility of TE (or s-polarization) modes. For the TE modes, the corresponding field components are [similar to the Eqs. (3.8) and (3.9) for TM modes]

\[
E_x(z) = A_d \exp(ik_y y - \kappa_d z), \quad z > 0, \quad (3.27)
\]

\[
E_x(z) = A_m \exp(ik_y y + \kappa_m z), \quad z < 0. \quad (3.28)
\]
From Eq. (3.12) we can get similar equations for $H_y$. Therefore, continuity of $E_x$ and $H_y$ leads to the condition

$$A_d(\kappa_d + \kappa_m) = 0. \tag{3.29}$$

Since confinement to the surface requires $\text{Re}[\kappa_d] > 0$ and $\text{Re}[\kappa_m] > 0$, this condition is only fulfilled if $A_d = 0$, so that also $A_m = A_d = 0$. Thus, no surface modes exist for TE (or $s$-polarization) modes. *Surface plasmon polaritons only exist for TM ($p$-polarization) modes.*

### 3.4 Dispersion relation

From here onward in this Chapter, I will consider the frequency dependent dielectric function for the metal as

$$\varepsilon_m(\omega) = \text{Re}[\varepsilon_m(\omega)] + i\text{Im}[\varepsilon_m(\omega)], \tag{3.30}$$

and permittivity for the dielectric medium is real (negligible losses), i.e., $\varepsilon_d \equiv \text{Re}[\varepsilon_d]$. To accommodate losses associated with electron scattering the term $\text{Im}[\varepsilon_m(\omega)]$ has been introduced. Using the real values for $\omega$ and $\varepsilon_d$ with the condition $|\text{Re}[\varepsilon_m(\omega)]| \gg |\text{Im}[\varepsilon_m(\omega)]|$, one can rewrite the Eq. (3.19) as complex wave vector:

$$k_y(\omega) = \text{Re}[k_y(\omega)] + i\text{Im}[k_y(\omega)] \tag{3.31}$$

in particular in more details manor,

$$k_y(\omega) \approx \frac{\omega}{c} \left[ \left( \frac{\varepsilon_d \text{Re}[\varepsilon_m(\omega)]}{\varepsilon_d + \text{Re}[\varepsilon_m(\omega)]} \right)^{1/2} \right] + i \left[ \frac{\omega}{c} \left( \frac{\varepsilon_d \text{Re}[\varepsilon_m(\omega)]}{\varepsilon_d + \text{Re}[\varepsilon_m(\omega)]} \right) \right]^{3/2} \frac{|\text{Im}[\varepsilon_m(\omega)]|}{2(\text{Re}[\varepsilon_m(\omega)])^2}. \tag{3.32}$$
The $\text{Re}[k_y(\omega)]$ determines the surface plasmon polariton wavelength, while the $\text{Im}[k_y(\omega)]$ contributes the losses associated with the damping of the surface plasmon polariton as it propagates along the interface. As I mentioned earlier, for $\text{Re}[k_y(\omega)]$ one needs $\text{Re}[\varepsilon_m(\omega)] < 0$ and $|\text{Re}[\varepsilon_m(\omega)]| > \varepsilon_d$, which can be fulfilled in a metal and also in a doped semiconductor.

From Eq. (3.19), we can see that under conditions (3.25) and (3.26) the surface plasmon polariton dispersion relation lies outside the light cone for the surrounding dielectric, which means that

$$k_y(\omega) > \frac{\omega}{c} \sqrt{\varepsilon_d}.$$  \hspace{1cm} (3.33)

The dispersion relation [see Fig. 3.3] approaches the light line $\sqrt{\varepsilon_d} \omega/c$ at small $k_y$, but remains larger than $\sqrt{\varepsilon_d} \omega/c$. Therefore the surface plasmon polaritons are dark modes/nonradiative, i.e., they do not couple to light waves in the surrounding dielectric and cannot be either emitted or excited by electromagnetic radiation from the far zone.

From Eq. (3.19) it is obvious that surface plasmon polariton wave vector $k_y$ becomes very large compared to that of wave vector in free space when the real part of the denominator becomes small and vanishes at a particular frequency, $\omega_{sp}$, which is the so-called surface plasma frequency for flat surfaces. On the other hand this is the upper limit of the plasmonic region, since at higher frequencies Eq. 3.23 is violated. The $\omega_{sp}$ satisfies the following condition,

$$\text{Re}[\varepsilon_m(\omega_{sp})] = -\varepsilon_d.$$  \hspace{1cm} (3.34)
Figure 3.3: The relationship [see Eq. (3.19)] between $h \omega$ vs. $k_y$ for silver ($\varepsilon_m$) and a dielectric ($\varepsilon_d$) interface. Where $\varepsilon_d = 1$ for the solid curve and $\varepsilon_d = 10$ for the dashed curve. (a) Calculated real part of the permittivity for silver. Here horizontal lines represent the surface plasmon frequencies. (b) Same plot as (a), but including the imaginary part of the permittivity for silver.

The surface plasmon polariton wavelength, $\lambda_{SPP}$, can be defined as:

$$
\lambda_{SPP} = \frac{2\pi}{\text{Re}[k_y(\omega)]} \approx \lambda \sqrt{\frac{\text{Re}[\varepsilon_m(\omega)] + \varepsilon_d}{\text{Re}[\varepsilon_m(\omega)] \varepsilon_d}},
$$

where $\lambda$ is the wavelength of the excitation light in vacuum.

Under the condition $\text{Re}[\varepsilon_m(\omega_{sp})] \rightarrow -\varepsilon_d$, the wavelength $\lambda_{SPP}$ of the surface plasmon polariton modes becomes very small. In other words, under the condition (3.34) the effective refractive index $n_{eff} = \lambda/\lambda_{SPP}$ for surface plasmon polaritons becomes very large. This may reduce the theoretical diffraction limit of resolution with surface plasmon polaritons, which is determined by $\lambda_{SP}/2$. This value may reach a scale of a few nanometers. Note that, a wave cannot be localized much shorter than half of its wavelength $\lambda/2$ in vacuum. However, this has to be corrected as $\lambda/2n$ for any medium other than vacuum due to the shorter wavelength $\lambda/n$ of light in the
medium with refractive index $n$. From the practical point of view, the Ohmic losses in a metal limit the wavelength and propagation length of the short wavelength surface plasmon polaritons, therefore, this will severely limit the resolution.

The behavior of the surface plasmon polariton dispersion relation given in Eq. (3.19) is illustrated in Fig. 3.3. The panel (a) shows the relations for an ideal metal, i.e., no losses are present. The solid curves represent the results for the silver-vacuum interface, where $\varepsilon_d = 1$ and for silver, the experimental dielectric values of the bulk silver have been used [17]. However, the imaginary part of the experimental dielectric values of the bulk silver have been ignored. The results in Fig. 3.3(a) and the previous discussion of the properties of surface plasmon polariton dispersion relation are in good agreement. Here, the horizontal solid line represents the upper limit of the plasmonic frequency, $\omega \to \omega_{sp}$, for the silver-vacuum interface $\omega_{sp} \approx 3.67$ eV. In other words, at this frequency range the wave vector related to the surface plasmon polariton becomes infinity, i.e., $k \to \infty$. As a result, both the phase velocity, $v_p$, and group velocity, $v_g$, of surface plasmon polaritons tend to zero, which corresponds to standing surface plasmons [87]. Note that the phase velocity and group velocity of surface plasmon polaritons are defined as for any other wave by the following relations [24],

$$v_p = \text{Re} \frac{\omega}{k}, \quad v_g = \text{Re} \frac{\partial \omega}{\partial k}$$  \hspace{1cm} (3.36)

The dashed curve in Fig. 3.3(a) is similar to the one we discussed above, i.e., silver-vacuum interface, but for the silver-semiconductor interface, where $\varepsilon_d = 10$. The
panel (b) shows the relations for an actual metal, i.e., when losses are present, where the dispersion relation is significantly different. In this case, the wave vector $k_y$ is complex, therefore, $\text{Re}[k_y]$ has been shown in Fig. 3.3(b). As shown in panel (b) the dispersion curve ends at some maximum value of $k$, with a cusp which is limited by the dielectric losses at the surface plasmon frequency. The maximum value of $k$, which is related to the dielectric losses, defines the minimum possible localization size of the surface plasmon polaritons in a nanosystem.

3.5 Surface plasmon polaritons at a metal-vacuum interface

Now consider the properties of the electromagnetic fields at metal-vacuum interfaces that exist due to surface plasmon polaritons propagation. The relative distributions (relative magnitude) of the local electric field for a silver-vacuum interface are shown in Fig. 3.4. Panels (a), (c) and (e) show the transverse electric field component, $E_z$, and (b), (d) and (f) display the longitudinal electric field component, $E_y$. The evanescent nature of the fields in the normal direction to the interface can be seen in all the panels. In all the panels the penetration of the fields into the vacuum is much greater than the surface plasmon polariton wavelength [see Eq. (3.35)], but the penetration into the metal (skin depth) is much shorter than the wavelength, which can be clearly seen in panels (c) and (d). Note that this is for the same frequency as for
Figure 3.4: (color) Distribution of local electric fields shown in yz plane, which is normal to the interface with y (horizontal coordinate) being the direction of surface plasmon polariton propagation, and z (the vertical coordinate) being normal to the surface. The magnitude is coded by colors as shown in a bar at the bottom. For panels (a), (b), (c) and (d) the frequency is 2.01 eV, for (c) and (d) it is 3.0 eV, as indicated.
Figure 3.5: Vector diagrams of local electric fields in the yz plane, which is same coordinate system as Fig. 3.4. The spatial scale and the corresponding frequencies are indicated in the figure.

The panels (a) and (b). It can be seen, from the comparison of the panels (a) and (b) with (e) and (f) that the plasmon polaritons propagation wavelength and evanescent extensions decrease close to the plasmonic frequency region. To get a better look at the local electric fields, the vector behavior of the local electric field $E$ is shown in Fig. 3.5. As one can see, the local electric field is neither longitudinal nor transverse. The vector of $E$ changes in each quarter period between transverse and longitudinal, alternating its direction each half period. As given in Eq. (3.8) the magnitude of the magnetic field $H_x$ is proportional to the transverse component of the electric field $E_z$. 
3.6 Propagation length, skin depth and plasmon lifetime

Before we discuss the propagation length and skin depth of surface plasmon polaritons, let’s consider spatial quality factor $Q$ of the surface plasmon polariton waves which is defined as

$$Q = \frac{\text{Re}[k_y(\omega)]}{\text{Im}[k_y(\omega)]},$$

(3.37)

where Re[$k_y(\omega)$] and Im[$k_y(\omega)$] can be found in the Eq. (3.32). Physically, the quality factor determines the number of oscillations that a surface plasmon polariton wave undergoes before it dissipates due to the dielectric losses in real metal. As we can see from the Fig. 3.6, the quality factor dramatically decreases with increasing frequencies. When $\omega \rightarrow \omega_{sp}$, the quality factor $Q \rightarrow 1$, which means that: closer to the plasmonic frequency surface plasmon polaritons do not propagate. In other words, at this point they do behave like localized surface plasmons, which we discussed in Chapter 2. The effect of different dielectric media are also shown in the figure. With increasing dielectric constant of the dielectric medium both quality factor and stopping frequency of polaritons drop significantly.

The propagation length, $L_{sp}$, of the surface plasmon polariton along the interface is determined by the Im[$k_y(\omega)$], which is given in second part of the Eq. (3.32). Im[$k_y(\omega)$] is shown in Fig. 3.7, as a function of $\hbar\omega$ for two different dielectric media, i.e., $\varepsilon_d = 1$ and 10 as indicated in the figure. The metal is silver, and here the experimental data
Figure 3.6: Spatial quality factor $Q$ as a function of frequency for two different dielectric media, i.e., $\varepsilon_d = 1$ and 10 as indicated in the figure. The metal is silver, here the experimental data from [17] have been used for the dielectric constant of silver. From [17] have been used for the metal dielectric $\varepsilon_m$. As one can see, the $\text{Im}[k_y(\omega)]$ significantly increases around the plasmon resonance frequency, where it becomes on the same order of magnitude as $\text{Re}[k_y(\omega)]$ (not shown). Therefore, according to the Eq. (3.37) we have not the surface plasmon polaritons but the localized surface plasmons. Also note that, due to the dielectric screening $\text{Im}[k_y(\omega)]$ is significantly higher for high $\varepsilon_d$ [see the curve for $\varepsilon_d = 10$]. The electric field of surface plasmon polaritons along a smooth surface decreases as $\exp(-\text{Im}[k_y(\omega)]y)$ [18]. Therefore, the propagation length $L_{sp}$ is defined as: the length after which the electric field decreases to $1/e$, which is given by,

$$L_{sp} = \frac{1}{\text{Im}[k_y(\omega)]}.$$  

(3.38)

The propagation length of the surface plasmon polariton for silver is shown in
Figure 3.7: $\text{Im}[k]$ as a function of $\hbar \omega$ for two different dielectric media, i.e., $\varepsilon_d = 1$ and 10 as indicated in the figure. The metal is silver, here the experimental data from [17] have been used for the dielectric constant of silver.

Fig. 3.8, where panel (a) shows the results for the silver-vacuum interface while (b) shows the same results as panel (a) but for the silver-dielectric interface, where $\varepsilon_d = 10$. This shows very good agreement with what we discussed under quality factor. In particular, one can see from the figure that when $\omega \rightarrow \omega_{sp}$, the propagation almost comes to an end. Note that the $\omega_{sp} = 3.67$ eV for the silver-vacuum interface, while $\omega_{sp} = 2.46$ eV for silver-dielectric interface, where $\varepsilon_d = 10$. More importantly, contrast to the nano-scale the propagation length of the surface plasmon polariton is very large, which is one of the most important properties in nanoplasmatics.

There is another important length parameter, which is called decay length (or skin depth, for metal), $\delta$, of the surface plasmon polariton electric fields. In the propagation length we considered the fields along the interface (along the $y$-axis), while in the decay length we consider the surface plasmon polariton electric fields
away from the interface (along the $z$-axes in both directions). It can be shown from Eqs. (3.20) and (3.21) that $\kappa_m$ and $\kappa_d$ can be approximated to first order in $\text{Im}[\varepsilon_m(\omega)]/\text{Re}[\varepsilon_m(\omega)]$ as

$$
\kappa_m = \frac{\omega}{c} \left[ \frac{\text{Re}[\varepsilon_m(\omega)]^2}{\text{Re}[\varepsilon_m(\omega)] + \varepsilon_d} \right]^{1/2} \left[ 1 + \frac{\text{Im}[\varepsilon_m(\omega)]}{2\text{Re}[\varepsilon_m(\omega)]} \right] \tag{3.39}
$$

$$
\kappa_d = \frac{\omega}{c} \left[ \frac{[\varepsilon_d]^2}{\text{Re}[\varepsilon_m(\omega)] + \varepsilon_d} \right]^{1/2} \left[ 1 - \frac{\text{Im}[\varepsilon_m(\omega)]}{2(\text{Re}[\varepsilon_m(\omega)] + \varepsilon_d)} \right] \tag{3.40}
$$

Following the same argument as before, the decay length, $\delta$ can be defined as

$$
\delta_m = \frac{1}{\text{Re}[\kappa_m]} \quad \text{and} \quad \delta_d = \frac{1}{\text{Re}[\kappa_d]}, \tag{3.41}
$$

where $\delta_m$ indicates metal and $\delta_d$ indicates dielectric decay length. The skin depth, $\delta_m$ in silver and decay length, $\delta_d$ in dielectric medium is shown in Fig. 3.9 as a function of frequency. In the case of silver in vacuum, $\delta_m$ does not change very much over the entire frequency range, $\delta_m \approx 20 - 30$ nm. At the both dielectric values, as expected the skin depth is much smaller than the decay length, i.e., $\delta_m \ll \delta_d$. However, due to
the dielectric screening with the dielectric medium, where $\varepsilon_d = 10$, the decay length has been significantly suppressed [see Fig. 3.9] while $\delta_m$ remains at the same order. Therefore, there is no significant difference between $\delta_m$ and $\delta_d$ at high frequencies.

Before introducing the lifetime of surface plasmons $\tau(\omega)$, I first consider the related parameter: the relaxation rate $\gamma(\omega)$ [28] which describes the relaxation due to the dielectric losses in metal. In other words, this is the dephasing of surface plasmons and it also defines their population life time or lifetime $\tau(\omega)$ through the following relation

$$\tau(\omega) = \frac{1}{2\gamma(\omega)}.$$  \hspace{1cm} (3.42)

Since, $1/\gamma(\omega)$ is amplitude of the relaxation or dephasing time of the surface plasmons, the factor of 2 in the denominator has been taken into account. Therefore, the proper term for the lifetime, $\tau(\omega)$ would be: the decay time of the energy of the surface plasmons.
Figure 3.10: Lifetime of surface plasmons $\tau(\omega)$, computed from the experimental data of Ref.[17]. Panel (a) shows the data for silver and panel (b) for gold.

The lifetime of surface plasmons $\tau(\omega)$, computed from the experimental data of Ref.[17] is shown in Fig. 3.10. The results for both silver, panel (a) and gold, panel (b) are shown. The surface plasmons lifetime for silver is much longer than for gold, in particular in between 1 and 2 eV, which is near-IR to red region. For silver $\tau(\omega)$ is $\sim 60$ fs while for gold it is $\sim 10$ fs. One of the interesting aspects is the cutoff of the plasmonic region around 2.6 eV for gold [see Fig. 3.10(b)], which is due to the strong absorption by the transitions from the $d$ to $sp$ band in gold. For silver this is around 4 eV, which is not shown in the graph. These highly localized electrons in $d$ band are contributing to the absorption and decay of the surface plasmons, but, they do not contribute directly to the plasmonic nature of noble metals.
Chapter 4

Enhancement of optical sensitivity of photodetectors

4.1 Introduction

In this Chapter I will study theoretically an enhancement of the intensity of mid-infrared light transmitted through a metallic diffraction grating. I show that for s-polarized light the enhancement of the transmitted light is much stronger than for p-polarized light. By tuning the parameters of the diffraction grating, the enhancement of the transmitted light can be increased by a few orders of magnitude. The spatial distribution of the transmitted light is highly nonuniform with very sharp peaks, which have spatial widths of about 10 nm. The main results in this chapter has been published in the following journals, J. Phys. Condens. [52], Physica E [53] and
Infrared Physics and Technology [54].

As we discussed in Chapter 2, it is clear now that due to generation of the surface plasmon polaritons at the boundary between metal and dielectric media the local electromagnetic field can be strongly enhanced [12]. For the surface plasmon polaritons the enhancement is observed only near the metal-dielectric interface and away from the interface the effect of the surface plasmons is exponentially suppressed.

The grating coupler method [12], which is widely used to generate the surface plasmons at the metal-dielectric interface, is based on the diffraction grating placed on the top of the plasmon waveguide [12, 55, 56]. In this case the grating vector provides the momentum required by the momentum conservation between the incident light and the surface plasmons. The diffraction grating has been widely used to generate not only the surface plasmons, but also the plasmon excitations in low dimensional semiconductor systems [57, 58, 45].

In the present Chapter, I will address another important problem related to interaction of electromagnetic waves with the excitations near metal-dielectric interface. Namely, the enhancement of optical sensitivity of infrared photodetectors in the presence of the metallic surfaces has been studied. For a $p$-polarized incident light (magnetic field in the wave is parallel to the metal-dielectric interface) this enhancement is due to generation of the surface plasmons at the metal-dielectric interface. Similar to other applications of the surface plasmons we should expect a strong local enhancement of the electromagnetic field near the metal surface. In the present work
the generation of the surface plasmons is realized by introducing a metallic diffraction grating. The metallic diffraction grating opens also a possibility to enhance the intensity of the $s$-polarized transmitted light (electric field is parallel to the metal-dielectric interface). This enhancement is due to generation of the local modes of the diffraction grating. In this case these modes are not the surface plasmons. The enhancement of electromagnetic field near the metal-dielectric interface will be considered for both $s$- and $p$-polarizations. If the active element of the photodetector is placed in the region of enhancement of the wave field then we should expect the increase of the sensitivity of the photodetector. There are two main types of infrared photodetectors, which are different by their active elements. Namely, in one type of photodetectors the active element is a quantum well [57], while in the other type the active element is a quantum dot [58].

We will see below that the distribution of the light, transmitted through the diffraction grating, is highly nonuniform with very bright spots, which have a size of the order of 10 nm. In this case it is more appropriate to use quantum dots as active elements of the photodetector. This is because the quantum dots have small size, so they can be placed completely inside of the regions of high intensity. This cannot be done for quantum wells. Another advantage of quantum dots is that they can be sensitive to both $s$-polarized and $p$-polarized light, while the quantum well is only sensitive to the $p$-polarized light. The quantum dots can be also used to detect the terahertz radiation [45].
Therefore, only the quantum dot photodetectors will be discussed. To characterize the effect of the metal grating on the optical properties of the photodetector, the distribution of the electromagnetic field inside of the active region of the photodetector has been calculated. The exact structure and distribution of quantum dots will not be considered here. I assume that the effect of the quantum dots on the distribution of the electromagnetic field is negligibly small, i.e., the active region of a photodetector has been considered as a homogeneous medium with uniform dielectric constant. The distribution of the electromagnetic field determines the optical, i.e., absorption, properties of the quantum dot system. In this description, the structure and the sizes of the quantum dots will not be discussed. Therefore, my main goal is to calculate the distribution of the electromagnetic field inside the metallic and dielectric media to understand finally how strong the enhancement of the absorption coefficient of quantum dots can be in such systems.

The frequency range of the incident light, which I used in the present work, corresponds to the typical interval spacing in small (∼10 nm) quantum dots. Namely, I consider the frequency around \( \omega \sim 70 \text{ THz} \), i.e., the energy is ∼ 250 meV.

The effect of the metal grid gate on the absorption efficiency of the terahertz electromagnetic radiation has been studied recently both theoretically and experimentally [59, 60]. The metal grating described in Popov et al. and Shaner et al. has been used to introduce the coupling of the incident light to the plasmon excitations within the double quantum well system of the field-effect transistor [59, 60]. The
main difference between my study and the results of Popov et al. and Shaner et al. is that in my case the main effect of the diffraction grating is the redistribution of the electromagnetic field intensity within the active region of an infrared photodetector [59, 60]. As a result of this redistribution we expect the local enhancement of the intensity of the electromagnetic field and finally the enhancement of the absorption efficiency of the photodetector. Therefore, in this work the diffraction grating introduces the coupling not between the incident light and the excitations of the active region of photodetector, but between the incident light and the local excitations of the diffraction grating.

4.2 Main system of equations

The first step in the analysis of the problem is to find the distribution of the electromagnetic field inside the diffraction grating and the active elements of the photodetector. At this stage I assume that the active region of the photodetector is uniform and does not contain active elements of the photodetector. Therefore, the system under consideration consists of three regions: region-I (air) with dielectric constant $\varepsilon_I = 1$, region-II (metallic diffraction grating with period $d$ and height $h$), and region-III (dielectric) with dielectric constant $\varepsilon_d$. The system is shown schematically in Fig. 4.1. It has been assumed that the dielectric constant of the metal, $\varepsilon_m(\omega)$, has the Drude dependence on the frequency
Figure 4.1: Schematic illustration of the metal grating on the surface of a dielectric medium. Here, grating period is $d$ and the grating height is $h$. The grating consists of periodic strips of metal with dielectric constant $\varepsilon_m(\omega)$ and air with dielectric constant $\varepsilon_I = 1$. The width of a metallic strips is $a$. The region III is filled by a material with dielectric constant $\varepsilon_d$. Here $\mathbf{E}$ is the electric field vector and $\mathbf{H}$ is the magnetic field vector. The angle $\theta$ is the incident angle.

$$\varepsilon_m(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i/\tau)}, \quad (4.1)$$

where $\omega_p$ is the plasma frequency and $\tau$ is the phenomenological relaxation time. Below it will be assumed that the metal is gold and $\omega_p = 3.39 \times 10^{15}\text{s}^{-1}$ and $\tau = 1.075 \times 10^{-14}\text{s}$ [17].

