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ELECTRON-PHOTON INTERACTION AT THE NANOSCALE

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ELECTRON-PHOTON INTERACTION AT THE NANOSCALE

INTERAKCE ELEKTRONŮ A FOTONŮ V NANOMĚŘÍTKU

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IN APPLIED PHYSICS

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Contents

Author

Andrea Konečná is currently a researcher and lecturer at the Institute of Physical Engineering (IPE) of Faculty of Mechanical Engineering (FME), Brno University of Technology (BUT). She is leading a newly established research group **AR**t of **T**heory in **E**lectron **MI**croscopy and **S**pectroscopy (ARTEMIS), under a prestigious Junior Star funding scheme of the Czech Science Foundation.

After obtaining the Engineering Physics Master's degree at FME, BUT, Andrea Konečná pursued PhD studies within the programme "Physics of Nanostructures and Advanced Materials" of the University of the Basque Country under the supervision of Javier Aizpurua and Rainer Hillenbrand. She defended her PhD thesis entitled "Theoretical Description of Low-Energy Excitations in Nanostructures as Probed by Fast Electrons" in May 2019. She further developed her expertise in theory of electron-matter interaction at the Institute of Photonic Sciences in Barcelona (Spain) and spent two years as a post-doctoral researcher in the Nanophotonics Theory Group led by Javier García de Abajo.

Research topics of Andrea Konečná are at the interface of nanophotonics and state-of-the-art electron microscopy and spectroscopy. In particular, she has been dealing with theoretical description of the interaction of fast electron beams with nanostructured matter and optical fields at the nanoscale within the following topics:

- Probing optical excitations (phonons and vibrations, plasmons, excitons) by electron energy-loss spectroscopy (EELS) in scanning transmission electron microscopy (STEM). She has been modelling and interpreting various STEM-EELS experiments that involved understanding hyperbolic phonon polaritons in thin films of hexagonal boron nitride, plasmons in metallic nanoparticles, low-energy nanoparticle plasmons in unconventional plasmonic materials such as MXenes or highly-doped semiconductors.

- Shaping electron beams via the interaction with optical fields. She has contributed to suggestions of versatile and fast setups using structured light beams whose phase and intensity profile can be imprinted on electron beams. Such optical phase plates for electrons could be implemented in future electron microscopes.

- Use of shaped electron beams in probing symmetries of excitations in matter and for low-dose imaging.

- Thermal effects in EELS, spatial dependence of thermally-driven phase transitions.

To address the research interests above, Andrea Konečná combines analytical and numerical methods (boudary- and finite-element methods) to describe electromagnetic fields emerging in the interaction of fast electrons, arbitrarily shaped nanostructures and nanoscale optical fields. She also uses various theoretical approaches to solve for the electron propagation through nanoscale electromagnetic fields.

1 Introduction

This habilitation thesis stands topically at the interface of two seemingly distinct fields: **electron microscopy and spectroscopy**, aiming at developing methods for materials analysis with electron beams, and **nanophotonics** dealing with confined optical fields and low-energy excitations in nanostructures. However, one of the main motivations stimulating developments in both fields is identical – to inspect samples with better spatial resolution than we can achieve with conventional light microscopes.

The smallest resolvable details in an image are restricted according to the Abbe diffraction limit $d = \lambda/(2\mathrm{NA})$, where λ is the probing wavelength and NA is the numerical aperture. A possible solution to overcome the limit is to decrease λ. In nanophotonics, we reduce photon wavelength by tightly confining the optical fields at interfaces, thin films, or specifically designed nanostructures. On the other hand, electron microscopes rely on the fact that electrons accelerated to energies $\sim 10^4 - 10^5$ eV can be associated with wavelengths as small as units of picometers and can be used to probe matter at single-atom resolution. Both fields, however, go well beyond "just" improved imaging and have many other applications.

In SECTION 1.1 and SECTION 1.2, we will separately introduce electron microscopy and spectroscopy, and nanophotonics. This will provide a basis for discussing the possible synergy between the two fields in SECTION 1.3, which is essential for this thesis.

1.1 Electron microscopy and spectroscopy

Since the invention and construction of the first electron microscope by Max Knoll and Ernst Ruska in early 1930s[1], electron microscopes have evolved into irreplaceable instruments in many areas of research and technology. Due to the sustainable development of electron-microscope instrumentation and related imaging and spectroscopic techniques, modern instruments are powerful analytical tools in material, physical and chemical sciences, as well as in biology or nanotechnology. The electron beams are not only passive probes but can also be used as fabrication tools to sculpt nanostructures and nanodevices. State-of-the-art microscopes can operate at sub-Ångstrom spatial resolution[2], attosecond time resolution[3], and can resolve sample excitations with few-meV spectral resolution[4].

Electron microscopes are commonly divided into two main categories: **scanning electron microscopes** (SEMs) are typically operated at acceleration voltages up to 30 kV, and we usually collect secondary electrons (SEs) emitted due to the interaction of the sample atoms with a focused primary electron beam. On the other hand, in **transmission electron microscopes** (TEMs) operated at higher voltages (between ~ 30 and 300 kV), we detect the primary-beam electrons after their transmission through the sample. Electron beams in TEM can be transversely extended, resembling plane waves, or tightly focused and scanned across the sample. In the latter case, we talk about **scanning transmission electron microscopes** (STEMs).

The interaction between an energetic electron beam and the sample can generate a "zoo" of signals and excitations. Part of the signal comprises electrons: primary electrons transmitted through the sample, back-scattered primary electrons (BSEs), and secondary and Auger electrons (SEs and AEs) emitted from the sampled material. Moreover, the interaction process can lead to the emission of photons, either in the visible-ultraviolet spectral range (cathodoluminescence (CL) process) or in the X-ray region. The electron-sample interaction processes can also be sorted based on the difference between initial and final electron beam energy (energy loss ΔE) as elastic ($\Delta E = 0$) or inelastic ($\Delta E \neq 0$). The inelastic processes can involve excitations in the sample, such as magnons, vibrational excitations, plasmons, excitons or other electronic excitations.

