Nanoparticle sensing using whispering-gallery-mode resonators: Plasmonic and Rayleigh scatterers

Yuecheng Shen and Jung-Tsung Shen*
Department of Electrical and Systems Engineering, Washington University in St. Louis, St. Louis, Missouri 63130, USA
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The theory of nanoparticle sensing using whispering-gallery-mode resonators is investigated for both plasmonic and Rayleigh scatterers. In particular, we describe how to extract critical information, such as the number of particles adsorbed, from the transmission spectrum. The effects of the interference due to multiple interparticle scatterings are elucidated. Analytical expressions are derived so as to enable further numerical analysis.

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I. INTRODUCTION

Nanoparticle sensing and monitoring have become increasingly important in many fields. Atmospheric nanoparticles, for example, have crucial effects on climate change [1] and human health [2]. Nanoparticles also appear as pathogens in bioterrorism [3] and as contaminants in manufacturing processes. In medicine, metallic nanoparticles can be used as cancer-fighting agents [4]. In many practical situations, especially in the low-particle-flux or low-particle-concentration regimes, a measurement sensitivity which enables detection of label-free single particles is often desired. Nonetheless, nanoparticles scatter probing light weakly if the size of the particles is much smaller than the wavelength of the light; to bypass this fundamental difficulty and to increase measurement sensitivity and resolution, one possibility is to exploit the phase coherence between the probing- and scattered-light signals by coupling nanoparticles to optical waveguides and resonators [5]. Very recently, the system consisting of high-quality-factor whispering-gallery-mode (WGM) resonators and tapered fibers has been proposed theoretically [6–8] and demonstrated experimentally to achieve single-particle resolution [6,9,10]. Despite these accomplishments, critical questions remain in such a detecting scheme, such as the determination from the transmission spectrum of the number of the particles adsorbed and their angular positions. In this paper, we investigate the theoretical aspects of nanoparticle detection using WGM resonators and address these critical issues. In particular, we provide a complete and coherent description for the two most common and important types of nanoparticles in particle sensing, i.e., plasmonic and Rayleigh scatterers, and provide criteria for extracting information from measurable transmission spectra. Analytic results are also derived so as to enable further numerical analysis for the determination of other characteristics, such as the intrinsic dissipation rates, resonance frequencies, and sizes of the nanoparticles. Thermal effects due to finite temperatures are also discussed; we show that the number of adsorbed particles can still be determined at finite temperatures for Rayleigh scatterers.

The system of interest is depicted schematically in Fig. 1. The system consists of a WGM resonator side-coupled to a tapered single-moded optical fiber. The nanoparticles are adsorbed onto the surface of the resonator and sensed by an evanescent field coupling due to the guided WGM in the resonator. Based upon the nature of the scattering, two types of nanoparticles are of particular interest: (i) a plasmonic particle, such as a metallic particle or an on-resonant molecule, that has a sharp resonance peak in the frequency range of interest, and (ii) a Rayleigh-type particle, such as a polystyrene particle or an off-resonant molecule, that does not have a distinct resonance peak in the frequency range of interest. In a typical experimental setup, a weak coherent laser beam is coupled into the fiber; after propagating around the WGM resonator and interacting with the adsorbed particles, the transmitted signal in the fiber is measured. The transmission spectrum contains the information of photon-nanoparticle interactions, which characterizes the scattering nature of the particles. In the following, we will show how to quantitatively extract useful information from the transmission spectrum.

Here, we start by explaining the physics, in particular the effects of the number of particles and their angular positions, so as to provide some insights. An ideal WGM resonator supports a pair of degenerate counterclockwise (CCW) and clockwise (CW) propagating modes [11]. An adsorbed nanoparticle on the surface backscatters CCW mode into CW mode, and vice versa. Thus, the nanoparticle effectively acts as a localized surface imperfection that breaks the mode degeneracy and induces mode splitting [12]. For a single Rayleigh particle, the mode splitting gives rise to two dips in the transmission spectrum; while for a single plasmonic particle, the mode splitting results in three dips in the spectrum, due to the additional resonance [5]. When more than one particle is adsorbed, multiple scatterings between particles occur. These coherent interparticle scattering processes depend on the relative angular positions of the particles, and give rise to an interference term in the transmission amplitude that modifies the spectral separation between the transmission dips. For plasmonic particles, two adjacent transmission dips could even merge for certain relative angles between the particles; for Rayleigh particles (identical or not), the collection of the particles acts jointly as surface imperfection so that the transmission spectrum maintains two dips, regardless of the relative angles.

