

# Perturbation theory for plasmonic eigenvalues

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We develop a perturbative approach for calculating the shift of surface resonances in response to a deformation of a dielectric volume within the electrostatic approximation. Our strategy is based on the conversion of the homogeneous system for the potential which determines the plasmonic eigenvalues into an inhomogeneous system for the potential's derivative with respect to the deformation strength, and on the exploitation of the corresponding compatibility condition. The resulting general expression for the first-order shift is verified for two explicitly solvable cases.

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## I. INTRODUCTION

Recent advances in plasmonics, *i.e.*, in the use of surface plasmons for subwavelength optics<sup>1-3</sup>, have led to renewed interest in the physics of plasmon excitations bound to smooth or rough surfaces<sup>4</sup>. In particular, it has been proposed to transport electromagnetic energy along linear chains of nanoparticles<sup>5</sup>, possibly embedded in a gain medium<sup>6</sup>, and proof-of-principle experiments have been made<sup>7-9</sup>. In setups such as this, fabrication-induced imperfections of the nanoparticles inevitably will result in slight shifts of their resonance frequencies, and it might be crucial to estimate the maximum size of such fluctuations which can still be tolerated. Although sophisticated numerical methods for computing the optical response of nanoparticles do exist<sup>10,11</sup>, it would still be helpful to have a flexible analytical tool which exploits the fact that the shape of an unintentionally deformed nanoparticle is close to some theoretical ideal.

In the present paper we develop such a perturbative approach to the computation of surface resonances. Our strategy is quite general, relying on concepts borrowed from differential geometry<sup>12</sup>. The mathematical arguments are given in the following Sec. II; some technical details have been deferred to the appendix. The main results are the expressions (26) and (28), which quantify the shifts of the resonance frequencies to first order in the deformation strength. Section III then provides two illustrative examples. The paper closes with some concluding remarks in Sec. IV.

## II. PERTURBATION THEORY FOR PLASMONICS

Consider a volume  $\Omega \subset \mathbb{R}^3$  filled with a dielectric medium which is characterized by an isotropic, frequency-dependent dielectric function  $\epsilon(\omega)$ ; this volume  $\Omega$  be surrounded by vacuum. Within the electrostatic approximation, which is valid if the characteristic linear extensions of  $\Omega$  are small in comparison with the wavelengths of impinging radiation, the Fourier components  $u(\mathbf{r}|\omega)$  of the potential are given by the solutions to the set of equations

$$\Delta u = 0 \quad \text{in } \mathbb{R}^3 \setminus \partial\Omega \quad (1)$$

$$u_- - u_+ = 0 \quad \text{on } \partial\Omega \quad (2)$$

$$\epsilon \partial_n u_- - \partial_n u_+ = 0 \quad \text{on } \partial\Omega. \quad (3)$$

Here  $u_-$  is the restriction of  $u$  to the interior  $\Omega$  and  $u_+$  its restriction to the exterior  $\mathbb{R}^3 \setminus \bar{\Omega}$ ; both  $u_-$  and  $u_+$  are smooth everywhere except at the boundary  $\partial\Omega$ . We stipulate that  $\partial\Omega$  be sufficiently smooth to substantiate the following operations, and suppress the dependence of  $u$  on the frequency  $\omega$  altogether. The expressions  $\partial_n u_{\pm} = \mathbf{n} \cdot \nabla u_{\pm}$  in Eq. (3) are the derivatives of the potential in the direction of the outward unit normal  $\mathbf{n}$ .

Observe that at this point the knowledge of the dielectric function  $\epsilon(\omega)$  is not yet required. Rather, we take  $\epsilon$  on the l.h.s. of Eq. (3) as a real number and regard it as an eigenvalue, henceforth dubbed as *plasmonic eigenvalue*, if the system (1) – (3) with that particular  $\epsilon$  possesses a nontrivial solution  $u$  which vanishes at least quadratically with increasing distance from  $\partial\Omega$ . This nomenclature is formally justified by reformulating the system (1) – (3) in terms of Dirichlet-to-Neumann operators, so that the desired values of  $\epsilon$  explicitly appear as inverse eigenvalues of a combination of such operators<sup>13</sup>. This somewhat unfamiliar view offers conceptual advantages: On the one hand, the material-specific aspects of the problem, embodied in the function  $\epsilon(\omega)$ , are separated from the geometric ones; only these geometric aspects matter

