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Acceleration of Chemical Reactions in Hybrid One-Dimensional Photonic Crystals Based on High-Index Metamaterials

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Abstract—Metamaterials with highly tunable refractive indices greatly enhance light-matter interaction in one-dimensional photonic crystals. As has been recently shown, the ionization energies of atoms placed in air voids of photonic crystals can be dramatically changed. The origin of the effect is the modification of the interaction of an electron with its own radiation field that gives rise to the change of the electron electromagnetic mass. For the first time the electromagnetic mass comes to play in describing physical processes. The mass correction is anisotropic and depends on the electron states. The photonic crystal mass correction is an observable and is described by an operator. The effect is strongly enhanced when the photonic crystal is made from highly tunable refractive index metamaterials, and the controllability of these materials gives rise to the controllability of the ionization energies and, hence, the physicochemical properties of atoms over a wide range. Thus, we assume that this quantum electrodynamic effect can be one of the main mechanisms for the acceleration of chemical reactions. In this work, the method of experimental verification of this effect based on the observation of shifts in the spectral lines of helium atoms injected in the gas phase in air voids of a hybrid one-dimensional photonic crystal by optical spectroscopy techniques is suggested. We believe that experimental verification of the effect under study can open new opportunities for the study of chemical and biochemical reactions and for the synthesis exceptional chemical compounds in confined environment that could be used in pharmaceutics and medical applications.

Keywords: photonic crystals, metamaterials, quantum electrodynamics, electron mass, ionization energy, acceleration of chemical reactions in confined environment

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INTRODUCTION

Artificial materials such as photonic crystals (PCs) are promising media for creating various photonics devices such as optical filters, waveguides, microlasers [1] and for studying quantum-electrodynamic (QED) effects such as control of spontaneous emission of quantum emitters placed in the periodic structure of PCs [2], enhancement of quantum interference effects, creation of dark states [3], control of electron mass [4] and others. In [4] it has been shown that a strong modification of the electromagnetic field in the PCs leads to a significant change in the interaction of an electron with its own radiation field, which leads to a significant change in the electromagnetic mass of a charged particle. The electromagnetic mass is not measurable in the experiment due to the ultraviolet divergence [5]. However, the considered modification of the electromagnetic interaction in the PC environment leads to the correction of the electromagnetic mass δm_{pc}. The contribution to the electron energy in the PC medium will differ from the contribution in the case of vacuum due to the strong modification of the photonic density of states in the periodical medium [6] and, consequently, the modification of the interaction of a charged particle with its own radiation field. It is important to note that the self-energy correction δm_{pc} is a finite and anisotropic value depending on the direction of the electron pulse in the PCs. The magnitude of the self-energy correction leads to a significant shift in the energy levels of atoms placed in the cavity of the periodic structure, comparable in magnitude to conventional atomic transitions. As has been recently shown [7], the consequence of this effect is the possibility of controlling the ionization energy of atoms in the periodic PC medium. The magnitude of the ionization energy change of hydrogen atom and alkali metals is of order of eV. The effect is strongly enhanced when the photonic crystal is made from highly tunable refractive index metamaterials [8–10], and the controllability of these materials gives rise to the controllability of the ionization energies over a wide range.

Nowadays one of the most important physicochemical problems is acceleration of chemical and biochemical reactions in confined environment, such as microdroplets [11], nanoporous organic frameworks and colloidal nanocrystal assemblies [12]. This is significant for the study of chemical kinetics in confined volume and for the synthesis new chemical compounds that are difficult to create in bulk solvent. This study is dedicated to suggestion of the experimental verification method of the considered QED effect. The verification method is based on the observation of shifts in the spectral lines of helium atoms injected in the gas phase in air voids of a hybrid one-dimensional PC by optical spectroscopy techniques. The experimental verification of the electron electromagnetic mass change in confined environment such as air voids of the PC structure can trigger the study and the synthesis of new chemical compounds and can provide the solving of new fundamental problems.