Having the microscope capable of operating with a focused beam (SEM or STEM) allows not only for imaging but also for highly localized spectroscopy. By analyzing the energy distribution of SEs, AEs, or X-rays, we can retrieve the sample's elemental composition. The CL signal can provide characteristics of material band gaps or optical excitations. Spatial localization of these signals is highly dependent on the type of material, primary beam energy and focus, but nanometric details are often routinely resolved. The most essential spectroscopic technique for this habilitation thesis is **electron energy-loss spectroscopy** (EELS), which analyses the energy of the primary electron beam after the interaction with the sample with the help of an electron energy-loss spectrometer, typically a magnetic prism[5].

After recent instrumental developments in electron monochromation, determining initial energy of the primary beam more precisely, and in energy-loss spectrometers, EELS can achieve a few-meV energy resolution, unlocking the energy region where phonons and molecular vibrations appear[6]. It is equally interesting to study valence electron excitations in the energy range $\sim 1-50$ eV, such as plasmons, excitons, and electronic transitions governing matter's optical and electronic properties[7]. Chemical composition can be determined from EELS at energies of hundreds of eVs corresponding to core electron excitations[8]. The unprecedented combined spectral/spatial meV/sub-Ångstrom resolution, breadth of the analysable energy region ($10^{-3}-10^{3}$ eV), and richness of analytic possibilities achievable with modern STEM-EELS instruments facilitate the correlation of various material and functional properties and make STEM-EELS a unique technique.

Another development direction of state-of-the-art electron microscopes goes towards improvements in time resolution. Conventional microscopes and related spectroscopic techniques rely on the accumulation of electron and photon counts over relatively long time periods ($10^{-3}-10^{2}$ s), which averages many dynamical processes in the studied samples, such as dynamics of phase transitions or optical excitations. These typical time-resolution limits can be overcome by preparing a pulse of primary electrons whose arrival towards the sample is synchronized with an external stimulus pre-exciting the sample within a "pump-probe" experiment. We currently distinguish between

dynamic TEM (DTEM) and **ultrafast TEM** (UTEM) used to probe irreversible or reversible processes, respectively. UTEM is closely linked to the so-called **photon-induced near-field electron microscopy** (PINEM), which probes the evolution of near-fields associated with the optical excitation in nanostructured samples in a stroboscopic way by varying the delay between the arrival of the electrons and the sample stimulated by a laser pulse.

Besides improvements in spectral and time resolution, there have been many efforts to achieve high spatial resolution in all microscope types and to develop new imaging techniques. A key aspect determining the microscope's resolving power is our capability to eliminate aberrations of electron lenses to form and image the electron beams perfectly. The electron beam distortions can be significantly reduced nowadays by involving aberration correctors[2,9].

The constant development of new imaging techniques, either improving the resolution or introducing new capabilities, is also responsible for making electron microscopes so powerful. For instance, samples that are thin and composed of light elements (such as 2D materials or biological specimens) impose mainly a phase modulation in the transmitted electron wave function in TEM, while the contrast in the conventional setup mostly provides amplitude information (*i.e.*, we detect intensity $I \propto |\psi_{\mathrm{f,prop}}|^2$, where $\psi_{\mathrm{f,prop}}$ is the post-interaction and propagated electron wave function). This limitation have been overcome by introducing electron holography[10], or phase plates[11], using the concepts adopted from light optics to retrieve the phase information. Another possibility to reconstruct the sample phase is electron ptychography[12].

1.2 Nanophotonics

To introduce one of the main concepts of nanophotonics, we can start with basic considerations of waves propagating in a bulk, homogeneous, and isotropic medium. An electric field describing a harmonic plane wave of light in such an environment can be expressed as $\mathbf{E}(\mathbf{r},t) = \mathrm{Re}\{\mathbf{E}_0\,\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}-\mathrm{i}\omega t}\}$, where $(\mathbf{r},t)$ are spatial coordinates and time, $\mathbf{E}_0$ is a vector describing amplitude and polarization, $\mathbf{k}$ is a wave vector determining the direction of propagation, and ω is the angular frequency. To ensure fulfillment of the wave equation in an isotropic medium described by relative permittivity ε and relative permeability μ, we have $k = \sqrt{\varepsilon\mu}\,\omega/c$, where c is the speed of light in vacuum.

Nanophotonics very often deals with materials and frequency ranges, where $\mu = 1$, and $\mathrm{Re}\{\varepsilon\} < 0 \wedge \mathrm{Im}\{\varepsilon\} \ll \mathrm{Re}\{\varepsilon\}$, which can take place, *e.g.*, in noble metals in the visible spectral range[13], or ionic crystals in the infrared[14]. Such dielectric properties imply purely imaginary k and thus no propagation of plane waves in bulk. However, solutions taking the form of evanescent waves propagating along interfaces with such materials exist. For a planar interface between vacuum ($\varepsilon = 1$) and material described by the permittivity ε, the wave vector component in the direction of propagation along the interface has to fulfill $k_\parallel = \omega/c\sqrt{\varepsilon/(\varepsilon+1)}$.

One can easily check that the wave vector component perpendicular to the plane of propagation yields an exponential decay of the field from the interface and, importantly, $\mathrm{Re}\{k_\parallel\} > \omega/c$ if the dielectric response fulfills the abovementioned conditions. The evanescent waves corresponding to the so-called polaritons, hybrid light-matter waves, are thus associated with an effective wavelength $\lambda = 2\pi/k_{\|}$, which is smaller than the wavelength of a photon in free space $\lambda_0 = 2\pi c/\omega$. This result suggests that the polaritons could break the conventional Abbe diffraction limit and "shrink" light to much smaller dimensions compared to photon wavelengths in free space or in an infinitely extended homogeneous medium.

The flat interface represents only one of the many arrangements to achieve light confinement due to the surface polaritons. Other geometries often used in nanophotonics are flat or corrugated thin films, edges, or variously shaped nanoparticles, ranging from spheres to nanostars, where the so-called localized surface plasmons (LSPs) reside[13]. It is nowadays possible to tailor the confined optical field almost on demand by choosing the suitable material and designing the particular geometry concerning the operating frequency ranging from far infrared to ultraviolet region of the electromagnetic spectrum.

