Optical Spectra of Plasmon–Exciton Core–Shell Nanoparticles: A Heuristic Quantum Approach

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Light–matter coupling in plasmonic nanocavities has been widely studied in the past years. Yet, for core–shell particles, popular electromagnetic models that use the classical Lorentz oscillator to describe the shell predict extinction spectra with three maxima, if the plasmon and the shell absorption are in resonance. In contrast, experiments exhibit only two peaks as also expected from simple quantum models of hybrid states. In order to reconcile the convenient and widely used classical electromagnetic description with experimental data, we connect it to the quantum world by conceiving a heuristic quantum model. Our model is based on the permittivity of a two-level system in a classical electric field derived from the optical Bloch equations. The light–matter coupling is included via the collective vacuum Rabi frequency $\Omega_0$. Using our model, we obtain excellent agreement with a series of experimental extinction spectra of particles with various coupling strengths due to a systematic size variation. The suppression of the third maximum, which mainly stems from the absorption in the shell, can be interpreted as a vacuum induced power broadening, which may occur in lossy (plasmonic) cavities below the strong-coupling regime.

In recent years, advances in the fabrication of plasmonic nanostructures have pushed the limits of controlling light–matter coupling to the sub-diffraction scale. Applications like surface enhanced Raman spectroscopy,1 nanolasing,2,3 or plasmon assisted photovoltaics3 harvest the ultra-high electric fields concentrated in tiny mode volumes of the near-field. Placing quantum emitters inside those volumes gives rise to plasmon–exciton coupling with a wide range of coupling strengths. In the weak coupling regime, energy dissipates via decay channels such as Ohmic losses or radiation to the far-field, rather than being transferred back and forth between the subsystems. This regime can be utilized to enhance the emission via the Purcell effect.5 In the strong coupling regime, the interaction between plasmon and exciton dominates over losses, i.e. plasmon and exciton exchange energy coherently resulting in a splitting of the original resonances into two new polariton modes. Achieving this regime and controlling the energy transfer could allow for intriguing new applications like ultrafast optical switching,6 quantum networks,7 or manipulating chemical reactivity.8 When comparing strong coupling in plasmon–exciton systems to more traditional implementations, e.g. high finesse cavities with trapped atoms, the interesting question arises whether the vast differences in coupling strength and decay rates may lead to qualitatively different features and to potentially new applications.

The engineering of new applications often relies on accurate and easy-to-use models, which build up a correct intuition as they cover the essentials of the underlying physics and provide quantitative predictions. With respect to strong coupling in general, it has been pointed out that the most prominent features can be described with classical coupled oscillator models.9 Also in plasmonics, a rather simple electromagnetic model is often used to describe coupled systems: The excitonic material (loosely speaking "the emitters") is regarded as as an ensemble of two-level systems. Their optical response is modeled via a damped oscillator, i.e. a bulk medium is created that features a permittivity with a complex Lorentzian frequency dependence. Nanoparticles that consist of a plasmonic core and an emitter shell are typically modelled with classical electromagnetic tools like Mie theory or numerical Maxwell equation solvers. The increase and decrease of the real part of the Lorentz permittivity below and above its resonance leads to two opposing shifts of the original resonances: one to higher frequencies above and one to lower frequencies. This splitting is thus not explicitly included in the model but emerges as a result of the choice of material parameters as well as the geometry of the system. Experimental findings are typically modeled in qualitative,10–13 rarely quantitative14 agreement. On the other hand, Antoniewicz el al. found that the model predicts a third peak between the two polariton resonances, when specific parameter ranges are met. It was attributed to a so-called shell mode where the Lorentzian coating attains metallic character (a negative real part of the Lorentzian permittivity).15 This spurious third peak, which also appeared in other published simulations,16–18 marks a clear contradiction to the usual models, as the masses-and-springs model or a simple quantum mechanical model

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for strong coupling predict only two polariton peaks.\textsuperscript{19} And experimentally, such a third peak has never been observed. This means, the aforementioned frequently used classical model may possibly lead to false intuition and false predictions.