As the number of adsorbed Rayleigh particles increases, the spectral center of the two transmission dips experiences a spectral shift that is proportional to the real part of the total complex polarizability from all particles adsorbed \((\sum_{i=1}^{n} \text{Re}[\alpha_i])\), where \(n\) is the number of particles and \(\alpha_i\) is the polarizability of the \(i\)th particle, and thus allows the determination of the number of particles. In contrast,
plasmonic particles, the number of transmission dips depends on the number of particles adsorbed. In particular, when \( n \geq 2 \) identical particles are adsorbed, the transmission spectrum has at most four dips. As the total number of resonances is \( n + 2 \) (where \( 2 \) is the number of WGMs), it immediately indicates the existence of \( n - 2 \) “dark states,” which are the superpositions of the particle states only and not the WGMs. The dark states do not couple to the WGM resonator and thus could not be probed by the probing light. For plasmonic particles, one has to perform numerical fitting using the analytical expression for the transmission amplitude given below to obtain the information on the number of particles adsorbed.

\[ H/\hbar = \int dx c_R^\dagger(x) \left( \omega_0 - i v_g \frac{\partial}{\partial x} \right) c_R(x) + \int dx c_L^\dagger(x) \left( \omega_0 + i v_g \frac{\partial}{\partial x} \right) c_L(x) + \left( \omega_c - i \frac{1}{\tau_c} \right) a^\dagger a + \left( \omega_c - i \frac{1}{\tau_c} \right) b^\dagger b + \sum_j \left[ \Omega_j - i \frac{1}{\tau_j} a_j^\dagger a_j + \Omega_j \delta_{aj} \right] + \int dx \left[ V_{aj} c_R^\dagger(x) a + V_{aj}^* c_R(x) \right] + \int dx \left[ V_{bj} c_L^\dagger(x) b + V_{bj}^* c_L(x) \right] + (h b^\dagger a + h^* a^\dagger b) + \sum_j \left[ (g_{aj} b \sigma_{+j} + g_{aj}^* b^\dagger \sigma_{-j}) + (g_{aj} a \sigma_{+j} + g_{aj}^* a^\dagger \sigma_{-j}) \right]. \]

Here, \( c_R/L^\dagger(x) \) is a bosonic operator creating a right (R) or left (L) moving photon at position \( x \) along the fiber. \( \omega_0 \) is the reference frequency where the waveguide dispersion relation is linearized and \( v_g \) is the group velocity \([13]\). \( a^\dagger \) and \( b^\dagger \) denote the creation operator for the CCW and CW modes of the WGM resonator, respectively; \( \omega_c \) is the resonant frequency of the WGM resonator. \( 1/\tau_c \) is the intrinsic dissipation rate of each WGM, and \( 1/\tau_q \) is the intrinsic dissipation rate of each particle. \( h\Omega_j \) is the excitation energy of the particle, while \( h\Omega_q \) is the ground-state energy. \( \Omega \equiv \Omega_j - \Omega_q \) is the resonant frequency of the plasmonic particle. \( h \) is the intermediate scattering strength between CCW and CW modes due to the surface imperfection. \( \sigma_{+j} \) and \( \sigma_{-j} \) are the excitation and deexcitation operator of the \( j \)th nanoparticle, respectively. \( V_{aj/b} \) is the waveguide-resonator coupling strength. \( g_{aj} \) and \( g_{aj}^* \) denote the resonator-particle coupling strength between the \( j \)th particle and CCW, or CW mode, respectively.

The experiments are typically carried out such that the mean photon number in the system is much smaller than one \([14]\). The scattering events thus are dominantly one-photon processes. The general form of a one-photon and

\[ |\Phi(t)\rangle = \left\{ \int dx [\phi_R(x,t)c_R^\dagger(x) + \phi_L(x,t)c_L^\dagger(x)] + e_a(t)a^\dagger + e_b(t)b^\dagger + \sum_{j=1}^{n} e_{aj}(t)\sigma_{+j} \right\} |G\rangle, \]