In the next step the quantum dots and quantum wells are added into the dielectric medium, i.e., region III, at some distance $z$ from the diffraction grating, i.e., from the metal-dielectric interface. To describe the distribution of the electromagnetic field, the coordinate system with axis $z$ orthogonal to the metal-dielectric interface, and axis $x$ in the plane of the interface has been introduced [see Fig. 4.1].
The direction of the incident light is characterized by an incident angle $\theta$. The incident light can have two polarizations: $s$- and $p$-polarizations. For the $p$-polarized light the magnetic field of the electromagnetic wave is in the plane of the interface, while for the $s$-polarized light the electric field of the wave is in the interface plane.

To find the distribution of the electromagnetic field, the system of Maxwell’s equations has to be solved with the corresponding boundary conditions. Namely, the amplitude of the incident light (at $z > 0$) is given and there are no waves incident on the diffraction grating outside of the grating region at $z < -h$, i.e., in this region there are only waves propagating away from the metal-dielectric interface. Maxwell’s equations for $s$- and $p$-polarized lights become decoupled and the electric and magnetic fields can be described in terms of a single function: $\psi = E_y$ in the case of the $s$-polarized light and $\psi = \sqrt{\mu_0/\varepsilon_0} H_y$ in the case of the $p$-polarized light [61].

To solve the corresponding Maxwell’s equations, the well known modal expansion method [62] has been used. In this method the solutions of Maxwell’s equations are expressed in terms of the eigenmodes of electromagnetic field in all three regions. In regions-I and -III these eigenmodes are simple plane waves, which are characterized by wave vectors. The incident light has an $x$ component of the wave vector equal to

$$k_x = k \sin \theta,$$  \hspace{1cm} (4.2)

where $k$ is wave vector of the incident light and $k = \omega/c$. The diffraction grating with the period $d$ introduces the coupling of the incident light with the waves, the $x$
components of the wave vectors, $k_{xn}$, of which are given by the expression

$$
k_{xn} = k \left[ \sin \theta + n \lambda / d \right], \quad (4.3)
$$

where $n = 0, \pm 1, \pm 2, \ldots$ is a diffraction order, and $\lambda$ is the wavelength of the incident light.

Then the general solution of Maxwell’s equations in regions -I and -III can be written as [56]

$$
\psi^{(I)}(x, z, \omega) = A^{(I)} e^{i(k_{ex} - k_{z}^{(I)} z)} + \sum_{n} B^{(I)}_{n} e^{i(k_{xn} x + k_{zn}^{(I)} z)},
$$

$$
\psi^{(III)}(x, z, \omega) = \sum_{n} B^{(III)}_{n} e^{i(k_{xn} x + k_{zn}^{(III)} z)},
$$

where $A^{(I)}$ is the amplitude of the incident wave, $B^{(I)}_{n}$ is the amplitude of the $n$th reflected wave (in region I), $B^{(III)}_{n}$ is the amplitude of the $n$th transmitted wave (in region-III), and

$$
k^{(I)}_{zn} = \sqrt{\varepsilon_{1} k_{z}^{2} - k_{x}^{2}}, \quad (4.6)
$$

$$
k^{(III)}_{zn} = \sqrt{\varepsilon_{d} k_{z}^{2} - k_{x}^{2}}, \quad (4.7)
$$

The general solution of Maxwell’s equations in region-II can be expressed in terms of the eigenmodes of the diffraction grating. The eigenmodes of the wave equation in the grating region are characterized by parameter $\kappa_{z}$, which satisfies the following nonlinear equation [61]

$$
\frac{\xi_{j}^{2} + 1}{2\xi_{j}} \sin[\beta_{1}a] \sin[\beta_{2}a] - \cos[\beta_{1}a] \cos[\beta_{2}a] = - \cos(k_{z}d). \quad (4.8)
$$
Here \( j = p, s \), where \( p \) stands for the \( p \)-polarization and \( s \) stands for the \( s \)-polarization.

The following notations have been introduced,

\[
\xi_p = [\varepsilon_m(\omega)\beta_2/\beta_1], \quad \xi_s = [\beta_2/\beta_1], \quad (4.9)
\]

\[
\beta_1 = \sqrt{\varepsilon_m k^2 - \kappa_z^2}, \quad \beta_2 = \sqrt{\varepsilon_I k^2 - \kappa_z^2}.
\]

For a given frequency \( \omega \) and given parameters of the system, e.g. \( \varepsilon_m, d, a \) and \( \theta \), we obtain from Eq. (4.8) the infinite set of eigenmodes, which are characterized by the value of \( \kappa_z \). These eigenvalues, which are complex, have been found numerically by finding the roots of a transcendental Eq. (4.8). The roots have been found by tracing the roots trajectory in the complex plane with variation of dielectric constant of a metal [63].

The solution of Eq. (4.8) determines infinite number of eigenmodes. If we enumerate them by index \( \ell \), i.e. \( \kappa_{z\ell} \) is the \( \ell \)th solution of Eq. (4.8), then the general solution of Maxwell’s equations in the region-II can be presented in the following form [56]

\[
\psi^{(II)}(x, z, \omega) = \sum_{\ell=1}^{\infty} \chi_{\ell}(x) \zeta_{+\ell}(z), \quad (4.10)
\]

where the functions \( \chi_{\ell}(x) \) and \( \zeta_{+\ell}(z) \) are determined by the following expressions

\[
\chi_{\ell}(x) = C_{1\ell} e^{i\beta_1 x} + D_{1\ell} e^{-i\beta_1 x}, \quad 0 < x < a, \quad (4.11)
\]

\[
\chi_{\ell}(x) = C_{2\ell} e^{i\beta_2(x-a)} + D_{2\ell} e^{-i\beta_2(x-a)}, \quad a < x < d, \quad (4.12)
\]

\[
\zeta_{\pm\ell}(z) = \pm \left[ A_{\ell}^{(II)} e^{-i\kappa_{z\ell} z} \pm B_{\ell}^{(II)} e^{i\kappa_{z\ell} z} \right], \quad (4.13)
\]
and

\[
C_{1\ell} = 1, \quad D_{1\ell} = \frac{1 + \xi_{\ell}}{1 - \xi_{\ell}} e^{i\beta_{1\ell}a} - e^{i(k_2d - \beta_{2\ell}a)},
\]
\[
C_{2\ell} = \frac{(\xi_{\ell} + 1) e^{i\beta_{1\ell}a} + (\xi_{\ell} - 1) e^{-i\beta_{1\ell}a} D_{1\ell}}{2\xi_{\ell}},
\]
\[
D_{2\ell} = \frac{(\xi_{\ell} - 1) e^{i\beta_{1\ell}a} + (\xi_{\ell} + 1) e^{-i\beta_{1\ell}a} D_{1\ell}}{2\xi_{\ell}}.
\]

Here the numbers \(A_{\ell}^{(II)}\) and \(B_{\ell}^{(II)}\) are unknown coefficients.

The complete set of coefficients \(B_n^{(I)}\), \(A_{\ell}^{(II)}\), \(B_{\ell}^{(II)}\), and \(B_n^{(III)}\) were found from the boundary conditions at the interface between different regions. These boundary conditions correspond to continuity of the function \(\psi\) and its derivative \(\partial\psi/\partial z\) for the \(s\)-polarized light and continuity of the functions \(\psi\) and \(\varepsilon^{-1}\partial\psi/\partial z\) for the \(p\)-polarized light. The boundary conditions at the interfaces between regions -I and -II, and between regions -II and -III result in the following system of equations

\[
A^{(I)}\delta_{n0} + B_n^{(I)} = \sum_{\ell=1}^{\infty} \Gamma_{1,\ell n} \left[ A_{\ell}^{(II)} + B_{\ell}^{(II)} \right],
\]

\[
\frac{1}{\varepsilon} \left[ k^{(I)}_z A^{(I)}\delta_{n0} - k^{(I)}_n B_n^{(I)} \right] = \sum_{\ell=1}^{\infty} \kappa_{z\ell} \Gamma_{2,\ell n} \left[ A_{\ell}^{(II)} - B_{\ell}^{(II)} \right],
\]

\[
\sum_{\ell=1}^{\infty} \Gamma_{1,\ell n} \zeta_{+\ell}(h) = B_n^{(III)} e^{-ik^{(III)}_n h},
\]

\[
\sum_{\ell=1}^{\infty} \Gamma_{2,\ell n} \kappa_{z\ell} \zeta_{-\ell}(h) = \frac{B_n^{(III)}}{\varepsilon_d} k^{(III)}_n e^{-ik^{(III)}_n h},
\]
for the p-polarized light and
\[ A^{(I)}_n \delta_{n0} + B^{(I)}_n = \sum_{\ell=1}^{\infty} \Gamma_{1,\ell n} \left[ A^{(II)}_\ell + B^{(II)}_\ell \right], \] (4.17)
\[ \left[ k_z^{(I)} A^{(I)}_n \delta_{n0} - k_z^{(I)} B^{(I)}_n \right] = \sum_{\ell=1}^{\infty} \kappa_{z \ell} \Gamma_{1,\ell n} \left[ A^{(II)}_\ell - B^{(II)}_\ell \right], \]
\[ \sum_{\ell=1}^{\infty} \Gamma_{1,\ell n} \zeta_{+\ell}(h) = B^{(III)}_n e^{-ik_z^{(III)}h}, \] (4.18)
\[ \sum_{\ell=1}^{\infty} \Gamma_{1,\ell n} \kappa_{z \ell} \zeta_{-\ell}(h) = -B^{(III)}_n k_z^{(III)} e^{-ik_z^{(III)}h}, \] (4.19)
for the s-polarization. Here, following notations are being introduced
\[ \Gamma_{1,\ell n} = \frac{1}{d} \int_0^d dx \ e^{-ik_z x} \chi_\ell(x), \] (4.20)
and
\[ \Gamma_{2,\ell n} = \frac{1}{d} \int_0^d dx \ e^{-ik_z x} \chi_\ell(x) = \int_0^a dx \ e^{-ik_z x} \chi_\ell(x) \frac{\epsilon(x)}{\epsilon_\ell(x)} + \int_a^d dx \ e^{-ik_z x} \chi_\ell(x) \frac{\epsilon_m(\omega)}{\epsilon_\ell}. \] (4.21)

The solution of the system of linear Eqs. (4.14)-(4.19) determines the coefficients \( B^{(I)}_n, A^{(II)}_\ell, B^{(II)}_\ell, \) and \( B^{(III)}_n \) in units of the amplitude, \( A^{(I)} \), of the incident light. To make the system finite, the maximum value of the diffraction order, \( n_{\text{max}} \) has been introduced, so that \( |n| \leq n_{\text{max}} \). The value of \( n_{\text{max}} \) determines also the maximum number of eigenmodes of the diffraction grating. Namely, \( \ell \leq (2n_{\text{max}} + 1) \). Therefore the final size of the system is \( 2(2n_{\text{max}} + 1) \).

Since the frequency range, considered in the present paper, corresponds to a very large magnitude of the metal dielectric constant \( (\epsilon_m \approx -847 + 1127i) \), the numerical procedure of finding the eigenmodes of the diffraction grating becomes highly unstable. Usually the direct numerical solution of nonlinear Eq. (4.8) does not provide all
the eigenmodes of diffraction grating, i.e., some of the eigenmodes can be overlooked. To resolve this problem the method of tracing the root trajectory was applied [63], i.e., the roots of Eq. (4.8) were been found by tracing the root trajectory in the complex plane of dielectric constant [63]. Namely, at first, all necessary roots of Eq. (4.8) at small value of metal dielectric constant was calculated. Then a straight line in the complex plane of the dielectric constant was introduced. This line connects the initial small dielectric constant and the final large dielectric constant. Finally, the root trajectory along the straight line in the complex dielectric plane was found, i.e., the values of the roots when the dielectric constant is changed along the line were traced [63]. With this method we can find all necessary eigenmodes of the diffraction grating including the hidden modes for the \( p \) and \( s \)-polarized light [64].

The value of \( n_{\text{max}} \) is found from the condition of convergence of the reflection, transmission, and absorption coefficients. Within the range of parameters, considered in the present work, I have found that the method converges at \( n_{\text{max}} \approx 15 \) for the \( p \)-polarized light and at \( n_{\text{max}} \approx 30 \) for the \( s \)-polarized light. Therefore, throughout the paper I adopted \( n_{\text{max}} = 25 \) and \( n_{\text{max}} = 50 \) for \( p \)-polarization and \( s \)-polarization, respectively. With these values of \( n_{\text{max}} \) the corresponding system of linear equations have been numerically solved.
4.3 Intensity distribution within the active region of photodetector

Solution of the system of linear Eqs. (4.14)-(4.19) determines the values of the coefficients $B_n^{(III)}$. With these values, the wave intensity in the active region of photodetector, i.e., in the region III has been found.

In a real quantum dot photodetector there is a layer of quantum dots at some distance $z$ from the metal-dielectric interface. The photoresponse of the photodetector is proportional to the absorption intensity, which is proportional to the intensity of the electromagnetic field at the position of the quantum dots. Therefore, the contribution to the photocurrent due to a single quantum dot at the point with the coordinates $x$ and $z$ can be written as in the following form

$$J(x, z) = \alpha I(x, z),$$

where $\alpha$ is the coefficient, which includes the absorption coefficient of the quantum dot and other parameters of the photodetector, and $I(x, z)$ is the intensity of the electromagnetic field at the position of the quantum dot. The real dependence of the photocurrent on the intensity of the light, $I(x, z)$, can be nonlinear and more complicated, but in the present work only linear regime of the photodetector has been considered.

In the quantum dots there are two different types of optical transitions. The first one is due to the in-plane component (in our case $x$ or $y$ component) of electric field,
and the second one is due to perpendicular component ($z$ component) of electric field. The corresponding optical transitions have different frequencies. For the s-polarized light there is only a $y$ component of electric field and the intensity of electromagnetic field in Eq. (4.22), which is responsible for the optical transitions within the quantum dot, has the following expression

$$I(x, z) = |\psi^{(III)}(z, x)|^2. \quad (4.23)$$

For the p-polarized light there are both a $z$ component and an in-plane ($x$) component of electric field. Therefore, in this case there are two types of optical transitions. Below, in the case of p-polarized light, only the transitions due to perpendicular component have been studied, i.e., the $z$ component, of electric field. Then the intensity $I(x, z)$ in Eq. (4.22) becomes

$$I(x, z) = |\partial_x \psi^{(III)}(z, x)|^2. \quad (4.24)$$

If the quantum dots within a layer at fixed distance $z$ from the metal-dielectric interface have completely random spatial distribution, then the total light absorption and correspondingly the total photocurrent is proportional to the average wave intensity

$$I_{av}(z) = \frac{1}{d} \int_0^d I(x, z)dx. \quad (4.25)$$

Below I do not discuss the coefficient $\alpha$ in Eq. (4.22) and consider only the intensity distribution $I(x, z)$. To characterize the enhancement of the transmitted light due to the presence of the diffraction grating the intensity $I(x, z)$ will be measured in
the units of the intensity, $I_0$, of electromagnetic wave in the region III without the
diffraction grating. The intensity $I_0$ is given by the standard Fresnel’s equations.
Namely,

$$I_0 = \frac{4k_z^2}{[k_z + k_z^{(III)}]^2}$$

(4.26)

for the s-polarization and

$$I_0 = \frac{4k_z^2 \sin^2 \theta}{\varepsilon_d [\varepsilon_d k_z + k_z^{(III)}]^2}$$

(4.27)

for the p-polarization [24]. Here $k_z = k \cos \theta$.

Therefore, if $I(x, z)$ is greater than 1 (in units of $I_0$) then there is enhancement of
the optical absorption by the quantum dot layer due to the presence of the diffraction
grating.

4.4 Results and discussion

4.4.1 Average intensity

As we have already discussed in the Introduction the enhancement of the intensity
of the light transmitted through the diffraction grating can be expected. This
enhancement is due to generation of the local modes of the diffraction grating. Usually,
when such type of enhancement is discussed, it is due to generation of the surface
plasmons at the metal-dielectric interface. In the present problem the surface plasmons
are coupled only to the p-polarized incident light, while for the s-polarized light
the incident light is coupled to the general modes of the diffraction grating. Therefore
in general, much stronger enhancement will be expected for the p-polarized light. It happens that in the present problem the enhancement of the incident light is much stronger for the s-polarized light. This is mainly because I am considering a low frequency range for the incident light, within which the dielectric constant of the metal is relatively large. For the parameters of the system considered in the present work the dielectric constant of the metal is \( \approx -847 + 1127i \).

At first, the average intensity [see Eq. (4.25)] of the transmitted light will be analyzed. There are few parameters of the diffraction grating, which determine the properties of the average intensity. These parameters are the period of the diffraction grating, \( d \), the metallic coverage of the dielectric media, \( a/d \), the incident angle, \( \theta \), and the height, \( h \), of the diffraction grating.

As a function of the frequency of the incident light the average intensity has a maximum. This maximum corresponds to the resonant condition for the generation of the modes of the diffraction grating. In Fig. 4.2 the results of calculations are shown for the s-polarized light and in Fig. 4.3 for p-polarized light for different metallic coverage, \( a/d \), of the dielectric media. The difference between the s- and p-polarized light can be clearly seen. For the p-polarization there is very sharp maximum [see Fig. 4.3]. The position of the maximum has weak dependence on the metallic coverage, \( a/d \). This is an indication that the incident light is coupled to the surface plasmons, since for the surface plasmons the energy of the generated plasmon depends on its wave vector, which is determined only by \( \pi/d \). Therefore, there is no dependence
of the wave vector of the plasmon excitation within the diffraction grating on the parameter $a/d$. At the same time the average intensity, even at the maximum, is less than 1 (in units of $I_0$). It means that, on average, there is no enhancement of the intensity of the transmitted light due to diffraction grating. The results in Fig. 4.2 and Fig. 4.3 are shown for the incident angle $\theta = 45^0$. A completely different

![Graph showing calculated average intensity, $I_{av}$, for s-polarized light at distance 10 nm below the grating (i.e., in region III) in units of $I_0$ for different $a/d$ values as indicated in the panel. For all the panels the grating period $d = 2\mu m$, the incident angle $\theta = 45^0$, and the height of the diffraction grating $h = 50nm$.](image)

behavior is observed for the s-polarized light, see Fig. 4.3. The maximum now is broad and there is a strong dependence of the position of the maximum, $\omega_{max}$, and the maximum intensity on the value of $a/d$. With decreasing metallic coverage, i.e.,
$a/d$, the line becomes red shifted, and the maximum intensity increases. For example, if $a/d$ decreases from 0.5 to 0.3 then the maximum intensity increases in six times and becomes 3.5. Since at $a = 0$ the average intensity should be 1 (in units of $I_0$), then at small values of $a$ we should expect a decrease of the maximum intensity with decreasing $a/d$. It means that there is an optimal value of $a/d$ for which the maximum intensity is the largest. Due to the numerical instability of the problem, it is difficult to go below $a/d = 0.3$ and find the optimal value of $a/d$.

The reason why the maxima in Fig. 4.2 is broad and there is a strong dependence
on $a/d$ is that in the case of s-polarization the incident light is coupled not to the surface plasmons but to the modes of diffraction grating. Such modes depend on the actual structure of the diffraction grating, i.e., on the value of $a/d$.

The dependence of the position of the peak, $\omega_{\text{peak}}$, of the average intensity on the metallic coverage, $a/d$, is shown in Fig. 4.4. This figure illustrates again the facts discussed above. Namely, the frequency $\omega_{\text{peak}}$ does not depend on $a/d$ for the p-polarized light, while there is a strong dependence of $\omega_{\text{peak}}$ on $a/d$ for the s-polarization. Therefore, only for the s-polarization we can use $a/d$ as a tuning parameter, i.e., by changing $a/d$ we can change the position of the maximum of $I_{\text{av}}$.

![Figure 4.4](image.png)

Figure 4.4: The peak frequency, $\omega_{\text{peak}}$, at the maximum value of average intensity is shown as a function of $a/d$ for both s- and p-polarization. The grating period $d = 2\mu m$, the incident angle $\theta = 45^0$, and the height of the diffraction grating $h = 50nm$.

The position of the maxima of the average intensity depends on the period, $d$, 

of the diffraction grating for both p- and s-polarized light. These dependencies are shown in Fig. 4.5 and in terms of the wavelength of incident light can be approximately described by the linear functions. Then

$$\lambda_{peak} = 1.8d + 0.31 \quad (4.28)$$

for s-polarization and

$$\lambda_{peak} = 2.2d - 0.0047 \quad (4.29)$$

for p-polarization. For p-polarization this linear dependence is universal, i.e., it does not depend on the parameter $a/d$ and on the incident angle (as we will see below). For s-polarization the coefficients in Eq. (4.28) depend on the value of $a/d$. Another difference between s- and p-polarizations is that the peak wavelength of the s-polarized light is less than the peak wavelength of the p-polarized light. This is due to a different nature of the eigenmodes of the diffraction grating for the different polarizations of the light.

The slope of the $\lambda_{peak}(d)$ dependence for the p-polarized light is 2.2 [see Eq. (4.28)]. This value is very close to the value obtained experimentally in the terahertz frequency range [65]. The experimental result for the slope is 2.19. Although the experimental data [65] have been obtained at a terahertz frequency, i.e., $\approx 30 \text{ THz}$, and our results are for $\approx 70 \text{ THz}$, the fact that the slope is almost the same indicates that at these frequencies the position of the maxima of the average intensity does not depend on the parameters of the metal, i.e., on the dielectric constant of metal. This also indicates that the nature of the diffraction grating modes, responsible for the intensity maxima
Figure 4.5: The peak wavelength, $\lambda_{\text{peak}}$, is shown as a function of grating period $d$, for both p- and s-polarization. The ratio $a/d = 0.5$ and the incident angle $\theta = 45^\circ$.

of the p-polarized light, is the same across the terahertz frequency range. These modes are the surface plasmons.

The dependence of the average intensity on the incident angle, $\theta$ is shown in Fig. 4.6. It can be seen from the figure that for p- and s-polarizations the position of the maximum has a very weak dependence on the incident angle. This means that the eigenfrequencies of the modes of the diffraction grating have a weak dependence on $\theta$. At the same time the maximum intensity strongly depends on the angle, $\theta$. We can see that with decreasing the incident angle the maximum intensity increases and at small angles it can be much larger than 1. It means that at small incident angles the
Figure 4.6: The average intensity, $I_{av}$, at distance $z = 50$ nm below the grating (i.e., in region III) in units of $I_0$ for different incident angle $\theta$ as indicated in the panels. The panels (a)-(c) corresponds to p-polarization and (d)-(f) corresponds to s-polarization. For all the panels the grating period $d = 2 \mu m$ and the ratio $a/d$ is 0.5.

diffraction grating provides strong enhancement of the intensity of the transmitted light. For the s-polarization the diffraction grating can enhance the intensity of the transmitted light by almost two orders of magnitude. At all incident angles the enhancement of the transmitted wave is much stronger for the s-polarization than for the p-polarization.

