1 Introduction

1.1 Light and matter on a nanometer scale

The notion of "photonics" implies the science and technology related to generation, absorption, emission, harvesting, processing of light and their applications in various devices. Light is electromagnetic radiation available for direct human perception, in the wavelength range from approximately 400 to approximately 700 nanometers. Typically, adjacent far ultraviolet and near infrared ranges are also involved to give the approximate range of electromagnetic radiation from 100 nanometers to 1–2 micrometers as the subject of photonics. If the space has certain inhomogeneities on a similar scale to the wavelength of the light, then multiple scattering and interference phenomena arise modifying the propagation of light waves. Light scattering is the necessary prerequisite for vision. Shining colors in soap bubbles and thin films of gasoline on a wet road after rain are primary experiences of light-wave interference everybody gains in early childhood. To modifiy the conditions for light propagation, inhomogeneities in space which are not negligible as compared to the wavelength of the light, i.e. starting from the size range 10–100 nm to a few micrometers, become important. Space inhomogeneity for light waves implies inhomogeneity in dielectric permittivity.

Matter is formed from atoms which in turn can be subdivided into nuclei and electrons. An elementary atom of hydrogen has a radius for the first electron orbital of 0.053 nm. Atoms may form molecules and solids. Many typical organic molecules have sizes of the order of 1 nm. Typical crystalline solids feature a lattice period of approximately 0.5 nm. Interaction of light with matter actually reduces to the processes involved in the electron subsystem of molecules and solids. Therefore to understand light–matter interactions, electron properties must be examined in detail. Electrons are viewed as objects possessing wave properties in terms of wavelength, and corpuscular properties in terms of mass and charge. If an electron has gained kinetic energy as a result of acceleration in an electric field between a couple of plates with voltage 1 V (e.g. generated in a silicon photocell), then its kinetic energy of 1 eV results in an electron de Broglie wavelength close to 1 nm. For kinetic energies corresponding to a characteristic value of $k_{\mathrm{B}}T = 27$ meV at room temperature, the electron de Broglie wavelength in solids is of the order of 10 nm. Here k_{B} is the Boltzman constant and T is temperature. When space inhomogeneities present which are not negligible as compared to the electron wavelength then scattering and interference of electrons develop modifying in many instances the interaction of light with matter. Space inhomogeneities for electrons means inhomogeneity in charge or mass displacement, electric or magnetic field variations.

1.2 What is nanophotonics?

Nanophotonics is the recently emerged, but already well defined, field of science and technology aimed at establishing and using the peculiar properties of light and light–matter interaction in various nanostructures. Since it is the spatial confinement of light waves in complex media and electron waves in various nanostructured solids that determine multiple physical phenomena in nanophotonics, it is possible to characterize *nanophotonics as the science and technology of confined light waves and electron waves*. It can be tentatively divided into four sections.

The **first** section of nanophotonics is *electron confinement effects on the optical properties of matter*; mainly semiconductor and dielectric materials. These phenomena are typically referred to as *quantum confinement* effects since manifestations of *wavy properties of electrons are typically labeled as quantum phenomena*. The net optical manifestations of these effects are size-dependent optical absorption spectra, emission spectra and transition probabilities for solid matter purposefully structured on the scale of a few nanometers. Their potential applications are the variety of optical components with size-controlled, tuned and adjustable parameters including emitters, filters, lasers and components, optical switches, electro-optical modulators etc. This sub-field of nanophotonics has become the subject of systematic research since the 1970s. Different issues related to electron confinement phenomena and their optical manifestations have already been the subject of several books [1–3].

The **second** section of nanophotonics constitutes *light wave confinement phenomena* in structured dielectrics, including the fine concept of photonic solids in which light wave propagation is controlled in a similar manner to electron waves in solids. This subfield of nanophotonics is principally *classical* in its essence, i.e. it is based entirely on *wave optics* and does not imply any notion beyond classical Maxwell equations. It actually dates back to early identification of light interference phenomena by Isaac Newton in the eighteenth century and to genuine prediction by Lord Rayleigh of the remarkable reflective properties of periodic media in the 1880s. The main practical outcome for this field is ingenious photonic circuitry development, from ultrasmall but high-quality cavities to ultracompact waveguides. Different issues of light confinement phenomena and near-field optics have already been included in several books [4–8].