where \( \phi_R(x,t), \phi_L(x,t) \) are the photonic wave functions in the waveguide; \( e_a(t) \) and \( e_b(t) \) are the excitation amplitudes of the \( a \) and \( b \) WGM, respectively; and \( e_{aj}(t) \) is the excitation amplitude of the \( j \)th particle. \( |G\rangle = |0;0;0;-,\ldots,\rangle \) denotes the vacuum state (with zero photon in the fiber and WGM resonator, and where all of the plasmonic particles are in the ground state \(|-\rangle\)). By applying the time-dependent Schrödinger equation \( i\hbar \partial / \partial t |\Phi(t)\rangle = H |\Phi(t)\rangle \), one obtains the following set of equations of motion:

\begin{align}
-iv_g \frac{\partial}{\partial x} \phi_R(x,t) + \delta(x) V_a e_a(t) + (\omega_0 + n\Omega_q) \phi_R(x,t) = i \frac{\partial}{\partial t} \phi_R(x,t), \\
+iv_g \frac{\partial}{\partial x} \phi_L(x,t) + \delta(x) V_b e_b(t) + (\omega_0 + n\Omega_q) \phi_L(x,t) = i \frac{\partial}{\partial t} \phi_L(x,t), \\
(\omega_c + n\Omega_q - i \frac{1}{\tau_c}) e_a(t) + V_{aj}^* \phi_R(0,t) + \sum_j g_{aj}^* e_{aj}(t) + h^* e_b(t) = i \frac{\partial}{\partial t} e_a(t).
\end{align}
\[ (\omega_n + n\Omega_\phi - i \frac{1}{\tau_n}) e_b(t) + V_{\phi}^* \phi_L(0,t) + \sum_j g_{aj}^* e_{aj}(t) + \hbar e_a(t) = i \frac{\partial}{\partial t} e_b(t). \]  

\[ (n - 1)\Omega_\phi + \Omega_\delta - i \frac{1}{\tau_q} \]  

For a given initial state, the full spatiotemporal dynamics of the system can be obtained by numerically solving the above set of equations. Here, we derive the steady-state solution to find the energy eigenstates of the system. For a steady state, one has \(|\Phi(t)\rangle = e^{-i\epsilon t}|\epsilon^+\rangle\), where \(\epsilon = \omega + n\Omega_\phi\) is the initial energy of the system divided by \(\hbar\), and \(\omega = \omega_0 + v_\phi k\) is the frequency of the incoming photon (\(k\) is the wave vector of the photon). Thus, \(\phi(x,t) = \phi(x)e^{-i\epsilon t}\), and similar expressions for the other terms. To compute the transport properties of the photon, one takes \(\phi_R(x) = e^{ikx}[\theta(-x) + t\theta(x)]\), and \(\phi_L(x) = re^{i(kx)}[\theta(-x)\), where \(t\) and \(r\) are the transmission and reflection amplitude, respectively. The set of equations (3) can be solved straightforwardly [5] and yields the solution for the transmission amplitude \(t(\omega)\) as follows:

\[ t = \frac{\Delta \tilde{\omega}_c (\Delta \tilde{\omega}_c \Delta \tilde{\omega}_d - G_2^2) + \Delta \tilde{\omega}_d \Gamma^2 - I_1 - |h|^2 \Delta \tilde{\omega}_q + iG_2 \Gamma + I_2/\Delta \tilde{\omega}_q}{(\Delta \tilde{\omega}_c + i\Gamma)(\Delta \tilde{\omega}_q (\Delta \tilde{\omega}_c + i\Gamma) - G_2^2) - I_1 - |h|^2 \Delta \tilde{\omega}_q + I_2/\Delta \tilde{\omega}_q}, \]  

where \(\Delta \tilde{\omega}_c = \omega - \omega_c + i(1/\tau_c)\), \(\Delta \tilde{\omega}_q = \omega - \omega_q + i(1/\tau_q)\), \(G_2^2 = \sum_j(|g_{aj}|^2 + |g_{bj}|^2)\), \(G_2^2 = \sum_j(|g_{aj}|^2 - |g_{bj}|^2)\), \(0, \Gamma = V^2/2\kappa\) is the coupling strength between the resonator and fiber, and

\[ I_1 = \sum_j (g_{aj}^* g_{bj} h + g_{aj} g_{bj}^* h^*) = 2g^2|h| \sum \cos(2m\theta_j - \theta_h), \]  

\[ I_2 = \sum_{j,k} (g_{aj}^* g_{bk} h - g_{aj} g_{bk}^* h^* \langle k | g_{ak} g_{bk} \rangle) = 2g^4 \left[ \frac{n(n-1)}{2} - \sum_{j<k} \cos 2m(\theta_j - \theta_k) \right]. \]  