THE MODIFICATION OF THE SELF-ENERGY INTERACTION OF AN ELECTRON IN PCS

For a long time the electromagnetic mass of an electron has been a mystery due to the nonrenormalizable ultraviolet divergences [5]. Then, the renormalization procedure had been introduced in solving of the Lamb shift problem [13]. In accordance with this procedure, the physical mass m_e of an electron is a sum of its bare mass m_0 and the electromagnetic mass m_{em}:

$$m_e = m_0 + m_{em}. \tag{1}$$

In [4] it is shown that the modification of the interaction of an electron trapped in air voids of a PC with its own radiation field results in the change of its electromagnetic mass. The virtual photons emitted and reabsorbed by a charged particle have Bloch structure [14] due to the periodical boundary conditions of PCs, and the self-energy of an electron in the periodical medium is different from the case of vacuum. In contrast to the electromagnetic mass of an electron in vacuum, the PC correction to this mass is an observable. For the first time the electromagnetic mass comes into play in describing physical processes. It is important that the electromagnetic mass of an electron is a first contribution to the self-energy and the subsequent contribution is the Coulomb energy correction (Lamb shift), having the order of 10^{-6} eV in vacuum [13]. The PC correction δm_{pc} corresponds to the self-energy operator [4], and this operator of the electromagnetic field of an electron trapped in air voids of a PC can be represented as

$$\begin{aligned}\delta m_{pc}\left(\hat{\vec{I}}_{\vec{p}}\right) = \frac{\alpha}{\pi^2}\Bigg[&\sum_n \int_{FBZ} \frac{d^3\vec{k}}{\omega^2_{\vec{k}n}} \sum_{\vec{G}} \left|\hat{\vec{I}}_{\vec{p}} \cdot \vec{E}_{\vec{k}n}\left(\vec{G}\right)\right|^2 \\ &- \int \frac{d^3\vec{k}}{2\vec{k}^2} \sum_{\lambda=1}^{2} \left|\hat{\vec{I}}_{\vec{p}} \cdot \vec{\varepsilon}_\lambda\left(\vec{k}\right)\right|^2\Bigg],\end{aligned} \tag{2}$$

where α is the fine-structure constant, $\hat{\vec{I}}_{\vec{p}} = \hat{\vec{p}}/\left|\hat{\vec{p}}\right|$ is the operator of the direction of the electron momentum, the eigenvectors of Maxwell's equations $\vec{E}_{\vec{k}n}(\vec{G})$ are the amplitudes of the Bloch plane waves $\vec{E}_{\vec{k}n}(\vec{r}) = \sum_{\vec{G}} \vec{E}_{\vec{k}n}(\vec{G}) e^{i(\vec{k}+\vec{G})\cdot\vec{r}}$, the corresponding eigenvalues $\omega_{\vec{k}n}(\vec{k})$ are the dispersion relations [14], n is a band index, $\vec{\varepsilon}_\lambda(\vec{k})$ denotes the unit vector of the field polarization (λ) in free space. The value of wave vectors $\vec{k}$ is limited by the first Brillouin zone (FBZ) and $\vec{G}$ is the reciprocal lattice vector of the PC ($\vec{G} = N_1\vec{b}_1 + N_2\vec{b}_2 + N_3\vec{b}_3$, where $\vec{b}_i$ are primitive basis vectors of a reciprocal lattice). The first term on the right-hand part of Eq. (2) is the modified self-energy in the PC medium, whereas the second term is just the ordinary low-energy part of the self-energy of an electron in vacuum, which appears in the second-order perturbation theory [13].