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when studying deformations of  $\Omega$ . On the other hand, standard theorems concerning the behavior of eigenvalues of linear operators under perturbations can now be employed. After such a plasmonic eigenvalue has been found for a particular geometry, *i.e.*, for some domain  $\Omega$  with a given shape, that eigenvalue then determines the frequency  $\omega_s$  of a surface resonance through the equation  $\epsilon = \text{Re}(\epsilon(\omega_s))$ . For example, a half space with planar boundary  $\partial\Omega$  yields  $\epsilon = -1$ , and the dielectric function can be taken as

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2} \quad (4)$$

for metallic materials with plasma frequency  $\omega_p$ , describing the free electron motion. This then leads to the familiar expression  $\omega_s = \omega_p/\sqrt{2}$  for the surface plasmon resonance at a planar metal-vacuum interface in the quasistatic limit<sup>4</sup>. Typical plasma frequencies for good conductors are on the order of  $10^{16} \text{ s}^{-1}$ .

We now consider the response of a plasmonic eigenvalue  $\epsilon$  to a small deformation of  $\Omega$ . This deformation is modeled in terms of a shape function  $a : \partial\Omega \rightarrow \mathbb{R}$  and a dimensionless parameter  $h$ , such that the surface of the deformed volume is given by

$$\partial\Omega(h) = \{\mathbf{r} + ha(\mathbf{r}) \mathbf{n}(\mathbf{r}) : \mathbf{r} \in \partial\Omega\}. \quad (5)$$

We assume that one has solutions  $\epsilon(h)$ ,  $u(\mathbf{r}, h)$  to the problem (1) – (3) with  $\Omega$  replaced by  $\Omega(h)$ , and that  $\epsilon(h)$  and  $u(\mathbf{r}, h)$  depend differentiably on  $h$ . We denote the derivatives in  $h$  by a dot and write  $\dot{\epsilon} = \dot{\epsilon}(0)$  and  $\dot{u}(\mathbf{r}) = \dot{u}(\mathbf{r}, 0)$  for brevity.

In what follows we derive a system of equations for  $\dot{\epsilon}$  and  $\dot{u}(\mathbf{r})$ , and therefrom an explicit expression for  $\dot{\epsilon}$ . To this end, we take the derivative of the system (1) – (3) with respect to  $h$ . First, for any  $\mathbf{r} \notin \partial\Omega = \partial\Omega(0)$  one has  $\mathbf{r} \notin \partial\Omega(h)$  for  $h$  sufficiently close to zero; therefore, Eq. (1) readily yields

$$\Delta \dot{u} = 0 \quad \text{in } \mathbb{R}^3 \setminus \partial\Omega. \quad (6)$$

Next we differentiate Eq. (2). In a more explicit form, this equation reads

$$u_-(\mathbf{r} + ha(\mathbf{r}) \mathbf{n}(\mathbf{r}), h) - u_+(\mathbf{r} + ha(\mathbf{r}) \mathbf{n}(\mathbf{r}), h) = 0 \quad (7)$$

and hence gives

$$a\mathbf{n} \cdot \nabla u_- + \dot{u}_- - (a\mathbf{n} \cdot \nabla u_+ + \dot{u}_+) = 0 \quad (8)$$

or

$$\begin{aligned} \dot{u}_- - \dot{u}_+ &= a\mathbf{n} \cdot \nabla u_+ - a\mathbf{n} \cdot \nabla u_- \\ &= (\epsilon - 1)a\partial_n u_-, \end{aligned} \quad (9)$$

where Eq. (3) has been used for eliminating  $u_+$ .

Similarly we differentiate Eq. (3), keeping in mind that  $\partial_n u_{\pm} = \mathbf{n} \cdot \nabla u_{\pm}$ , and taking into account that  $\mathbf{n}$  also depends on  $h$ . Thus, one has

$$(\mathbf{n} \cdot \nabla u_{\pm})' = \dot{\mathbf{n}} \cdot \nabla u_{\pm} + \mathbf{n} \cdot (\nabla u_{\pm})'. \quad (10)$$

