

Perspective on molecular quantum plasmonic nanoantennas

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2017 J. Opt. 19 060401

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Editorial

Perspective on molecular quantum plasmonic nanoantennas

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Introduction

One of the ultimate goals of modern science is the precise control of single photons at the atomic level, the excitation of plasmons allows nanoscale localisation of electromagnetic (EM) energy and is a promising path towards this aim. Quantum plasmonics is the study of plasmonics in tiny systems where confinement of the valence electrons modifies the optical response. Recently there has been much interest in exploring the ultimate small size limit of quantum plasmonics in molecules. By the manipulation of individual atoms/molecules, properties of light, such as the local field enhancement, gradient and polarisation, can be controlled on the angstrom scale. This paves the way for new systems in quantum optics, as well as nano-localised photochemistry and the design of efficient molecules for light–matter interaction. In this perspective, we discuss the theoretical modelling of quantum plasmonic nanoantennas and the analogies to classical antennas. We also discuss the importance of phonons in quantum plasmonics, the generation of hot electrons and justify the concept of molecular antennas.

Classical antennas

Antennas are prevalent in modern technology due to the need to precisely control and emit/receive EM radiation. There is currently a large effort in the nano-optics community in designing nanoantennas that work at optical frequencies, which involves shrinking antennas down to ever smaller sizes. A nanoantenna can be defined as a device, usually smaller than the incident wavelength, which efficiently converts EM waves into localised fields, analogously to antennas in radio technology that convert EM waves into electric and magnetic currents. In this perspective, we will concentrate on metal nanoantennas but there also exists dielectric, semiconductor and hybrid nanoantennas. At optical frequencies, the penetration depth of light into a metal can become comparable to the dimensions of the nanoparticle and the optical response becomes dominated by *localised surface plasmons* (LSPs) [1]. A LSP is a coherent oscillation of the electron gas in response to a light field. The periodic transfer of EM energy to kinetic energy of the electrons allows subdiffraction confinement of the light and results in large field enhancements, which have a wealth of applications including sensing [2], metamaterials/metasurfaces [3], controlling chemical reactions [4] and energy conversion [5]. As all the valence electrons take part in the oscillation, the plasmon has a huge cross section which can be many times larger than the physical cross section of the nanoparticle. This is clearly a very appealing attribute for a nanoantenna as it allows for the efficient collection of free space EM radiation. Furthermore, the concentration of EM energy into a small spatial region in the near

field allows coupling with small emitters/absorbers, thus the nanoantenna acts as an intermediate link between the small system and the far field: overriding the cross section and wavelength mismatch ($R \ll \lambda$) that usually stops them talking. By changing the dimensions, shape or material (of either the particle or the background material) one can achieve a huge degree of control over the spectral position of the plasmon resonance.

With the strong analogies between traditional antennas in the radio and microwave regime, and nanoantennas in the optical, it is only natural that plasmonic nanoantenna research has borrowed many of the concepts. For instance, it is highly desirable to have nanoantennas with large directivity and high efficiency (i.e. low internal and radiative loss). There are many examples of nanoantenna designs directly borrowed from radio wave technology, such as dipole [6], monopole [7], bowtie [8] and Yagi-Uda designs [9]. For example, it has been shown that the theory of thin half-wave dipole antennas translates into the plasmonic regime but with the caveat that the simple scaling law $L = \lambda/2$ is modified to take into account significant penetration of the light into the metal [10].

Quantum plasmonics

It is natural to ask, what happens if we continue to shrink down the dimensions of antennas? For systems below about 5 nm we are in the regime of *quantum plasmonics* [11, 12] which is a flourishing new field of research (here defined as the regime where (non-bulk) quantum effects of the material are important; there is another area of plasmonics which shares the name, where the quantum nature of light is considered. Of course, the ultimate goal would be to consider both simultaneously). In this regime bulk dielectric functions will not work due to quantum size effects. There are two approaches to this problem. One is to continue using the intuitive classical framework and add quantum effects as a correction, this is the nonlocal approach and is usually implemented in the hydrodynamic model [13]. The second approach relies on performing a complete quantum calculation and considering the plasmon as constructed from a linear combination of electron-hole transitions, this is normally performed within time-dependent density-functional theory (TDDFT) which is a popular method for evaluating optical properties of quantum systems [11]. The TDDFT method allows the description of the correlated dynamics of a many body system by solving an auxiliary system of independent particles in a mean field. Which approach to take, *ab initio* or hydrodynamic, comes down to necessity, rather than taste, in most cases. TDDFT is feasible for a few hundred electrons (core electrons are usually considered by a suitable pseudopotential and do not need to be explicitly calculated), so for nanoparticles above about 1–2 nm radius full quantum calculations become increasingly infeasible. Nonlocal models have mixed success, often predicting the wrong spectral shift for nanoparticles (the usual neglect of electron spill out in the nonlocal model leads to only blue shifts which can match with experimental result for noble metals but this is a fluke! This blue shift comes from the screening of d electrons, not considered in the nonlocal model), but do correctly describe the smearing of surface charge at material boundaries which limit the possible field enhancements.