We consider a one-dimensional PC due to the simplicity of its theoretical and practical investigations. The polarization structure of the electric field can be represented as

$$\vec{E}_{\vec{k}n}(\vec{G}) = \sum_{\lambda=1}^{2} E_{\vec{k}n\lambda}(G)\vec{\varepsilon}_\lambda(\vec{k}_{\vec{G}}), \tag{3}$$

where $\vec{\varepsilon}_1(\vec{k}_{\vec{G}})$ and $\vec{\varepsilon}_2(\vec{k}_{\vec{G}})$ are the unit vectors of the electromagnetic field TE (transverse-electric) and TM (transverse-magnetic)-polarization, correspondingly, $\vec{k}_{\vec{G}} = \vec{k} + G\vec{e}_z$.

The operator of the self-energy correction to the electromagnetic mass of a free electron trapped in air voids of a one-dimensional PC having the cylindrical symmetry can be written in the form

$$\delta m_{pc}\left(\hat{\vec{I}}_{\vec{p}}\right) = A + \left(\hat{\vec{I}}_{\vec{p}} \cdot \hat{\vec{I}}_{pc}\right)^2 B, \tag{4}$$

where $\hat{\vec{I}}_{pc}$ is the unit vector of a given periodicity Z-axis of a one-dimensional PC medium,

$$\begin{aligned}A = &\frac{\alpha}{\pi}\sum_{n,\,G}\int k_\rho dk_\rho \\ &\times \int_{FBZ} dk_z \left(\frac{\left|E_{\vec{k}n1}(G)\right|^2}{\omega^2_{\vec{k}n1}} \frac{k^2_{Gz}}{k^2_\rho + k^2_{Gz}} + \frac{\left|E_{\vec{k}n2}(G)\right|^2}{\omega^2_{\vec{k}n2}}\right) - \frac{4\alpha}{3\pi}\int dk,\end{aligned}$$

$$B = \frac{\alpha}{\pi}\sum_{n,G}\int k_\rho dk_\rho \times \int_{FBZ} dk_z \left(\frac{\left|E_{\vec{k}n1}(G)\right|^2}{\omega_{\vec{k}n1}^2}\frac{2k_\rho^2 - k_{Gz}^2}{k_\rho^2 + k_{Gz}^2} - \frac{\left|E_{\vec{k}n2}(G)\right|^2}{\omega_{\vec{k}n2}^2} \right)$$

[7]. Here, $\omega_{\vec{k}n1}$ and $\omega_{\vec{k}n2}$ are dispersion relations for the TE and TM Bloch modes satisfying transcendental equation [14]. For estimation of the self-energy correction to the electromagnetic mass of an atomic electron in state $|\Psi\rangle$ the corresponding matrix element $\langle\Psi|\delta m_{pc}\left(\hat{\vec{I}}_{\vec{p}}\right)|\Psi\rangle$ should be calculated.

THE PC CORRECTION TO THE ELECTROMAGNETIC MASS OF HELIUM ATOM ELECTRONS AND METAMATERIALS WITH HIGHLY TUNABLE REFRACTIVE INDEX

As has been shown in [7], the Hamiltonian of atoms in the PC medium must be completed with the operators $\delta m_{pc}\left(\hat{\vec{I}}_{\vec{p}}\right)$ for each electron due to the modification of the interaction of an electron with its own radiation field. The Hamiltonian of the atomic hydrogen takes the form

$$\hat{H}_{pc} = \delta m_{pc}\left(\hat{\vec{I}}_{\vec{p}}\right) + \hat{H}, \tag{5}$$

where $\hat{H}$ is the ordinary Hamiltonian of hydrogen atom in free space. The states and energies of an atom are determined by the Schrödinger equation

$$\hat{H}_{pc}|\Psi_{i,pc}\rangle = E_{i,pc}|\Psi_{i,pc}\rangle. \tag{6}$$

This equation can be solved with perturbation theory expanding the solution in powers of $\delta m_{pc}\left(\hat{\vec{I}}_{\vec{p}}\right)$. At the first approximation we get