Our understanding of the behavior of light at the nanoscale, together with improvements in nanofabrication and chemical synthesis of specifically shaped nanoparticles, leads to a broad scope of applications, *e.g.*, in light nanofocusing and waveguiding[15–17], energy storage and conversion[18], biosensing[19], or quantum computing[20]. Other efforts of the nanophotonics community are in the development of near-field-based imaging and spectroscopic techniques, such as scanning-near field optical microscopy and nano Fourier Transform Infrared spectroscopy (nano-FTIR)[21] or tip-enhanced Raman spectroscopy[22].

1.3 Marriage of electrons and photons

As the confined near field features spatial details much smaller than the free-space photon wavelength, it is understandable that the "conventional" photons cannot probe the spatial characteristics of such nanoscale optical fields. And very often, the free-space photon cannot even excite such fields. On the other hand, a beam of fast electrons is accompanied by an evanescent field, thus representing a natural excitation source and/or probe for polaritons in nanophotonics structures. The interaction of fast electrons with confined polaritonic near fields is then imprinted in electron spectra. Interestingly, this interaction can be either spontaneous or stimulated if an external source is used to pre-excited the sample, as schematically visualized in FIGURE 1.1.

In CHAPTER 2, we introduce several works discussing how fast electrons probe the polaritonic waves in the infrared (IR) and visible (VIS) energy range, respectively. We will show several material platforms, ranging from ionic crystals supporting phonon polaritons (PhPs) to doped semiconductors and metals where free-charge carriers yield plasmon polaritons (PPs). As another example, we will introduce the excitation of localized vibrational modes of both optical and acoustic nature in an isolated inorganic molecule.

Although our description of the capabilities of electron microscopy and spectroscopy in SECTION 1.1 might result in the impression that everything we need has already been developed and all issues are resolved, but the opposite is true. Many solutions or techniques mentioned are complex

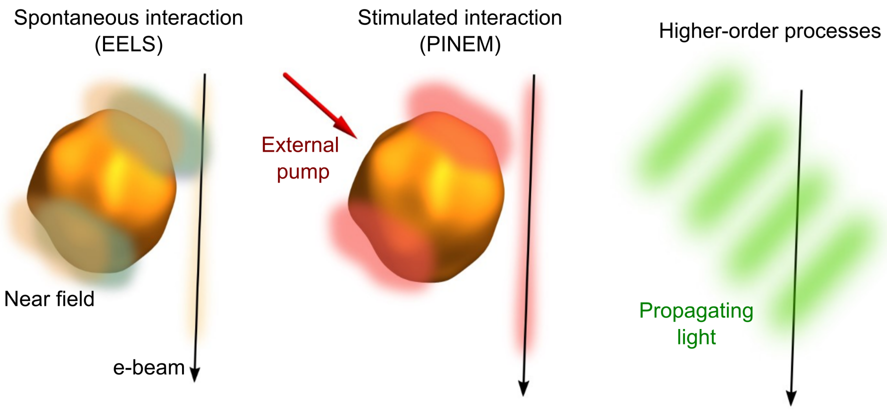

Figure 1.1: Three scenarios of electron-light interaction discussed in this Thesis. Left: electron beams can induce optical near fields, which results in energy losses visible in electron spectra. Middle: if an electron beam passes close to an already excited near field (*e.g.,* by an external light source), it can experience multiple photon exchanges. Right: electrons can also interact with freely propagating photons through higher-order processes. Such interaction is thus possible, but rather inefficient.

regarding instrumentation, operation and/or post-processing[12]. Therefore, there is still a search for alternative and out-of-the-box solutions. Exploiting the electron-photon interaction could be one of them: in CHAPTER 3 we discuss how the optical fields can be used to actively modify the electron beams in different scenarios and suggest setups to correct for electron-beam aberrations and generate on-demand electron beam shapes.

The electron-photon interaction could be introduced in an electron microscope in two (or even more) steps: in the first one, we could perform the on-demand tailoring of electron wave functions, as shown in FIGURE 1.2, while in the second step, the tailored electrons would interact with a sample. CHAPTER 3 outlines several possible applications of the shaped electron beams in both imaging and spectroscopy and finally, in CHAPTER 4 we summarize the presented work and present an outlook and personal viewpoint of the future development of electron spectro-microscopy hand in hand with (nano)photonics.

This thesis is comprised of brief commentaries of original work co-authored by Andrea Konečná. A reference to the related publication accompanies each commentary.

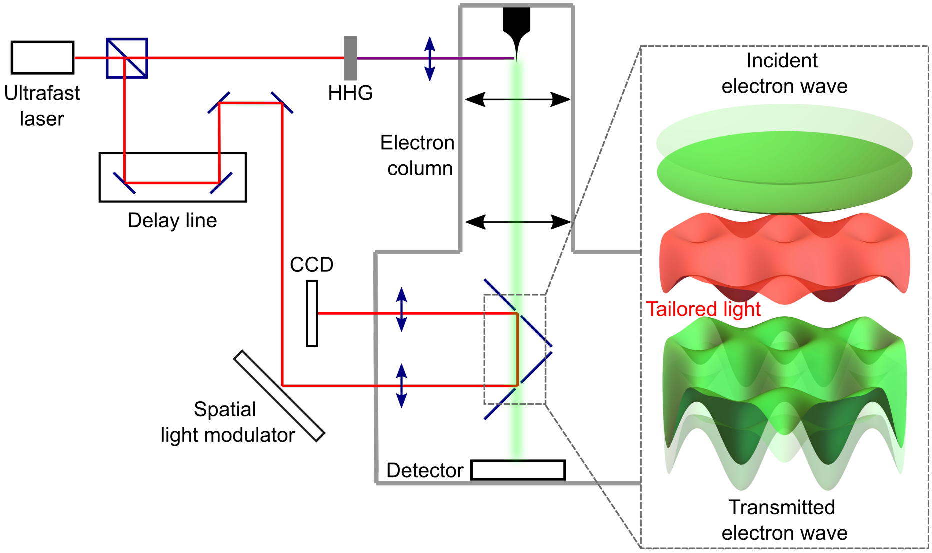

Figure 1.2: Implementation of electron-light interaction in an electron microscope. A schematic of a possible experimental setup as introduced in Ref.[23]. The setup is based on a femtosecond laser source attached to a SEM. The laser extracts electrons from the electron gun and in the second path it is structured by a spatial light modulator to modify the electron wave function as visualized in the inset.