Therefore we can expect strong enhancement of the intensity of the transmitted
light at small incident angle. The enhancement is the strongest for the s-polarized light. The behavior of the enhancement as a function of the incident angle for the p-polarized light is unexpected. The modes, which are responsible for the enhancements of the p-polarized light are the surface plasmons. At the same time, it has been known that the coupling of the light to the surface plasmons is determined by the component of electric field orthogonal to the metal-dielectric interface. Therefore we should expect that if we increase the orthogonal component of electric field then generation of the surface plasmons, and correspondingly the enhancement of the transmitted light is increased. But for the p-polarized light we can see in Fig. 4.7 the opposite tendency: with decreasing the angle, i.e., decreasing \( z \) component of the electric field, the enhancement is increased. This fact shows that for the p-polarized light the modes of the diffraction grating are not purely surface plasmons. These modes contains both the orthogonal and the in-plane components of the electric field. These modes can be identified as the surface plasmon modes since, as we will see below, the light in these modes is mainly localized near the metal-dielectric interface.

As we can see from Fig. 4.7 the enhancement, i.e., the average intensity of the transmitted light in the units of \( I_0 \), increases with decreasing the incident angle. At the same time, for the p-polarized light, the intensity \( I_0 \) has strong dependence on the incident angle, \( \theta \), itself. Namely, the intensity \( I_0 \) decreases with decreasing \( \theta \), see Eq. (4.27). Therefore there is an optimal value of the incident angle, \( \theta \), which is determined by the condition that the intensity (not the enhancement) of the trans-
Figure 4.7: The maximum average intensity (peak value), $I_{av(max)}$, for the p- and s-polarized light at distance $z = 10nm$ below the grating (i.e., in region III) is shown as a function of incident angle, $\theta$. The intensity is in the units of $I_0$. The grating period $d = 2\mu m$, the ratio $a/d = 0.5$, and the height of the diffraction grating $h = 50nm$.

Emitted light is maximum. To find the actual intensity of the transmitted light we just need to multiply the data shown in Fig. 4.7 by $I_0(\theta)$. In Fig. 4.8 the dependence of the intensity of transmitted light on the incident angle for p- and s-polarized light is shown. For the s-polarized light, a monotonic dependence can be seen on the incident angle and the maximum intensity of the transmitted light is achieved for the normal incident light. For the p-polarized light we can clearly see that there is an optimal value of the incident angle. This angle is around $\theta \approx 50^\circ$. We can also see a general tendency that the intensity of the s-polarized transmitted light is much larger than the intensity of the p-polarized transmitted light.
Figure 4.8: The maximum average intensity (peak value), $I_{av}^{(max)}$, for the p-polarized light (scaled by a factor of 5) and s-polarized light at distance $z = 10$ nm below the grating (i.e., in region III) is shown as a function of incident angle $\theta$. The intensity is in units of the intensity of the incident light. The grating period $d = 2\mu m$, the ratio $a/d = 0.5$, and the height of the diffraction grating $h = 50$ nm.

Another parameter of the diffraction grating, which can be varied to optimize the performance of the photodetector, is the height of the grating, $h$. When the height of the grating is large then the intensity of the transmitted wave should be small and $I_{av} \approx 0$. At zero height, i.e., without a diffraction grating, the average intensity is 1 (in units of $I_0$). Then, if at the intermediate values of $h$ there is an enhancement of the intensity of the transmitted light, i.e. $I_{av} > 1$, then the dependence of $I_{av}$ on $h$ is non-monotonic and at some value of $h$ we should see the maximum of the average intensity. This is an optimal value of the height of the diffraction grating.

The dependence of the average intensity on the height $h$, of the diffraction grating is shown in Fig. 4.9, for the p-polarized light. The specific feature of this dependence
is that it is non-monotonic even for the parameters of the system, for which the average intensity is less than 1 at all values of $h$. For example [see Fig. 4.9(a)], at the incident angle $\theta = 45^0$ the average intensity is less than 1 at all $h$, but there is a local maximum at $h \approx 50nm$. At smaller incident angle, e.g. $\theta = 5^0$ [see Fig. 4.9(b)], there is an enhancement of the transmitted light and we have an absolute maximum at $h \approx 50nm$. The position of the absolute maximum determines the optimal value of the height of the diffraction grating. We can also notice the local minima at small $h$, $h \approx 8nm$.

![Figure 4.9: (a) The average intensity, $I_{av}$, for p-polarized light at distance $z = 50nm$ below the grating (i.e., in region III) is shown in units of $I_0$ as a function of $h$ for $a/d = 0.5$ (a) at $\omega = 68$ THz for $\theta = 45^0$ and (b) at $\omega = 67.8$ THz for $\theta = 5^0$. For all the panels the grating period $d = 2\mu m$.](image)

A different behavior is observed for the s-polarized light, see Fig. 4.10. In this case if the average intensity is less than 1 then the dependence of $I_{av}$ on $h$ is monotonic, i.e., there is no local maximum, which is different from the p-polarization [see Fig. 4.9]. The typical dependence is shown in Fig. 4.10(a), where for $a/d = 0.5$ the average
intensity is less than 1. If the average intensity is greater than 1, then there is an 
absolute maximum at some finite value of $h$. For example, at $a/d = 0.3$ the maximum 
of the average intensity is achieved at $h \approx 55$ nm.

Finally, the properties of the average intensity of the transmitted light for the s- 
and p-polarizations can be summarized. From the data shown above we can conclude 
that the enhancement of the transmitted light is the largest for the s-polarized light. 
For s-polarization, the frequency position of the intensity maxima can be tuned by 
varying the period of the diffraction grating, $d$, and the metallic coverage of the 
dielectric media, $a/d$. For the p-polarized light only the period of the diffraction 
grating affects the frequency position of the maximum. For p- and for s-polarized 
light there is no dependence of the position of the intensity maxima on the incident 
angle.

Figure 4.10: The average intensity, $I_{av}$, for s-polarized light at distance $z = 50$ nm 
below the grating (i.e., in region III) is shown in units of $I_0$ as a function of $h$ (a) at 
$\omega = 75$ THz and $a/d = 0.5$ and (b) at $\omega = 69$ THz and for $a/d = 0.3$. For all the 
panels the grating period $d = 2\mu$m and the incident angle $\theta = 45^0$. 

\[ I_{av} \]
\[ \begin{array}{c}
\begin{align*}
0.9 & \\
0.7 & \\
0.5 & \\
\hline
20 & \\
60 & \\
100 & \\
\end{align*}
\end{array} \]
\[ \begin{array}{c}
\begin{align*}
\omega = 75 \text{ THz} & \\
\omega = 69 \text{ THz} & \\
\hline
20 & \\
60 & \\
100 & \\
\end{align*}
\end{array} \]
It is possible to find the optimal parameters of the diffraction grating so that the enhancement of the transmitted intensity is the largest. For the s-polarized light the decrease of the metallic coverage, $a/d$, and the incident angle, $\theta$, results in increase of the average intensity, while for the p-polarized light only the incident angle changes the intensity of the transmitted light. As a function of the height of the diffraction grating the average intensity has a maximum for both p- and s-polarizations. For the parameters of the system considered in the present work the maximum is achieved at $h \approx 50\text{nm}$.

4.4.2 Intensity distribution and the modes of the diffraction grating

The important property of quantum dots is that they are sensitive to the local electromagnetic field. Therefore it is possible to enhance the sensitivity of the quantum dot photodetector by placing the quantum dots at the points with high intensity of the transmitted wave.

In this relation it is important to understand the distribution of the transmitted electromagnetic wave in the active region of the photodetector, i.e., in the region III. In this distribution the bright spots, i.e., spots with high intensity can be expected.

The distribution of the transmitted electromagnetic field in region III is shown in Fig. 4.11 for the p-polarized light. The main tendency, is that the intensity of the transmitted wave is non-uniform with maxima at points $x = nd$ and $x = a + nd$, i.e.,
Figure 4.11: (color) The distribution of electric field intensity for p-polarized light is shown in region III. (a) Intensity $I(x, z)$ at peak frequency, $\omega = 67.95$ THz, for $\theta = 45^0$ and $a = 0.3d$. (b) The same plot for $a = 0.5d$. (c) Similar plot for $\theta = 5^0$ and $a = 0.5d$. (d) Electric field intensity in the vicinity of the first peak in panel (c) is shown in the $x - z$ plane. The scale of the intensity is indicated by the color bar on the top. For all the panels the grating period $d = 2\mu m$ and the height of the diffraction grating $h = 50$ nm.

at the points corresponding to the boundaries between the metallic strips and air.

With increasing enhancement of the transmitted light, i.e., with increasing average intensity, the peaks become more sharp and more localized. There is a weak effect of metallic coverage, $a/d$, on the distribution of the intensity of electric field [see
Fig. 4.11(a) and 4.11(b)]. For large incident angles, i.e., for small values of $I_{av}$, the peaks are broad, and the contrasts of the peaks are small, i.e., the ratio of the maximum intensity and the minimum intensity is around 2. When we change the parameters of the grating, which results in the enhancement of the average intensity, then the peaks become very sharp [see Fig. 4.11(c)]. The widths of the peaks are around 10 nm. Such a peak can accommodate one quantum dot. The contrasts of the peaks are large. For example, in Fig. 4.11(c) the ratio of the maximum value of the intensity to the minimum value is around 40.

The same results for the s-polarized light is shown in Fig. 4.12. In comparison to the p-polarized light we have much stronger local enhancement of the intensity of the transmitted waves. Another difference from the p-polarization is that now the bright spots are located at the points corresponding to only one side of the metal-air interface, i.e., at $x = nd$, while at points $x = a + nd$ the enhancement is much weaker. The contrast of the bright spots can be up to 200. The intensity at the peak decreases with the distance from the metal-dielectric interface, and the characteristic distance is around 20 nm. The widths of the peaks are the same as for the p-polarized light and are around 10-20 nm. Similar to the p-polarized light the peaks become more localized when the average intensity is increased. Comparing to the average value of the intensity we can say that the intensity at the peak can be 10-100 times larger than the average value.

To clarify the differences between the p- and s-polarized light the distribution of
the intensity of electric field in the grating and dielectric regions (regions II and III) is shown in Fig. 4.13. We can see that the peaks for the p-polarized light are more localized in the $x$ direction than the corresponding peaks for the s-polarized light. At the same time for the s-polarization the peaks are more extended in the $z$ direction. Therefore, if we need to use the advantage of the bright spots in the transmitted
waves then, for the s-polarization there are more restrictions on the positions of the quantum dots in the growth direction (z-direction). The quantum dots should be placed at the distance from the metal-dielectric interface less than 30-40 nm.

Another crucial difference between the p- and s-polarized light is that the number of the bright spots for the p-polarization is twice as large as the number of the bright spots for the s-polarization. This follows from the fact (see Fig. 4.13) that the bright spots for the s-polarized light appear only at one side of the metal-air interface.

![Image](image_url)

Figure 4.13: (color) Distribution of $I(x, y)$ is shown for the grating region (region II) and below the grating region (region III) for (a) p-polarization and (b) s-polarization. For all the panels: $d = 2\mu m$, $a/d = 0.5$, $\theta = 10^\circ$, and $h = 50$ nm.

The behavior of the waves inside the diffraction region is also different for the p- and s-polarized light. We can see that electromagnetic field is mainly localized
inside the metal region for the p-polarized light and inside the air region (between metallic strips) for the s-polarized light. In the $z$-direction the electromagnetic field is localized in both cases at the interface with region III. Based on this behavior of the field inside the diffraction grating we can say that the modes, which are responsible for the enhancements of the incident light, are the surface plasmon modes for the p-polarized light and the modes trapped in the air region between two metallic strips for the s-polarized light. For the s-polarization the dependence of the energy of the trapped modes on the width of the air region, i.e., on the value of $(d - a)$, explains the dependence of the average intensity of the transmitted light on the ratio $a/d$ [see Fig. 4.2]. We can see from the figure that with decreasing $a/d$ the frequency position of the intensity maximum decreases. This is because with decreasing $a$ the width, $(d - a)$, of the air regions increases. Then the size of the trapped mode also increases and correspondingly the energy of this mode decreases. With increasing the size of the trapped mode the coupling of the incident light with the mode is increased, which results in increase of the maximum intensity, shown in Fig. 4.2.

4.5 Conclusion

It has been shown that the enhancement of the electromagnetic field due to the presence of the diffraction grating is much stronger for the s-polarized light than for the p-polarized light. This is opposite to what we should expect if we assume that the enhancement of the light is due to generation of the surface plasmons, since the
surface plasmons can be generated only by the p-polarized light, but not by the s-polarized light. The manifestation of the surface plasmons is not so strong in our system since I am working in the low-frequency range, where the coupling of the incident light to the surface plasmons is weak.

For the s-polarized light the enhancement of the transmitted light is due to generation of the modes of electromagnetic field, which are trapped between the metallic strips in the diffraction grating region. For the p-polarized light, the modes responsible for the light enhancements are the surface plasmon modes. As a result the light in the diffraction grating is localized in the metallic region for the p-polarized light and in the air region for the s-polarized light.

The dependence of the enhancement of the transmitted light on the parameters of the diffraction grating can be summarized as follows

- Decreasing the metallic coverage, i.e., $a/d$, of the dielectric media increases the intensity of the s-polarized light, but does not affect the p-polarized light. For the s-polarized light there is an optimal value of $a/d$ for which the enhancement is maximum.

- Decreasing the incident angle increases the enhancement of the light for both p- and s-polarizations. At the same time for both polarizations the incident angle does not change the frequency positions of the intensity maxima. For the actual value of the transmitted light there is an optimal incident angle, $\theta \approx 5^\circ$, for the p-polarized light, at which the intensity of the transmitted light is the
maximum. For the s-polarized light the actual intensity of the transmitted light has a monotonic dependence on the incident angle and the maximum of the intensity is realized at zero incident angle.

- The intensity of the transmitted light for both p- and s-polarizations has a nonmonotonic dependence on the height, $h$, of the diffraction grating. There is an optimal value of $h$, at which the intensity has a maximum. This value is around 50 nm for the parameters of the system considered in the present work.

- The intensity of the transmitted wave decreases with the distance from the metal-dielectric interface. The characteristic length is around 50 nm.

- The spatial distribution of the intensity of transmitted light is highly nonuniform with the sharp peaks. The spatial size of the peaks is around 10 nm. For the s-polarized light the intensity at the peak is two order of magnitude larger than the average intensity.

Therefore, to have the largest enhancement of the transmitted light in the active region of the quantum dot photodetector we need to use the s-polarized light. In addition, the metallic coverage, $a/d$, and the incident angle should be small. The height of the diffraction grating should have the optimal value, which is around 50 nm. The strongest effect is achieved if the quantum dots are placed at the bright spots of the transmitted wave. For the s-polarized light the bright spots are near only one type of the metal-air interface. The distance between the quantum dot layer and the
metal-dielectric interface should not exceed the characteristic size of the enhancement region in the growth direction. This size is around 30-40 nm. Under these conditions the enhancement of the signal could be a few orders of magnitude.

For a general system of quantum dots we can estimate the strength of the local enhancement, $I_{\text{max}}$, of the transmitted wave so that the net effect of the diffraction grating is the enhancement of the absorption coefficient. If the average distance between the quantum dots is $d_{av}$, then only part of the quantum dots will experience the high electric field in the photodetectors with the diffraction grating. We can estimate this part as $d_{av}/d$. Then the maximum enhancement should satisfy the following condition $I_{\text{max}} > d/d_{av}$. For $d_{av} \sim 50\text{nm}$ and $d = 2000\text{nm}$, $I_{\text{max}} > 40$ has been obtained. This value can be easily achieved for some values of parameters of the diffraction grating.

This results can be also applied to a single quantum dot. Namely, by placing the quantum dot at the bright spots of the diffraction grating we can enhance the optical properties of the dot.
Chapter 5

Plasmonic enhancing nanoantennas for photodetection

5.1 Introduction

In this Chapter I will discuss the use of plasmonic nanostructured systems as nanoantennas for photodetection. Even though semiconductors and their heterostructures have many useful properties and widely used in photodetection, their electron density is very small compared to that of metals and, therefore, they have low absorption cross sections. The idea of using metal nanostructured antennas is to combine the high optical responses of metals with the functional electric properties of semiconductors. The main results in this chapter has been published in Infrared Physics and Technology [66].
Nanostructured metals have a wide spectral range of surface plasmon resonances from near-ultraviolet to infrared. One particular example is a collection of thin metal wires where the electron density $n$ averaged over the volume is low, and so is the electron plasma frequency $\omega_p \propto \sqrt{n}$. Metal nanostructures, that have sharp edges or tips also possess low surface-plasmon resonance frequencies. Such nanostructures, when excited by a resonant optical radiation, create high local fields at these sharp features that may be up to three orders of magnitude higher in amplitude than the excitation optical field. For lower THz-range frequencies, the dielectric function of metals becomes mostly imaginary with its real part being positive, which precludes the surface plasmon resonances. In these cases, there are two types of plasmonic systems still available. The first type of the systems is highly-doped semiconductors that possess metallic-like optical behavior in the far-infrared region. Second, dielectrics and intrinsic semiconductors between their TO and LO phonon frequencies which exhibit dielectric permittivity with a large negative real part and relatively small imaginary part (reststrahlen band), which is necessary for a pronounced plasmonic behavior. Microstructures and nanostructures made out of such materials exhibit high-Q plasmonic resonances and enhanced fields.

5.2 Nanoantennas

Nanoantennas [66] designed to receive optical energy in the ultraviolet, visible, infrared, and beyond are the smallest detectors available. They can be scaled to
a fraction of the radiation wavelength. Such optical antennas are specifically engineered to focus micrometer scale light into nanoscale volumes with high spatial and spectral control of the greatly enhanced fields in visible and near-infrared regions [67]. The subwavelength antennas whose size is much smaller than wavelength will be considered. In most cases, resonant conventional antennas in radio-frequency or microwave range have size comparable to and scaling with wavelength. In contrast, plasmonic nanoantennas have internal, plasmonic resonances that do not depend on their size but rather on their shape only. The resonance frequencies of known types of plasmonic nanoantennas span the entire optical range from near-ultraviolet to near-infrared. Nanostructured antennas are related to nanoantennas: they consist of elements with nanoscale sizes but their total size may be comparable or larger than the wavelength. In this case too, the resonance frequency is determined by the nanostructure shapes and not necessarily by the size of the entire antenna. A particular type is a nanostructured system which generates propagating electromagnetic waves at the interfaces of plasmonic materials known as surface plasmon polaritons [68].

By nature, the nanoantennas are direction, wavelength, and polarization sensitive elements. There are two types of plasmonic nanoantennas discussed in this work. The first type is based on surface plasmons which are standing quasielectrostatic waves [69, 70, 71]. Such nanoantennas are capable of producing very high local fields in small volumes. They may be used to improve signal/noise characteristic of IR photodetectors. The semiconductor detector should have size on the nanoscale and
be positioned near the *hot spot* (nanofocus) of the nanoantenna.

One of the most efficient optical antennas is bowtie plasmonic nanoantenna and their arrays. For example, the fractal bowtie plasmonic nanoantenna array shown in Ref. [70] is designed to detect five bands centered at wavelengths of $\lambda, 2\lambda, 4\lambda, 8\lambda$ and $16\lambda$. Typically the bowtie nanoantenna consists of two triangular pieces of gold, each about 75 nm long, and whose tips face each other in the shape of a bowtie. The bowtie takes energy from near-infrared light and squeezes it into a 20 nm gap that separates the two gold triangles [67]. As shown in Ref. [67], the result is a concentrated spike of light that is several order of magnitude intense than the exciting field.

There has recently been great interest in the spherical metal nanoshells as nanoantennas consisting of a dielectric core covered by a thin gold layer. By varying the relative dimensions of the core and the shell, the resonance frequency of the nanoparticles can be precisely varied from the near-ultraviolet to the mid-infrared [71]. The plasmon resonance frequency of the nanoshell shifts as a function of nanoshell composition: for thinner metal shells the resonance shifts toward the red and infrared.

### 5.3 Chain of metal nanospheres

As an efficient nanoantenna, self-similar linear chain of several metal nanospheres with progressively decreasing sizes and separations [69] has been considered. To introduce our idea, consider a finite chain of metal nanospheres where for an $i$th nanosphere the radius is $R_i$ and its surface-to-surface separation from the $(i + 1)$th
Figure 5.1: Local fields (absolute value relative to that of the excitation field) in the equatorial plane of symmetry for linear self-similar chain of three silver nanospheres. The ratio of the consecutive radii is \( R_{i+1}/R_i = 1/3 \); the distance between the surfaces of the consecutive nanospheres \( d_{i,i+1} = 0.6R_{i+1} \). Inset: the geometry of the system in the cross section trough the equatorial plane of symmetry.

A nanosphere is \( d_{i,i+1} \). Self-similarity will be assumed, i.e., \( R_{i+1} = \kappa d_{i,i+1} \) and \( d_{i+1,i+2} = \kappa d_{i,i+1} \), where \( \kappa = \text{constant} \); see a schematic in inset in Fig. 5.1(a). Consider \( \kappa \ll 1 \), so the local field of a given nanoparticle is only weakly perturbed by the next one.
Figure 5.2: Local fields (absolute value relative to that of the excitation field) in linear symmetric self-similar chain of six silver nanospheres. The ratio of the consecutive radii is 3; the distance between the surfaces of the consecutive nanospheres 0.6 of the smaller sphere’s radius. Inset: the geometry of the system (in the cross section through the equatorial plane).

The local field in the proximity of the biggest nanosphere is enhanced with respect to exciting field $E_0$ by the resonance quality factor, $Q \sim \text{Re}[\varepsilon(\omega)]/\text{Im}[\varepsilon(\omega)]$, where $\varepsilon(\omega)$ is the relative dielectric function of the spheres’ metal, and $\omega$ is the light frequency.
Note that $Q \gg 1$ for a good metal, which is assumed. This local field is uniform on the scale of that next smaller nanosphere and plays role of the excitation field for it. Thus, in the proximity of the second nanosphere, the local field is enhanced by the factor of $Q^2$. Continuing this chain, at the $n^{th}$ nanosphere, the local field is estimated as $Q^n E_0 \gg E_0$. For example, for a realistic value of $Q = 10$ and $n = 3$ nanospheres, a very large local field at the smallest nanosphere $E \sim 10^3 E_0$ has been obtained, corresponding to Raman scattering enhancement by a factor of $E^4 \sim 10^{12} E_0$.

The local electric field, $\mathbf{E} = -\nabla \varphi$, in the equatorial plane of the nanosphere chain for three particles are shown in Fig. 5.1, where $R_{i+1} = (1/3)R_i$, and $d_{i+1,i+2} = 0.6R_{i,i+1}$. For instance, possible values of radii are: $R_1 = 45 \text{ nm}$, $R_2 = 15 \text{ nm}$, and $R_3 = 5 \text{ nm}$. In Fig. 5.1, there is the cascade, multiplicative enhancement of the local fields from larger to smaller nanospheres. The highest enhancement is by a factor $\sim 580$, found close to the surface plasmon frequency of an isolated nanosphere at $\hbar \omega = 3.37 \text{ eV}$ ($\lambda = 369 \text{ nm}$ in vacuum) [Fig. 5.1(a)]. The hottest spot (nanofocus), where the local field is located between the smallest nanospheres and not at the geometric apex of the system (outside the chain at the smallest nanosphere) as one might intuitively expect. Centrally symmetric chains have been considered; one of them of six nanospheres, is illustrated in Fig. 5.2 for the nanosphere separation $d_{i+1,i+2} = 0.6R_{i,i+1}$. In this case, the hot spot of the local field occurs at the center of symmetry.
5.4 Tapered nanoplasmonic waveguide

Figure 5.3: (color) Geometry of the nanoplasmonic waveguide. The propagation direction of the surface plasmon polaritons is indicated by the arrow. Intensity of the local fields relative to the excitation field is shown by color. The scale of the intensities is indicated by the color bar in the center. (b) Local electric field intensity is shown in the longitudinal cross section of the system. The coordinates are indicated in the units of the reduced radiation wavelength in vacuum, \( \lambda_{\text{vac}} = 100 \) nm. The radius of the waveguide gradually decreases from 50 to 2 nm.