In this paper, we introduce a heuristic quantum model (HQM) for the permittivity of an emitter shell reconciling measurement data and theory. The model takes into account the influence of the plasmonic cavity onto the optical properties of the emitters. It is based on a semi-classical description of a two-level system in a classical electric field, but uses the vacuum Rabi frequency arising from the interaction between the collective emitter dipole and the quantized plasmonic mode. This results in the so-called power broadening of the emitters that suppresses the spurious peak. We compare the model to experimental extinction spectra of core–shell nanospheroids. We then discuss the appearance of the spurious peak for the classical Lorentz approach to model the shell into account. After that, we will apply both classical description of a two-level system in a classical model via our heuristic quantum mechanical model that takes the two-level nature of the shell into account. After that, we will apply both models to experimental data for core-shell nanorods of various sizes. We find that the HQM recovers measured data with high accuracy while the classical model fails. We will then close by discussing the nature and the implications of the HQM.

**CLASSICAL LORENTZ MODEL FOR CORE–SHELL SPHEROIDS**

Here, we shortly introduce the Mie–Gans theory to model the extinction of core–shell nanospheroids. We then describe the classical Lorentz approach to model the shell and discuss the appearance of the spurious peak for the simplest example of plasmonic nanoparticles: A spherical particle with Drude response. In this way, we can exemplify how the HQM that we will introduce in the following section modifies the extinction of core–shell particles.

Mie–Gans theory provides a transparent analytical expression for the polarizability $\alpha_k$ of a general core–shell nanospheroids:\textsuperscript{10,20}

$$\alpha_k = V \frac{(\epsilon_2 - \epsilon_3)\epsilon_a + g\epsilon_2(\epsilon_1 - \epsilon_2)}{\epsilon_3 + L_k^{(2)}(\epsilon_2 - \epsilon_3)\epsilon_a + gL_k^{(2)}\epsilon_2(\epsilon_1 - \epsilon_2)}. \quad (1)$$

From this polarizability, the calculation of the optical cross sections (absorption, scattering or extinction) is straightforward.\textsuperscript{20} The index $k$ stands for different polarizations of incoming light along the long ($k = a$) or short ($k = b$) axis, respectively. The $\epsilon_i$ represent the permittivity of the core ($i = 1$), the shell ($i = 2$) and the surrounding medium ($i = 3$) and $\epsilon_a = \epsilon_2 + (\epsilon_1 - \epsilon_3)(L_k^{(1)} - gL_k^{(2)}).$ $L_k^{(1,2)}$ are geometrical factors of the inner (1) and outer (2) spheroid, $g$ is the inner spheroid’s volume fraction of the total volume $V$. Details on the model are presented in the Supplementary Information.

In a purely classical approach, a shell within this Mie–Gans model is described as a Lorentz oscillator with resonance $\omega_0$, linewidth $\gamma$ and oscillator strength $f$. That means that the permittivity $\epsilon_2$ is given by

$$\epsilon_{\text{class}}(\omega) = \epsilon_\infty + \frac{f\omega_0}{\omega_0 - \omega + i\gamma/2}$$

for frequencies $\omega$ around the resonance frequency $\omega_0$ far exceeding the linewidth $\gamma$. Here, $\epsilon_\infty$ describes the influence of transitions with higher energy.

Figure 1a presents the extinction spectra for the simple example of a sphere consisting of a Drude metal described by $\epsilon_1 = \epsilon_\infty.\text{D} + \omega_p^2/(\omega^2 - i\Gamma\omega)$ with its plasma frequency $\omega_p$ and damping $\Gamma$. The core diameter is set to 25 nm. The shell with a thickness of 3 nm is described by eq 2 with a resonance at $\lambda_0 = 495$ nm, close to the plasmon resonance. The linewidth $\gamma$ is set to 50 meV and the oscillator strength $f$ varies between 0 and 0.2. Details on the parameters are presented in Figure 1e together with a sketch of the model system. We included the modified long wavelength approximation\textsuperscript{21} to extend the validity of the dipole approximation in eq 1 to larger particle sizes.