2 Electron spectroscopy

This Chapter summarizes our contributions to the field of vibrational STEM-EELS as well as to electron-based spectroscopies applied on excitations in the visible spectral range.

2.1 Vibrational electron energy-loss spectroscopy

When energetic primary electrons in STEM interact with a sample without any other external stimulation, the probability of nonzero energy exchange between the electrons and the sample is very low. If we employ an electron energy-loss spectrometer, most of the electrons contribute to the so-called zero-loss peak (ZLP) with a natural width determined by the primary electrons' monochromaticity (energy spread). As the energy spread limits the resolution over the entire EEL spectrum, the aim is to reduce it. The best results can be achieved by employing cold field-emission guns producing the smallest $\sim$ 250-meV broadening[24] and by further improving the energy spread with monochromators.

So far, the most successful STEM-EELS design can reach the ZLP width as small as a few meV[4,6]. Such resolution yields unprecedented details in the EEL spectra in core-loss and valence-loss regions that can be simultaneously linked with the precisely defined electron-beam position. Notably, the narrowness of the ZLP also uncovers the spectral region, where magnons, phonons, low-energy plasmons, and molecular vibrations exist. Although the ultra-low-energy or high-resolution STEM-EELS is a relatively young technique, it has already been applied to various material systems summarized below, where either localized vibrational excitations or low-energy quasi-particles emerge.

2.1.1 Molecular vibrations

Konečná, A., Iyikanat, F. & García de Abajo, F. J. Theory of Atomic-Scale Vibrational Mapping and Isotope Identification with Electron Beams. *ACS Nano* **15,** 9890–9899 (2021).

Localized vibrational modes have been detected by STEM-EELS in molecular crystals, particularly in guanine[26,27], in clusters or alanine molecules, where different isotopes were distinguished[28], in molecular adsorbates on surfaces[29], and even in liquid water encapsulated in a liquid cell[30]. Fast electrons are typically quite harmful to sensitive organic molecules, which has been experimentally overcome by taking advantage of long-range interaction with optical-like vibrational modes featuring non-zero net dipole moment. Such vibrations are detectable even with an electron beam placed in aloof geometry, probing the molecules remotely. We confirm and extend these observations with a case study of an inorganic h-BN-like molecule, where we observe different localization of the acoustic- and optical-like vibrations, and suggest that single-isotope impurities could be detected down to the single-atom level[25].

2.1.2 Phonon polaritons

Maciel-Escudero, C., Konečná, A., Hillenbrand, R. & Aizpurua, J. Probing and steering bulk and surface phonon polaritons in uniaxial materials using fast electrons: Hexagonal boron nitride. *Phys. Rev. B* **102,** 115431 (2020).

Konečná, A., Li, J., Edgar, J. H., García de Abajo, F. J. & Hachtel, J. A. Revealing Nanoscale Confinement Effects on Hyperbolic Phonon Polaritons with an Electron Beam. *Small* **17,** 2103404 (2021).

Solid-state systems with periodic atomic lattices feature acoustic and optical phonon branches. It turns out that the largest energy-loss probability arises when the electrons interact with ionic or polar crystals featuring optical modes with a non-zero net dipole moment. In such a scenario, the crystal can support PhPs[33], which can be, similarly to the optically active molecular vibrations, excited even with aloof electrons[34]. As we mentioned, the electrons naturally couple to the polaritons and can be used to map the associated near field and its confinement.

Even the first STEM-EELS spectra in the infrared[6] showed the PhPs in different ionic and polar crystals, including hexagonal BN (h-BN), SiO_2, SiC, and TiH_2. However, the complete and correct interpretation of the spectra was presented in follow-up works, which could get some inspiration from works published a few decades earlier[35]. Several studies demonstrated the emergence of rather damped PhPs in thin films and at edges of SiO_2[36–38]. Confined PhPs were observed in MgO nanocubes[39] and ZnO nanowires[40].

PhPs in h-BN represent a special case because of the material anisotropy. Due to the covalent in-plane and weak out-of-plane van-der-Waals bonds, h-BN features distinct vibrational properties in the two directions. The anisotropy then yields a peculiar propagation of waves on h-BN surfaces in different frequency regions when excited by focused electron beams[31].

When the h-BN crystal takes the form of a thin film, waveguide-like modes that offer promising applications in nanophotonic devices can be excited and probed[41]. Interestingly, by precisely positioning the electron beam with respect to thin-film boundaries, we can control the preferred polariton wavelength to be probed by the electrons, which allows us to reconstruct the polariton dispersion. We first suggested this polariton interferometry scheme in Ref.[42], but we were able to exploit its full potential only in the more recent work[32]. We were able to reconstruct dispersions of polaritonic modes propagating along sheet or edge surfaces, where we revealed that an exact edge geometry plays a significant role in determining the resulting polaritonic properties.

2.1.3 Infrared plasmon polaritons

Yang, H., Konečná, A., Xu, X., Cheong, S.-W., Garfunkel, E., García de Abajo, F. J. & Batson, P. E. Low-Loss Tunable Infrared Plasmons in the High-Mobility Perovskite (Ba, La) SnO3. *Small* **18,** 2106897 (2022).

Yang, H., Konečná, A., Xu, X., Cheong, S.-W., Batson, P. E., García de Abajo, F. J. & Garfunkel, E. Simultaneous Imaging of Dopants and Free Charge Carriers by Monochromated EELS. *ACS Nano* **16,** 18795–18805 (2022).

Compared to polar crystals, where the PhPs are formed due to the lattice vibrations, materials with free-charge carriers can feature PPs. In the infrared, PPs emerge either in large metallic cavities (*e.g.*, micrometer-sized particles)[45,46] or in doped semiconductors[47], where the free-carrier oscillations naturally occur at lower frequencies due to smaller carrier concentrations.

We investigated a perovskite material $BaSnO_3$ (BSO) which becomes plasmonic due to the doping by La atoms (BLSO)[43]. In particular, we performed spatially-resolved EELS mapping of BLSO nanoparticles forming nanocubes or nanoblocks and thoroughly analyzed the localized plasmonic modes formed in these nanoresonators. We focused on evaluating the resonance broadenings $\Delta\omega_\mathrm{r}$ and quality factors $Q = \omega_\mathrm{r}/(\Delta\omega_\mathrm{r})$, where ω_r denotes the resonant frequency. These quantities are tightly related to the energy loss associated with the resonances and, thus, the potential applicability of the plasmonic nanoparticles. Interestingly, we found out that the plasmonic resonances in the smallest particles are more damped than initially expected due to additional scattering and very tight confinement of the conduction electrons.