To introduce the second type of nanoantennas, tapered nanoplasmonic waveguide will be introduced. It is theoretically predicted that surface plasmon polaritons propagating toward the tip of a tapered plasmonic waveguide are slowed down and
asymptotically stopped when they tend to the tip, never actually reaching it [68]. This phenomenon causes accumulation of energy and giant local fields at the tip. In our example, the tapered nanoplasmonic waveguide is a silver cone in vacuum; its angle of opening is 0.04 radian, as shown in Fig. 5.3(a). The vacuum reduced wavelength of the excitation radiation is $\lambda/2\pi = 100$ nm, which corresponds to red light of $\lambda = 630$ nm. The surface plasmon polaritons are efficiently excited at the wide end of the waveguide nanowire by using, e.g., grating or Kretschman [72] geometry and propagate to the tip as indicated. This propagation causes accumulation of the surface plasmon polariton energy at the tip and the corresponding increase of the local field intensity by more than three orders of magnitude. As shown in Fig. 5.3(b), the intensity of the local optical field is sharply concentrated in 3D in a nanolayer at the surface of the metal, which is a signature of surface plasmon polaritons. The hot spot of local fields is created in a nanosize region at the very tip.

The physical reason is that both the phase and group velocity of surface plasmon polaritons asymptotically tend to zero toward the nanotip. Consequently, the surface plasmon polaritons are slowed down and adiabatically stopped at $z \to 0$, which leads to their accumulation at the tip. For this example, it has been selected that the minimum radius of the wire to be $R_{\text{min}} = 0.02\lambda/2\pi = 2$ nm to avoid effects of the spatial dispersion of the dielectric response that are important at shorter distances, cf. Refs.[81, 74], and the maximum radius (at $z = -25\lambda/2\pi = -2.5$ $\mu$m) to be $R_{\text{max}} = 0.02\lambda/2\pi = 50$ nm. In Fig. 5.4, it has been shown that the amplitudes of the
Figure 5.4: (color) Snapshot of instantaneous fields (at some arbitrary moment $t=0$): Normal component $E_x(a)$ and longitudinal component $E_z(b)$ of the local optical electric field are shown in the longitudinal cross section $(x - z)$ plane of the system. The fields are in the units of the far-zone (excitation) field.

Local optical fields in the cross section of the system for the normal and longitudinal (with respect to the axis) components of the optical electric field. The longitudinal field in the metal is very small, proportional to a factor of $|\varepsilon_d/\varepsilon_m| \ll 1$, as should be from the boundary conditions. Therefore, the guide itself is clearly seen in panel (a) as the acute triangular region of low fields. The transverse $x$ component grows by an order of magnitude as the surface plasmon polaritons approach the tip of the guide, while the longitudinal $z$ component, which is very small far from the tip, grows relatively much stronger. Close to the tip, both these components are on the same order of magnitude, as is expected for the localized excitations. This growth in magnitude is concurrent with the energy localization in 3D and the significant
reduction of the wavelength, which are due to the dramatic slowing down of the surface plasmon polariton’s. Note the surface plasmon polaritons in Fig. 5.4 are not standing but running waves; the fields shown represent an instantaneous snapshot of these waves.

5.5 Conclusion

In conclusion, optical antennas are becoming a promising candidate for nanophotonic, and optoelectronic applications, such as detecting, and emitting, optical radiation in nanoscale devices. The plasmonic nanoantennas (e.g., nanoshell, nanolens and bowtie) are capable of producing very high local fields in small volumes. They may be used to improve the signal characteristics of infrared photodetectors. The proposed nanolenses can be used as a nanoantenna for wide range of applications, in particular, for photodetection in the visible, infrared, and beyond. In addition, one can use the nanoshell as a tunable optical antenna to detect several wavelength bands. The plasmonic nanoantennas (plasmonic waveguides) are capable of working similar to the microwave region antennas. They intercept the energy of the excitation radiation over a large area and propagate as surface plasmon polaritons toward a small IR photodetector crystal which can be attached at the end of the nanoplasmonic waveguide. In particular, in such a system optical area of the detector is much larger than the electrical area, therefore, detectivity can be significantly improved. The rapid adiabatic nanofocusing promises to find various applications in nanoop-
tics and nanotechnology, where greatly enhanced local optical fields are required, in particular, for probing, spectroscopy, detection, and modification on the nanoscale in physics, chemistry, biology, electrical engineering, etc.
Chapter 6

Ultrafast optical responses of metal nanostructures

6.1 Introduction

In this Chapter I will predict that nonlinear ultrafast electron photoemission by strong optical fields and, potentially, other nonlinear optical responses of metal nanostructures significantly depend on the absolute (carrier-envelope) phase of excitation pulses. Strong enhancement of the local optical fields produces these responses at excitation intensities lower by order(s) of magnitude than for known systems. The main results in this chapter has been published in Appl. Phys. A [75]

Recently there has been great deal of interest in ultrafast science to understand the nonlinear optical responses of atoms, molecules, and condensed matter to ultrashort
(one or a few oscillations) pulses critically depend on the phase between the carrier oscillation of a laser pulse and its envelope [76, 77, 78], which is also called the absolute phase. Therefore, the understanding of the absolute phase is very important for the ultrafast science. The measurements of the absolute phase using smooth metal surfaces has been reported [77, 78]. Since they are using high pulse intensity with amplifiers it impossible to determine the absolute phase directly from the laser oscillators.

The importances of metal nanostructure to enhance the ultrashort fields and make possible the determination of the absolute phase at relatively low intensities will be discussed in the following chapters. This effect is nontrivial because relaxation times of the surface plasmon eigenmodes responsible for the ultrafast responses of metal nanostructures are rather long, typically tens of femtoseconds in the red to near-infrared spectral region for noble metals such as silver [90]. This long relaxation time ($\gtrsim 10 - 50$ fs) has been used to predict a possibility of the coherent control of the nanoscale femtosecond optical responses [80, 81]. Such a control has been experimentally observed recently [88]. The sensitivity to the absolute phase requires reaction within an optical cycle ($\sim 100$ fs). Metal nanostructures also possess a very short reaction time that is inverse to their total spectral width, $\tau \sim \Delta \omega^{-1} \sim 100$ fs. This defines the minimum rise time of the nanosystem response, which potentially makes it sensitive to the absolute phase.
6.2 Strong-field electron emission

It has been considered that strong-field electron emission that takes place when the energy barrier separating the metal electrons from the surrounding space (whose height is defined by workfunction $W_f$) is slanted by a quasistationary, instantaneous electric optical field $E$ causing the electron tunneling. I will use the term *quasistationary* instead of the usual physics term of ultrastrong fields *quasistatic*, because the latter term in nanoplasmonics is reserved for the case when all sizes of the system are much less than the light wavelength. Such a process occurs for relatively small values of the Keldysh parameter, which is defined by,

$$\gamma = \left( \frac{W_f}{U_p} \right)^{1/2} \lesssim 1,$$

where $U_p = \frac{m}{2} \left( \frac{eE}{m\omega} \right)^2$ is the electron quiver energy, $m$ is the electron (effective) mass, $e$ is the elementary charge, and $\omega$ is the optical frequency [93]. The quasistationary emission is of advantage for our purpose since its dependence on the parameters of the problem, absolute phase in particular, is exponentially strong.

It can be separated the electron emission process into two stages [94]: an essentially quantum tunneling stage and the subsequent almost classical motion in the free space. For the tunneling stage, the probability per unit time of tunneling [85] integrated over the electron states at the Fermi surface is given by

$$w(t) = 8 \frac{\hbar}{me^2} \varepsilon_F W_f^2 \nu_F \exp \left( \frac{E_W}{E(t)} \right) \Theta[-E(t)]\Theta[-A(t)],$$

where $E_W = \frac{4}{3e\hbar} \left( 2mW_f^2 \right)^{1/2}$, $\Theta[\ldots]$ is the unit-step function, $\varepsilon_F$ is the Fermi energy,
$\nu_F$ is the electron state density at the Fermi surface, $E(t)$ is a component of the time-dependent local electric field normal to the surface of the system [our convention is that the positive value of $E(t)$ corresponds to the field directed away from the surface towards the free space, i.e., in the direction of an electron detector], and the vector potential is chosen in the following gauge:

$$A(t) = c \int_{t}^{\infty} E(t) dt,$$

and $c$ is the speed of light. Throughout, It has been considered that the electron charge to be $-e$. In Eq. (6.2), $E_W$ is the characteristic, workfunction field that defines a scale for the local field $E(t)$ that efficiently causes the photoelectron emission. Note that it has been neglected that the effects of the electron interaction with its electrostatic image that are not expected to radically change the predicted phase dependence that originates, as shown below (see Fig. 6.2 and its discussion), from the corresponding phase sensitivity of the local electric fields that are the cause of the tunneling process, and themselves do not depend on it. After the tunneling, the electron velocity is given by

$$v(t) = \frac{e}{mc} A(t) + v_d, \quad v_d = -\frac{e}{mc} A(t_0),$$

where $t_0$ is the time of emergence of an electron in the free space, which is assumed to occur by tunneling at zero velocity [94], and $v_d$ is the drift velocity, which is the asymptotic (final) velocity of the electron reached after the end of the excitation pulse. Note that the $\Theta[-E(t)]$ factor in Eq. (6.2) assures that the electron intially accelerates away from the metal surface, and $\Theta[-A(t)]$ guarantees that the drift velocity of the
electron is likewise directed from the metal surface into the free space. An excitation pulse generates a bunch of electrons that drift away from the metal surface generating a current density
\[ j = -env_d \int_{-\infty}^{\infty} w(t) dt, \tag{6.5} \]
where \( n \) is the density of electrons in the emitting layer, and \( v_d \) is the component of the drift velocity normal to the metal surface and directed away from the metal.

It has been known that only nonlinear processes are coherently controllable when integrated over time \([80, 81]\). The strong-field photoemission has been chosen because it is a highly-nonlinear optical process and as such is the most sensitive to the absolute phase. The electron photoemission current as given by Eqs. (6.2)-(6.5) exponentially depends on the time-kinetics of the local optical electric field \( E(t) \) at every point of the metal nanosystem. To find this field in a general case for a strong excitation field \( E_0 \) would have been an extremely complicated, unrealistic task. However, there are the following two properties of the metal nanosystems that make an approximate solution possible.

(i) In the optical spectral region, the dielectric permittivity \( \varepsilon \) of noble metals is very large and negative, \( \varepsilon \ll -1 [17] \). Correspondingly, the normal field, which only causes the photoemission, can be strong enough outside the metal to slant the workfunction barrier sufficiently to produce the photoemission, but inside the metal this local field may still be small enough to be treated by linear response theory.

(ii) To have the Keldysh parameter \( \gamma [93] \) sufficiently small for moderate light
intensities, the near-ir spectral region has been considered. In this case, the quality factor of the metal plasmon resonances is high enough, i.e., $\text{Im}[\varepsilon] \ll -\text{Re}[\varepsilon]$. This implies that normal field in the metal is almost real and opposite in sign to (out of phase with) the normal field outside. Because for the emission the outside field should be directed outward from the metal, the inside field is necessarily directed inward and cannot cause the photoemission. Consequently, the strong-field photoemission under such conditions can only occur from a very thin (on order of the Debye or Thomas-Fermi length, which is on a tenth of a nanometer scale for metals) layer at the surface where the local field $E(t)$ is the exterior (outside of the metal) optical field at the surface.

6.3 Numerical example

In accordance with the above-given arguments, it has been used that a previously-developed linear-response Green-function numerical approach [81] yielding the local field at each spatio-temporal point, $E(\mathbf{r},t)$. The current density $j(\mathbf{r})$ is computed by a numerical integration over the time in Eq. (6.5) at each spatial point. For our numerical computations, silver has been selected as the metal because it has the smallest optical losses of any natural metal in the visible and infrared spectrum [17]. Two planar nanosystems have been considered whose geometry is illustrated in Fig. 6.1: V-shape [panel (a)] and random planar composite (RPC) [panel (b)]. A coordinate frame has been chosen in such a way that the nanosystem is in the $xz$
Figure 6.1: The geometry of the nanosystems in the cross section through the \(xz\) plane of symmetry: V-shape (a) and random planar composite (b). The units in \(x\) and \(z\) axes are are nm. The thickness of both the systems in the \(y\) direction is set to be 4 nm.

plane with the \(z\) polarization of the excitation pulse; the V-shape axis of symmetry is oriented along the \(z\) axis. The positive \(y\) axis direction is set toward the electron detectors, so it is the \(y\) component of the local field to cause the photoemission.

6.4 Discussion

The physical basis of the absolute-phase dependence of the optical effects in nanos-structured metals can be traced in Fig.6.2 where display the local optical fields at the apex of the V-shape (in units of the excitation field \(E_0\)). The corresponding single-oscillation excitation pulses are shown in the insets; the medium (carrier) frequency \(\hbar \omega_0 = 1.55\) eV corresponds to the radiation of Ti sapphire laser. The most important feature is the evident dependence of the first few oscillations of the local fields on
the absolute phase: each of the shape, magnitude, and darkness of the points in the graphs, which describes the ability to contribute to the photocurrent, change with $\varphi$. The change of the sign of the current (corresponding to the change from the black squares to gray triangles in the graphs) does not occur exactly at the minimums of $E$ that would have been if these oscillations were purely harmonic. This and the non-harmonic shape of the early oscillations indicate that many surface plasmon eigenmodes contribute to these oscillations, which is a major factor determining the absolute-phase sensitivity. This sensitivity is due to the large bandwidth of the optical response of metals. Note that in contrast, the later oscillations (fifth and subsequent in the figure) are not $\varphi$-sensitive.

In contrast to linear-response fields, the tunneling current exponentially depends on the scale of the local optical fields [cf. Eq. (6.2)]. In our computations, for the sake of definiteness, the excitation field has been chosen such a way that the maximum local field $E_m = \max[-E(r,t)]$ yields the maximum exponential in Eq. (6.2) equal to $\exp(-E_W/E_m) = 10^{-3}$. The distributions of the photoelectron current density over the surface of a V-shape are shown Fig. 6.3. Here and below, only the phase dependence of the current will be considered. Therefore the current dependence is given relative to its global maximum in time and space (which is arbitrarily ascribed a value of 1). From this figure, it is evidenced that, irrespectively of $\varphi$, the maximum photocurrent density is concentrated at a hot spot at the apex (tip) with weak emitting spots elsewhere on the surface. Importantly, the magnitude of the current
Figure 6.2: Temporal dependencies of local electric optical field (the \(y\) component, in units of excitation field \(E_0\)) at the apex of V-shape for values of absolute phase \(\varphi\) indicated in panels. The black squares denote the temporal points contributing to the current in Eq. (6.2) where the \(\Theta\) function arguments are positive; the gray triangles denote the points that do not contribute to the photocurrent. The corresponding excitation pulses are shown in the insets at the upper right corners of the corresponding panels.
changes by 60%, which is a very strong absolute-phase dependence.

Integrating \( j(r) \) over the surface of the V-shape, it has been obtained the following result and it can be seen in Fig. 6.4(a) the total current as a function of the absolute phase, \( J(\varphi) \). It has been seen that this function has multiple maxima, but one of these maxima, at \( \varphi \approx \frac{3\pi}{2} \), dominates. Given the large amplitude of the \( \varphi \)-dependence, this maximum is quite suitable for the calibration of the absolute phase. To understand the physical origin of this maximum and generally the absolute phase sensitivity of the photoemission, let us compare with Fig. 6.2. Only at this value of \( \varphi = \frac{3\pi}{2} \), the minimum (negative maximum) of the field occurs at \( A(t) < 0 \) (as described by the black squares in contrast to the gray triangles). This implies that electrons, which are most efficiently emitted at the negative field maximum, drift \textit{toward} the free space and create the observable current, in contrast to the other \( \varphi \)
Figure 6.4: Total current $J$ as a function of absolute phase $\varphi$ for: (a) V-shape at $\hbar \omega_0 = 1.55$ eV, and (b) RPC at $\hbar \omega_0 = 1.25$ eV. The current $J(\varphi)$ is plotted in relative units where its maximum is ascribed a value of 1.

While it is possible to find the absolute phase from the electron emission at smooth surfaces [77, 78], the advantage of using a metal nanostructured system for this purpose is a relatively large value of the local field, enhanced by a factor of $\approx 5$ (cf. Fig. 6.2), which allows one to observe the same photocurrent at the excitation intensities $\approx 25$ times lower than for a flat metal surface. As an example, in our case the peak instantaneous intensity of local field can be estimated to be $1.2 \cdot 10^{14}$ W/cm$^2$ corresponding to the Keldysh parameter that is reasonable small, $\gamma \approx 0.9$. At the same time, the required peak intensity of the excitation radiation is much smaller, $4.8 \cdot 10^{12}$ W/cm$^2$. 
Now consider the RPC nanosystem whose geometry is shown in Fig. 6.1(b) where it have been carried out that the computations for $\hbar \omega_0 = 1.25$ eV radiation, close to the communications range. They show that the peak amplitude of the local fields is in this case significantly higher, $E_m \approx 20$, which corresponds to the peak local-field intensity enhanced by a factor of $\approx 400$ (the data not shown). Similar to the case of a V-shape, for the RPC the spatial distributions of the emission current are not significantly dependent on $\varphi$, as the data shown in Fig. 6.5 show. The corresponding dependence of the total photocurrent on the absolute phase shown in Fig. 6.4(b) shows high enough modulation $\approx 30\%$ that is also quite suitable for the absolute phase determination. Note that the maxima in Figs. 6.4 (a) and (b) are reached at different phases $\varphi$ which certainly is related to different proximities to the corresponding surface plasmon resonances.
6.5 Conclusion

To conclude, strong optical-field emission of electrons from a metal nanostructure excited by extremely short (one optical oscillation) pulses have been investigated. This photoemission is shown to be highly sensitive to the absolute (carrier-envelope) phase of these pulses. The local optical field enhancement taking place in metal plasmonic nanostructures results in this effect to occur at an order of magnitude or more lower intensities than in other systems, including flat metal surfaces. These results have a two-pronged significance. First, this effect opens up new possibilities in the physics of a wide class of enhanced optical phenomena and their spatio-temporal control on the fastest possible temporal scale $\sim 100$ as, within single or a few optical oscillations. There are prospective direct applications of this effect in the ultrafast nanoscale optoelectronics, e.g., for attosecond, phase-controlled injection of carriers from metal to other systems: molecular, metal, and semiconductor. Even wider class’ applications are foreseen as a tool in the study of ultrafast phenomena in other systems. This includes in particular, the absolute phase determination of relatively low intensify ultrashort laser pulses and those of optical radiation emitted by various chemical and biological objects including atoms, molecules, clusters, and condensed matter.
Chapter 7

Nanolocalized nonlinear electron photoemission under coherent control

7.1 Introduction

In this Chapter I will theoretically show that two-photon coherent control yields electron photoemission from metal nanostructures that is localized in nanosize hot spots whose positions are controllable on a nanometer scale, in agreement with recent experiments. I propose to use silver V-shapes as tailored nanoantennas for which the position of the coherently controllable photoelectron emission hot spot can be deterministically predicted. The main results in this chapter has been published in
In various fields of nanoscience and nanotechnology, one of the key processes to achieve is controlled photoinduced injection of charges into nanoscopic regions of semiconductor or metal systems, or vacuum. It is very important to perform this injection as an ultrafast processes, on femtosecond or subfemtosecond scale and have a possibility to choose the injection nanosite dynamically with a nanometer-scale resolution. Such processes can be used, for instance, in site-specific, time-resolved electron-excitation spectroscopy of molecules and nano-objects; its technological applications are possible in superfast nano-optoelectronics to transfer signals from optical to electronic components. There are, however, major obstacles to implement such processes. One of them is that light cannot be focused to nanoscopic regions directly. Using the adiabatic transformation, it is possible to transfer the optical excitation energy and coherence to the nanoscale [87]; however, such a concentration and the electron photomission caused by it are static in space. Recently it has been proposed that to use the coherent control to dynamically concentrate the optical excitation energy in space and time on the nanometer-femtosecond scale [80, 81]. For nonlinear photoprocesses, not only such a concentration is possible, but also the time-integral is coherently controllable [81]. This phenomenon has been later observed for two-photon electron emission from random nanostructured metal systems [88] using two-pulse, interferometric coherent control in combination with electron microscopy.

In this work, it will be pursued that the following two related goals: (a) it will
be shown that the two-photon (interferometric) coherent control allows one to dynamically control electron emission from randomly rough surfaces, which is localized within a few nanometers; it has been also proposed that the metal nanoantennas whose photoelectron emission is predictable, highly localized, and coherently controllable. (b) The photoelectron emission from metal nanostructures in the strong-field (quasistationary) regime has been predicted. In this regime it allows coherent control with extremely high contrast, suitable for nanoelectronics applications.

Consider a specific variant of the coherent control where a femtosecond excitation pulse consists of two identical laser subpulses with a controllable temporal delay $\tau$ between them, as shown in Fig. 7.1(a), which excite a nanosystem of the type shown in Fig. 7.1(b). Such an excitation directly models the interferometric coherent control of experiments [88]. The physics of the coherent control in this case is very transparent. The first subpulse excites an oscillating polarization in the nanostructured system. Because different sites of a nanostructure have different eigenmodes localized at them [89], and these eigenmodes generally have different frequencies, there will be phase shifts accumulated between them during the first subpulse and subsequent delay $\tau$. When the second subpulse arrives, it will do a positive work on those oscillations that are in phase with it enhancing them and depleting energy of the out-of-phase oscillations. By a proper choice of $\tau$, any given “hot spot” of the polarization can be enhanced to its maximum or, to the opposite, suppressed.

The contrast of this control depends on the relaxation polarization time $T_p$ with
respect to the typical delay \( \tau \) which is on order or greater than the pulse length \( T \). In turn, the minimum difference \( \Delta \omega \) in eigenfrequencies that can be resolved (discriminated between) by this coherent control is \( \Delta \omega \gtrsim 1/\tau \gtrsim 1/T_p \). Time \( T_p \) depends on frequency \( \omega \) and ranges from several femtoseconds in the blue region to \( \sim 100 \) fs in the near infrared (ir) [90, 91, 92]. For \( \Delta \omega \gtrsim 1/T_p \) the control contrast is high, in the opposite case it becomes low.