The **third** section of nanophotonics is essentially the *quantum optics of nanostructures*. It deals with modified light–matter interaction in nanostructures with confined light waves. Spontaneous emission and scattering of light essentially modifies and becomes controllable since spontaneous photon emission and spontaneous photon scattering can be promoted or inhibited by engineering photon density of states often referred to as electromagnetic mode density. The ultimate case of this modified light–matter interaction is the development of confined light–matter states in microcavities and photonic crystals. This section of nanophotonics is relatively new. It has its root in the seminal paper by E. Purcell in 1946 predicting the modified spontaneous decay rate of a quantum sytem (e.g. an atom) in a cavity. In the 1970s V. P. Bykov suggested freezing spontaneous decay of excited atoms

in a periodic structure where no means is available to carry off the emitted radiation. Eventually these ideas evolved into the concept of *photonic crystals* and *photonic solids* through seminal papers in the 1980s by E. Yablonovitch who suggested thresholdless lasing in a device with inhibited spontaneous emission of radiation, and by S. John who indicated possible light wave localization in disordered structures. Modified light–matter interaction in microcavities and photonics crystals is the subject of a few books [9–11].

The **fourth** section of nanophotonics is optics and optical engineering based on *metal-dielectric nanostructures*. Typically metals are not considered an important subject in optical research and engineering. Our experience mainly reduces to everyday observation of ourselves in aluminium mirrors. However metal-dielectric nanostructures feature a number of amazing properties resulting from the development of electron excitations at metal–dielectric interfaces called *surface plasmons*. Structuring of metal-dielectric composites on the nanoscale (10–100 nm) makes surface effects dominant. Actually, the optical properties of metal nanoparticles have been used for many centuries in stained glass but nowadays the study of metal-dielectric composites in optics has evolved into the well-defined field of *nanoplasmonics*. High concentrations of electromagnetic radiation and modification of the rates of quantum transitions in the near vicinity of metallic singularities result in novel light emitting devices and ultrasensitive spectral analysis with ultimate detection of a single molecule by means of Raman scattering. A few issues of nanoplasmonics have been considered in books [12,13].

1.3 Where are the photons in nanophotonics and in this book?

The author takes the approach whereby temptation to use the term "photon" is purposefully avoided unless the concept of light quanta is essential in order to understand the phenomenon in question. It is anticipated by many scientists and has been clearly outlined by W. Lamb in his seminal paper entitled "Anti-photon" [14]. In nanophotonics photons become necessary when trying to understand the emission of light by an excited quantum system and the scattering of light when light frequencies change (Raman scattering). Then, eventually, *quantum electrodynamics* comes to the stage. Not all phenomena of light propagation need the involvement of photons and the vast majority of light absorption phenomena can be treated in a semiclassical way when the matter is described in terms of quantum mechanics (more accurately speaking, *wave mechanics*), but light is understood as classical electromagnetic waves.

The rest of the book is organized as follows. Fifteen chapters, from Chapter 2 to Chapter 16, are organized in the form of two large parts.

Part I is entitled "*Electrons and electromagnetic waves in nanostructures*" and contains Chapters 2 to 12. It considers electrons in complex media and nanostructures in terms of *wave mechanics*, and electromagnetic radiation in complex media and nanostructures in terms of *wave optics*. Parallel consideration of wave phenomena in the theory of matter and in the theory of light in complex structures is pursued purposefully to highlight the conformity of wave phenomena in nature, both for electrons in matter and for classical waves

in complex media. This harmony did result in amazing interactions between wave optics and wave mechanics in the past century. At first, in the 1920s, wave optics stimulated basic ideas of wave mechanics to conform mechanics with optics, not only in the classical parts (geometrical ray optics versus classical mass-point mechanics), but also in the other part, i.e. wave mechanics versus wave optics. Furthermore, dedicated advances in wave mechanics in explaining electron properties of solids stimulated, in the 1980s, a systematic transfer of its results to wave optics to provide a fine concept of photonic solids. Part I includes basic properties of quantum particles and light waves (Chapter 2), systematic analysis of textbook problems from quantum mechanics and wave optics revealing conformity of the main laws and formulas in these two seemingly unlinked fields of physics (Chapter 3), introduction to electron theory and optics of solids and quantum confinement phenomena in nanostructures (Chapter 4), consideration of semiconductor (Chapter 5) and metal (Chapter 6) nanoparticles, properties of light in periodic (Chapter 7) and non-periodic (Chapter 8) dielectric media, brief description of optical nano-circuitry (Chapter 9), tunneling of light (Chapter 10) and principal properties of metal-dielectric nanostructures (Chapter 11). Chapter 12 summarizes parallelism in electronic and optical phenomena based on wave properties of electrons and light.