We also investigated the effects of inhomogeneous doping by La in some of the nanoparticles[44]. We used the full potential of STEM-EELS and correlated the information from high-resolution imaging, EEL spectra in the core-loss, valence, and vibrational energy regions. Although the images did not reveal any apparent inhomogeneities, we could extract dopant densities by analyzing ratios of the peaks associated with La and Ba atoms in the core-loss EELS. In the visible range, we could evaluate the band gap, which, together with Hall measurements, led to our estimation of the Burstein-Moss (B-M) shift. We could also observe local energies of bulk plasmons in the (near)infrared spectral range, which correlated with the dopant densities and values with the most significant B-M shifts. Very interestingly, the inhomogeneities in doping led to non-trivial localized plasmon modes, and we could even observe waveguiding-like modes arising between areas with a local increase of doping. We also concluded that not all La atoms provide carriers and found a carrier-activation percentage of about 50 %.

2.1.4 Coupled plasmon-phonon polaritons

Gallina, P., Konečná, A., Liška, J., Idrobo, J. C. & Šikola, T. Strongly Coupled Plasmon and Phonon Polaritons as Seen by Photon and Electron Probes. *Phys. Rev. Appl.* **19,** 024042 (2023).

If we deal with a system composed of several elements (*e.g.*, nanoparticles), each supporting a polaritonic excitation, we must consider a possible coupling between the elements. Such coupling occurs via the electromagnetic near field associated with each polaritonic excitation and can influence all other elements yielding a new modal structure[49]. We can imagine a system of coupled oscillators, where each oscillator represents one polaritonic excitation, and the springs emerge due to the electromagnetic interaction between them[50]. Coupled polaritonic systems are extensively studied in nanophotonics[51,52]. The coupling offers more degrees of freedom to tailor the nanoscale fields on demand and brings applications in energy transport, sensing, or field enhancement[53].

The coupling of two or more plasmonic particles has also been studied in various STEM-EELS works, which revealed both the energy structure of the new hybridized modes and the related near field distributions[45,54–56]. As the infrared frequency range became accessible only recently in STEM-EELS, only a few pioneering works[57,58] addressed the coupling between PhPs, residing exclusively in the infrared, and low-energy PPs. Our contribution[48] deals with the interaction of previously studied infrared polaritons in SiO_2 and localized plasmonic excitations in micron-sized gold particles[52]. We revealed that by precisely positioning the electron beam, we could actively control the coupling, which could be used to characterize both the coupled system and individual system constituents without any need to prepare several samples. We also compared the spatially-resolved STEM-EELS measurements to far-field optical spectra, which lack spatial information and, on the other hand, bring better spectral resolution.

2.2 Electron spectroscopy in the visible spectral range

STEM-EELS in the infrared range is undoubtedly one of the exciting directions among electron-based spectroscopic techniques. Here we first discuss another STEM-EELS work, but compared to the results in the previous chapter applied solely in the visible spectral range. We also extend the scope to an alternative interferometric technique based on the collection of CL signal, and PINEM as applied in the detection of the nonlinear optical response of gold nanoparticles.

2.2.1 Excitons

Reidy, K., Majchrzak, P. E., Haas, B., Thomsen, J. D., Konečná, A., Park, E., Klein, J., Jones, A. J. H., Volckaert, K., Biswas, D., Watson, M. D., Cacho, C., Narang, P., Koch, C. T., Ulstrup, S., Ross, F. M. & Idrobo, J. C. Direct Visualization of Subnanometer Variations in the Excitonic Spectra of 2D/3D Semiconductor/Metal Heterostructures. *Nano Lett.* **23,** 1068–1076 (2023).

Besides plasmons, excitons are other electronic excitations of high interest in nanophotonics. They emerge due to the formation of an electron-hole pair, typically in semiconductors. Similarly to plasmons, excitons can be largely influenced by nanoconfinement, with an extreme case represented by the so-called quantum dots. Our ability to control the excitonic states offers applications in generating single- (or few-) photon sources for quantum communication, in photovoltaics or sensing.

STEM-EELS has recently emerged as a possible technique to study the excitonic properties at the nanoscale. In our work, we studied the difference in the excitonic structure in a plain few-layer transition metal dichalcogenide (TMD) MoS_2 with respect to areas with epitaxially grown gold nanoparticles on top of MoS_2. We reveal that the gold contact is responsible for the dielectric screening of the exciton and the emergence of a new peak in the EEL spectra. Such an arrangement of metal-TMD contacts can be found in TMD-based nanodevices and understanding the changes in the excitonic properties induced by the metal contacts is even technologically important.

2.2.2 Localized surface plasmons and plasmon polaritons

Sannomiya, T., Konečná, A., Matsukata, T., Thollar, Z., Okamoto, T., García de Abajo, F. J. & Yamamoto, N. Cathodoluminescence Phase Extraction of the Coupling between Nanoparticles and Surface Plasmon Polaritons. *Nano Lett.* **20,** 592–598 (2020).

When a focused electron beam impinges on a metallic film, it produces the so-called transition radiation (TR) due to the annihilation of a mirror charge. Simultaneously, the beam launches a surface PP (SPP) propagating along the boundary. The polaritonic wave propagates until it gets damped due to the absorption of the metal or adsorbate layers, but it can also reach a grating or a scatterer through which the energy can be radiated to the far field.

In our work, the scatterers are represented by silver nanospheres separated by a thin dielectric spacer from a thick metallic film. This geometry leads to the hybridization of localized plasmon modes of a free-standing particle with the corresponding mirror charges in the metal film underneath[61]. By placing the electron beam close to the particle, we can directly excite the hybridized modes and detect them through radiation in the far field in the CL setup. We identify bonding and anti-bonding dipolar modes with polarization parallel to the metal-dielectric interface, as well as an out-of-plane (perpendicular to the interface) bonding dipolar mode and higher-order quadrupolar modes.