The spectra exhibit a peak splitting as a consequence of the coupling between the excitonic shell and the plasmonic core. Larger oscillator strengths result in higher coupling strengths and consequently in a larger peak splitting between the upper and lower polariton peak. In addition to the polariton resonances, a third peak emerges roughly at the uncoupled resonance position. This peak arises not only in the dipolar approximation discussed here, but also in the full Mie solution as well as in numerical Maxwell simulations and is an intrinsic feature of the classical material model, i.e. the Lorentzian permittivity.\textsuperscript{15} To underline how the additional resonance grows larger with respect to the polariton peaks, Figure 1b) presents the extinction cross sections for $f = 0.03$, $f = 0.08$ and $f = 0.13$ (blue, orange and red line). For $f = 0.03$, only the two polariton peaks are visible, for $f = 0.08$, the additional peak is clearly visible and for $f = 0.13$, it is already of comparable magnitude. The nature of this additional peak has been comprehensively discussed by Antosiewicz et al.\textsuperscript{15} It has been attributed to a so-called shell mode that resonates over the whole particle and that absorbs the electric energy predominantly in the shell. Despite the fact that the third peak is predicted by such a well-established
and frequently used model, it has not been observed in experiments. Furthermore, other models for strong coupling do not predict another (polariton) mode.\textsuperscript{19} In the following we show that this discrepancy can be lifted by taking the quantum character of the system into account.

**HEURISTIC QUANTUM MODEL FOR AN EXCITONIC SHELL**

We take the quantum character into account by starting with a semi-classical model that can be derived from Bloch equations: A two-level system is placed in a classical electric field $E = E_0 \cos(\omega t)$ where its permittivity is determined within the rotating wave approximation. The expression is only slightly different from the classical approach:\textsuperscript{19,22}

$$\epsilon_{\text{two-level}}(\omega) = \epsilon_{\infty} + \frac{f}{2} \frac{\omega_0 - \omega + i \gamma}{(\omega_0 - \omega)^2 + \frac{\gamma^2}{4} + \frac{\Omega^2}{2}}. \quad (3)$$

The Rabi frequency $\Omega$ accounts for the coupling between the electric field and the two-level system via $\Omega = \mu E_0 / \hbar$ where $\mu$ describes the transition dipole moment. The non-linearity that distinguishes eq 3 from its linear counterpart eq 2 originates from the Rabi frequency in the denominator. This textbook formula is a more correct approach to describe the response of a two-level system to an electric field. Why is it usually not applied in excitonic material models?

For weak interactions between light and matter, $\Omega$ can be neglected in eq 3 and the classical Lorentz solution is recovered. For larger interaction strengths, $\Omega$ causes the so-called power broadening.\textsuperscript{22} As $\Omega \propto E_0$, it is usually argued that a non-negligible $\Omega$ requires many photons to reach sufficiently high field strengths.\textsuperscript{19} However, it is the electric field that scales the Rabi frequency and not the number of photons. Plasmonic nanoparticles provide such small mode volumes that even for very low photon numbers, the electric fields can be very strong. In fact, cavity QED determines that even the vacuum state $|0\rangle$ in an optical cavity is of finite energy. This leads to a finite coupling energy between light and matter that is expressed by the vacuum Rabi frequency $\Omega_0$ as\textsuperscript{23}

$$\hbar \Omega_0 = \mu \sqrt{\frac{2 I_{\text{vac}}}{\epsilon_0}}. \quad (4)$$

Here, $I_{\text{vac}}$ represents the (non-vanishing) average intensity of a cavity mode’s vacuum state which is given by\textsuperscript{22}

$$I_{\text{vac}} = \frac{1}{2} \epsilon_0 \langle 0 | E^2 | 0 \rangle = \frac{\hbar \omega_M c}{4 V_M}. \quad (5)$$