$$\left|\Psi_{i,pc}^{(1)}\right\rangle = |\Psi_i\rangle, \quad E_i^{(1)} = \langle\Psi_i|\delta m_{pc}\left(\hat{\vec{I}}_{\vec{p}}\right)|\Psi_i\rangle + E_i, \tag{7}$$

where E_i is the energy of the state $|\Psi_i\rangle$ of an atom in free space. The correction $E_i^{(1)} - E_i$ depends only on the orbital l and the magnetic m_l quantum numbers, and what is important does not depend on the electron coordinate: $\langle\Psi|\delta m_{pc}\left(\hat{\vec{I}}_{\vec{p}}\right)|\Psi\rangle = \langle l, m_l|\delta m_{pc}\left(\hat{\vec{I}}_{\vec{p}}\right)|l, m_l\rangle$.

In this work, we suggest the experimental verification method of the QED effect under study. The method is based on the observation of shifts in the spectral lines of helium atoms injected in the gas phase in air voids of a hybrid one-dimensional PC by optical spectroscopy methods. These spectral shifts are caused by the PC correction to the electron self-energy. We suggest considering helium atoms due to the simplicity of the experiment. Helium is inert to interaction with microstructure of the periodical medium and a quite well-studied system [15]. This two-electron system has one electron in the ground state 1*s*. The other electron will make transitions. It is necessary to use transitions between triplet states of the helium-orthohelium atom. The choice of the initial state of the second electron of the helium atom in the triplet metastable state 2^3S_1 is because its lifetime is about 7.9 yr, which is important in the experimental measurements. To do this, the parahelium atoms (with the singlet state 1^1S_0) must first be excited by an electron beam to the metastable state of 2^3S_1 orthohelium.

In addition, we assume that a disordered structure made of similar material like a one-dimensional PC must be used in the optical spectra measurements of helium atoms. It is important for extraction of surface effects from consideration. The principal scheme of the experimental verification of the modification of the helium electrons self-interaction with its own radiation field in periodical structure of a one-dimensional PC is depicted in Fig. 1.

Metamaterials have attracted considerable attention because of their abnormal electromagnetic response which is not found in naturally occurring material. Materials with a high and controllable refractive index are crucial for diverse optical devices [8]. The key of achieving high refractive index of metamaterials is to maximize the effective permittivity ($\varepsilon = 1 + (P/\varepsilon_0 E)$, where P and ε_0 are polarization and permittivity in free space, respectively), while simultaneously the diamagnetic effect and the resultant reduction of effective permeability ($\mu = 1 + (M/H)$, where M denotes magnetization) should be suppressed as possible. Thus, the polarization and magnetization within the artificial medium should be maximized and suppressed respectively toward unnaturally high refractive index [8, 9]. Then, the effective refractive index n_{eff} of such metamaterial can be represented in the form

$$n_{\text{eff}}(\omega) = \left[(a/g)\varepsilon_d(\omega)\right]^{1/2}, \tag{8}$$

where a is the size of the metal nanoparticles, g is the gap between particles and $\varepsilon_d(\omega)$ is the permittivity of the gap-filling dielectric [10]. The control of these parameters gives rise to the strong near-field coupling between nanoparticles and light, and, hence, to an increase of effective refractive index of a metamaterial. As has been recently shown [7], the QED effect under study is strongly enhanced with using the hybrid photonic crystal which is made from a highly tunable refractive index metamaterial. This is because the PC correction to the electron self-energy, therefore, the shifts of energy levels of atoms depend quadratically on the refractive index of the PC material host. The controllability of these materials gives rise to the controllability of the atom energy shifts over a wide range.