If the electron beam is focused at larger distances from the particles, it excites the TR and simultaneously the SPP, which in turn excites in-plane hybridized plasmonic modes of the nanosphere-on-mirror system. The plasmons radiate to the far field and interfere with the TR. By scanning the electron beam with respect to the nanoparticle, we can retrieve the relative phase shifts between the events. By applying a conformal mapping scheme, it is then possible to visualize the phase flip between the SPP excitation and the scattered field around the resonance energy of the localized mode.

2.2.3 Nonlinear plasmonic response

Konečná, A., Di Giulio, V., Mkhitaryan, V., Ropers, C. & García de Abajo, F. J. Nanoscale Nonlinear Spectroscopy with Electron Beams. *ACS Photonics* **7,** 1290–1296 (2020).

A non-linear optical response can be observed in a broad range of nanophotonic systems, including metallic nanoparticles and interfaces when stimulated by an intense excitation field. As PINEM often relies on intense laser fields, it could naturally become a technique suitable for probing the non-linear optical response at the nanoscale.

The PINEM spectrum is symmetric for electrons interacting with the field at a single frequency (*i.e.*, only the linear field) – the probability that an electron gains a quantum of photon energy $l\hbar\omega$, P_l, is equal to the probability of losing a quantum of photon energy $-l\hbar\omega$, P_{-l}. However, we theoretically find that this is not true anymore when the nonlinear field components emerge, *i.e.*, $P_l \neq P_{-l}$. We further present two particular cases of electrons interacting with metallic nanoparticles in the form of a sphere or a nanorod excited by strong laser fields inducing the second-harmonic (SH) response. We confirm that the asymmetries in the PINEM spectra, from which we could deduce the strength of the SH field, are achievable for realistic laser powers.

3 Generation and applications of shaped electron beams

A possible solution to overcome some drawbacks and introduce new applications of STEM-EELS is to perform electron beam shaping. We can employ electron phase plates (EPPs) that can be inserted in an electron microscope [see the scheme in FIGURE 3.1(a)] to prepare an electron wave function with on-demand amplitude and phase profile. Such shaping could also compensate for a phase distortion introduced by the other electron-optics elements and thus eliminate the need for expensive aberration correctors. A conceptually well-known EPP design is a diffraction grating used as a beam splitter[63] or a generator of vortex electron beams (VEBs)[64,65], see FIGURE 3.1(b). Another option to imprint the phase varying transversely to the beam axis is to let an extended beam transmit through a thin film with a nontrivial thickness profile. Sculpted thin films have been successfully used to compensate for a spherical aberration[66] or VEB generation[67]. However, these EPPs have a major drawback: they cannot be modified or tuned when plugged into the microscope.

So far, several designs of tunable EPPs have been proposed. The first design relies on an array of micron-scale einzel lenses whose voltage and thus the relative phase of electrons transmitted through different lenses can be adjusted independently. Preliminary proof-of-concept experiments with the einzel-lens modulator (ELM)[68] demonstrated the successful generation of variously shaped electron beams (SEBs). An example of an ELM featuring six einzel lenses and the corresponding phase profile of the transmitted electron wave function is shown in FIGURE 3.1(c). Another microelectronics-based EPP relies on metallic electrodes forming a non-trivial electrostatic potential around the edges of an aperture. Here we suggest two alternatives based on the electron-photon interaction, such as the scheme shown in FIGURE 3.1(d).

3.1 Generation of shaped electron beams with light

García de Abajo, F. J. & Konečná, A. Optical Modulation of Electron Beams in Free Space. *Phys. Rev. Lett.* **126,** 123901 (12 2021).

The optical free-electron modulator (OFEM) is based on the interaction of fast electrons with optical fields in free space. The free-space interaction is due to an electron-photon momentum mismatch typically very inefficient but still feasible if an intense laser field is involved. If the optical field features a tailored amplitude and phase profile, achieved, *e.g.*, by incorporating a spatial light modulator

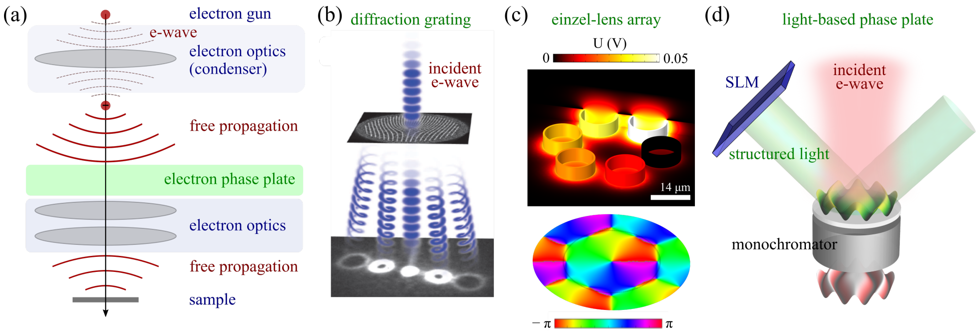

Figure 3.1: Electron phase plates. (a) A simplified scheme of an electron microscope with an electron phase plate. (b) Diffraction grating for generation of electron vortex beams (taken from Ref.[64]). (c) An array of six einzel lenses representing a tunable EPP. (d) PINEM-based EPP.

(SLM), the electron wave function exhibits a nontrivial spatial variation after the interaction. Our theoretical suggestion was recently reproduced experimentally[23], confirming the predictions.

Konečná, A. & García de Abajo, F. J. Electron Beam Aberration Correction Using Optical Near Fields. *Phys. Rev. Lett.* **125,** 030801 (3 2020).

The SLM is also used in the second possible design when tailored light is reflected off a thin film opaque for light but transparent for electrons. The presence of the film makes the electron-photon interaction more efficient, which is well known from other PINEM experiments[71]. The PINEM-based EPP, which we exploited theoretically, could be straightforwardly used for correcting electron-microscope aberrations or for reaching on-demand electron beam shapes. Recent experimental realization confirmed our predictions and demonstrated the generation of Laguerre-Gauss beams in a setup very similar to the theoretically proposed one[72].