Part II is entitled "*Light–matter interaction in nanostructures*" and contains four Chapters, from Chapter 13 to 16. It gives a brief introduction to quantum electrodynamics (Chapter 13), discussion of modification of spontaneous decay rates and spontaneous scattering rates resulting from modified density of photon states in nanostructures (Chapter 14), as well as brief consideration of light–matter states beyond the perturbational approach in microcavities and photonic crystals (Chapter 15). Finally, in Chapter 16, plasmonic enhancement of luminescence and Raman scattering is considered as the bright example of light–matter interaction engineered on a nanoscale.

The author hopes the reader will be successfully introduced into the amazing world of nanophotonics by going through this book. The book is written in a style appropriate to senior students at university, the more advanced reader being referred to original and review articles cited therein. The reader is expected to enjoy the beauty of the photonic nanoworld and to be capable of contributing properly to the "bright future" outlined in the Strategic Research Agenda [15] with the nanophotonic roadmap of how to get there, highlighted recently by the European network of excellence "Nanophotonics to realize molecular scale technologies" (PhoREMOST) [16].

References

[1] J. H. Davies. *The Physics of Low-Dimensional Semiconductors* (Cambridge: Cambridge University Press, 1998).
[2] C. Klingshirn. *Semiconductor Optics* (Berlin: Springer, 1995).
[3] S. V. Gaponenko. *Optical Properties of Semiconductor Nanocrystals* (Cambridge: Cambridge University Press, 1998).
[4] M. Born and E. Wolf. *Principles of Optics* (New York: MacMillan, 1964).

[5] A. Yariv and P. Yeh. *Optical Waves in Crystals* (New York: John Wiley and Sons, 1984).
[6] J. D. Joannopoulos, R. D. Meade and J. N. Winn. *Photonic Crystals: Molding the Flow of Light* (Princeton: University Press, 1995).
[7] L. Novotny and B. Hecht. *Principles of Nano-Optics*. (Cambridge: Cambridge University Press, 2007).
[8] A. M. Zheltikov. *Optics of Microstructured Fibers* (Moscow: Nauka, 2004) – in Russian.
[9] Y. Yamamoto, F. Tassone and H. Cao. *Semiconductor Cavity Quantum Electrodynamics* (Berlin: Springer-Verlag, 2000).
[10] V. P. Bykov. *Radiation of Atoms in a Resonant Environment* (Singapore: World Scientific, 1993).
[11] D. S. Mogilevtsev and S. Ya. Kilin. *Quantum Optics Methods of Structured Reservoirs.* (Minsk: Belorusskaya Nauka, 2007) – *in Russian.*
[12] U. Kreibig and M. Vollmer. *Optical Properties of Metal Clusters* (Berlin: Springer 1995).
[13] S. A. Maier. *Plasmonics: Fundamentals and Applications* (Berlin: Springer Verlag, 2007).
[14] W. E. Lamb. Anti-photon. *Appl. Phys. B*, **60** (1995), 77–80.
[15] *Towards a Bright Future for Europe. Strategic Research Agenda in Photonics* (Düsseldorf: VDI Technologiezentrum, 2006).
[16] *Emerging Nanophotonics. PhoREMOST Network of Excellence* (Cork: Tyndall National Institute, 2008), www.phoremost.org.

PART I

ELECTRONS AND ELECTROMAGNETIC WAVES IN NANOSTRUCTURES

2 Basic properties of electromagnetic waves and quantum particles

It seemed as if Nature had realized one and the same law twice by entirely different means.

Erwin Schrödinger (Nobel lecture, 1933)

2.1 Wavelengths and dispersion laws

A classical wave is described in terms of its frequency ν, amplitude A and wave vector $\mathbf{k}$. Along with ν, circular frequency $\omega = 2\pi\nu$ is often used. Frequencies ν and ω are related to the period T of oscillations

$$T = \frac{1}{\nu} = \frac{2\pi}{\omega}. \tag{2.1}$$

The wavelength λ can be defined as a distance over which the wave travels during a single period T or as a distance between two points obeying the same phase of oscillations. It is related to the wave vector $\mathbf{k}$ as,

$$k = |\mathbf{k}| = \frac{2\pi}{\lambda}, \tag{2.2}$$

where k is referred to as the wave number. The wave vector direction coincides with the direction of the phase motion. The propagation speed of the wave v can be considered in terms of phase velocity and group velocity. Phase velocity decribes the speed of motion of a plane with constant phase:

$$v = \frac{\lambda}{T} = \lambda\nu = \frac{\omega}{k}. \tag{2.3}$$

Group velocity v_g describes the speed and direction of energy transfer in the course of a wave process. It reads as a vector in a 2- and 3-dimensional case,

$$\mathbf{v}_g = \frac{d\omega}{d\mathbf{k}} \tag{2.4}$$

and reduces to a scalar value in a one-dimensional problem, i.e.

$$v_g = \frac{d\omega}{dk}. \tag{2.5}$$

In the particular case of a linear $\omega(k)$ relation, phase and group velocities coincide. In isotropic media the group velocity has direction, coinciding with the wave vector.