Plasmonics at the ultimate small size scale

There has been a huge amount of work on molecular plasmonic systems, using TDDFT, within the last few years. Much of this has been on exactly how to identify a plasmon in such tiny systems, not a simple task! There now exist several different methods to characterize plasmons in ultra-small systems, which include

the scaling method [14], plasmonicity index [15], dynamics of the electron populations [16], and collectivity [17, 18]. With the conceptual difficulties in identifying plasmons increasingly well understood by a combination of ideas from classical plasmonics and excited state structural analysis from electronic structure theory, attention must now turn to the potential practical benefits of quantum plasmonics. In our recent work [18], we concentrated on the field localisation/enhancement of small single-atom-thick sodium chains, a well-studied system of quantum plasmonics. A difficulty apparent straight away is that the line broadening of excitations, which is usually introduced by hand in a rather arbitrary way in TDDFT calculations, strongly impacts the local field: a fact well known in classical plasmonics. At best one can use experimental data to pick the line broadening, but this is not satisfactory. For quantum plasmonics to become a 'practical' field of research, loss must be included in an *ab initio* way. Our first approach is to identify that at this length scale the broadening will be mainly from phonon–electron interactions. This *vibron–electron coupling* is well known in spectroscopy [19] and it is an important ingredient in quantum plasmonics. Thus, we calculated the phonon normal modes, also within the DFT formalism, and use the energy of the highest energy mode as an approximate value for the broadening. This is a simple method and treats the phonons as a perturbation on the electronic spectra. Larger plasmon–phonon coupling gives richer spectral features, as recently shown for aromatic hydrocarbons [20]. We found that 10 atom chains and 20 atom dimer chains act very similar to larger plasmonic systems, with maximum field enhancement of around 80. Of course, there are some differences, for instance the field enhancement drops off very rapidly (on the order of the bond length) which may limit some applications, although high field gradients could be useful for exciting non-dipole transitions and breaking the usual selection rules, for instance it can be shown that the quadrupolar transition rate is proportional to $\left(\frac{\lambda}{R}\right)^2$ [21]. This could be particularly useful for increasing the light interaction of molecules with no dipole moment such as oxygen, carbon dioxide and methane. Quantum plasmonics is increasingly proving to be a fascinating union between plasmonics and electronic structure with the flow of ideas from each field enriching the other. It is well known that plasmonics has benefited via concepts such as the plasmon hybridisation model [22], which borrows heavily from atomic orbital theory. We believe the use of plasmonic concepts in electronic structure could prove to be equally fruitful.

Hot electrons

One of the most exciting topics in quantum plasmonics is the generation of *hot electrons*. These highly energetic electrons, generated by plasmon decay, can be harvested for energy in solar cells and hold promise for plasmon-assisted photochemistry [23]. For example, water splitting close to a gold nanoparticle of radius 0.95 nm has been demonstrated theoretically using TDDFT [4], it was shown that odd modes are more efficient at water splitting as the plasmon-induced hot electron energies match the antibonding orbital of water. It can be expected that this will become an intense area of research in quantum plasmonics: by careful control of cluster size and structure, hot electrons can be injected into desired molecular states to induce chemical reactions. Whilst the proof of concept has been shown, there is much that can be improved in the theoretical modelling. For example, the authors in [4] use the jellium approximation and place the water molecule by hand (the alignment is important due to the dipole moment of the water), future, more advanced calculations, should include the full atomic structure of the nanoparticle and relax the total structure (nanoparticle plus molecule) to find how the molecules bind to the surface. It has been demonstrated,

with TDDFT, that it is important to model the full atomic structure of metallic nanoparticles, especially for local fields close to the surface [11].

The molecular nanoantenna concept

Finally, we remark that at such small scales, it is necessary to justify the title of ‘nanoantenna’, a requirement for an antenna is that it *efficiently* converts energy from far to near field (or vice versa). It is well known that the scattering and absorption cross section scale as R^3 and R^6 respectively for spheres (where R is the radius) [1]. Here we justify the use of the title in three ways. One, we are interested in designing antennas that are efficient for their size, by considering the collectivity of an excitation we can design molecular systems with the biggest possible cross section. Often the size will be dictated by other requirements such as catalytic behaviour. It is also worth pointing out that small size comes with added benefits such as tunability. For example, it was shown that for polycyclic aromatic hydrocarbons, the addition/removal of a single electron can reversibly switch on/switch off a molecular plasmon excitation [24]. Future quantum plasmonic devices will work within the compromise of a large cross section and tunability. Two, using the analogy of antennas can help understand complicated quantum systems. It is well known that atoms/molecules can be considered as tiny antennas and we recently demonstrated that the complicated spectra from a sodium chain dimer can be interpreted within a plasmonic picture [18]. Three, quantum antennas do not necessarily have to act in isolation and could be coupled to larger classical antennas. For instance, a quantum antenna could be part of an arrangement of antennas to give a cascade effect for massive field enhancements [25], or many could be arranged periodically to form a *quantum metamaterial* (i.e. the small cross section of each individual element can be compensated by arranging the meta-molecules closely: similar to the case of a crystal solid which, despite the small size of the constituent atoms, can interact strongly with light). Thus, to conclude, we believe it is sensible to push the antenna concept down to the smallest possible scale and that quantum plasmonic nanoantennas will be a rich area of research for many years to come.

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