3.2 Applications of shaped electron beams

The shaped electron beams offer many applications. As already shown, the rapidly tunable EPPs, such as those based on the electron-light interaction, can eliminate aberrations of conventional electro- and magnetostatic electron lenses and serve as aberration correctors. However, the EPPs could be used to introduce previously impossible approaches in imaging and spectroscopy.

Konečná, A., Rotunno, E., Grillo, V., García de Abajo, F. J. & Vanacore, G. M. Single-Pixel Imaging in Space and Time with Optically Modulated Free Electrons. *ACS Photonics* **10,** 1463–1472 (2023).

In light optics, the detection of light reflected off or transmitted through a sample is typically done using detectors with multiple pixels. Such detectors are however relatively slow and cannot operate at all wavelengths. Imaging with a detector featuring only one pixel was developed to overcome these drawbacks. Of course, a single pixel only carries information on the integrated intensity of the transmitted or reflected light, and we would lack spatial resolution. The sample morphology is therefore reconstructed using variable illumination with differently shaped incoming light beams.

We studied if the same approach is suitable for electron microscopy. We found that by tailoring the electron wave function amplitude with the PINEM-based EPP, we can reconstruct the structure of amplitude objects even when considering limitations of a realistic setup. We have also suggested that the same reconstruction algorithm could be used in time instead of the spatial domain to reconstruct the temporal evolution of a reversible event modifying the sample image contrast.

Konečná, A., Iyikanat, F. & García de Abajo, F. J. Entangling free electrons and optical excitations. *Sci. Adv.* **8,** eabo7853 (2022).

It can be shown that the interaction of fast electrons with a sample featuring optical modes results in an entangled electron-sample state which we describe in terms of excited sample states and final electron scattering directions. We formulate an inverse problem when we target a specific final entangled state, which can be achieved by precisely shaping and positioning the incident electron wave function with respect to the sample.

We studied two specific cases of a plasmonic nanotriangle with localized surface plasmon modes and a hBN-like molecule supporting vibrational excitations. In both scenarios we could find suitable shapes of incident electron wave functions to achieve the desired final entangled states within a specific energy and momentum window (*i.e.*, we need to perform energy and momentum post-filtering). It is also possible to target excitation of only one sample mode and eliminate the electron interaction with other modes. In such case, we can achieve a selective excitation similar to shown previously[75].

4 Conclusion and outlook

This habilitation thesis can be divided into two main parts: I) CHAPTER 2 summarizes works applying already existing imaging and spectroscopic techniques in electron microscopy to solid-state nanosystems. We discussed the coupling of fast electrons with the confined optical fields over a broad spectral range, which makes the electron beams ideal in probing phonon and plasmon polaritons or excitons in nanostructures. II) In CHAPTER 3, we demonstrated the high potential of non-trivially shaped electron beams to improve already existing microscopes or develop entirely new microscopic and spectroscopic methods, for which we can seek inspiration in light optics.

I foresee a range of research directions I would like to deal with in the upcoming years. Some of the research topics listed below are already included in the "Junior Star" grant proposal, awarded for years 2023 – 2027 by the Czech Science Foundation to start a new research group.

4.1 Improvements in instrumentation

Development of light-based phase plates

We discussed two possible designs of light-based phase plates in CHAPTER 3. However, many modifications or other options could be adapted, such as polariton-based phase plate[76] or shaping through the interaction of fields confined at edges of an aperture[71], schematically shown in FIGURE 4.1. Further research is also required for solving inverse problems related to using such light-based phase plates, *e.g.*, for a given desired shaped electron wave function, we need to find the needed optical field. We will also focus on a technologically simple, robust, and easy-to-use solution suitable for experimental implementation.

Generation of electron beams modulated in time

Information on the temporal evolution of the sample morphology or response is another important piece for understanding the basic physical properties and functionalities of nanostructures and nanodevices. Some of the current technological solutions offering temporal resolution in electron microscopy rely on generating well-defined electron pulses. We could, however, think about the possibility of generating other types of temporal modulation of the beam, which could be used for the reconstruction technique as suggested in Ref.[73].

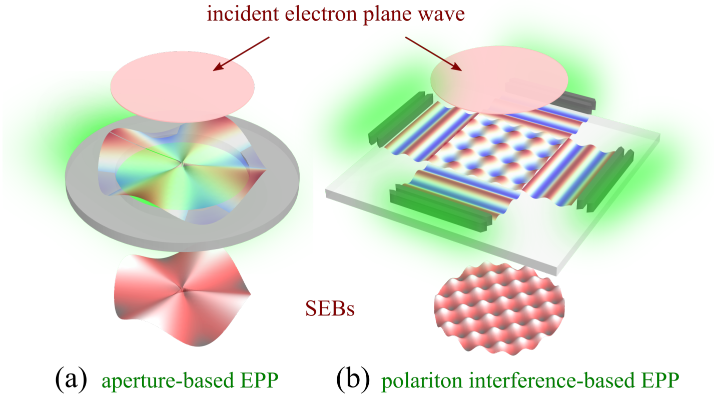

Figure 4.1: Light-based electron phase plates. Two possible schemes for shaping the electron wave function with light. (a) Interaction of electrons with optical field confined at edges of an aperture. (b) Electron beam shaping via the interaction with interfering polaritons.

Improvements in spectral resolution in electron energy-loss spectroscopy

The current spectral resolution of a few meV in EELS might still be improved by studying mechanisms that are limiting it. One such limitation could arise due to both elastic and inelastic thermally-induced interactions of the beam with liner tubes through which the electrons are propagating. Calculations should reveal if these limitations play an essential role, and if yes, find materials and geometries to reduce them.

4.2 New applications and methodology in electron microscopy and spectroscopy

Probing beam-sensitive samples

One of the most difficult challenges in electron microscopy is probing organic or other beam-sensitive samples. In such samples, a high dose of electrons causes damage to bonds through ionization, or light atoms can be completely removed from the sample due to the impact of energetic electrons. To overcome this drawback, we can probe many representatives (samples) of the same system, as utilized, *e.g.*, for reconstructing protein structure in “single-particle analysis”[77]. Another approach for probing the sensitive samples is to control and reduce the electron dose significantly. As most of the beam-sensitive samples are phase objects, it is thus also desirable to enhance the contrast without increasing the dose. This could be done by taking advantage of shaped or even pulsed and shaped electron beams in connection with reconstruction algorithms, as suggested in FIGURE 4.2(a).