In the equalities above, \(g_{aj} = g_a e^{im\theta_j}\) and \(g_{bj} = g_b e^{-im\theta_j}\) are employed with \(m\) being the order of the WGM; also, \(g_a = g_b \equiv g\) is used for the induced dipole moment. \(\theta_j\) is the angular position of the \(j\)th particle. The \(\theta = 0\) axis is chosen to point perpendicular to the fiber direction and bisects the resonator so that \(V_a = V_b = V\) can be taken as real numbers [5]. The interference term \(I_2\) involves the relative angular positions and is due to multiple scattering between particles.

(2) Rayleigh scatterer: For a Rayleigh scatterer, the interaction between the particle and the photon is given by \(H_I = -\tilde{d} \cdot \tilde{E}\), where \(\tilde{d} = \tilde{a} \tilde{E}\) is the induced dipole moment of the particle, and the polarizability \(\tilde{a} = 4\pi \epsilon_0 a^3(\epsilon_{\text{particle}} - \epsilon_{\text{medium}})(\epsilon_{\text{particle}} + 2\epsilon_{\text{medium}}) \equiv a_1 + i\alpha_2\). Here, \(\epsilon_{\text{particle}}\) is the complex effective permittivity for the spherical particle and \(\epsilon_{\text{medium}}\) is the permittivity for its surrounding environment. The electrodynamic profile of the particle is expanded as \(\tilde{E} = (a + b^\dagger)\tilde{\phi}_n + (a^\dagger + b)\tilde{\phi}_n^\dagger\) [5], where \(\phi_n = \tilde{E}_n e^{im\theta}\) is the \(m\)th order WGM and \(\tilde{E}_0\) is the radial part of the electrical field, \(E_0 = |\tilde{E}_0|\) denotes the magnitude of the field. Using these expressions, \(H_I\) now becomes

\[ H_I = -2n\alpha \tilde{E}_0^2 (a^\dagger a + b^\dagger b) - 2 \sum_k e^{2im\theta_k} a^\dagger b \]  

where the last two terms indicate that all of the particles collectively backscatter the WGMs into each other, effectively acting as an intermode coupling. Thus, the Hamiltonian for the Rayleigh case can be written as

\[ H/I = \int dx c_I^\dagger(x) \left( \omega_0 - i \nu_k \frac{\partial}{\partial x} \right) c_I(x) = \int dx c_L^\dagger(x) \left( \omega_0 + i \nu_k \frac{\partial}{\partial x} \right) c_L(x) \]  

\[ + (\Omega_c - i\gamma)c^\dagger a^\dagger (a + \Omega_c - i\gamma)b^\dagger b \]  

\[ + \int dx \left( [V_a c_R^\dagger(x)a + V_b c_R^\dagger(x)b + V_a c_L^\dagger(x)a + V_b c_L^\dagger(x)b] \right) \]  

\[ + \left( h - 2\alpha \tilde{E}_0^2 \sum_j e^{2im\theta_j} \right) b^\dagger a \]  

\[ + \left( h^* - 2\alpha \tilde{E}_0^2 \sum_k e^{-2im\theta_k} \right) a^\dagger b, \]  

where \(\Omega_c = \omega_c - 2n\alpha_1 \tilde{E}_0^2\) and \(\gamma = \frac{1}{T} + 2n\alpha_1 \tilde{E}_0^2\) (here \(\alpha \equiv \tilde{a}/\hbar\)). In contrast to the plasmonic case, the notable feature here is that both the WGM resonator frequency \(\omega_c\) and damping rate
1/\tau_c are renormalized. Specifically, both terms are shifted by an amount proportional to the number of the particles \( n \). The renormalization predicts a red shift of the resonance frequency when the dielectric function of the particle is larger than that of the ambient surrounding medium (\( \text{Re}\{\epsilon_{\text{particle}}\} > \text{Re}\{\epsilon_{\text{medium}}\} \), i.e., \( \alpha_1 > 0 \)), and a blue shift when the dielectric function of the particle becomes smaller (\( \text{Re}\{\epsilon_{\text{particle}}\} < \text{Re}\{\epsilon_{\text{medium}}\} \), i.e., \( \alpha_1 < 0 \)). The latter case describes the situation wherein the nanoparticles are embedded in an aqueous solution with a higher refractive index. Moreover, for dissipative materials, \( \alpha_2 \) is positive and thus the damping rate increases, in accord with physical intuition. On the other hand, when there is a gain in the particle (e.g., due to external pumping and the nonlinearity in the particle), \( \alpha_2 \leq 0 \), the damping rate decreases. The transmission amplitude can be computed straightforwardly to yield