### 7.2 Two photon emission

First consider an excitation pulse not too intense, so the response of the nanosystem to it is linear. It has been also assumed that the size of the system is much less than the wavelength and use the quasistatic approximation. Then the local field potential \( \varphi(\mathbf{r}, t) \), induced by the external (excitation) potential \( \varphi_0(\mathbf{r}, t) \), is determined by the retarded Green’s function \( G^r(\mathbf{r}, \mathbf{r}'; t) \) of the system [80, 81]

\[
\varphi(\mathbf{r}, t) = \varphi_0(\mathbf{r}, t) - \int \varphi_0(\mathbf{r}', t') \frac{\partial^2}{\partial \mathbf{r}^2} G^r(\mathbf{r}, \mathbf{r}'; t - t') \, d^3 r' \, dt'. \tag{7.1}
\]

It has been considered that each of the two subpulses to have a Gaussian envelope with carrier frequency \( \omega_0 \), duration \( T \), linear \( z \) polarization, and amplitude \( E_0 \),

\[
\varphi_0(\mathbf{r}, t) = -zE_0 \exp \left[ -(t/T)^2 \right] \cos (\omega_0t). \tag{7.2}
\]

Then the local electric field in the nanosystem is given by
Figure 7.1: (a) Example of electric field of excitation pulse ($\tau = 5$ fs, $T = 8$ fs). (b) Geometry of nanosystem in the cross section through the $xz$ plane of symmetry. The units in $x$ and $z$ axes are are nm; the thickness of the system in the $y$ direction is 4 nm.
\[ \mathbf{E}(\mathbf{r}, t) = -\nabla \left[ \varphi(\mathbf{r}, t - \tau) + \varphi(\mathbf{r}, t) \right], \]  
\[(7.3)\]

where \( \varphi(\mathbf{r}, t) \) is computed from Eq. (7.1) with \( \varphi_0(\mathbf{r}, t) \) given by Eq. (7.2).

It has been assumed that \( W_f > h\omega_0 > W_f/2 \), where \( W_f \) is the metal workfunction. Then the electron emission is predominantly two-photon. It has been considered that the nanosystems that are planar in the \( xz \) plane [cf. Fig. 7.1(b)] with some small thickness \( b \approx 4 \text{ nm} \) in the \( y \) direction. It has been assumed that only the electrons emitted in the positive \( y \) direction are detected. Under these conditions, the electron current density \( J(x, z) \) in the plane \( (xz) \) of the nanostructure, integrated over time, is proportional to

\[ J(x, z, \tau) \propto \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dy \Theta(\mathbf{r}) E(\mathbf{r}, t)^2, \]
\[(7.4)\]

where \( \Theta \) is a characteristic function equal to 1 inside the metal nanostructure and zero otherwise. Note that the time-integrated current \( J(x, z, \tau) \) depends on the delay time, \( \tau \), between the subpulses as a parameter.

### 7.3 Numerical example

Numerical computations have been performed for an example of the random planar nanostructure shown in Fig. 7.1(b) using Eqs. (7.1)-(7.4). I chose silver as the metal because it has the smallest optical losses of any natural metal in the visible and ir
spectrum [17]. The results are shown in Fig. 7.2. As one can see, for two delay times, \( \tau = 4.45 \) fs and \( \tau = 5.09 \) fs, that differ only by 0.64 fs (approximately half of optical period), the hot spot of electron emission (shown by the red) moves within 2 nm to the neighboring position [panels (a) and (b)], and then returns back in a fraction of the optical period [panel (c)]. For a longer delay [panel(d)], this hot spot moves by \( \sim 10 \) nm to a new position. Thus, it is possible to coherently control the position of the two-photon excitation of the electron emission within the entire nanostructure with a resolution of just a few nm. Note that this kinetics of hot spots “blinking” with the delay time, shown in Fig. 7.2, is in an excellent qualitative agreement with the experimental data [88].

Also similar to the experiment [88], there are two problems with this picture. First, this is a random nanostructure, and the position of any hot spot is completely random, which may not be desirable for various applications. Second, the contrast of the coherent control is not very high: the ratio of the maximum to minimum intensity of any hot spot as a function of \( \tau \) does not exceed 10 : 1, which may not be enough for certain applications. The cause of a moderate contrast is certainly insufficiently long polarization relaxation time in the near-uv region. However, if the photon energy is significantly decreased to increase \( T_p \), then the two-photon electron emission from clean silver is impossible. This can be remedied in by using a coverage with a thin layer of an alkali metal to decrease \( W_f \), as is made industrially in photomultipliers. Also, one can use the photoemission not into vacuum, but into a semiconductor, with
Figure 7.2: (color) Density of the integrated photoemission current in the plane of the nanosystem shown in Fig. 7.1, made of silver, for $\hbar \omega = 3$ eV. Scales are in nm, the maximum current (in relative but consistent units) and the delay are shown above the corresponding plots. Color scale of the current density is shown to the right of the panels.

the corresponding electric bias. Below, it has been considered that the photoemission in the near-ir, for $\hbar \omega_0 = 1.25$ eV.

Next, I consider not a random planar system as above, but V-shapes with different angles: Fig. 7.3 shows the geometry of two such V-shapes with the central angles of 28 and 51 deg. By this it has been pursued to have a completely reproducible nanoantenna- photoelectron emitter with controllable properties. From Fig. 7.3 it can
Figure 7.3: (color) (a)-(d): Same as in Fig. 7.2 but for the V-shapes of the geometry shown in the plots where the angle of a V-shape is shown on the plots. (e): Integrated current density at the hot spots (relative units) as a function of delay $\tau$ at the openings of the two V-shapes, identified by color.
be seen that the hot spot of the photon-emission for each of the V-shapes, depending on the delay $\tau$, can localize either at the opening of a V-shape [(a) and (d)] or in its middle [(b) and (c)]. This allows for the coherent control of the hot spot localization both within a given type of the nanoantennas, or between them. More insight into this controllability can be obtained from Fig. 7.3(e) where it has been shown that the electron currents from the openings of these two V-shapes as functions of the delay. For relatively small delays, $\tau < 30$ fs, these two dependencies oscillate practically in phase. However, at longer delays, there is a phase shift accumulating between them, that reaches approximately a half of the optical cycle for $\tau \approx 80$ fs. This is certainly due to the different frequencies of the eigenmodes that are localized at the openings of these two V-shapes. Note that the decay of the photocurrent with $\tau$ is certainly not monoexponential, which shows involvement of several eigenmodes, as also was noticed in the experiment [88].

### 7.4 Conclusion

To summarize the major results of this work, theory of localized optically-nonlinear photoelectron emission from metal nanostructures under two-pulse (interferometric) coherent control has been developed. For two-photon emission from random metal nanostructures, it has been shown that the coherent control allows one to move the hot spots of the electron emission within distances of $\sim 1 - 10$ nm. However the contrast of the dependence on the control parameter (delay $\tau$ between the pulses)
is not extremely high, and the positions of the hot spots are quasirandom. These findings are in a good qualitative agreement with experiments [88]. Silver V-shape nanostructures with different angles have been proposed as engineered nanoantennas, for which the position of the hot spots and the delays required to move these hotspots along the nanostructures are deterministically predicted.

To radically increase the spatial selectivity (contrast) of the coherent control, it has been proposed that to employ the high-field [see Chapter 6], low frequency (quasistationary) electron photoemission for which the dependence on the control parameter is exponentially strong. The theory for such photoemission from metal nanostructures has been developed. As a result, it has been shown that any of the two nano-V-shapes can be extremely selectively excited depending on the interpulse delay. Such systems can be used in different applications (nanospectroscopy, nanoelectronics, etc.) for nanolocalized, controllable photoinjection of electrons.
Chapter 8

Electronic properties of graphene

8.1 Introduction

The recent discovery of elusive two-dimensional form of carbon called graphene [95] has unusual electronic properties that may be useful in the design of new electronic devices. Recently there has been a great deal of interest in this high mobility conducting material [96, 97, 98]. One of the factors which makes graphene so attractive for research is the low-energy dynamics of electrons in graphene. Those electrons can be described by a two dimensional Dirac-Weyl equation and electrons in graphene behave as massless chiral fermions [99], i.e., “relativistic” electrons. The chiral nature [see Sec.8.4] of electron states in single-layer, as well as bilayer [100], graphene is of crucial importance for electron tunneling through potential barriers, and thus for the physics of electronic devices such as carbon transistors [98]. From the point of view of
its electronic properties, graphene is a two-dimensional zero-gap semiconductor and its low-energy quasiparticles are formally described by the Dirac-like Hamiltonian [101, 102, 103]

$$\mathcal{H} = -i\hbar v_F \sigma \nabla,$$

(8.1)

where $v_F \approx 10^6 m.s^{-1}$ is the Fermi velocity, $\sigma = (\sigma_x, \sigma_y)$ are the Pauli matrices and $\nabla = (\partial_x, \partial_y)$. This description is theoretically accurate [101, 102, 103] and has also
been experimentally proven [96].

The fact that charge carriers in graphene are described by the Dirac-like equation Eq. (8.1) rather than the usual Schrodinger equation. This is a consequence of graphene’s crystal structure, which consists of two equivalent carbon sublattices A and B [101, 102, 103] [see Fig. 8.1]. Quantum mechanical hopping between the sublattices leads to the formation of two energy bands, and their intersection near the edges of the Brillouin zone yields the conical energy spectrum near the “Dirac” points $K$ and $K’$ which introduce two valleys into the problem. Therefore, quasiparticles in graphene exhibit the linear dispersion relation

$$E = \hbar kv_F,$$  \hspace{1cm} (8.2)

with double valley degeneracy. In contrast to the conventional metals and semiconductors, where the energy spectrum can be approximated by a parabolic (free-electron-like) dispersion relation one can expect that graphene’s quasiparticles behave differently due to the linear spectrum.

Graphene is made up of carbon atoms arranged in a hexagonal lattice shown schematically in Fig. 8.1. This lattice can be described by the following two vectors [106]

$$\mathbf{a}_1 = \left( \frac{3}{2}a_0, \frac{\sqrt{3}}{2}a_0 \right) \quad \text{and} \quad \mathbf{a}_2 = \left( \frac{3}{2}a_0, -\frac{\sqrt{3}}{2}a_0 \right)$$  \hspace{1cm} (8.3)

The unit cell contains two carbon atoms corresponding to the positions marked A and B in Fig. 8.1. Here $a_0 = 0.136$ nm represents the distance between two nearest-neighbor carbon atoms.
8.2 Bonding in Carbon

2s and 2p orbitals of Carbon have very similar energies [see Fig. 8.2] [104]. Therefore, like many of the first-row elements of the Periodic Table, Carbon has atomic orbitals that can hybridize. As a result, carbon can adapt to form chemical bonds with different geometries. Carbon has four electrons to form bonds: two 2s electrons and two 2p electrons. All four electrons are in the \( n = 2 \) (\( n \)-principal quantum number) quantum energy state of the atom.

Depending on the chemical circumstances, carbon atom forms a number of hybridized atomic orbitals. Carbon atoms in the elemental substances (e.g., diamond, graphite, fullerenes) bonds to each other covalently, by sharing of electron pairs. The covalent bonds have directional properties. It gives remarkable properties to the car-
bon, in particular, to adapt into various molecular and crystalline structures. Each carbon atom makes bonds with three neighboring atoms [see Fig. 8.1] where the three nearest neighbor vectors in real space are given by:

\[
\tau_1 = \frac{a_0}{2} \left( 1, \sqrt{3} \right), \quad \tau_2 = \frac{a_0}{2} \left( 1, -\sqrt{3} \right) \quad \text{and} \quad \tau_3 = (a_0, 0). \quad (8.4)
\]

There are two types of bonds: a bonds involving electrons in the \(2s, 2p_x\) and \(2p_y\) orbitals of carbon, and \(\pi\) bonds involving electrons in the \(2p_z\) orbitals [105]. Electrons can occupy the following orbitals [see Fig. 8.3].

- \(4sp^3\), Fig.8.3(a), no \(\pi\) orbitals (no p-orbitals available for bonding).
- \(3sp^2\), Fig.8.3(b), one \(\pi\) orbitals (one p-orbitals available for bonding).
- \(2sp\), Fig.8.3(c), two \(\pi\) orbitals (two p-orbitals available for bonding).

Figure 8.3: Orbital configurations of bonding in Carbon. From [105]
8.3 Electronic band structure: Nearest-neighbor tight-binding model

The electronic band structure of graphene can be calculated using the tight-binding approximation [106]. Only electrons in the \(2p_z\) orbitals which give rise to the \(\pi\) band and account for the transport properties of graphene are considered. To calculate the electronic band structure of graphene, I will denote the functions with subscript 1 and 2 corresponding to the sublattices of carbon atoms A and B, respectively [107]:

\[
\xi_1 = \frac{1}{\sqrt{N}} \sum_n e^{ik_{1n}} \varphi_1(r - R_{1n}),
\]

\[
\xi_2 = \frac{1}{\sqrt{N}} \sum_n e^{ik_{2n}} \varphi_2(r - R_{2n}),
\]

where, \(k\) is the wave vector, \(N\) is the arbitrarily large number of unit cells considered, \(\varphi_1(r)\) and \(\varphi_2(r)\) represent the \(p_z\) orbitals of carbon atoms A and B respectively, \(n\) denotes the unit cell and \(R_{1n}\) and \(R_{2n}\) correspond to the positions of carbon atoms A and B, respectively, in cell \(n\). The two Bloch functions \((\xi_1, \xi_2)\), constructed from atomic orbitals for the two inequivalent carbon atoms at A and B, in Fig. 8.1, provide the basis functions for 2D graphite (graphene). In order to solve the Schrödinger equation, a linear combination of Bloch functions has been considered, i.e., \(\xi = a\xi_1 + b\xi_2\).

Let \(\mathcal{H}\) be the Hamiltonian for an electron in the atomic potential given the atoms in the graphene lattice. Before we calculate the eigenvalues, we should start with the
Figure 8.4: (color) Electronic band structure of graphene. The conductance band touches the valence band at the $K$ and $K'$ points.

terms $\mathcal{H}_{ij} = \langle \xi_i | \mathcal{H} | \xi_j \rangle$. In the tight-binding approximation, only the following terms are considered: (i) $\langle \varphi_a | \mathcal{H} | \varphi_a \rangle = \alpha$, and $\varphi_a$ is the $2p_z$ atomic orbital of a carbon atom $a$, (ii) $\langle \varphi_a | \mathcal{H} | \varphi_b \rangle = \gamma_0$, if the carbon atoms $a$ and $b$ are nearest neighbors where $\gamma_0$ is the transfer integral between the nearest-neighbor carbon atoms and (iii) $\langle \varphi_a | \varphi_b \rangle = \delta_{ab}$.

Without losing generality, we shall set $\alpha = 0$, which corresponds to a simple shift in the zero energy. It follows that

$$\mathcal{H}_{11} = \mathcal{H}_{22} = \langle \xi_1 | \mathcal{H} | \xi_1 \rangle = \alpha = 0,$$

$$\mathcal{H}_{12} = \mathcal{H}_{21} = \langle \xi_1 | \mathcal{H} | \xi_2 \rangle.$$

These matrix elements can be calculated by considering that each atom is surrounded by three neighbors. For an atom of type A, neighbors are of type B, [Fig. 8.1].
Finally we can get the following two equations,

\[ \langle \xi_1 | \mathcal{H} | \xi \rangle \Rightarrow a \mathcal{H}_{11} + b \mathcal{H}_{12} = a \mathcal{E}(k), \quad \langle \xi_2 | \mathcal{H} | \xi \rangle \Rightarrow a \mathcal{H}_{21} + b \mathcal{H}_{22} = b \mathcal{E}(k). \quad (8.9) \]

The nonzero solution for the coefficients \( a \) and \( b \) exists only if the corresponding determinant is zero.

\[ \begin{vmatrix} -\mathcal{E}(k) & \mathcal{H}_{12} \\ \mathcal{H}_{21} & -\mathcal{E}(k) \end{vmatrix} = 0. \quad (8.10) \]

As we discussed, for the off diagonal matrix element \( \mathcal{H}_{12} \) (and \( \mathcal{H}_{12}^* \)), we must consider the three nearest neighbor B atoms relative to an A atom, which were denoted by vectors \( \tau_1, \tau_2 \) and \( \tau_3 \). Therefore, \( \mathcal{H}_{12} \) can be written as [107];

\[ \mathcal{H}_{12} = \gamma_0 \ f(k) = \gamma_0 \left( e^{i k \cdot \tau_1} + e^{i k \cdot \tau_2} + e^{i k \cdot \tau_3} \right) \quad (8.11) \]

where \( f(k) \) is a function of the sum of the phase factors of \( e^{ik \cdot \tau_j} \) \( (j = 1, 2, 3) \). Using the coordinates in Fig. 8.1, \( f(k) \) can be written as:

\[ f(k) = e^{-ia_0 k_x} + 2 \ e^{ia_0 k_x} \ \frac{\sqrt{3}a_0 k_y}{2} \cos \left( \frac{\sqrt{3}a_0 k_y}{2} \right) \quad (8.12) \]

The solution of the determinant gives the dispersion relation [107]

\[ \mathcal{E}(k) = \pm \gamma_0 \sqrt{|f(k)|^2} \quad (8.13) \]

which can be rewritten in the form

\[ \mathcal{E}(k_x, k_y) = \pm \gamma_0 \sqrt{1 + 4 \cos \left( \frac{\sqrt{3}a_0}{2} k_y \right) \cos \left( \frac{a_0}{2} k_x \right) + 4 \cos^2 \left( \frac{a_0}{2} k_x \right)} \quad (8.14) \]
It is clear that $\mathcal{E}(\mathbf{K}) = \mathcal{E}(\mathbf{K}') = 0$, where the $\mathbf{K}$ and $\mathbf{K}'$ points at the corners of the Brillouin zone are given as

$$K = \frac{2\pi}{a_0} \left( \frac{1}{3}, \frac{1}{\sqrt{3}} \right) \quad \text{and} \quad K' = \frac{2\pi}{a_0} \left( \frac{1}{3}, -\frac{1}{3\sqrt{3}} \right)$$

(8.15)

respectively. Near the $\mathbf{K}$ and $\mathbf{K}'$ we have $\mathcal{E}(\mathbf{k} + \mathbf{K}) = \mathcal{E}(\mathbf{k} + \mathbf{K}') \approx \gamma \sqrt{k_x^2 + k_y^2}$ for $|\mathbf{k}| a_0 \ll 1$ where, $\gamma = \frac{\sqrt{3}}{2} \gamma_0$ with $a = 0.246$ nm is the lattice constant and $\gamma_0 = 3.03$ eV. This linear dispersion in the vicinity of the $\mathbf{K}$ and $\mathbf{K}'$ plays decisive roles in electronic and transport properties of graphene.

The electronic band structure of graphene is shown in Fig. 8.4. The conduction band is corresponding to positive energies, meanwhile, the valance band is corresponding to negative energies, which are totally filled. This is due to the fact that the number of electrons is equal to the number of orbitals. The Fermi level corresponds to zero energy [see Fig. (8.5)].
Figure 8.6: Reciprocal lattice and first Brillouin zone of graphene (shaded). The vectors $\mathbf{b}_1$ and $\mathbf{b}_2$ are the basis vectors of the lattice, where $K$ and $K'$ are Dirac points.

One can clearly see in the Fig. 8.4 that the valance band and the conduction band touch one another at six points. As we discussed in Sec. 8.1, these are the Dirac points. These points are also shown in Fig. 8.6, which illustrates the first Brillouin zone of graphene in the reciprocal lattice. Note that the first Brillouin zone is the smallest volume entirely enclosed between the mediating planes of the reciprocal lattice vectors. In this figure the basis vectors $\mathbf{b}_1$ and $\mathbf{b}_2$ of the reciprocal lattice are defined by the following two equations [see Eq. (8.16)], with the condition $\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij}$,

$$
\bar{\mathbf{b}}_1 = \frac{2\pi}{3a_0} \left( 1, \sqrt{3} \right), \quad \bar{\mathbf{b}}_2 = \frac{2\pi}{3a_0} \left( 1, -\sqrt{3} \right)
$$

(8.16)
8.4 Effective mass description: k-p model

In this section I will discuss key steps to determine the effective mass or \( k \cdot p \) model describing states in the vicinity of \( K \) and \( K' \) based on the nearest neighbor tight binding model. The states in the vicinity of the Fermi level of the graphene can be written as [108]:

\[
\psi_A(R_A) = \chi_a(R_A)F_A(R_A), \quad \psi_B(R_B) = \chi_b(R_B)F_B(R_B) \tag{8.17}
\]

where \( \chi_a(R_A), \chi_b(R_B) \) are two component vectors with \( R_A = n_a a_1 + n_b b_1 + \tau_1 \) and \( R_B = n_a a_1 + n_b b_1 \). Here \( n_a, n_b \) are integers, and \( F_A = (F^K_A, F'^K_A) \) and \( F_B = (F^K_B, F'^K_B) \) are the slowly varying envelope functions defined in Ref. [108]. Since I am interested in the final result of the \( k \cdot p \) model, I will not show all the steps in the calculation here. Detailed calculations can be found in Ref. [108].

As a final result, the equation for \( F_B(r) \) can be written as [108]:

\[
E_F A(r) = \gamma \begin{pmatrix} \hat{k}_x - i\hat{k}_y & 0 \\ 0 & \hat{k}_x + i\hat{k}_y \end{pmatrix} F_B(r), \tag{8.18}
\]

where \( \hat{k} \equiv -i \nabla \). Similar equation can be written for \( F_A(r) \) as

\[
E_F B(r) = \gamma \begin{pmatrix} \hat{k}_x + i\hat{k}_y & 0 \\ 0 & \hat{k}_x - i\hat{k}_y \end{pmatrix} F_A(r). \tag{8.19}
\]

Using Eqs. (8.18) and (8.19) the full Schrödinger equation is given by

\[
\mathcal{H}F(r) = E F(r) \tag{8.20}
\]
where,
\[
\mathcal{H} = \gamma \begin{pmatrix}
KA & KB & K'A & K'B \\
0 & (\hat{k}_x - i\hat{k}_y) & 0 & 0 \\
(\hat{k}_x + i\hat{k}_y) & 0 & 0 & 0 \\
0 & 0 & 0 & (\hat{k}_x + i\hat{k}_y) \\
0 & 0 & (\hat{k}_x - i\hat{k}_y) & 0
\end{pmatrix}
\]
(8.21)

\[
F(r) = \begin{pmatrix} F^K_A(r) \\ F^K_B(r) \\ F^{K'}_A(r) \\ F^{K'}_B(r) \end{pmatrix}
\]
(8.23)

It can be easily shown from Eq. (8.22), that the Hamiltonian of a single valley system is given by an expression (near the K points),
\[
\mathcal{H} = \gamma \begin{pmatrix}
K A & K B \\
0 & (\hat{k}_x - i\hat{k}_y) \\
(\hat{k}_x + i\hat{k}_y) & 0
\end{pmatrix}
= \frac{\gamma}{\hbar} (\vec{\sigma} \cdot \vec{p}),
\]
(8.25)

where \(\vec{\sigma}\) are the Pauli matrices, \(\vec{p} = -i\partial/\partial\vec{r}\).