It has been shown that electron energy-loss spectroscopy of sensitive samples can be performed remotely at the expense of losing some spatial resolution[26,28,30,78]. With some prior knowledge of the sample morphology, we could also apply reconstruction algorithms together with shaped electron beams to EELS of molecular samples.

Optical properties of phase-changing materials at the nanoscale

Due to the tunability of their optical, thermal, or electrical properties, phase-changing materials represent interesting platforms for designing switchable nanodevices. One such material is vanadium dioxide (VO_2), which exhibits insulator-to-metal transition relatively close to room temperature at around 335 K. Electron spectro-microscopy with in-situ heating is a very suitable technique for correlating local composition (through X-ray and core-loss EELS signals), optical and thermal properties (low-loss EELS) with the change in crystallinity or shape (diffraction and (high-resolution) imaging), everything as a function of applied temperature. Such experiments would reveal the relation between the phase transition and relevant physical properties at the truly microscopic level. They could complement other measurements often done with bulk samples or nanoparticle assemblies, where some effects are averaged out.

Nanoscale thermometry

EELS with meV resolution can detect not only energy losses but also energy gains which can the electron beam experience when interacting with a sample at non-zero temperature. If we know occupation statistics of low-energy sample excitations (typically Bose-Einstein for vibrations and phonons), we can determine the local temperature at the sample from the ratio of the energy loss and gain peaks[79,80]. We could study potential of this technique to explore samples with inhomogeneous temperature spread or study radiative near-field thermal transport.

Optical dichroism

Detecting chiral samples' dichroic optical and vibrational response is essential in many fields. In pharmacy, different molecular enantiomers often play a role in drug effectiveness and safety. At the same time, chiral centres in inorganic materials emerging due to atomic defects or a specific band structure (as in some TMDs) find applications in information storage and processing. At the atomic or nanoscale level, dichroism could be studied with a particular class of shaped electron beams, vortex electron beams (VEBs), featuring a non-zero orbital angular momentum (OAM), as schematically shown in FIGURE 4.2(c). So far, only several theoretical works suggest the feasibility of energy- and OAM-filtered EELS to reveal the optical dichroic signal[81–83], but first experimental attempts have been inconclusive[84]. We will explore the robustness of the dichroic signal concerning the exact beam-sample geometry and suggest practical schemes for reliable and practical measurement schemes.

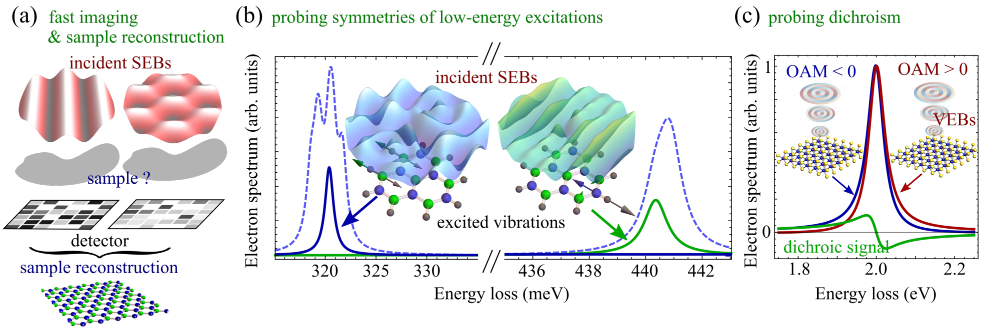

Figure 4.2: Applications of shaped electron beams in microscopy and spectroscopy. (a) Fast imaging and (3D) reconstruction of sample structure with the aid of SEBs. Extended SEBs interact with an unknown sample while the corresponding intensities of the transmitted waves are collected at a multi-pixel detector. The intensities associated with different incident SEBs are then used to reconstruct sample structure down to the atomic scale. (b) SEBs featuring different symmetries can selectively excite specific vibrational modes of a molecule as demonstrated in the S-EEL spectra (dashed curve corresponds to the spectrum acquired with a conventional beam). Such information can be used to reconstruct the localisation and symmetry of the modes with a low electron dose. (c) Dichroic signal is acquired when probing chiral nanostructures, lattices (here we show an example of monolayer MoS_2) and molecules with VEBs having positive and negative OAM.

Controlling excitations in nanophotonics systems

We have already discussed in CHAPTER 3 that by controlling the incident beam shape, we can selectively excite only desired excitations in the sample[75,83], see also FIGURE 4.2(b). We will further explore the applications of the shaped electron beams and reconstruction schemes in energy-loss spectroscopy to acquire information on excitations' localisation or symmetries with increased spatial or spectral resolution.

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Abstract

This habilitation thesis summarizes the author's contributions to several research topics at the interface of nanophotonics, electron microscopy, and spectroscopy. Electron energy-loss spectroscopy, photon-induced near-field electron microscopy, and cathodoluminescence spectroscopy are introduced as techniques suitable for probing electromagnetic fields produced by vibrational and electronic excitations in nanostructured matter. The thesis also deals with the utilization of both spatially confined and extended electromagnetic fields in the active modification of electron wave functions and discusses several applications of on-demand shaped electron beams in new electron microscopy and spectroscopy techniques. The last part of the thesis provides an overview of new research directions that the author will follow in the coming years.

Abstrakt

Tato habilitační práce shrnuje příspěvky autorky k několika výzkumným tématům na pomezí nanofotoniky, elektronové mikroskopie a spektroskopie. Spektroskopie energiových ztrát elektronů, fotony indukovaná elektronová mikroskopie blízkého pole a katodoluminiscenční spektroskopie jsou představeny jako techniky vhodné pro zkoumání elektromagnetických polí vznikajících díky vibračním a elektronickým excitacím v nanostrukturách. Práce se zabývá také použitím prostorově lokalizovaných i rozlehlých elektromagnetických polí pro aktivní modifikaci vlnových funkcí elektronů a diskutuje několik aplikací na míru tvarovaných elektronových svazků v nových technikách elektronové mikroskopie a spektroskopie. Poslední část práce poskytuje přehled nových výzkumných směrů, kterými se bude autorka v nadcházejících letech zabývat.