Here, $\omega_M$ is the mode’s resonance frequency. The intensity of these vacuum fluctuations is thus largely determined by the geometrical confinement $V_M$ of the electromagnetic mode. It can be extremely small in plasmonic
cavities,24,25 with accordingly high vacuum intensities. On the other hand, power broadening occurs when the field intensity exceeds the threshold intensity \( I_{\text{ph}} \) (also referred to as saturation intensity):22,26,27

\[
I_{\text{ph}} = \frac{1}{4} c \varepsilon_0 \frac{h^2 \gamma^2}{\mu^2}.
\]

From \( I_{\text{vac}} > I_{\text{ph}} \), we find the condition for a non-negligible power broadening for the vacuum Rabi frequency from the above equations:

\[
\Omega_0^2 > \gamma^2 / 2.
\]

Since \( \Omega_0 \) grows stronger for decreasing mode volumes, this criterion can easily be fulfilled in plasmonic cavities. We therefore propose that eq 3 should be applied when modelling the spectra of nanoparticles with a plasmonic core and an excitonic shell. A similar relation is often expressed with the term ”saturation photon number” \( n_0 \approx \gamma^2 / \Omega_0^2 \) in cavity QED.28

The switch to this slightly more complicated permittivity model of eq 3 is further motivated by the fact that the third peak (in the extinction spectra of Figure 1a and b) results to a considerable extent from the particle’s absorption and not its scattering.15 The sole absorption of the excitonic shell can be straightforwardly quantified within a numerical Maxwell solver (see supplementary information and Ref. 15). In the classical model, this absorption can be even stronger than that of the metallic core although the number of involved charge carriers is significantly lower. It is plausible that a correction of the classical model includes a mechanism that suppresses the emergence of this presumably unphysical peak via some form of damping which is more or less the effect of \( \Omega \) in eq 3 (see also the discussion section).

Now, the remaining question is which value needs to be inserted for \( \Omega \). First, we want to restrict ourselves to the low-excitation limit. If not utilizing well-designed ultrashort laser pulses, it is unrealistic to excite the plasmonic systems twice within the typical plasmon lifetime of about 100 fs. We therefore consider the case that on average, only individual photons probe the otherwise unexcited system, and therefore propose that it is the vacuum Rabi frequency \( \Omega_0 \) that must be inserted in eq 3. Moreover, the shell does not consist of only one but several two-level systems. Yet, it is argued that these form a collective system (sometimes referred to as ”giant oscillator”) in the plasmonic cavity.29 This collective nature and the corresponding coherence means that each individual subsystem is directly affected by the electric field induced by the respective others. Consequently, Rabi oscillations30 and the vacuum Rabi splitting30,31 of individual two-level systems as well as for example chemical reactivity8 are directly modified by the number of involved entities. We therefore suggest that the value for \( \Omega \) that has to be inserted in the permittivity is retrieved from the collective coupling strength of the complete core–shell system. Until now, we regard this approach (i.e. using eq (3) and inserting the collective vacuum Rabi frequency for the light–matter coupling) as a heuristic quantum model (HQM) that is derived from the semi-classical approach. We assume that quantum mechanical treatments that also capture the effect discussed here can be derived more rigorously. We suspect that the reason, why this effect is still not discussed in literature might be the vast difference in effective rates i.e. coupling strength and exciton/plasmon/photon decay rates between traditional quantum electrodynamics (QED) systems and plasmon–exciton coupling. We believe that this effect is not necessarily exclusive though much more pronounced in plasmon–exciton systems. In the following, we want to present the consequences of applying this new HQM to the model of the core–shell sphere with a core formed by a Drude metal which is illustrated in Figure 1.