Using the Eq. (8.25) one can clearly understand the chiral nature of electron states in graphene. For a one dimensional system (say \(k_y = 0\)), Eq. (8.25) can be reduced to the following simple form of Hamiltonian,
\[
\mathcal{H} = \gamma \begin{pmatrix}
0 & k_x \\
k_x & 0
\end{pmatrix},
\]
(8.26)
and the corresponding determinant is

\[
\begin{vmatrix}
-\mathcal{E} & \gamma k_x \\
\gamma k_x & -\mathcal{E}
\end{vmatrix} = 0.
\]

(8.27)

Therefore, the dispersion relation can be written as

\[
\mathcal{E} = \gamma k_x, \quad \text{with} \quad \begin{pmatrix} F^K_A \\ F^K_B \end{pmatrix} = e^{ikr} \begin{pmatrix} 1 \\ 1 \end{pmatrix}
\]

(8.28)

and

\[
\mathcal{E} = -\gamma k_x, \quad \text{with} \quad \begin{pmatrix} F^K_A \\ F^K_B \end{pmatrix} = e^{ikr} \begin{pmatrix} 1 \\ -1 \end{pmatrix}.
\]

(8.29)

This relation can be seen in Fig. 8.7(a). One can see clearly from the figure (a), that for a linear dispersion relation, the electron can have both positive and negative energies, while in Fig. 8.7(b) for the parabolic dispersion relation it can have only
positive energies. Owing to the linear spectrum, it is expected that graphene quasiparticles will behave differently from those in conventional metals and semiconductors where the energy spectrum can be approximated by a parabolic (free-electron-like) dispersion relation [panel (b)]. From Fig. 8.7(a) we can clearly see that backscattering, i.e., scattering from $k_x$ to $-k_x$, is strongly suppressed, because they are different states.
Chapter 9

Electron localization in graphene quantum dots

9.1 Introduction

In this Chapter I will discuss a localized state of an electron in a graphene quantum dot with a sharp boundary. Due to Klein’s tunneling, the “relativistic” electron in graphene cannot be localized by any confinement potential. In this case the electronic states in a graphene quantum dot become resonances with finite trapping time. I consider these resonances as the states with complex energy. To find the energy of these states we solve the time-independent Schrödinger equation with outgoing boundary conditions at infinity. The imaginary part of the energy determines the width of the resonances and the trapping time of an electron within quantum dot. I
will show that if the parameters of the confinement potential satisfy a special condition then the electron can be strongly localized in such quantum dot, i.e., the trapping time is infinitely large. In this case the electron localization is due to interference effects. I will theoretically show how the deviation from this condition affects the trapping time of an electron. I also analyze the energy spectra of an electron in a graphene quantum ring with a sharp boundary. The main results in this chapter has been published in Phys. Rev. B [109].

Due to the unique nature, which we discussed in Chapter-8, electronic properties of elusive purely two-dimensional form of carbon called graphene [95], have been intensively studied since the discovery of the anomalous quantum Hall effect [96, 97, 110]. Graphene is a gapless semiconductor, in which the conduction and the valence bands are touching in two inequivalent points [see Fig. 8.4], corresponding to two valleys. Due to the unique band structure of graphene, the charge carriers are massless chiral fermions [99], i.e., massless “relativistic” electrons. Such electrons can cross large potential barriers with almost unity probability [98]. Therefore, the electrons in graphene cannot be localized by any confinement potential. This effect is called Klein’s paradox [111] and is related to the fact that electrons in graphene can have both positive and negative energies.

Also we can understand this remarkable property of electrons in graphene in the following way: when a potential barrier is smaller than the gap separating electron and hole bands in semiconductors, the penetration probability decays exponentially
with the barrier height and width. Otherwise, resonant tunneling is possible when the energy of the propagating electron coincides with one of the hole energy levels inside the barrier. In graphene the gap is zero, therefore the transmission probability for normally incident electrons is always equal to unity, irrespective of the height and width of the barrier [98].

In quantum electrodynamics, this behavior is related to the Klein paradox. This phenomenon usually refers to a counterintuitive relativistic process in which an incoming electron starts penetrating through a potential barrier, if the barrier height exceeds twice the electron’s rest energy $m_0c^2$. In this case, the transmission probability $t$ only depends weakly on barrier height, approaching perfect transparency for very high barriers, in stark contrast to conventional, nonrelativistic tunneling. This relativistic effect can be attributed to the fact that a sufficiently strong potential, being repulsive for electrons, is attractive to positrons, and results in positron states inside the barrier. These align in energy with the electron continuum outside the barrier. Matching between electron and positron wave functions across the barrier leads to the high-probability tunneling described by the Klein paradox. In other words, it reflects an essential difference between nonrelativistic and relativistic quantum mechanics. In the former case, we can accurately measure either the position of the electron or its velocity, but not both simultaneously. In relativistic quantum mechanics, we even cannot measure electron position with arbitrary accuracy since, if we try to do this, we create electron-positron pairs from the vacuum and we cannot
Figure 9.1: (color) Tunnelling through a potential barrier in graphene. (a) Schematic diagrams of the spectrum of quasiparticles in single-layer graphene. The pseudospin denoted by $\sigma$ is parallel (antiparallel) to the direction of motion of electrons (holes), which also means that $\sigma$ keeps a fixed direction along the red and green branches of the electronic spectrum. (b) Potential barrier of height $V_0$ and width $D$. For the both panels $E$ is the Fermi energy.

distinguish our original electron from these newly created electrons. Graphene opens a way to investigate this counterintuitive behavior in a relatively simple benchtop experiment, whereas previously the Klein paradox was only connected with some very exotic phenomena, such as collisions of ultraheavy nuclei or black hole evaporation [112].

Therefore, when a propagating electron reaches the potential barrier it penetrates through it and emerges inside of the barrier in the state with a negative energy-hole state. This tunneling, known as Klein’s tunneling, introduces an efficient escape channel from any trapping potential.
This behavior is shown in Fig. 9.1. The red and green curves in Fig. 9.1(a) emphasize the origin of the linear spectrum, which is the crossing between the energy bands associated with crystal sublattices A and B. The cross points represent the Dirac points. The three diagrams show schematically the positions of the Fermi energy $E$ across such a barrier. The Fermi level (dotted lines) lies in the conduction band outside the barrier and the valence band inside it. The green filled areas indicate occupied states. The corresponding potential barrier of height $V_0$ and width $D$ is shown on Fig. 9.1(b).

The conical spectrum of graphene is the result of intersection of the energy bands originating from sublattices A and B [see Fig. 9.1(a)] and, accordingly, an electron with energy $E$ propagating in the positive direction originates from the same branch of the electronic spectrum (shown in red) as the hole with energy $-E$ propagating in the opposite direction. This means that electrons and holes belonging to the same branch have pseudospin $\sigma$ pointing in the same direction, which is parallel to the momentum $(k)$ for electrons and antiparallel to the momentum $(q)$ for holes [see Fig. 9.1(a)]. This allows the introduction of chirality, that is formally a projection of pseudospin on the direction of motion, which is positive and negative for electrons and holes, respectively.

Therefore, when Klein’s tunneling is taking into account, we can conclude that there are no conventional quantum dots in graphene, i.e., quantum dots [113], which can localize electrons within finite spatial regions. At the same time for future elec-
tronic applications of graphene it is quite important to realize the quantum dot trapping potential for “relativistic” electrons. Therefore, from a fundamental point of view, it is desirable to find a feasible and controllable way to realize the quantum dot trapping potential for relativistic electrons in graphene. A zero dimensionality of quantum dots and possibility of tuning the confinement potential and the electron density externally result in very broad applications of quantum dots in conventional semiconductors, ranging from lasers [114] and photodetectors [115] to quantum information processing and quantum computers [116]. Recently quantum dots created in carbon nanotubes [117, 118] and graphitic systems [119] have been also reported.

Since the electron in graphene cannot be localized we need to discuss not the localization but the trapping of an electron. Here trapping means that the electron should stay within finite spatial region for a very long time. The problem of trapping of an electron has been studied in the case of a one-dimensional wire in zero [120, 121, 122] and in finite [123] magnetic fields, and for a quantum dot with smooth [124] and sharp [125] boundaries. It was shown that the trapping potential for a “relativistic” electron in graphene is produced by transverse momentum [120, 124, 128]. In the case of a quantum dot the transverse potential is related to an electron angular momentum [124]. The larger the angular momentum, the more efficient trapping potential is created. Another factor, which strongly affects the trapping time, is the sharpness of the quantum dot boundaries, i.e., the sharpness of the confinement potential. The sharpness of the boundary of a quantum dot determines the width of the trapping
potential. Therefore the most efficient trapping is realized in a smooth confinement potential and for electronic states with large angular momentum. The trapping time of an electron in a quantum dot has exponential dependence on the angular momentum and the slope of the confinement potential [124]. Since the electron with a large trapping time can be considered as almost localized, below both terms *trapping* and *localized* have been used to describe electron states in graphene quantum dots.

Although the most efficient trapping is realized in a smooth potential, some trapping should be expected in the confinement potential with sharp boundaries [125]. In this case the trapping time has not the exponential but the power dependence on the parameters of the confinement potential.

In the present work, it has been shown that even in the case of confinement potential with sharp boundaries we can realize the trapping of the “relativistic” electron for a very long time. For special parameters of the confinement potential, which can be achieved by an additional tuning of the potential, the escape rate from some states of the quantum dot can be even exactly zero. Therefore, the “relativistic” electrons in such states are *strongly localized* with infinite trapping time. This localization is achieved not due to a large trapping potential barrier, but due to interference effects within the quantum dot. It means that the trapping properties of the quantum dot with sharp boundaries depend on the distribution of the confinement potential within the whole region of the quantum dot. This opens another possibility for tuning of the trapping properties of an electron in quantum dots. I show below that by introducing
additional holes in the quantum dots we can strongly suppress the escape rate of
an electron from the quantum dot. This effect will be illustrated by considering the
trapping properties of quantum rings with sharp boundaries.

The quantum dot considered in this work has the same structure as the one studied
in Ref. [125]. The authors of Ref. [125] discussed the resonances of the quantum dots,
which are revealed as peaks in the scattering cross section [126]. From the width of the
peaks, the lifetime or escape rate can be extracted. My approach to the problem of
the trapped states of the quantum dots is different from Ref. [125]. The trapped states
or decaying states of the quantum dot system are revealed as peaks, i.e., resonances,
in the scattering cross section or as the first-order poles of the scattering matrix in the
complex energy plane. The poles are complex, where the real part corresponds to the
energy of the resonance and the inverse of the imaginary part describes the lifetime
of the decaying state. In the present paper we use different approach to the problem
of resonances, i.e., trapped states, of the quantum dot system. This approach was
originally introduced by Gamow in Ref. [127]. In this approach the resonances are
described by eigenfunctions, Gamow’s vectors, with complex eigenvalues. The real
part of the complex eigenvalue is associated with the energy of the resonance, and
the inverse of the imaginary part of the eigenenergy is associated with the lifetime
of the decaying state. Namely, if $E$ is the complex energy of the localized state,
then the trapping time is $\tau = \hbar/\text{Im}[E]$. Here $\text{Im}[E]$ is the imaginary part of the
electron energy and $\hbar$ is the reduced Planck constant. Therefore the resonances in
this approach have complex energy and are considered as the long-lived states in the decay process [126]. Such states can be found as the time-independent solutions of the Schrödinger equation with purely outgoing boundary conditions. The stationary solutions with such boundary conditions exist only at complex eigenenergies. This approach allows us to obtain the closed form of the equation for the complex energy of the trapped states of the quantum dot. From this equation we can obtain the condition of strong localization of an electron within the quantum dot and derive some analytical results for the imaginary part of the electron energy.

9.2 Main equations: single quantum dot

To introduce a quantum dot in graphene we consider a cylindrically symmetric confinement potential, which has the following form

\[
V(r) = \begin{cases} 
0 & \text{if } r < R \\
V_0 & \text{if } r > R
\end{cases},
\]

(9.1)

where \(V_0 > 0\) and as shown in Fig. 9.2, \(R\) is the radius of the quantum dot. This shape of confinement potential allows us to obtain analytical expressions for the trapping time of the states of the quantum dot. The confinement potential in Eq. (9.1) has sharp boundaries and based on the analysis of Ref. [124] we can conclude that the trapping time of the electron within such a quantum dot is relatively small. This means that any trapping of the electron in a such potential should be related to the behavior of the wavefunctions within the whole region of quantum dot, i.e., the
trapping properties are determined by the interference effects within the quantum dot.

The Hamiltonian of a single electron in graphene with potential, determined by Eq. (9.1), is given by an expression [137] [see Sec. 8.4]

\[
\mathcal{H} = \frac{\gamma}{\hbar}(\vec{\sigma} \cdot \vec{p}) + V(r).
\]  \hspace{1cm} (9.2)

In expression (9.2) for the Hamiltonian of the system we consider a single valley only, taking into account the double valley degeneracy of the energy levels. The potential in Eq. (9.1) does not introduce any mixture between the different valleys and does not lift the valley degeneracy. In addition to the valley degeneracy each level has double spin degeneracy. Therefore, each energy level discussed below, has a fourfold degeneracy.

The wavefunction, \( \psi(\vec{r}) \), corresponding to the Hamiltonian (9.2), is a two component function. These two-components correspond to two different sublattices of
graphene honeycomb lattice. For cylindrically symmetric confinement potential the
two-component wavefunction has the following form

$$\psi(r, \theta) = e^{i(m-1/2)\theta} \begin{pmatrix} \chi_1(r) \\ \chi_2(r)e^{i\theta} \end{pmatrix},$$

(9.3)

where $r$ and $\theta$ are cylindrical coordinates, and $m = \pm 1/2, \pm 3/2, \ldots$ is orbital angular momentum. With this form of the wavefunction, the Schrödinger equation corresponding to the Hamiltonian in Eq. (9.2) becomes

$$V(r)\chi_1 - i\gamma \frac{d\chi_2}{dr} - i\gamma \frac{m + 1/2}{r} \chi_2 = E\chi_1,$$

(9.4)

$$V(r)\chi_2 - i\gamma \frac{d\chi_1}{dr} + i\gamma \frac{m - 1/2}{r} \chi_1 = E\chi_2.$$  

(9.5)

To find the energy, $E$, of the level we need to solve the system of Eqs. (9.4)-(9.5) with the following boundary conditions: (i) at $r = 0$ both $\chi_1$ and $\chi_2$ should be finite and (ii) at infinity we have outgoing boundary conditions, i.e., $\chi_1, \chi_2 \propto \exp(ikr)$.

By eliminating $\chi_1$ or $\chi_2$ in the system Eqs. (9.4)-(9.5) we can easily obtain that $\chi_1$ and $\chi_2$ satisfy Bessel’s differential equations of the order $|m - 1/2|$ for functions $\chi_1$ and of the order $|m + 1/2|$ for function $\chi_2$. Then the general solution of the system of Eqs. (9.4)-(9.5) inside the quantum dot, where $V = 0$, has the form

$$\begin{pmatrix} \chi_1(r) \\ \chi_2(r) \end{pmatrix} = A \begin{pmatrix} J_{|m-1/2|}(\varepsilon r/R) \\ iJ_{|m+1/2|}(\varepsilon r/R) \end{pmatrix},$$

(9.6)

where $J_n$ is the Bessel function of the $n$th order and we introduced the dimensionless energy $\varepsilon = RE/\gamma$. The energy and correspondingly the dimensionless energy is complex in our approach.
Outside the quantum dot, i.e., at $r > R$, the solutions of the corresponding Bessel differential equations should describe the outgoing waves, $\propto \exp(ikr)$. Therefore at $r > R$, the solution of Eqs. (9.4)-(9.5) are Hankel functions of the first kind. Then the general solution of the system of Eqs. (9.4)-(9.5) at $r > R$, where $V = V_0$, is

$$
\begin{pmatrix}
\chi_1(r) \\
\chi_2(r)
\end{pmatrix} = B
\begin{pmatrix}
H^{(1)}_{|m-1/2|}(\varepsilon - \nu_0) r/R \\
iH^{(1)}_{|m+1/2|}(\varepsilon - \nu_0) r/R
\end{pmatrix},
$$

(9.7)

where $H_n^{(1)}$ is the Hankel function of the first kind and of the $n$th order and we introduced the dimensionless confinement potential $\nu_0 = RV_0/\gamma$.

At the boundary of the quantum dot, i.e., at $r = R$, the two-component wave-function should be continuous. From this condition we can find the energy eigenvalue equation, which takes the form

$$
\frac{H^{(1)}_{|m-1/2|}(\varepsilon - \nu_0)}{H^{(1)}_{|m+1/2|}(\varepsilon - \nu_0)} = \frac{J_{|m-1/2|}(\varepsilon)}{J_{|m+1/2|}(\varepsilon)}.
$$

(9.8)

The solution of the eigenvalue equation, Eq. (9.8), determines the complex energy spectrum of the quantum dot. The imaginary part of the energy characterizes the electron trapping time at the corresponding state of the dot.

One can see that Eq. (9.8), is symmetric with respect to the change of the sign of the angular momentum, $m \rightarrow -m$. It means that the energy spectra of an electron with positive and negative angular momenta are identical. Therefore below we consider only positive values of $m$, $m = 1/2, 3/2, \ldots$
9.3 Strongly localized states in quantum dots

For a given angular momentum, $m$, the eigenvalue equation, Eq. (9.8), has been solved numerically. The results of calculations are shown in Fig. 9.3 for a few lowest values of $m$. The results are plotted in the complex energy plane. As we can see from these data the typical imaginary part of the energy is of the order of 1 (in dimensionless units). This is valid for all values of $m$. These results are consistent with the main conclusion of Ref. [124], where it was shown that the strong trapping can be achieved only in a smooth confinement potential, in which the trapping time is exponentially large.

Based on the data shown in Fig. 9.3 we can estimate the typical trapping time of the electron within the quantum dot. In the real units the imaginary part of the energy is of the order of $\gamma/R$. Then the trapping time $\tau \sim \hbar R/\gamma$. For a quantum dot of size $R = 50\,nm$ we obtain $\tau \sim 10^{-13}\,s$. This is a relatively small time and we should consider the electron in such a quantum dot as weakly trapped.

Although an electron in the confinement potential as in Eq. (9.1) is only weakly localized (the typical imaginary part of the energy is large), we can see in Fig. 9.3 that there is a region of energies, where the imaginary part of the energy becomes small. Within this region the real part of the energy is close to the trapping potential, $\nu_0$. This observation has already been reported in Ref. [125]. In addition to a strong electron trapping at $\varepsilon \approx \nu_0$, we can have the exact localization of an electron in the quantum dot if the potential, $\nu_0$, satisfies a special condition. Namely, we can see
Figure 9.3: The energy spectra of an electron in the graphene quantum dot is shown for different angular momenta, $m$ (as indicated) in the complex energy plane. For all the panels $\nu_0 = 20$.

from Eq. (9.8) that if the potential strength, $\nu_0$, is the root of the Bessel function of the order $(m - 1/2)$, i.e., $J_{m-1/2}(\nu_0) = 0$, then there is a solution of eigenvalue equation, $\varepsilon = \nu_0$, with zero imaginary part, and the electron at this level is strongly localized. Therefore, the strongly localized state of the electron in the quantum dot exists only if the potential satisfies the condition

$$\nu_0 = \lambda_{n,i},$$

(9.9)

where $\lambda_{n,i}$ is the $i$th root of the Bessel function of the order $n = 0, 1, 2, \ldots$ and $n$ is related to the angular momentum: $n = m - 1/2$. We can rewrite the expression
(9.9) in the original units. Taking into account that the unit of the energy is $\gamma/R$, we obtain

$$V_0 = \frac{\gamma}{R} \lambda_{n,i}.$$  \hfill (9.10)

For example, for $R = 50 \text{ nm}$ and $\gamma = 645 \text{ meV} \cdot \text{nm}$ we have

$$V_0 = 12.9 \lambda_{n,i}(\text{meV}).$$  \hfill (9.11)

Then for each $n$ we can find a set of the heights of the confinement potential, at which an electron can be strongly localized. These heights are shown in Table 9.1 for a few lowest values of $n$ and $i$.

Table 9.1: The heights of the confinement potential, $V_0$, at which the electron can be strongly localized, is shown for a few lowest values of $n$ and $i$. The potential satisfies Eq. (9.11). The potential strength is in units of meV. The radius of the quantum dot is $R = 50 \text{ nm}$.

<table>
<thead>
<tr>
<th></th>
<th>$n = 0$</th>
<th>$n = 1$</th>
<th>$n = 2$</th>
<th>$n = 3$</th>
<th>$n = 4$</th>
<th>$n = 5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i = 1$</td>
<td>31</td>
<td>50</td>
<td>66</td>
<td>82</td>
<td>98</td>
<td>113</td>
</tr>
<tr>
<td>$i = 2$</td>
<td>71</td>
<td>91</td>
<td>109</td>
<td>126</td>
<td>143</td>
<td>159</td>
</tr>
<tr>
<td>$i = 3$</td>
<td>112</td>
<td>131</td>
<td>150</td>
<td>168</td>
<td>185</td>
<td>203</td>
</tr>
<tr>
<td>$i = 4$</td>
<td>152</td>
<td>172</td>
<td>191</td>
<td>209</td>
<td>227</td>
<td>245</td>
</tr>
<tr>
<td>$i = 5$</td>
<td>193</td>
<td>213</td>
<td>232</td>
<td>250</td>
<td>269</td>
<td>287</td>
</tr>
<tr>
<td>$i = 6$</td>
<td>233</td>
<td>253</td>
<td>272</td>
<td>291</td>
<td>310</td>
<td>328</td>
</tr>
<tr>
<td>$i = 7$</td>
<td>274</td>
<td>294</td>
<td>313</td>
<td>332</td>
<td>351</td>
<td>369</td>
</tr>
</tbody>
</table>

Any violation of the condition $\nu_0 = \lambda_{n,i}$ introduces an escape of the electron from the quantum dot. In this relation the following question has to be addressed: How large is the trapping time of an electron in the quantum dot if the condition of localization is weakly violated, i.e., $\delta_{\nu} \equiv \nu_0 - \lambda_{m-1/2,i}$ is small and nonzero? I expect that in this case the escape rate from the quantum dot and correspondingly
the imaginary part of the energy is small. To find the imaginary part of the energy
\[ \varepsilon \approx \nu_0 \approx \lambda_{m-1/2,i} \]
of the almost localized state we can consider \( \delta_\nu = \nu_0 - \lambda_{m-1/2,i} \) as a small parameter and then from Eq. (9.8) obtain the first non-zero corrections to \( \text{Im}[\varepsilon] \).

The following notation has been introduced, \( \delta_\varepsilon \equiv \varepsilon - \nu_0 \), and I consider \( \delta_\varepsilon \) and \( \delta_\nu = \nu_0 - \lambda_{m,i} \) as small parameters. Then

\[ \varepsilon = \lambda_{m,i} + \delta_\varepsilon + \delta_\nu \quad (9.12) \]

and the right hand side of Eq. (9.8) can be rewritten in the following form

\[ \frac{J_{m-1/2}(\varepsilon)}{J_{m+1/2}(\varepsilon)} = \frac{J_{m-1/2}(\lambda_{m,i} + \delta_\varepsilon + \delta_\nu)}{J_{m+1/2}(\lambda_{m,i} + \delta_\varepsilon + \delta_\nu)}. \quad (9.13) \]

The left hand side of Eq. (9.8) in these notations becomes

\[ \frac{H^{(1)}_{m-1/2}(\varepsilon - \nu_0)}{H^{(1)}_{m+1/2}(\varepsilon - \nu_0)} = \frac{H^{(1)}_{m-1/2}(\delta_\varepsilon)}{H^{(1)}_{m+1/2}(\delta_\varepsilon)}. \quad (9.14) \]

Then the eigenvalue equation, Eq. (9.8) takes the form

\[ \frac{J_{m-1/2}(\lambda_{m,i} + \delta_\varepsilon + \delta_\nu)}{J_{m+1/2}(\lambda_{m,i} + \delta_\varepsilon + \delta_\nu)} = \frac{H^{(1)}_{m-1/2}(\delta_\varepsilon)}{H^{(1)}_{m+1/2}(\delta_\varepsilon)}. \quad (9.15) \]

The next step is to find the small-\( \delta_\varepsilon \) and small-\( \delta_\nu \) expansions of the right and left hand sides of Eq. (9.15). Since the imaginary part of the energy is searched, then we need to find both the real and imaginary terms in Eq. (9.15). The left hand side of Eq. (9.15) contains only the Bessel functions. For a real argument the expansion of the Bessel function is always real. Therefore the left hand side of Eq. (9.15) gives
the contribution only to the real terms in Eq. (9.15). Keeping only the lowest order corrections in the right hand side of Eq. (9.15), I obtain

\[
(\delta_\varepsilon + \delta_\nu) \frac{J'_{m-1/2}(\lambda_{m,i})}{J_{m+1/2}(\lambda_{m,i})} = \frac{H^{(1)}_{m-1/2}(\delta_\varepsilon)}{H^{(1)}_{m+1/2}(\delta_\varepsilon)}. \tag{9.16}
\]

The left hand side of Eq. (9.16) contains the Hankel functions. Even for the real argument the expansion of the Hankel function contains both the real and imaginary terms. Finally, the imaginary terms will determine the imaginary part of the energy. The small argument expansion of the Hankel function depends on its order, i.e., on the value of \(m\). Therefore we need to consider two cases: (i) \(m > 1/2\) and (ii) \(m = 1/2\).