For electromagnetic waves in a vacuum the group and phase velocities are equal to $c = 299\,792\,458\,\mathrm{ms}^{-1}$.

Within the scale of electromagnetic waves the visible part occupies a rather narrow band of wavelengths from 400 nm (violet light) to 700 nm (red light). Typically adjacent near-ultraviolet (UV) and near-infrared (IR) bands are also considered as the subject of optical science to form the optical range of electromagnetic waves from 100-200 nm to several micrometers. For example, the most efficient conversion of electrical energy into light occurs in a gas of mercury atoms at 253 nm, which is the basic light source in luminescent lamps (finally converted into the visible by means of luminophores, for example Na vapor in street lamps). Similar or even shorter light wavelengths are used in modern microelectronics technology to get the image of desirable microchip circuitry onto a silicon wafer with submicron resolution. From the IR side, 1550 nm is probably the most representative electromagnetic wavelength since it is the principal wavelength of optical communication, falling within the transparency of commercial silica waveguides and the erbium amplifiers band to provide low-loss propagation over long distances and amplification options to compensate for losses. It is due to this favorable combination of silica and erbium properties that everyone can enjoy worldwide PC-networking.

Quantum particles, e.g. electrons, are believed to exhibit wave properties with wave vector and wavelength being related to their momentum $\mathbf{p}$ in accordance with the relations first proposed by de Broglie in 1923 [1]

$$\mathbf{p} = \hbar\mathbf{k}, \quad \lambda = \frac{h}{p} \tag{2.6}$$

Here $h = 6.626069 \times 10^{-34}$ Js is the Planck constant and $\hbar \equiv h/2\pi$. Kinetic energy E is related to wave number as

$$E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}. \tag{2.7}$$

In terms of kinetic energy E, the particle de Broglie wavelength, using Eq. (2.6), is

$$\lambda = \frac{h}{\sqrt{2mE}}. \tag{2.8}$$

The last relation is instructive in obtaining an immediate intuitive idea about the typical wavelength scale inherent in the electron world. For example, if an electron with rest mass $m_0 = 9.109534 \times 10^{-31}$ kg has gained kinetic energy $E = 10$ eV while being accelerated in a vacuum between a couple of electrodes with potential difference 10 V, its de Broglie wavelength equals 3.88×10^{-10} m $= 0.388$ nm.

We arrive at the following important conclusion. When considering spatial structuring of matter on the nanometer scale, one has electron confinement phenomena at the very short end of the scale (of the order of 1 nm) and confinement of light waves at the very long end of the scale (of the order of 1000 nm). Accordingly, the whole variety of optical manifestations of electron and light wave spatial confinement in nanostructured materials, composites, devices constitute the field of *nanophotonics*.

Relations $\omega(k)$ between frequency ω and wave number k for classical waves and $E(p)$ between kinetic energy E and momentum p for a particle are called the *dispersion laws*.

When considering electromagnetic waves in a vacuum, in accordance with Eq. (2.3) one has the linear dispersion law,

$$\omega = ck. \tag{2.9}$$

By adding the $\hbar$ factor in both parts of Eq. (2.9) the $\omega(k)$ function readily transforms into $E(p)$ recalling Eq. (2.6) along with the other cornerstone relation proposed by Max Planck in 1900 [2],

$$E = \hbar\omega \tag{2.10}$$

where E now stands for the energy quantum of electromagnetic radiation, the *photon* energy. Then we can replace the dispersion law, Eq. (2.9), by

$$E = pc \tag{2.11}$$

referring to this as "the photon dispersion law".

Using electronvolts as convenient energy units, one has a typical range of photon energies from approximately 1 eV to 10 eV to be considered in optics, with 1.770 eV and 3.097 eV corresponding to the visible limits of 700 and 400 nm, respectively. The photon wavelength – photon energy relation in a vacuum reads,

$$E = \frac{hc}{\lambda}, \quad E[\text{electronvolts}] = \frac{1239.85\ldots}{\lambda[\text{nanometers}]} \tag{2.12}$$

which is a consequence of Eqs. (2.11) and (2.6). To compare electronvolts to joules, $1\text{ eV} = 1.602\,189 \times 10^{-19}$ J where the coefficient equals the electron charge value in coulombs.