An \textit{ab initio} calculation of \( \Omega \) might in principle be possible but would at the very least be prone to errors.32 But even if there was a non-controversial way, to determine \( \Omega \) within the framework of quasi normal modes,33,34 it would be very sensitive to the exact material parameters, the geometry and emitter position. To allow for an easy comparison with real measured data, we strive for a more practical way to retrieve the collective coupling strength by making use of the fact that \( \Omega_0 \) is directly reflected in the splitting \( \Delta \) of the polariton peaks. In the example presented in Figure 1a, both linewidths and resonance positions of plasmon and dye coincide. In that case, \( \Delta = 2 \Omega_0 \). Note that for deviating resonance positions, the splitting would be smaller.25

We now use eq 3 instead of eq 2 in the Mie–Gans model to model the extinction of the Drude metal core–shell sphere. To do so, we determine \( \Omega_0 \) from the peak splitting of the outer peaks of each classical spectrum presented in Figure 1a and insert it into the expression of the semi-classical permittivity of a two-level system, leaving all other parameters unchanged. The resulting extinction spectra are presented in Figure 1c. We again see the splitting into upper and lower polariton resonance. However, in contrast to the classical model, no additional peak emerges between the two polariton peaks since this region is exactly the region where the power broadening weakens the transition between ground and excited state in the dye. Stronger coupling strengths (and thus higher \( \Omega_0 \)) are met by a stronger power broadening and consequently, the additional peak is suppressed effectively even for high oscillator strengths of the dye.

**EXPERIMENTAL DATA**

Is the heuristic quantum model we present here a more suitable approach to determine the spectra in such coupled core–shell particles? The well established expression in eq 3 for the permittivity is more precise than a pure Lorentz approximation, and we gave convincing arguments for using the collective vacuum Rabi frequency
In the following, we want to test the model’s validity by comparing it to experimental data of core–shell nanorods. We turned to gold nanorods, because their aspect ratio can be used to tune the longitudinal plasmon resonance (i.e., electron oscillations along the long axis) to about 600 nm, where the excitonic absorption resonance of the shell is formed by J-aggregates of the dye molecules TDBC (5,5’,6,6’-tetrachloro-1,1’-diethyl-3,3’-di(4sulfobutyl)benzimidazolocarbocyanine). See the Supplementary Information for details on the aqueous solution of the system. Using our HQM, we are able to reproduce the measured extinction quite accurately while we did not succeed with a purely classical model.

Figure 2a presents the Mie–Gans simulated normalized extinction spectrum of a gold nanospheroid (dash-dotted blue line) in comparison to an experimentally measured spectrum of an aqueous nanorod dispersion (orange line). Now, the core is not modelled as a simple Drude metal which disregards interband transitions, but with the dielectric function derived from measured literature data. Its short axis diameter was determined by transmission electron microscopy (TEM) to be 18 nm, the long axis is left adjustable to fit the plasmon resonance. A 1 nm thick citrate capping layer is included. The two resonances in both simulation and experiment correspond to the transverse (520 nm – short axis) and the longitudinal plasmon mode (600 nm – long axis) of the rod. The discrepancy in the magnitude of the transverse resonance is a known issue in EM nanorod simulations. We mainly attribute the differences to agglomerations of rods and secondary particles like spheres in the ensemble spectrum.

As discussed in the previous sections, the experimental spectrum changes considerably after the gold particles are coated with a layer of the J-aggregate forming dye TDBC (orange line in Figure 2b). In particular, the coupling between core and shell induces the longitudinal plasmon resonance to split into two new polariton resonances.

The classical simulation can reproduce the splitting of the longitudinal mode with good accuracy (dashed red line in Figure 2b). However, an additional peak emerges close to the uncoupled dye resonance frequency. Its origin is the same as for the additional peak in Figure 1. Yet, this additional peak is not visible in the experimental spectrum.

For the simulation in Figure 2b, we chose the emitter parameters in accordance with literature. We use \( \epsilon_{\infty} = 1.7, \) an emitter linewidth of \( h \gamma = 47 \text{ meV} \) together with an oscillator strength of \( f = 0.08 \) and an emitter resonance of \( h \omega_0 = 2.0 \text{ eV} \) (612 nm). This resonance position is red-shifted in comparison to the resonance of TDBC in water (590 nm), which can be rationalized by the adsorption on the particle surface. The shell thickness of 3 nm was determined by TEM (see Supplementary Information). Altering these parameters, also well outside the range found in literature, does not remove the additional peak when we keep the experimentally observed mode separation.