Case (i): \(m > 1/2\). For \(m > 1/2\) the order of the Hankel function is greater than 0, then the small-\(\delta_\varepsilon\) expansion of the right hand side of Eq. (9.16) is

\[
\frac{H^{(1)}_{m-1/2}(\delta_\varepsilon)}{H^{(1)}_{m+1/2}(\delta_\varepsilon)} = \frac{\delta_\varepsilon}{2m - 1} + i \frac{\pi \delta_\varepsilon^{2m}}{2^{2m}[(m - 1/2)!]^2}, \tag{9.17}
\]

where both the real and imaginary terms have been considered. Combining Eqs. (9.16) and (9.17), the following equation for the correction has been obtained, \(\delta_\varepsilon\), to the energy of the electronic state in the quantum dot

\[
\frac{2m}{2m - 1} \delta_\varepsilon = -\delta_\nu - i \frac{\pi}{2^{2m}[(m - 1/2)!]^2} \delta_\varepsilon^{2m}, \tag{9.18}
\]

where the relation \(J'_{m-1/2}(\lambda_{m,i}) = -J_{m+1/2}(\lambda_{m,i})\) has been used. From this equation we can find both the real and imaginary parts of \(\delta_\varepsilon\)

\[
\delta_\varepsilon = -\left(1 - \frac{1}{2m}\right) \delta_\nu - i \frac{\pi}{2^{m}[(m - 1/2)!]^2} \left[1 - \frac{1}{2m}\right]^{2m+1} \delta_\nu^{2m}, \tag{9.19}
\]
Since \( \text{Im} \varepsilon = \text{Im} \delta \), then, if the energy of the state is close to \( \nu_0 \approx \lambda_{m-1/2,i} \), then the imaginary part of the energy has the form

\[
\text{Im}[\varepsilon] = \frac{\pi}{[2^m(m - 1/2)!]^2} \left[ 1 - \frac{1}{2m} \right]^{2m+1} \delta_\nu^{2m} \tag{9.20}
\]

for \( m > 1/2 \).

Case (ii): \( m = 1/2 \). Now in Eq. (9.16) we have Hankel functions of the zeroth order. Then the small-\( \delta \varepsilon \) expansion of the Hankel function contains the logarithm and the right hand side of Eq. (9.16) becomes

\[
\frac{H_0^{(1)}(\delta \varepsilon)}{H_1^{(1)}(\delta \varepsilon)} = -\delta \varepsilon \ln \delta \varepsilon + i \frac{\pi}{2} \delta \varepsilon. \tag{9.21}
\]

Taking into account that \( m \) in Eq. (9.16) is equal to 1/2, the following equation has been obtained for \( \delta \varepsilon \)

\[
(\delta \varepsilon + \delta \nu) \frac{J'_0(\lambda_0,i)}{J_1(\lambda_0,i)} = -\delta \varepsilon \ln \delta \varepsilon + i \frac{\pi}{2} \delta \varepsilon. \tag{9.22}
\]

Since \( \delta \varepsilon \ln \delta \varepsilon \gg \delta \varepsilon \) then in the real part of Eq. (9.22) we need to keep only \( \delta \varepsilon \ln \delta \varepsilon \) term. Taking into account that \( J'_0(\lambda_0,i) = -J_1(\lambda_0,i) \), the final equation has been obtained for \( \delta \varepsilon \)

\[
\delta \varepsilon \ln \delta \varepsilon = \delta \nu + i \frac{\pi}{2} \delta \varepsilon. \tag{9.23}
\]

This equation can be solved to find the imaginary part of the energy

\[
\delta \varepsilon = \frac{\delta \nu}{\ln \delta \nu} + i \frac{\pi}{2} \left( \frac{\delta \nu}{\ln \delta \nu} \right). \tag{9.24}
\]

Finally, Eq. (9.25) is being obtained, if we consider that \( \text{Im} \varepsilon = \text{Im} \delta \varepsilon \).

\[
\text{Im}[\varepsilon] = \frac{\pi}{2} \left( \frac{\delta \nu}{\ln \delta \nu} \right) \tag{9.25}
\]
for \( m = 1/2 \).

We can see from Eq. (9.20) that the imaginary part of the energy has an exponential dependence on \( m \), of the quasilocalized state: \( \text{Im}[\varepsilon] \propto \exp[-2m|\ln \delta\nu|] \).

Therefore, the states with large angular momentum can be trapped for a longer time than the states with small values of \( m \). At the same time the imaginary part of the energy has a weak power-law dependence on \( \delta\nu \). Another interesting fact about expressions (9.20) and (9.25) is that the coefficients in these expressions depend only on the angular momentum, \( m \), but not on the value of \( \lambda_{m-1/2,i} \).

Since \( \nu_0 = R V_0 / \gamma \), the condition of strong localization can be expressed in terms of the original parameters of the confinement potential, i.e., the strength of the potential, \( V_0 \), and \( R \),

\[
RV_0 = \gamma \lambda_{n,i},
\]

where \( n = 0, 1, 2, \ldots \) and \( i = 1, 2, \ldots \). From Eqs. (9.20)-(9.25) and (9.26) we can estimate the trapping time of the quasilocalized states for the quantum dots with spatially fluctuating parameters. For example, if the radius of the quantum dot varies within the range \( \delta R \), then from Eq. (9.20) we can find that the escape rate, i.e., imaginary part of the energy, from quasilocalized state of the dot is proportional to \( (\delta R / R)^{2m} \).

One of the manifestations of the strongly trapped state in the quantum dot is a sharp peak in the electron density of states, which can be measured in the resonant tunneling experiments or in the resonant scattering experiments. The density of states
can be expressed through the real part of the energy and the imaginary part of the energy, which now becomes the width of the resonance, by the following equation [131]

\[ g(\varepsilon) = \frac{1}{\pi} \sum_j \frac{|\text{Im}(\varepsilon_j)|}{[\varepsilon - \text{Re}(\varepsilon_j)]^2 + |\text{Im}(\varepsilon_j)|^2}, \]  

(9.27)

where the density is expressed in the dimensionless units. The density of states for \( \nu_0 = 20 \) and \( m = 3/2 \) is shown in Fig. 9.4. We can clearly see a sharp maximum at the energy close to \( \nu_0 \). This maximum corresponds to the highly trapped state of electron within the quantum dot.

The existence of a highly trapped state of electron in the quantum dot, i.e., the state with small imaginary part of the energy is due to the interference effect. It means that the imaginary part of the energy of such a state is very sensitive to the
exact profile of the confinement potential. The deviation from the box-like shape of the confinement potential of quantum dot [see Eq. (9.1)] can increase or decrease the escape rate from the quantum dot, i.e., increase or decrease the imaginary part of the energy. To illustrate this behavior we consider a quantum dot with an additional hole at the center of the dot, i.e., a quantum ring. I show below that, by varying the size of the hole we can tune the trapping time of the quasilocalized state of an electron in the quantum dot.

9.4 Main equations: Quantum ring

![Figure 9.5: The geometry of the graphene ring with the outer radius $R$ and the inner radius $a$.](image)

The quantum ring is shown schematically in Fig. 9.5 and is described by the
following confinement potential

\[
V(r) = \begin{cases} 
V_0 & \text{if } r < a \\
0 & \text{if } a < r < R \\
V_0 & \text{if } r > R 
\end{cases}
\] (9.28)

where \( R \) is the external radius of the ring and \( a \) is the internal radius of the ring. The quantum ring can also be considered as a quantum dot of radius \( R \) with an additional hole of radius \( a \) at the center of the dot.

Now we have three different regions, within which the confinement potential is constant and the functions \( \chi_1 \) or \( \chi_2 \) satisfy the corresponding Bessel equations. Similar to the quantum dot system, only the positive values of angular momentum, \( m = 1/2, 3/2, \ldots \) will be considered. Then the general solution of the system of Eqs. (9.4)-(9.5) has the following form

\[
\begin{pmatrix} \chi_1(r) \\ \chi_2(r) \end{pmatrix} = A \begin{pmatrix} J_{m-1/2}(\varepsilon - \nu_0) r/R \\ \i J_{m+1/2}(\varepsilon - \nu_0) r/R \end{pmatrix}
\] (9.29)

for \( r < a \),

\[
\begin{pmatrix} \chi_1(r) \\ \chi_2(r) \end{pmatrix} = B \begin{pmatrix} H^{(1)}_{m-1/2}(\varepsilon r/R) \\ \i H^{(1)}_{m+1/2}(\varepsilon r/R) \end{pmatrix} + C \begin{pmatrix} H^{(2)}_{m-1/2}(\varepsilon r/R) \\ \i H^{(2)}_{m+1/2}(\varepsilon r/R) \end{pmatrix}
\] (9.30)

for \( a < r < R \) and

\[
\begin{pmatrix} \chi_1(r) \\ \chi_2(r) \end{pmatrix} = D \begin{pmatrix} H^{(1)}_{m-1/2}(\varepsilon - \nu_0) r/R \\ \i H^{(1)}_{m+1/2}(\varepsilon - \nu_0) r/R \end{pmatrix}
\] (9.31)
for $r > R$. Here $H_n^{(2)}$ is the Hankel function of the second kind. In these expressions it has been taken into account that the wavefunction should be finite at $r = 0$ and outside the quantum ring we have outgoing waves.

From the continuity of the wavefunctions at $r = a$ and $r = R$ the energy eigenvalue equation has been obtained.

$$\frac{\alpha_1 H_{m+1/2}^{(1)}(\beta \varepsilon) - H_{m-1/2}^{(1)}(\beta \varepsilon)}{\alpha_1 H_{m+1/2}^{(2)}(\beta \varepsilon) - H_{m-1/2}^{(2)}(\beta \varepsilon)} = \frac{\alpha_2 H_{m+1/2}^{(1)}(\varepsilon) - H_{m-1/2}^{(1)}(\varepsilon)}{\alpha_2 H_{m+1/2}^{(2)}(\varepsilon) - H_{m-1/2}^{(2)}(\varepsilon)}, \quad (9.32)$$

Figure 9.6: The imaginary part of the energy, $\text{Im}[\varepsilon]$, of the quasilocalized state as a function of $\beta$ for a graphene quantum ring for different values of angular momentum, $m$, and different strengths of confinement potential, $\nu_0$ (as indicated).
where the following notations have been introduced $\beta = a/R$ and

$$\alpha_1 = \frac{J_{m-1/2}[\beta(\varepsilon - \nu)]}{J_{m+1/2}[\beta(\varepsilon - \nu)]}, \quad \alpha_2 = \frac{H^{(1)}_{m-1/2}(\varepsilon - \nu)}{H^{(1)}_{m+1/2}(\varepsilon - \nu)}$$

(9.33)

In the limit of small $\beta$, $\beta \to 0$, Eq. (9.32) transforms into Eq. (9.8) for an ideal quantum dot.

### 9.5 Quantum ring: Fine tuning of the trapping time

In the case of the quantum ring, I am interested in the effect of an additional structure, i.e., a hole, in the quantum dot on the electron escape rate from the highly trapped state of the quantum dot. From the above section we know that for an ideal quantum dot the energy of highly trapped state is close to the confinement potential strength, $\varepsilon \approx \nu_0$. If the condition of localization [see Eq. (9.26)] is satisfied then the energy of localized state is exactly equal to $\nu_0$ and the imaginary part of the energy is zero. When the condition (9.26) is violated then the imaginary part of the energy is nonzero. Now I consider the effect of additional hole at the center of the quantum dot on the magnitude of the imaginary part of the energy of the highly trapped quasilocalized state. Therefore the dependence of the imaginary part of the energy on the parameter $\beta = a/R$ of the ring will be studied. This dependence can be found from Eq. (9.32).

The results of numerical solution of Eq. (9.32) are shown in Fig. 9.6, where the
imaginary part of the energy of the quasilocalized state is shown as a function of $\beta$. We can clearly see that by increasing the inner radius of the ring we can strongly decrease the imaginary part of the energy of the quasilocalized state. This is valid for all values of $m$. Therefore the additional internal structure of the quantum dot can produce “constructive interference”, which suppresses the electron escape rate from the highly trapped state of the quantum dot. In Fig. 9.6 different values have been used for the heights of the confinement potential. The reason for this is that we need to choose the confinement potential height close to the value determined by the condition of strong localization, Eq. (9.9). Therefore in Fig. 9.6(a) we have $\nu_0 = 12$ and $|\nu_0 - \lambda_{0,4}| = 0.2$, in Fig. 3(b) we have $\nu_0 = 20$ and $|\nu_0 - \lambda_{1,6}| = 0.4$, and in Fig. 3(c) we have $\nu_0 = 20$ and $|\nu_0 - \lambda_{4,5}| = 0.6$. We can also see another property of confinement potential, which has already been discussed in Sec. 9.3. Namely, with increasing the angular momentum, $m$, the imaginary part decreases.

We can also see from Fig. 9.6 that there is a general tendency in the dependence of the imaginary part on the inner radius of the quantum ring. Namely, the sensitivity of the imaginary part of the energy to the inner radius of the ring decreases with increasing the angular momentum of the state. We can see that the imaginary part of the energy remains constant at small values of $\beta$ and we can see the changes in the imaginary part of the energy only at $\beta > 0.02$ for $m = 1/2$, at $\beta > 0.03$ for $m = 3/2$, and at $\beta > 0.15$ for $m = 9/2$. This behavior can be understood from the fact that with increasing the electron angular momentum the corresponding wavefunction becomes
more localized near the outer radius of the ring. In this case the energy of such a
wavefunction becomes less sensitive to the inner radius of the ring.

It happens that the dependence, shown in Fig. 9.6, can be observed only if the
confinement potential, $\nu_0$, is greater than the value corresponding to the condition
of strong localization. It means that only if $\nu_0 > \lambda_{m,i}$ ($\nu_0 - \lambda_{m,i} \ll 1$) then the
additional hole in the quantum dot suppresses the escape rate of an electron from the
quantum dot. To illustrate this effect the dependence of $\text{Im}[\varepsilon]$ on the parameter $\beta$
for different values of $\nu_0$ has been shown in Fig. 9.7(a)-(b). In Fig. 9.7(a) the data
are shown for $m = 1/2$. In this case the condition of strong localization is satisfied at
$\nu_0 \approx 11.5$. We can see from Fig. 9.7(a) that if $\nu_0 > 11.5$ then the function $\text{Im}[\varepsilon(\beta)]$ has
a minimum, while if $\nu_0 < 11.5$ then the function $\text{Im}[\varepsilon(\beta)]$ increases with increasing
the inner radius of the ring, $a$. Similar behavior, which is shown in Fig. 9.7(b), is
observed for $m = 3/2$. Now the condition of strong localization for the quantum dot
is satisfied at $\nu_0 \approx 19.5$.

We can understand this behavior from the analysis of the energy eigenequation
Eq. (9.32). Similar to the quantum dot system the real solution of this equation in
the form $\varepsilon = \nu_0$ is being searched. Under this condition we can easily obtain $\alpha_1 \to \infty$
and $\alpha_2 \to 0$. Then equation (9.32) becomes

$$
\frac{H_{m+1/2}^{(1)}(\beta \nu_0)}{H_{m+1/2}^{(2)}(\beta \nu_0)} = \frac{H_{m-1/2}^{(1)}(\nu_0)}{H_{m-1/2}^{(2)}(\nu_0)}.
$$

(9.34)

With a real argument, the Hankel function of the second kind is complex conjugated
to the Hankel function of the first kind. Then Eq. (9.34) becomes

\[ \frac{J_{m+1/2}(\beta \nu_0)}{Y_{m+1/2}(\beta \nu_0)} = \frac{J_{m-1/2}(\nu_0)}{Y_{m-1/2}(\nu_0)} \tag{9.35} \]

where \( Y_n \) is the Neumann function of the order \( n \). From Eq. (9.35), at fixed value of potential strength, \( \nu_0 \), we can find the, \( \beta \), at which we have a strongly localized state within the quantum ring, i.e., imaginary part of the energy of this state is zero. If the potential strength, \( \nu_0 \), satisfies the Eq. (9.9) then the solution of Eq. (9.35) is \( \beta = 0 \).

Let’s assume that there is a small violation of the condition (9.9), i.e., \( \delta \nu = \nu_0 - \lambda_{m,i} \) is small, but it can be positive or negative. In this case, if the solution of Eq. (9.35)
exists, then the corresponding value of $\beta$ is small, i.e., $\beta \nu_0 \ll 1$. Then for small $\beta$ the left hand side of Eq. (9.35) becomes
\[
-\frac{\pi (\beta \nu_0 / 2)^{2(m+1/2)}}{(m + 1/2)!(m - 1/2)!} = \frac{J_{m-1/2}(\nu_0)}{Y_{m-1/2}(\nu_0)}. \tag{9.36}
\]
Since $\delta_{\nu} = \nu_0 - \lambda_{m,i}$ is small, we can rewrite the right hand side of Eq. (9.36) in the following form
\[
-\frac{\pi (\beta \lambda_{m,i}/2)^{2(m+1/2)}}{(m + 1/2)!(m - 1/2)!} = \frac{J'_{m-1/2}(\lambda_{m,i})}{Y_{m-1/2}(\lambda_{m,i})} \delta_{\nu}, \tag{9.37}
\]
where it has been taken into account that $J_{m-1/2}(\lambda_{m,i}) = 0$. Then from Eq. (9.37) we can find $\beta$
\[
\beta = \Lambda_{m,i} \left( -\frac{J'_{m-1/2}(\lambda_{m,i})}{Y_{m-1/2}(\lambda_{m,i})} \delta_{\nu} \right)^{1/2(m+1/2)}, \tag{9.38}
\]
where the following notation has been introduced
\[
\Lambda_{m,i} = \frac{2}{\lambda_{m,i}} \left( \frac{(m + 1/2)!(m - 1/2)!}{\pi} \right)^{1/2(m+1/2)}. \tag{9.39}
\]
The solution of equation (9.38) exists only if
\[
-\frac{J'_{m-1/2}(\lambda_{m,i})}{Y_{m-1/2}(\lambda_{m,i})} \delta_{\nu} > 0 \tag{9.40}
\]
The typical behavior of the functions $J_n$ and $Y_n$ is shown in Fig. 9.7(c). Taking into account that $\lambda_{m,i}$ are zeros of the Bessel function $J_{m-1/2}$ we can conclude that for all values of $\lambda_{m,i}$ the ratio $J'_{m-1/2}(\lambda_{m,i})/Y_{m-1/2}(\lambda_{m,i})$ is negative. Then the solution of Eq. (9.38) and correspondingly the solution of Eq. (9.32) exists only for positive $\delta_{\nu}$, i.e., only if $\nu_0 > \lambda_{m,i}$. Therefore only for $\nu_0 > \lambda_{m,i}$ an additional hole at the center of the quantum dot can suppress the escape rate from the quasilocalized state of the dot.
9.6 Conclusion

There are two different mechanisms of trapping of an electron in graphene quantum dot. The first one is due to generation of the trapping barrier, which is induced by the transverse momentum, i.e., by the angular momentum for cylindrically symmetric quantum dots. In this case the trapping time is determined by electron tunneling through the trapping barrier. The width of the trapping barrier depends on the slope of the confinement potential. Therefore the most efficient trapping of the electron is achieved for a smooth confinement potential [124]. Since the electron angular momentum determines the height of the trapping barrier then the trapping time also has a strong exponential dependence on the magnitude of the angular momentum. For such mechanism of trapping the electron escape rate from the quantum dot is robust with respect to variations of the parameters of the confinement potential.

In this work another mechanism of trapping has been discussed. This mechanism occurs in a quantum dot with a sharp boundary. In this case the width of the trapping barrier is very small, and the trapping is realized not only due to electron tunneling but also due to interference effects. Since the interference is very sensitive to the parameters of the confinement potential, then for a given electron angular momentum, $m$, a strong electron localization can occur only at one energy level. The energy of this level is equal to the strength of the confinement potential, $\nu_0$. Therefore, the imaginary part of the energy of this level is zero and the electron trapping time at this level is infinitely large. In addition the potential should satisfy
a special condition, Eq. (9.26). As a result, only a discrete but infinite set of values of the height of the confinement potential can produce a strongly localized electronic state.

Although experimentally it is more easier to create a confinement potential with smooth boundary, the sharp boundary are also important. As we have shown in the present work, for the quantum dots with sharp boundaries there is a completely new mechanism of trapping. This trapping is due to the interference effect and as a result, it can be observed for all values of angular momentum, even for a small $m$. For a smooth boundary the trapping is due to a tunneling and can be achieved only for large values of angular momentum [124]. This shows the advantage of sharp boundaries of the quantum dots. Namely, if we correctly choose the parameters of the confinement potential with sharp boundaries, then the electrons with small values of $m$ can be strongly localized. The finite width (say $w$) of the boundary of the quantum dot introduces an additional escape from the quantum dot due to violation of the condition (9.26). Then the escape rate from such a quantum dot can be estimated as $(w/R)^{2m}$. When the electron trapping is due to interference effects, any variation of the profile of the confinement potential strongly affects the trapping time. This opens a possibility of efficient tuning of the trapping properties of an electron in quantum dots by introducing an internal structure in the quantum dot and by varying the parameters of this structure. This behavior has been illustrated, where the internal radius of the ring affects the trapping properties of the ring.
Chapter 10

Trapping of an electron in coupled quantum dots in graphene

10.1 Introduction

In this Chapter I will discuss a system of quantum dots in graphene theoretically by analyzing the complex energy spectra of the quantum dot system. I found that in a double dot system some energy levels becomes strongly localized with an infinite trapping time. Such strongly localized states are achieved only at one value of the inter-dot separation. I also study a periodic array of quantum dots in graphene within a tight-binding mode for a quantum dot system. The values of the hopping integrals in the tight-binding model are found from the expression for the energy spectra of the double quantum dot system.
One of the directions of conventional quantum dot research is related to coupled quantum dots, i.e., “artificial molecules”. The coupled quantum dots have been proposed as building blocks of quantum computing [132]. Recently the problem of coupled quantum dots in graphene has been addressed in the literature [133]. In this relation it is very important to understand the trapping properties of the coupled quantum dots. In this Chapter I will consider the effect of the coupling of quantum dots on the electron trapping time.

In the conventional coupled quantum dot systems [134] there are two types of inter-dot coupling. The first one is a direct inter-dot tunneling, which shifts the energy levels of the individual quantum dots. The second type of coupling is realized in systems, where the states of the quantum dots are degenerate with the continuum states, e.g. the continuous states of the leads in resonant tunneling experiments [135, 136]. In this case the states of the quantum dots have finite widths, which are the widths of the tunneling conductance maxima. Then the second type of coupling is the coupling through the continuum states of the leads. This type of coupling has interference nature and affects the width of the quantum dot levels [136]. As a result some levels of the coupled quantum dots become narrow and the other levels become broad. Therefore in the conventional quantum dot systems, the real part of the inter-dot coupling matrix elements are determined by the direct inter-dot tunneling, while the imaginary part is due to coupling through the continuum states.

