Optical properties of spatially dispersive
Mie-resonant halide perovskite nanoparticles

A S Berestennikov\textsuperscript{1}, I V Iorsh\textsuperscript{1} and S V Makarov\textsuperscript{1}

\textsuperscript{1} Department of Nanophotonics and Metamaterials, ITMO University, St. Petersburg 199034, Russia
E-mail: a.berestennikov@metalab.ifmo.ru

Abstract. We have proposed a mechanism explaining the unusual blue shift of photoluminescence peak in relatively large perovskite nanoparticles, where the quantum confinement effect is insignificant. We performed theoretical analysis of the absorption and scattering cross-sections of incident light in such nanoparticles in classical (local) and nonlocal cases. The blue shift for the scattering and absorption features in spectra around the exciton peak was obtained from the model, which can be related to that the previously observed shift of the luminescence peak in perovskite nanoparticles with a diameter less than 100 nm owing to the exciton nonlocality.

1. Introduction
Organic-inorganic perovskites, such as CH\textsubscript{3}NH\textsubscript{3}PbX\textsubscript{3} family, where X is I, Br or Cl, are very promising class of material for effective nanoscale light sources, solar cells, light emitters and photodetectors, which have excitonic states at room temperature, high enough refractive index, low losses at the exciton wavelength [1]. These excellent properties along with low cost of their fabrication by wet-chemistry allowed for creation of hybrid perovskite nanoantennas [2] and metasurfaces [3].

The materials based on perovskite nanoparticles have a favourable combination of quantum-size effects (if the radius of the particle is less than or of the order of the Bohr radius of exciton), improving their optical properties in comparison with bulk analogues, Mie resonances and the ability to disperse in a variety of solvents and matrices, which allows them to be introduced into various devices. In order to create effective and tunable light-emitting nanoantennas, it is necessary to be able to change the optical properties of nanoparticles, such as the wavelength of the luminescence, the absorption/scattering cross-sections and the radiation direction [4].

In recent works [5, 6], it was found that in nanocrystals of perovskites with a radius less than 100 nm, the photoluminescence peak is a blue-shifted. This effect is known for nanoparticles of several nanometers and associated with quantum-size effects. However, this effect has not yet been explained for the case of large perovskite nanoparticles.

In this work, we show theoretically that exciton-induced nonlocality can affect resonant properties of CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} perovskite nanoparticles with relatively big sizes and shift the photoluminescence, absorption and scattering cross-section peaks to shorter wavelengths.
2. Model of spatially dispersive dielectric spheres

The Mie theory explains the optical properties of sphere of arbitrary diameters, consisting of an isotropic material, which is characterized by a local dielectric constant. It depends only on the frequency of the incident wave:

$$\varepsilon(\omega, k) = \varepsilon_0 + \frac{\omega_p^2}{\omega_{exc}^2 - \omega^2 - i\gamma\omega}, \quad (1)$$

where $\varepsilon_0$ is background dielectric constant, $\omega_p$ is the dipole oscillator strength, $\gamma$ is the damping term and $\omega_{exc}$ is the excitonic transition frequency.

However, in the general case the dielectric function of the medium $\varepsilon$ depends on the wave vector, or in other words has a nonlocal response. Therefore, metallic and dielectric spheres can have interesting optical effects, which cannot be explained by the classical local model. In this case, the observed effects can be explained by using a modified Mie theory, in which spatial dispersion is included by adding a nonlocal term to the equation of the classical local dielectric function [7]:

$$\varepsilon(\omega, k) = \varepsilon_0 + \frac{\omega_p^2}{\omega_{exc}^2 - \omega^2 + Dk^2 - i\gamma\omega}, \quad (2)$$

where $Dk^2 = \hbar^2 k^2 \omega_{exc}/2m_{exc}$ is the spatial dispersion term.

By using classic Maxwell boundary conditions, which require the tangential components of $E$ and $H$ be continuous at $r = R$ and Pekar additional boundary conditions, which impose a condition of zero polarization at the surface of the particle $P = 0$, we can determine the expansion coefficients of the scattered wave and obtain the scattering, extinction and absorption cross-sections of spatially dispersive dielectric nanoparticles

$$Q_{\text{scat}} = \frac{2}{k_0^2 r^2} \sum_{n=1}^{\infty} (2n + 1)(|a_n|^2 + |b_n|^2), \quad (3)$$

$$Q_{\text{abs}} = \frac{2}{k_0^2 r^2} \sum_{n=1}^{\infty} (2n + 1) \text{Re}(a_n + b_n) - Q_{\text{scat}}, \quad (4)$$

where $a_n$ and $b_n$ are expansion coefficients, $r$ is the radius of the particle, $k_0 = \omega/c\sqrt{\varepsilon_M}$ and $\varepsilon_M$ is the dielectric permittivity of surrounding medium.

3. Results and discussions

To explain the blue shift of the photoluminescence we applied the generalized Mie theory of spatially dispersive spheres to the calculation of the optical properties of the CH$_3$NH$_3$PbI$_3$ (or MAPbI$_3$) nanoparticles. In figure 1 the plots of local and nonlocal absorption and scattering cross-sections of the MAPbI$_3$ nanoparticles with different radii are calculated. In the classical (local) case with dielectric function from equation (1), the blue shift of the absorption (figure 1a) and scattering (figure 1c,d) black line peaks are not observed. However, we found that in nonlocal case with $\varepsilon(\omega, k)$ from equation (2), the main scattering (figure 1c, red line) and absorption (figure 1b) peaks shifts to lower wavelengths by 45 nm with decreasing of the nanoparticle radius. This shift is due to the fact that the exciton is not stationary and has the kinetic energy, so it emits photons at a higher frequency.
4. Conclusions
We proposed that a mechanism where the blueshift of the luminescence peak in perovskite nanoparticles is associated with nonlocality of material around an exciton. We performed analytical calculations of the absorption and scattering cross-sections of incident light in such nanoparticles in the local and nonlocal cases. Using this results, we plotted the spectral and radii dependences of the absorption and scattering cross-sections in both cases. Our investigations showed that the possible mechanism of the photoluminescence peak blue shift in perovskite nanoparticles is associated with the nonlocality of excitons.

5. Acknowledgements
This work was supported by Russian Science Foundation (grant 17-73-20336).

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