\[
T(\omega) = \frac{(\omega - \Omega_c + i\gamma)^2 - (h - 2\alpha E_0^2 \sum_j e^{2im\theta_j})(h^* - 2\alpha E_0^2 \sum_k e^{-2im\theta_k})}{(\omega - \Omega_c + i\gamma + i\Gamma)^2 - (h - 2\alpha E_0^2 \sum_j e^{2im\theta_j})(h^* - 2\alpha E_0^2 \sum_k e^{-2im\theta_k})}.
\]

The term in the amplitude that is proportional to \( \sum_{j<k} e^{2im(\theta_j - \theta_k)} \) is the interference term.

The two amplitudes, given by Eqs. (4) and (8), contain all of the information but, in general, are very complicated. With the advent of microfabrication techniques, resonators can be fabricated with an extremely high quality factor. Thus, in the following, we will take the intermode scattering strength \( h \) to be 0, which simplifies the expression.

### III. Transmission Spectra

We now investigate the evolution of the transmission spectra \( T(\omega) = |t(\omega)|^2 \) as the number of the adsorbed particles increases. To begin with, Fig. 2 plots a typical transmission spectrum for the null case, i.e., the bare system of the resonator and fiber with no particles adsorbed. For this case, \( t = (\omega - \omega_c + i/\tau_c - i\Gamma)/(\omega - \omega_c + i/\tau_c + i\Gamma) \), and the relevant parameters of the setup, i.e., \( 1/\tau_c \), \( \Gamma \), and \( \omega_c \), can be extracted from a simple fitting scheme (e.g., the method of least squares). When single particles are progressively adsorbed, the transmission spectra are as plotted in Fig. 3. For the Rayleigh case (left panel of Fig. 3), one of the notable features is that all spectra exhibit only two dips, as the presence of the particles breaks the degeneracy of the two WGMs by acting as a surface imperfection. We also note that the spectrum is asymmetric with respect to \( \Omega_c \) when \( \alpha_2 \) is nonzero, and both dips have different linewidths and heights: when \( \alpha_2 \) is not zero, such that \( \alpha \) is complex, the effective intermode scattering strengths in \( b^*a \) and \( a^*b \) in Eq. (7) are not complex conjugate to each other, which results in the asymmetry of the two dips. Moreover, it can be shown that the spectral separation of the two dips is always \( \text{Re}\{2\sqrt{T_0}\} \), where \( I_3 = 4\alpha^2 E_0^4 [n + 2 \sum_{j<k} \cos 2m(\theta_j - \theta_k)] \) is the interference term; the shift of the center of the spectrum (defined

![FIG. 2. (Color online) Schematic representation of the transmission spectrum for the null case (i.e., no particle is adsorbed). \( T_{\min} = (1/\tau_c - \Gamma)^2/(1/\tau_c + \Gamma)^2 \). The full linewidth at half minimum is \( 2(1/\tau_c + \Gamma) \).](image)

![FIG. 3. (Color online) Transmission spectra for different numbers of adsorbed nanoparticles. Left: Rayleigh; right: plasmonic. The angular positions of the particles are \( \theta = 0, \pi/8, \pi/6 \), and \( \pi/4 \). \( m = 17 \) and \( h = 0 \) for both cases. For Rayleigh scatterers, \( 1/\tau_c = 0.76, \Gamma = 0.44, \alpha_1 E_0^2 = 6 \), and \( \alpha_2 E_0^2 = 0.16 \) MHz. For plasmonic particles, \( 1/\tau_c = 0.76, \Gamma = 0.44, g = 6 \), and \( 1/\tau_q = 0.16 \) GHz [15]. All parameters are given in angular frequency.](image)
as the average of the location of the two dips) from \( \omega_c \) is given by \(-2n\alpha_1E_0^2\), which is a direct result of the renormalization of the center frequency. By measuring the shift in the one-particle case, \( \alpha_1E_0^2 \) can be determined. Consequently, the number of the particles adsorbed for any cases can be determined by measuring the corresponding spectral shift and dividing by \( 2n\alpha_1E_0^2 \).