In the graphene quantum dot system there is no direct tunneling between two
spatially separated quantum dots. The levels of the quantum dots in graphene are degenerate with the continuum states. Therefore the inter-dot coupling in graphene should be described as the coupling through its continuum states. In this case the coupling matrix elements have both real and imaginary parts and we should expect that the inter-dot coupling in graphene affects both the position and the width, i.e., the electron escape rate, of the levels of the dot system. I will show below that the inter-dot coupling in graphene can result in strong suppression of the escape rates from the dot system and under some conditions the escape rate can be even zero. This suppression is the result of the interference effect and is sensitive to the shape of the confinement potential. Below, the properties of the trapped states in a double quantum dot system and in periodic array of quantum dots are discussed.

10.2 Double quantum dot system: Main equations

The coupled quantum dots system is shown schematically in Fig. 10.1. Two identical cylindrically symmetric quantum dots will be considered, which are characterized by radius $R$. The distance between the centers of the quantum dots is $d$. Then the system under consideration consists of three regions: region I (quantum dot 1), region II (quantum dot 2) and region III [see Fig. 10.1]. To describe the system it is convenient to introduce the polar coordinates for each quantum dot: $r_1$ and $\theta_1$ for the first quantum dot, and $r_2$ and $\theta_2$ for the second quantum dot [see Fig. 10.1]. It has been assumed that the quantum dots have sharp boundaries [125, 109] and the
corresponding confinement potential has the following form

\[
V(\vec{r}) = \begin{cases} 
-V_1 & \text{if } r_1 < R, \text{ region I} \\
-V_2 & \text{if } r_2 < R, \text{ region II} \\
0 & \text{if } r_1, r_2 > R, \text{ region III}
\end{cases}, \quad (10.1)
\]

where \( V_1, V_2 > 0 \).

Figure 10.1: The geometry of the coupled graphene quantum dots. The quantum dots have the same radius \( R \). Here \( d \) is the distance between the centers of the quantum dots (inter-dot distance). To characterize the position of point \( P \), introduce the polar coordinates \( r_1, \theta_1 \) and \( r_2, \theta_2 \) for each quantum dot.

With the confinement potential in Eq. (10.1) the Hamiltonian of a single electron in graphene is given by Eq. (9.2).

To find the solution of the Schrödinger equation corresponding to the Hamiltonian (9.2) the basis states have been introduced, which have the same form as single quantum dot states [109]. Then the general solution of the Schrödinger equation for the double dot system has the following form,

\[
\psi_I(r_1, \theta_1) = \sum_m A_m \begin{pmatrix} J_{|m-1/2|}(\varepsilon_1 r_1/R) e^{i(m-1/2)\theta_1} \\
i J_{|m+1/2|}(\varepsilon_1 r_1/R) e^{im\theta_1} \end{pmatrix}, \quad (10.2)
\]
in region I \((r_1 < R)\), where \(\varepsilon_1 = R(E + V_1)/\gamma\) and \(J_n\) is the Bessel function of the \(n\)th order;

\[
\psi_{II}(r_2, \theta_2) = \sum_m C_m \left( \begin{array}{c} J_{|m-1/2|}(\varepsilon_2 r_2/R) e^{i(m-1/2)\theta_2} \\ i J_{|m+1/2|}(\varepsilon_2 r_2/R) e^{im\theta_2} \end{array} \right), \tag{10.3}
\]

in region II \((r_2 < R)\), where \(\varepsilon_2 = R(E + V_2)/\gamma\), and

\[
\psi_{III}(r_1, r_2, \theta_1, \theta_2) = \sum_m B_m \left( \begin{array}{c} H_{|m-1/2|}(\varepsilon r_1/R) e^{i(m-1/2)\theta_1} \\ i H_{|m+1/2|}(\varepsilon r_1/R) e^{im\theta_1} \end{array} \right) + \\
\sum_m D_m \left( \begin{array}{c} H_{|m-1/2|}(\varepsilon r_2/R) e^{i(m-1/2)\theta_2} \\ i H_{|m+1/2|}(\varepsilon r_2/R) e^{im\theta_2} \end{array} \right), \tag{10.4}
\]

in region III \((r_1, r_2 > R)\), where \(\varepsilon = RE/\gamma\), \(H_n\) is the Hankel function of the \(n\)th order of the first kind. Here \(m = \pm 1/2, \pm 3/2, ...\) is the orbital angular momentum, defined for each quantum dot separately. In these expressions it has been taken into account that the wave function should be finite at \(r_1 = r_2 = 0\) and outside the quantum dot system have outgoing waves.

The wavefunction should be continuous at the boundary between regions I and III \((r_1 = R)\) and at the boundary between regions II and III \((r_2 = R)\). The continuity condition, for example, at the boundary between regions I and III have the form

\[
\psi_I(R, \theta_1) = \psi_{III}[R, r_2(\theta_1), \theta_1, \theta_2(\theta_1)], \tag{10.5}
\]
where

\[ r_2(\theta_1) = \sqrt{R^2 + d^2 - 2dR \cos \theta_1} \]

\[ \theta_2(\theta_1) = \sin^{-1} \left( \frac{R \sin \theta_1}{r_2(\theta_1)} \right). \]  

(10.6)

Taking into account expressions (10.2) and (10.4) for the wavefunction in the regions I and III and integrating the boundary condition (10.5) over the boundary surface, the following equation has been obtained

\[ \frac{J_{m-1/2}[\varepsilon + \nu_1]}{J_{m+1/2}[\varepsilon + \nu_1]} = \frac{B_{mH|m-1/2}[\varepsilon] + \sum_{m'} D_{m'} \Gamma_{m,m'}^{(-)}}{B_{mH|m+1/2}[\varepsilon] + \sum_{m'} D_{m'} \Gamma_{m,m'}^{(+)}}. \]  

(10.7)

The similar equation can be derived from the continuity condition at the boundary between regions II and III

\[ \frac{J_{m-1/2}[\varepsilon + \nu_2]}{J_{m+1/2}[\varepsilon + \nu_2]} = \frac{\sum_{m'} B_{mH|m-1/2}[\varepsilon] + D_{mH|m-1/2}[\varepsilon]}{\sum_{m'} B_{mH|m+1/2}[\varepsilon] + D_{mH|m+1/2}[\varepsilon]} \]  

(10.8)

where, \( \nu_1 \equiv RV_1/\gamma, \nu_2 \equiv RV_2/\gamma \) and,

\[ \Gamma_{m,m'}^{(\pm)} = \int_{0}^{2\pi} H_{m'\pm1/2} \left[ \frac{\varepsilon r_2(\theta_1)}{R} \right] e^{-i[(m\pm1/2)\theta_1 -(m'\pm1/2)\theta_2(\theta_1) - \theta_2(\theta_1)]} d\theta_1. \]  

(10.9)

The solution of the system of Eqs. (10.7) and (10.8) determines the complex energy of the electronic states in the double quantum dot system, where the coefficients \( \Gamma_{m,m'}^{(\pm)} \) describe the inter-dot coupling. In the limit of large inter-dot separation, \( d \), the inter-dot coupling terms become small and Eqs. (10.7) and (10.8) transform into eigenvalue equations for two uncoupled single quantum dots [109]. At finite inter-dot separation
the coefficients $\Gamma_{m,m'}^{(\pm)}$ introduce the coupling between the states with different angular momentum, $m$. In Eqs. (10.7) and (10.8) the summation runs over all possible values of angular momentum, $m'$. Below, small values of angular momentum have been considered, $m$, and to make the system of Eqs. (10.7) and (10.8) finite the values of $m$ in Eqs. (10.7)-(10.8) have been restricted by inequality: $|m| \leq 5/2$. Under this restriction the system of Eqs. (10.7) and (10.8) has been solved numerically to find the complex energy spectra of the double dot system.

10.3 Double quantum dot system: Results and discussion

At large inter-dot separation the inter-dot coupling is small and the double quantum dot system becomes the system of uncoupled quantum dots. The energy spectra of each of the quantum dots are determined from the eigenvalue equation\[109\]
\[
\frac{J_{|m-1/2|}(\varepsilon + \nu)}{J_{|m+1/2|}(\varepsilon + \nu)} = \frac{H_{|m-1/2|}(\varepsilon)}{H_{|m+1/2|}(\varepsilon)}. \tag{10.10}
\]
This equation can be obtained from Eqs. (10.7)-(10.8) at zero inter-dot coupling, $\Gamma_{m,m'}^{(\pm)} = 0$. The solution of this equation is a complex energy spectrum, where the imaginary part of the energy determines the electron trapping time in the quantum dot. For identical quantum dots, i.e., $\nu = \nu_1 = \nu_2$, the energy spectra of two quantum dots become degenerate. At finite inter-dot separation we should expect the splitting of the degenerate energy levels. Since the coefficients $\Gamma_{m,m'}^{(\pm)}$, which determines the
inter-dot coupling, are complex then the finite inter-dot coupling modifies both the real and imaginary parts of the electron energy.

![Graph showing real and imaginary parts of energies](image)

Figure 10.2: (a)-(b) the imaginary parts of the energies, $\text{Im}[\varepsilon]$, of the quasilocalized states are shown as functions of $d/R$ for double quantum dot system in graphene for different values of angular momentum, $m$, (as indicated). (c)-(d) same diagram for the real part of the energy, $\text{Re}[\varepsilon]$. For all the panels $\nu_1 = \nu_2 = 20$.

To describe the effect of inter-dot coupling on the trapping properties of the double quantum dot system the splitting of the degenerate levels of double quantum dots has been traced with decreasing the inter-dot separation, $d$. We characterize the states at finite values of $d$ by the angular momentum of the original quantum dot states at large inter-dot separation. The results of the calculations are shown for the angular momenta $m = 1/2$ and $m = 3/2$ in Fig. 10.2. For each value of $m$ it has been shown
that only one set of energy levels, which corresponds to the lowest escape rate, i.e., the lowest imaginary part of the energy, at large inter-dot separation.

We can see from Fig. 10.2 that at finite inter-dot separation, \( d \), the inter-dot coupling introduces the splitting of the degenerate energy levels of the double dot system. The splitting occurs both for the real and for the imaginary parts of the energy. The escape from one of the states of the double quantum dots is suppressed, i.e., the imaginary part of the energy decreases. The most important property of this dependence is that at finite value of \( d \), \( d \approx 4R \), the imaginary part of the energy becomes zero. It means that the electron at this level becomes strongly localized, i.e., the trapping time is infinitely large. In addition to suppression of the escape rate from one of the levels of the double dot system we can see an enhancement of the escape rate from another level. This fact illustrates the splitting of the degenerate levels due to inter-dot coupling. The splitting of the real part of the energies has almost a linear dependence on the inter-dot separation, \( d \).

The suppression of the escape rate of an electron from the double quantum dot system is due to the interference effects. Therefore, this behavior is sensitive to the parameters and the positions of the quantum dots. The exact value of the inter-dot separation, at which the strongly localized state is realized, depends on the actual structure of the quantum dots.

The results shown in Fig. 10.3 correspond to the quantum dot system with two identical quantum dots. In this case the inter-dot coupling has the strongest effect
on the electron energy spectra and on the electron trapping time. This is because the energy spectra of two quantum dots at large inter-dot separation are identical.

If the quantum dots have different parameters, e.g. different strength of the confinement potential, then the effect of the inter-dot coupling is suppressed. The results of calculations for the double quantum dot system with the different values of the confinement potential strength, $\nu_1 \neq \nu_2$, are shown in Fig. 10.3. We can see that at large inter-dot separation, $d$, the energies of two quantum dots are different. With decreasing the distance, $d$, the inter-dot coupling introduces an additional splitting of the energy levels. The imaginary part of one of the levels of the double dot system becomes smaller, i.e., the electron in this state becomes more localized. We can see from Fig. 10.3 that the effect of the inter-dot coupling on the energy spectra is less than in the case of the identical quantum dots. As a result, the state with zero imaginary part is achieved at smaller values of the inter-dot separation, $d \approx 3R$.

The data shown in Fig. 10.3 illustrate the possibility of experimental control of the electron trapping in the quantum dot system. Namely, if we keep the same separation between the dots and change the strength of the confinement potential for one of the dots ($\nu_1$ or $\nu_2$), then we can switch between the states with different trapping times. For example, if the inter-dot separation is $d \approx 4R$ then, start from the identical quantum dots and then change the confinement potential of one of the dots, then the electron state transforms from the highly trapped to the weakly trapped state.

The finite trapping time of an electron has been illustrated in terms of the widths
Figure 10.3: The imaginary parts of the energies, $\text{Im}[\varepsilon]$, of the quasilocalized states are shown as functions of $d/R$ for double quantum dot system for angular momentum, $m = 3/2$, and different strength of confinement potentials, $\nu_1$ and $\nu_2$ (as indicated).

The density of states is shown in Fig. 10.4 for the double quantum dot system of identical quantum dots, i.e., $\nu_1 = \nu_2 = 20$. In this figure only the states with $m = 3/2$, which correspond to the results shown in Fig. 10.2(b) and (d), are taken into account. At large inter-dot separations [Fig. 10.4(a)] there is a broad peak, which corresponds to two degenerate states of the quantum dots. With decreasing the inter-dot distance, $d$, the formation of two peak structure is observed. Here the
low energy peak is narrowed and the higher energy peak is broadened. Finally at $d/R \approx 4$ the width of the lower energy peak becomes very small, which illustrates almost zero escape rate of the electron from the double quantum dot system.

### 10.4 Array of quantum dots

In the previous section the appearance of the strongly localized states of the electron in the double quantum dot system has been illustrated. Such states exist only at specific values of the inter-dot separation. Additional degree of freedom can
be introduced into the dot system if we increase the number of coupled quantum dots. One of the examples of such a system is the periodic array of identical quantum dots. Such an array is characterized by the radius of each quantum dot, $R$, and the inter-dot distance, $d$ [see Fig. 10.5]. Here the inter-dot distance, $d$, becomes the period of the quantum dot array system.

![Figure 10.5: The geometry of the quantum dots array system. Inter-dot spacing is $d$ and the radius of the dot is $R$.](image)

At large inter-dot distance, $d \gg R$, all quantum dots have the same energy spectrum. When the inter-dot distance decreases the inter-dot coupling results in splitting of the degenerate energy levels and formation of the band structure. To analyze this energy structure only one electron state per quantum dot will be considered. This state is characterized by the angular momentum, $m$, and the complex energy, $\varepsilon_m$. The inter-dot coupling will be introduced through the tight-binding model, which is described by the following tight-binding Hamiltonian

$$
\mathcal{H}_t = \sum_i \varepsilon_m a_i^\dagger a_i + \sum_i t_m a_i^\dagger a_{i+1} + h.c.,
$$

where $a_i$ is the annihilation operator of an electron in the state with energy $\varepsilon_m$ at the quantum dot $i$ and $t_m$ is the inter-dot hopping integral. The value of the hopping
integral can be found from the application of the Hamiltonian (10.11) to a double dot system. For the double dot system the energy spectra is found from the solution of the system of Eqs. (10.7) and (10.8). In this system of equations only one level per dot has been considered and then I compare the corresponding energy spectrum with the energy spectrum of the tight-binding model. This comparison gives the following value for the hopping integral in the tight-binding model

\[ t_m = -\frac{\varepsilon_m \varepsilon_{m,1}}{2m\nu} \frac{\Gamma_m^{(+)} J_{[m-1/2]}(\varepsilon_{m,1}) - \Gamma_m^{(-)} J_{[m+1/2]}(\varepsilon_{m,1})}{H_{[m+1/2]}(\varepsilon_m) J_{[m-1/2]}(\varepsilon_{m,1})} \]  

(10.12)

where, \( \varepsilon_{m,1} = R(E_m + V)/\gamma = \varepsilon_m + \nu \). The details of derivation of the hopping integral is as follows.

To find the hopping integral in the tight-binding model (10.11) a system of two identical quantum dots with only one state per dot will be considered. It has been assumed that the angular momentum of this state is \( m \) and the energy is \( \varepsilon_m \). In this case in the Eqs (10.7) and (10.8), which determine the energy spectrum of the system, we need to keep only the terms with \( m' = m \). Then equations (10.7) and (10.8) become

\[ \frac{J_{[m-1/2]}(\varepsilon + \nu)}{J_{[m+1/2]}(\varepsilon + \nu)} = \frac{B_m H_{[m-1/2]}(\varepsilon) + D_m \Gamma_m^{(-)}}{B_m H_{[m+1/2]}(\varepsilon) + D_m \Gamma_m^{(+)}}, \]  

(10.13)

\[ \frac{J_{[m-1/2]}(\varepsilon + \nu)}{J_{[m+1/2]}(\varepsilon + \nu)} = \frac{B_m \Gamma_m^{(-)} + D_m H_{[m-1/2]}(\varepsilon)}{B_m \Gamma_m^{(+)} + D_m H_{[m+1/2]}(\varepsilon)}, \]  

(10.14)

where \( \nu_1 = \nu_2 = \nu \). A nontrivial solution of Eqs. (10.13)-(10.14) can be found from
the condition that the determinant of the following matrix

\[
\mathbf{A} = \begin{pmatrix} A_1(\varepsilon) & A_2(\varepsilon) \\ A_2(\varepsilon) & A_1(\varepsilon) \end{pmatrix}
\]  

(10.15)
is zero. Here

\begin{align*}
A_1(\varepsilon) &= H_{|m+1/2|}(\varepsilon)J_{|m-1/2|}(\varepsilon + \nu) - H_{|m-1/2|}(\varepsilon)J_{|m+1/2|}(\varepsilon + \nu), \quad (10.16) \\
A_2(\varepsilon) &= \Gamma_{m,m}^{(+)}J_{|m-1/2|}(\varepsilon + \nu) - \Gamma_{m,m}^{(-)}J_{|m+1/2|}(\varepsilon + \nu). \quad (10.17)
\end{align*}

For uncoupled quantum dots the non-diagonal element, \( A_2 \), of the matrix is zero and the energy spectrum is determined by equation \( A_1(\varepsilon) = 0 \). This equation gives two degenerate energy levels with the energy equal to the energy of a single quantum dot, \( \varepsilon = \varepsilon_m \).

Here it has been assumed that the inter-dot coupling is small and the energy of the coupled quantum dots is close to \( \varepsilon_m \). Then, by expanding the diagonal element, \( A_1(\varepsilon) \), of the matrix around \( \varepsilon_m \),

\[
A_1(\varepsilon) = A_1[(\varepsilon - \varepsilon_m) + \varepsilon_m] \approx A_1(\varepsilon_m) + A_1'(\varepsilon_m)[\varepsilon - \varepsilon_m],
\]  

(10.18)

where, \( A_1' \) is the first derivative of the function. Since, \( A_1(\varepsilon_m) = 0 \), then Eq. (10.18) becomes

\[
A_1(\varepsilon) \approx A_1'(\varepsilon_m)[\varepsilon - \varepsilon_m].
\]  

(10.19)

With this expression the matrix \( \mathbf{A} \) takes the form

\[
\mathbf{A} = \begin{pmatrix} A_1'(\varepsilon_m)[\varepsilon - \varepsilon_m] & A_2(\varepsilon_m) \\ A_2(\varepsilon_m) & A_1'(\varepsilon_m)[\varepsilon - \varepsilon_m] \end{pmatrix}.
\]  

(10.20)
From the condition that the determinant of the matrix $A$ is zero we can find the energy of the double dot system

$$\varepsilon = \varepsilon_m \pm \frac{A_2(\varepsilon_m)}{A_1(\varepsilon_m)}. \quad (10.21)$$

In the tight-binding model (10.11) of double quantum dot system the energy spectrum is

$$\varepsilon = \varepsilon_m \pm t_m. \quad (10.22)$$

Comparing equations (10.21) and (10.22), we can obtain the expression for the hopping integral in the tight-binding model

$$t_m = \frac{A_2(\varepsilon_m)}{A_1(\varepsilon_m)}. \quad (10.23)$$

Using the properties of Bessel and Hankel functions, we can find the derivative $A_1'(\varepsilon_m)$ in the following form

$$A_1'(\varepsilon_m) = -\frac{2m\nu}{\varepsilon_m \varepsilon_{m,1}} H_{m+1/2}(\varepsilon_m) J_{m-1/2}(\varepsilon_{m,1}), \quad (10.24)$$

where $\varepsilon_{m,1} = \varepsilon_m + \nu$. Substituting Eqs. (10.17) and (10.24) in Eq. (10.23), we can obtain expression (10.12) for the hopping integral in the tight-binding model.

The states of the Hamiltonian (10.11) are characterized by a wave vector, $k$, and the corresponding energy spectrum has a form

$$\varepsilon(k) = \varepsilon_m + 2t_m \cos(kd), \quad (10.25)$$

where the wave vector $k$ is defined within the interval $0 \leq k < 2\pi/d$. 
Both the energy $\varepsilon_m$ and the hopping integral $t_m$ are complex. Then the energy spectrum, $\varepsilon(k)$, of the quantum dot system is complex, and the imaginary part of the energy determines the escape rate of an electron from the quantum dot array.

Figure 10.6: The imaginary part of the energy, $\text{Im}[\varepsilon]$, is shown as a function of the wave vector, $k$, for different values of $d/R$ (as indicated). Here $\nu_0 = 20$ and $m = 3/2$.

In Fig. 10.6 the imaginary part of the energy spectrum is shown as a function of the wave vector, $k$, at $m = 3/2$ and different values of the period, $d$. We can see from the figure that if the period, $d$, is less than some critical value, $d \lesssim 8R$, then there are always two states with zero imaginary part of the energy, which means that electron trapping time of these states is infinitely large. This property is different from the double quantum dot system, where the state with large trapping time can be realized only at one value of the inter-dot distance.

The manifestation of the specific behavior of the imaginary part of the energy
spectra could be the formation of the charge density wave in the periodic array of quantum dots in graphene. Indeed, if initially all quantum dots are occupied by electrons, then after some time the electrons at the states with small trapping time will escape from the quantum dot system. Finally, only the states with large trapping times will be occupied. Such states have non-zero momentum and the occupation of these states results in the charge density wave.

10.5 Conclusion

The unique feature of the quantum dots in graphene is that the discrete electron energy spectra of the quantum dot is degenerated with the continuum spectra of graphene. As a result the states of the quantum dot have finite width and the electrons at these states have finite lifetime. In this case the inter-dot coupling in the system of many quantum dots in graphene can be described as the combination of the following processes: (i) the electron escapes from a quantum dot into the continuum states of graphene; (ii) then the electron freely propagates outside the quantum dots; (iii) and finally the electron is trapped by another quantum dot. These types of processes introduce inter-dot coupling, which has both real and imaginary parts. As a result, the inter-dot coupling changes both the positions and the widths of the energy levels of the quantum dots. For some states of the quantum dot system the width of the energy levels, i.e., the escape rate from the quantum dots, is suppressed and can be even zero. For the double quantum dot system such states with infinitely large
trapping time are realized only at one value of the inter-dot distance. This distance depends on the parameters of the quantum dots, e.g. the radius of the dot, the strength of the confinement potential, and the shape of the quantum dot.

For a periodic array of quantum dots in graphene the inter-dot coupling results in the band structure of the energy spectra. In this case the strongly localized states with zero width exist at all values of inter-dot separation smaller than some critical value. The states with infinitely large trapping time have a non-zero wave vector.
Bibliography


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