To apply the HQM, we determined the coupling strength from a series of measurements by systematic variation of the dielectric environment for each particle size (see also Supplementary Information). This additional experimental effort was required as the peak splitting directly translates to the coupling strength only when the original plasmon and exciton resonances and the respective linewidths coincide. This exact coincidence is however experimentally difficult to realize. The more appropriate way to determine the coupling strength is therefore via the anti-crossing of the polariton peaks for various detunings. This way, we obtained a value of \( h \Omega_0 = 82 \text{ meV} \) for the 18 nm rod. Using now the (only slightly deviating) value of \( h \Omega = 85 \text{ meV} \) in eq 3, the simulated extinction spectrum reproduces the experimental spectrum almost perfectly (dash-dotted blue line in Figure 2b), except for the previously mentioned issue with the magnitude of the transverse resonance. We use...
FIG. 3. The upper row shows the extinction spectra of TDBC-coated gold nanorods of different sizes as measured (solid orange lines) and simulated with to the Mie–Gans model (dash-dotted blue lines) and FEM simulations (dashed dark blue lines). Both models use the HQM. All particles have the same aspect ratio but a varying transverse diameter of 11 nm, 18 nm, 34 nm, and 37 nm (from left to right). Both models nicely reproduce the measurement data. For a comparison, the lower row presents the same measured spectra for the same particles (orange lines) with Mie–Gans-simulated (dashed red lines) and FEM–simulated (dotted dark red lines) using the classical approach. The spurious peak becomes visible for all particle sizes in both the numerical and analytical model leading to a mismatch between simulations and experiments.

We further tested the model by investigating particles with different sizes and therefore with different coupling energies $\hbar \Omega_0$. In the purely classical approach, we expect the additional peak to be more pronounced for smaller particles as the relative amount of excitonic material rises. These effects are also observed for the simple model of a Drude sphere with a Lorentz shell (see Supplementary Information). On the other hand, smaller particles support larger coupling strengths. Consequently, when applying the HQM for decreasing particle sizes, the (classically larger) rogue peak is suppressed by a more pronounced power broadening. In addition to the analytical Mie–Gans calculation, we also used a numerical FEM solver to determine whether the exact particle shape influences the outcome. In both calculations, we used the particle dimensions as determined by TEM and simulated the bare nanoparticle spectra (see Supplementary Information). Moreover, we used the same parameter set for TDBC as indicated above, except for $\Omega_0$, which we varied according to the measured mode splittings. The upper row in Figure 3 presents measured (orange lines) and calculated spectra for particles with a transverse diameter of 11 nm, 18 nm, 34 nm, and 37 nm, using a vacuum Rabi splitting $\Omega_0$ of 100 meV, 85 meV, 77 meV, and 65 meV, respectively. The agreement between measured spectra and model is remarkable. Mie–Gans (dash dotted blue lines) and FEM simulations (dashed dark blue lines) are consistent, no shell resonances appear at the positions of the "bare" dye and in all cases, the peak splitting is very well reproduced. The slight mismatch for the smallest particles is probably caused by the increased surface damping in such small particles, which modifies the permittivity of gold and is not considered in our model.

The lower row in Figure 3 presents simulations for the same particles as in the upper row, using the same parameter set, except for using $\epsilon_{\text{class}}$ in the shell permittivity. In all cases, the additional dye peak emerges, both in the Mie–Gans (dashed red lines) and the FEM approach (dotted dark red lines). As predicted previously, the rogue resonance becomes more pronounced for smaller particles. In the HQM the spurious peak is suppressed by increasing power broadening.

The agreement between the simulation and the experimental data and the consistency for different particle sizes indicates that indeed, the heuristic quantum model as presented here, can be a suitable approach to describing the spectra of plasmon–exciton core–shell systems.