For identical plasmonic particles (right panel of Fig. 3), the spectrum is always symmetric with respect to the WGM resonance frequency \( \omega_c \), when the particles are on-resonance (\( \Omega = \omega_c \)). For a fixed number of particles, the number of the dips depends on the value of the interference term \( I_2 \). Specifically, when all cosine terms \( \cos 2m(\theta_j - \theta_k) \) for \( j < k \) become 1, \( I_2 \) reaches its minimum 0, and the spectrum has three dips for any number of particles. Also, for the special case of two particles, when \( \cos 2m(\theta_1 - \theta_2) = -1 \) (which is only possible for the two-particle case), the spectrum has only two dips. Normally, \( 0 < I_2 \), and the spectrum has four dips for any number \( (\geq 2) \) of particles, as shown in the right panel of Fig. 3. Here, we summarize the evolution of the structure of the dips: usually there are four dips; as each cosine term approaches 1, the two middle dips merge; and as each cosine term approaches \(-1\), the two dips on each side of \( \omega = \omega_c \) merge, giving the spectrum two dips. In contrast to the Rayleigh-type case, the number of the particles adsorbed, however, cannot directly be determined by measuring the spectral shift and requires a numerical fitting from the transmission spectrum. Also, from the one-particle case, \( \tau_q \), \( g_a \), and \( g_b \) can be extracted. Consequently, further information such as the relative angular positions and the number of particles can be obtained by numerically fitting with Eq. (4) for any number of particles.

### IV. MATRIX METHOD

The exact locations and number of the dips in the transmission spectrum are of particular interest, as they exhibit eigenfrequencies of the subsystem consisting of the resonator and the particles. Here, we describe a direct yet simple matrix method to derive these eigenfrequencies: The matrix essentially represents the Hamiltonian of the subsystem, with the diagonal terms being the unperturbed frequencies of the WGMs and nanoparticles, while the nondiagonal terms describe the couplings between the components. The eigenvalues of this matrix thus indicate the number and positions of dips in the transmission spectrum.

As a concrete example, we describe the case of \( n \) Rayleigh scatterers adsorbed to the resonator. There are only two bases, i.e., CCW and CW, so the matrix takes the following form:

\[
\begin{pmatrix}
\omega_c - 2n\alpha_1E_0^2 & -2\alpha_1E_0^2 \sum_{j,k} e^{2im\theta_j} \\
-2\alpha_1E_0^2 \sum_{j,k} e^{2im\theta_k} & \omega_c - 2n\alpha_1E_0^2
\end{pmatrix}
\]

The two eigenvalues of the matrix are \( \omega = \omega_c - 2n\alpha_1E_0^2 \pm 2\alpha_1E_0^2 \sqrt{\sum_{j,k} e^{2im(\theta_j - \theta_k)}} \). The real part of the eigenvalues gives the exact locations of the two transmission dips. Moreover, the spectral separation of two dips is given by \( \text{Re}[2\sqrt{F}] \), which is the same as using the full Hamiltonian.

As a second example, we describe the case of two identical plasmonic particles adsorbed. The bases for the matrix are chosen as CCW \((1, 0; -1, -1)\), CW \((0, 1; -1, -1)\), |0, 0; +, +\rangle, and \(|0, 0; -, -\rangle\), respectively. Using these bases, the matrix is given by

\[
\begin{pmatrix}
\omega_c & 0 & g_a e^{im\theta_1} & \ldots & g_a e^{im\theta_n} \\
0 & \omega_c & g_b e^{im\theta_1} & \ldots & g_b e^{im\theta_n} \\
g^a e^{-im\theta_1} & g^b e^{-im\theta_1} & \Omega & 0 & 0 \\
\vdots & \vdots & 0 & \ddots & \vdots \\
g^a e^{-im\theta_n} & g^b e^{-im\theta_n} & 0 & 0 & \Omega
\end{pmatrix}
\]