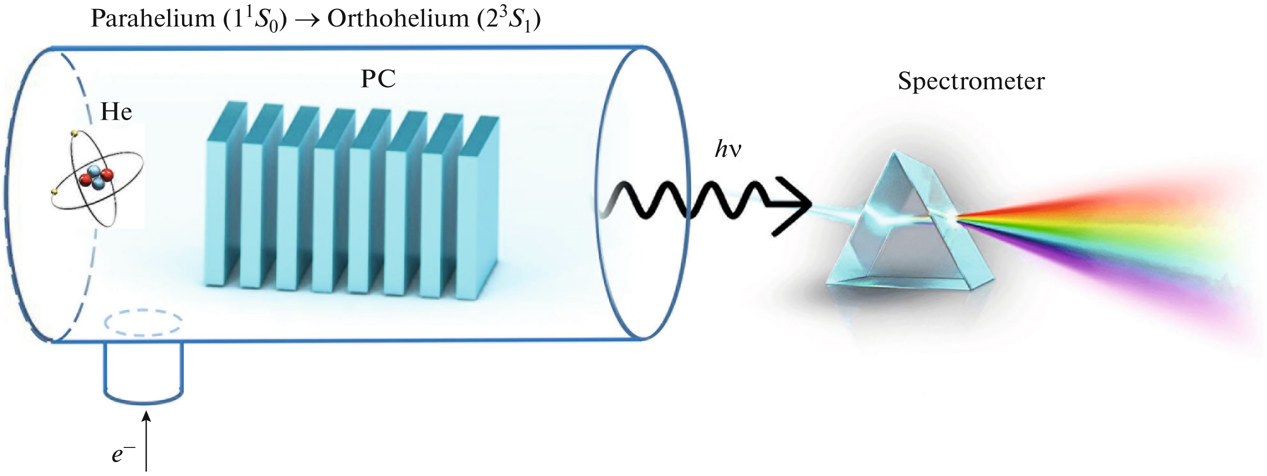

Fig. 1. Schematic of suggested experiment of the verification of the QED of the PC correction to the helium electrons masses. The method is based on the observation of shifts in the spectral lines of helium atoms injected in the gas phase in air voids of a hybrid one-dimensional photonic crystal by optical spectroscopy techniques. The parahelium atoms (with the singlet state 1^1S_0) are excited by an electron beam to the metastable state 2^3S_1 of orthohelium. Transitions between triplet states of the orthohelium atom can be observed due to the long lifetime of this metastable state which is about 7.9 yr.

On the base of standard model of particles collision, the kinetics for most chemical reactions are described by an Arrhenius equation [16] of the form

$$k = A\exp\left(-E_a/RT\right), \tag{9}$$

where k is the reaction rate constant, A is the reacting particles collision frequency, E_a is activation energy, R is the gas constant and T is the absolute temperature. Increasing of energy levels and, hence, decreasing of ionization energy of reacting atoms placed in confined air voids of the hybrid PC structure provides the significant decreasing of activation energy and acceleration of chemical reactions.

CONCLUSIONS

New artificial materials such as PCs, metamaterials, having unique optical properties, provide the opportunity for many applications in photonics, chemistry, biology, and quantum technology, and are the good testbed system for the study of the fundamental QED effects. In this work, the method of experimental verification of the QED effect of the electromagnetic mass change of an electron in artificial periodical materials like PCs is suggested. This method is based on the observation of spectral lines shifts of helium atoms injected in the gas phase in air voids of a hybrid one-dimensional PC by optical spectroscopy techniques. Helium atoms are inert to interaction with microstructure of the periodical medium, and a quite well-studied system which can be cost-effective in experimental verification of the PC correction to the helium electrons masses. Using a hybrid one-dimensional PC based on high-index metamaterials leads to enhance light-matter interaction and, hence, the effect under study. It is important, that the value of the PC correction to the energy levels and the ionization energy of atoms is of order of eV. Thus, for the first time the electromagnetic mass of an electron comes into play clearly in describing physical processes. The experimental verification of this QED effect can be very interesting and significant from the fundamental theory and possible practical applications. We believe that experimental verification of the effect under study can open up new opportunities for the study of chemical and biochemical reactions and for the synthesis of exceptional chemical compounds in confined environment that could be used in pharmaceutics and medical applications.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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