DISCUSSION

At this point, we shortly want to take a look at the impact of the power broadening on the shell permittivity. As directly seen in a comparison between eq 2 and eq 3, the only difference of the permittivities in the classical Lorentz and the HQM model is the additional term $\Omega^2$ in the denominator. Since it does not show up in the imaginary part of the nominator, it cannot be interpreted as a classical damping term. The classical permittivity $\epsilon_{\text{class}}(\omega)$ can be either matched to the real or the imag-
FIG. 4. Comparison between the HQM and the classical approach. The four columns represent the different particle sizes and consequently coupling strengths that were used for Figure 3. In the first two rows, the solid blue lines represent the respective real and imaginary parts of $\epsilon_{\text{two-level}}$. The dashed red lines represent the real and imaginary parts of $\epsilon_{\text{class}}$ when the parameters are chosen to match the real part of $\epsilon_{\text{two-level}}$. The dash-dotted orange lines represent the real and imaginary parts of $\epsilon_{\text{class}}$, as well, only now, parameters are chosen to match the imaginary part of $\epsilon_{\text{two-level}}$. The lower row presents the Mie–Gans modelled extinction for the particle dimensions that were also used for Figure 3. The different line styles stand for the respective parameters used in the graphs above.

inary part of $\epsilon_{\text{two-level}}(\omega)$. Figure 4 exemplifies the situation by comparing the classical and HQM permittivity for the four different $\Omega$ that were used to successfully reproduce the experimental data in Figure 3. To match either the real or the imaginary part of the permittivity of the classical model to the well fitting HQM model, a different choice of the oscillator strength $f$ and damping $\gamma$ would be required for each $\Omega$ (see legend).

Blue lines indicate the real (first row in Figure 3) and imaginary (second row) parts of the permittivity of the HQM, which were used for the model of the extinction spectra (third row) that matches the experiments in Figure 3. A classical permittivity with adjusted $f$ and $\gamma$ to match the real part (dashed red lines) of the permittivity (first row) recovers the peak splitting (last row), but a shoulder of the rogue peak is still visible. Decreasing the oscillator strength $f$ to match the imaginary part (dash-dotted orange lines) successfully suppresses this peak, but also results in a too small peak splitting.

This comparison allows for a few insights into the nature of the additional peak in the classical model. First, in contradiction to previous discussions in the literature, the plots illustrate that the third peak does not require a negative real part of the permittivity. In all examples it is clearly larger than zero, yet if the imaginary part becomes too large, the peak becomes visible. In fact, $\text{Re}(\epsilon)$ is not responsible for the additional peak to arise but it is the large imaginary part of the shell permittivity, that causes a maximum in the imaginary part of the particle polarizability $\alpha$. In contrast to the two polariton resonances, the additional peak in the classical model is not caused by a minimum in the denominator of $\alpha$, but by a maximum in its numerator caused by the large $\text{Im}(\epsilon_{\text{class}})$ (see also Supplementary Information). To suppress the peak, it is therefore necessary to decrease its maximum (without suppressing $\text{Re}(\epsilon)$ too much). This is exactly the effect of the power broadening. In fact, one could argue that the additional peak does not represent a single new mode, at all. An (eigen-)mode of a spherical particle is characterized by a vanishing denominator of the corresponding scattering coefficients and consequently of the polarizability $\alpha$. This is not the case for the additional peak in our parameter set of the classical model. Having said that, the classical model does not contradict standard models for strong coupling in predicting a novel or polariton state. We show that the third peak only emerges due to a highly polarizable and absorptive shell medium.