where \( \Omega \) is the excitation frequency of the particles. A direct computation reveals that there are \( n - 2 \) degenerate eigenstates with eigenvalue \( \Omega \); moreover, these eigenstates do not involve the CCW and CW states but are only a linear superposition.
of the particle states. Thus, these eigenstates are decoupled from the resonator and cannot be probed by the probing beam in the fiber; consequently, the transmission at the resonant frequency $\Omega$ is always 100%, regardless of the particle dissipations. These states are properly named as the “dark states.” Evidently, the maximum number of dips in the transmission spectrum is $(n + 2) - (n - 2) = 4$. For the case of four identical particles $(n = 4)$, which could be dissipative, the two dark states are given by $(0,0,\sin(\theta_1 - \theta_2), \sin(\theta_1 - \theta_3), \sin(\theta_1 - \theta_4), 0)$ and $(0,0,\sin(\theta_2 - \theta_4), \sin(\theta_2 - \theta_3), 0, \sin(\theta_2 - \theta_1))$, respectively. Thus the dark states are robust against the dissipations. These results can be generalized to the case when there are several species of plasmonic particles with different excitation frequencies. For example, when $M$ species of particles are adsorbed, with excitation frequency $\Omega_i$ and number $n_i$ $(i = 1, \ldots, M)$, the number of dark states is given by $D = \sum_{i=1}^{M} d(n_i)$, where $d(n_i) = n_i - 2$ if $n_i \geq 2$, and 0 if $n_i < 2$. Consequently, the maximum number of transmission dips is $(2 + \sum_{i=1}^{M} n_i) - D$. Although the simple matrix method gives directly the number and positions of the transmission dips, these sharp eigenfrequencies are broadened by the intrinsic dissipation of the particles, as well as by the resonator-fiber coupling $\Gamma$. To obtain the linewidth of each transmission dip, as well as the numerical value of the transmission, one must employ the full theory presented above. It can be further shown that the dissipations and $\Gamma$ do not affect the locations of the dips. We note that the matrix method could also deal with the case of a higher power of the probing light by employing bases with multiple plasmonic excitations. The dimension of the Hamiltonian matrix is accordingly enlarged, which gives rise to a more complicated transmission spectrum.

Here we describe possible schemes to reveal the signatures of the dark states. As the dark states are eigenstates formed by identical and independent plasmonic scatterers, the dark states can be transmuted into detectable bright states by alleviating either of these two requirements. For example, by imposing a spatially varying magnetic field, each plasmonic particle would experience a different amount of transition frequency shift so that the particles become nonidentical; additional transmission dips would thus emerge in the transmission spectrum, which provides the information about the number of particles. Alternatively, when two plasmonic particles are in close proximity to each other so that a direct scattering of photons between the particles becomes possible, additional transmission dips will also emerge in the transmission spectrum. Mathematically, both approaches modify the lower-right diagonal block of the Hamiltonian matrix of Eq. (11) so that in the former case, the identical $\Omega$’s are shifted to different values; while in the latter case, off-diagonal terms become nonzero due to the direct coupling. In both cases, all eigenstates couple to the WGMs and can be detected by the probing light.

V. CONCLUSIONS

Finally, we comment on some of the important issues in practical detection. First, we discuss the effects of the presence of the surface imperfections $(h \neq 0)$. The sensitivity as well as the accuracy for the estimation of the particle number and locations of the transmission dips degrade with increasing surface imperfection. The surface imperfection breaks the degeneracy of the two WGMs, and splits the single transmission dip into a doublet in the undercoupling regime [5,12]. As the adsorbed particles are intrinsically (spatially localized) surface imperfections, such a doublet structure from nonzero $h$ will superimpose upon the induced structures due to the particles in the transmission spectra, and therefore mask the information about the particles. We note, however, that one could still obtain the information by numerically fitting the transmission spectrum using Eqs. (4) or (8) for the nonzero $h$ case.

Second, all measurements are performed at finite temperatures. At a finite temperature $T$, the dominant thermal effects manifest in the temperature dependence of the index $n(T)$ of the resonator, and the radii $(r(T)$ and $a(T)$ of the WGM resonator and the particles. These thermal effects effectively give rise to a temperature-dependent resonator resonant frequency $\omega_1(T)$, evanescent field $E_0(T)$, and temperature-dependent polarizability $\alpha(T)$. Remarkably, for the Rayleigh case, our theory indicates that the number of particles adsorbed can still be determined even at finite temperatures. In this case, the spectral shift of the center of the transmission spectrum is given by the same expression, $2n\alpha_1(T)E_0^2(T)$. By measuring the spectral shift for the one-particle case, the number of particles can again be determined. Third, our formalism is capable of describing the full spatiotemporal dynamics of the system, and applies to other scenarios. For example, when nanoparticles fly by the resonator slowly and closely but do not get adsorbed (which is desired when washing off the adsorbed particles is not practical), the dynamics can be analyzed by the full theory presented here.

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