In a medium other than a vacuum c should be replaced by $c/n(\omega)$ with $n(\omega)$ being *the index of refraction* and Eqs. (2.10) and (2.12) read,

$$\omega = ck/n(\omega), \quad E = pc/n(\omega). \tag{2.13}$$

Figure 2.1 represents the dispersion laws for electromagnetic waves (photons) and for electrons. A straight line inherent in electromagnetic waves in a vacuum changes slope in a given homogeneous medium in accordance with the refractive index n. A parabolic $E(p)$ function for a particle with mass m, in accordance with Eq. (2.7), exhibits different steepness depending on the mass of the particle under consideration.

In a complex medium, refractive index n becomes wavelength dependent (typically reducing with increasing wavelength) and the dispersion law becomes non-linear. Then absolute values of phase and group velocities diverge. In anisotropic media, not only absolute v and v_g values but also directions of phase and energy transfer do not coincide. Notably, the refractive index for electromagnetic waves in a large variety of continuous dielectric media is a quite stable material parameter within the optical range. For all known dielectric and semiconductor materials, refractive index ranges from $n = 1$ for a vacuum to $n = 4$ for germanium monocrystals (in the near IR). For a given material, relative n variation typically measures about 10% within the optical range. Under conditions of high powered optical excitation, when a considerable portion of the electrons experience

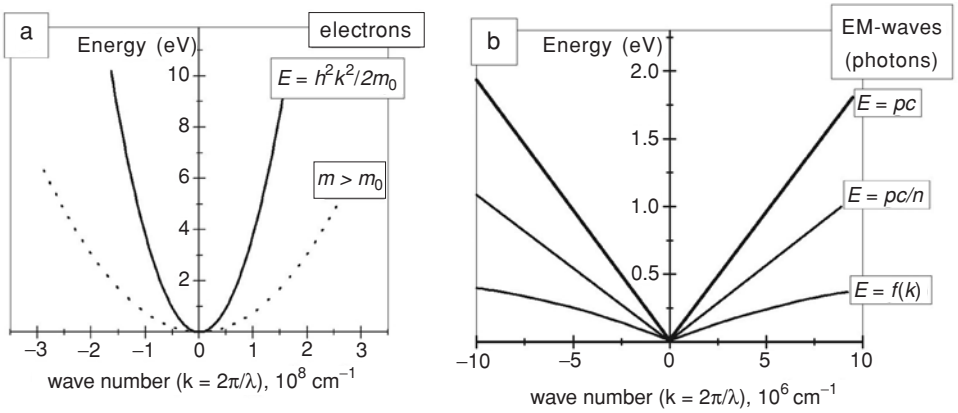

Fig. 2.1 **Dispersion curves (energy versus wave number) for (a) electrons and (b) electromagnetic waves (photons)**

upward transitions to higher states, refractive index can hardly be modified by a few percent as compared to its original value. Even $\Delta n/n = 0.01$ is considered to be distinguished nonlinear-optical behavior. Under the same conditions, the absorption coefficient may exhibit a ten-fold decrease (optical absorption saturation). Under the condition of an external electric field of the order of 10^5 V/cm, 0.1% variation in n is considered as pronounced electro-optical performance.

In complex media, quantum particle motion does not necessarily reduce to a simple parabolic $E(p)$ function, i.e. a particle sometimes cannot be ascribed a constant mass. This results in a generalized definition of particle mass,

$$m^{-1} = \frac{\mathrm{d}^2 E}{\mathrm{d}p^2}, \tag{2.14}$$

which for parabolic law coincides with the usual constant mass. An electron in a periodic lattice features multiple extrema in $E(p)$ dependence. Since every continuous function can be expanded in a series like,

$$E(p) = E(p_0) + (p - p_0)\left.\frac{\mathrm{d}E}{\mathrm{d}p}\right|_{p=p_0} + \frac{1}{2}(p - p_0)^2\left.\frac{\mathrm{d}^2 E}{\mathrm{d}p^2}\right|_{p=p_0} + \cdots, \tag{2.15}$$

one can count energy and momentum from a given extremum point to get the parabolic $E(p)$ relation provided that the first derivative at the extremum point equals zero, and cutting off the terms with derivatives higher than two. In a periodic anisotropic medium the tensor of *effective mass* is used with components determined as,

$$\frac{1}{m_{ij}*} = \frac{\partial^2 E}{\partial p_i \partial p_j}. \tag{2.16}$$

The tensor feature of effective mass means the acceleration the particle experiences under the action of an external force may not coincide with the direction of the force.