Figure 4 also shows that indeed, to recover the measured peak splitting for all particle sizes with the classical model, each particle size requires a new set of parameters due to the varying coupling strength. In previous classical simulations, different linewidths for the same dye needed to be assumed to model spectra for different coupling strengths. The HQM elegantly removes this necessity and for all particle sizes, the dye parameters can be kept constant and only the (measured) coupling strength is used as varying parameter.
Further studies will be necessary to explore the validity of the HQM. We regard this article as an invitation to a discussion, which we start by the question how to interpret the effect of the power broadening induced by a plasmonic cavity. An incoming photon that probes the unexcited system already detects the modified permittivity. In that sense, it is already the vacuum ground state of the plasmonic cavity that alters the optical properties of the excitonic system. We could thus regard the effect as some kind of 'vacuum induced power broadening'. At first, such an interpretation seems rather counterintuitive, although other vacuum induced effects such as the Purcell effect, spontaneous emission, parametric fluorescence and vacuum Rabi splitting are well-established. Vacuum fields have been proven to modify the properties of two-level quantum systems, and power broadening would represent another realization of such QED effects.

Such a vacuum effect would also allow for intriguing applications. Optical nonlinearities in the few photon limit could be harvested as each single photon would further change the permittivity. Similarly, the strong coupling regime allows for two-photon nonlinearities with the same origin: The Rabi frequency changes for the number of excitations in the system. Yet, for the nonlinearities that occur in the HQM, the strong coupling regime is no prerequisite. The strong coupling regime requires a combination of sufficiently low linewidths of both emitters and cavities. Typically, this criterion is quantified to \( 2\Omega > (\kappa + \gamma)/2 \). On the other hand, the comparison between the vacuum field and the threshold intensity for power broadening \( I_{pb} \) previously showed, that the requirement of power broadening does not regard the cavity linewidth at all, since only \( \Omega^2 > \gamma^2/2 \) is necessary. Power broadening is not about pushing energy back and forth between the two subsystems but about the energy that is fed into the emitters. In principle, it should be possible to also construct weakly coupled systems in which power broadening is relevant and low photon number nonlinearities can be exploited. This is an exclusive property of lossy (bad) cavities and thus of plasmonic systems. In high-finesse optical cavities, the onset of a cavity induced power broadening comes along with the onset of strong coupling, which already can be exploited for two photon nonlinearities. In a plasmonic system, \( \Omega^2 > \gamma^2/2 \) can be fulfilled far before strong coupling occurs, i.e. plasmonic systems indeed may lead to qualitatively different features with respect to cavity QED than conventional high quality cavities.

The precise treatment of weakly coupled systems in the HQM might be slightly different than the way we introduced here since we used the collective coupling strength as the value to be inserted in the expression for the permittivity. In fact, we presumed that the emitters were coherently coupled to the plasmonic cavity. Outside of the strong coupling limit, coherence becomes weaker and consequently, the value for \( \Omega \) that is to be used might be a bit lower than the collective coupling strength. The nanoparticle systems that we presented here are all strongly coupled. Single particle spectra of bare nanorods indicated a plasmon linewidth in the realm of 150 meV. Hence, even the largest particles verge on the strong coupling regime.

CONCLUSION

We presented a heuristic quantum approach to describe the permittivity of an excitonic system coupled to a plasmonic cavity. This way, we could reconcile theory and experimental data for core–shell particles with a metal core and an excitonic shell. Previous purely classical models predicted the occurrence of an additional peak that has not been observed in measurements. Our approach started from the semi-classical model of a two-level system that takes the power broadening into account, which is induced by the light–matter coupling. We argue that this power broadening occurs even in the low-excitation limit since in plasmonic cavities, even the intensity of the vacuum field is strong enough to noticeably alter the optical properties of the shell. This effect does not even require strong coupling, but can also arise in weakly coupled systems with lossy cavities. The power broadening suppresses the non-physical peak allowing for a remarkable match with experimental data. Using our model, we were able to recreate the extinction spectra of core–shell nanorods of various sizes. The necessity to alter the dye parameters individually vanishes and we only need to consider the varying coupling strengths. The fact that already vacuum fluctuations can cause the effect and that the power broadening occurs already in the ground state, implies that this might be a vacuum effect similar to e.g. the vacuum Rabi splitting. This would allow for low-photon nonlinearities, even outside the strong coupling regime.

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COMPETING INTERESTS

The authors declare no competing interest.