The required derivatives  $\dot{\mathbf{n}}$  and  $\mathbf{n} \cdot (\nabla u_{\pm})'$  are calculated in Appendix A. According to Eq. (A12),  $\dot{\mathbf{n}} = -\nabla_{\partial} a$  coincides with the negative gradient of the shape function inside the surface  $\partial\Omega$ , while Eq. (A21) expresses  $\mathbf{n} \cdot (\nabla u_{\pm})'$  in terms of the Laplace-Beltrami operator  $\Delta_{\partial} = \text{div}_{\partial} \nabla_{\partial}$  applied to  $u_{\pm}$ , and the mean curvature  $H$  of  $\partial\Omega$ . Combining these results, we find

$$\begin{aligned} (\mathbf{n} \cdot \nabla u_{\pm})' &= -\nabla_{\partial} a \cdot \nabla_{\partial} u_{\pm} - a\Delta_{\partial} u_{\pm} + 2aH\partial_n u_{\pm} + \partial_n \dot{u}_{\pm} \\ &= -\text{div}_{\partial}(a\nabla_{\partial} u_{\pm}) + 2aH\partial_n u_{\pm} + \partial_n \dot{u}_{\pm}. \end{aligned} \quad (11)$$

Thus, taking the  $h$ -derivative of Eq. (3) leads to

$$\begin{aligned} (\epsilon\partial_n u_- - \partial_n u_+)' &= \dot{\epsilon}\partial_n u_- + \epsilon(\partial_n u_-)' - (\partial_n u_+)' \\ &= \dot{\epsilon}\partial_n u_- \\ &\quad - \text{div}_{\partial}(a(\epsilon\nabla_{\partial} u_- - \nabla_{\partial} u_+)) \\ &\quad + 2aH(\epsilon\partial_n u_- - \partial_n u_+) \\ &\quad + \epsilon\partial_n \dot{u}_- - \partial_n \dot{u}_+. \end{aligned} \quad (12)$$

The l.h.s. now vanishes identically, and the third term on the r.h.s. vanishes because of Eq. (3) itself. Moreover, since  $u_+ = u_-$  on  $\partial\Omega$  according to Eq. (2), and  $\nabla_{\partial}$  differentiates inside  $\partial\Omega$  only, we can replace  $\nabla_{\partial} u_+$  by  $\nabla_{\partial} u_-$  in the second term, finally leaving us with

$$\epsilon\partial_n \dot{u}_- - \partial_n \dot{u}_+ = -\dot{\epsilon}\partial_n u_- + (\epsilon - 1) \text{div}_{\partial}(a\nabla_{\partial} u_-). \quad (13)$$

Summarizing, the differentiation of the homogeneous system (1) – (3) has led to the inhomogeneous system

$$\Delta \dot{u} = 0 \quad \text{in } \mathbb{R}^3 \setminus \partial\Omega \quad (14)$$

$$\dot{u}_- - \dot{u}_+ = F \quad \text{on } \partial\Omega \quad (15)$$

$$\epsilon\partial_n \dot{u}_- - \partial_n \dot{u}_+ = -\dot{\epsilon}\partial_n u_- + G \quad \text{on } \partial\Omega, \quad (16)$$

where

$$F = (\epsilon - 1)a\partial_n u_- \quad (17)$$

$$G = (\epsilon - 1) \text{div}_{\partial}(a\nabla_{\partial} u_-). \quad (18)$$

Since the homogeneous system has a nontrivial solution (the given  $u$ ), its inhomogeneous descendant can admit a solution only if the right hand sides  $F$ ,  $-\dot{\epsilon}\partial_n u_- + G$  satisfy a certain compatibility condition. Since by assumption there is a solution (the  $h$ -derivative of the given family  $u(\mathbf{r}, h)$ ), this condition actually is fulfilled, and yields a formula for  $\dot{\epsilon}$ , which we will derive now. Starting from  $\Delta u_- = \Delta \dot{u}_- = 0$  in  $\Omega$ , Green's formula gives

$$\begin{aligned} 0 &= \int_{\Omega} d^3 r (u_- \Delta \dot{u}_- - (\Delta u_-) \dot{u}_-) \\ &= \int_{\partial\Omega} d^2 S (u_- \partial_n \dot{u}_- - (\partial_n u_-) \dot{u}_-), \end{aligned} \quad (19)$$

where  $d^2 S$  denotes the surface area element. Thus, one has

$$\int_{\partial\Omega} d^2 S u_- \partial_n \dot{u}_- = \int_{\partial\Omega} d^2 S (\partial_n u_-) \dot{u}_-; \quad (20)$$

a corresponding identity holds for  $u_+$ ,  $\dot{u}_+$ . Therefore,

$$\begin{aligned} & \int_{\partial\Omega} d^2S (u_- \epsilon \partial_n \dot{u}_- - u_+ \partial_n \dot{u}_+) \\ &= \int_{\partial\Omega} d^2S (\epsilon (\partial_n u_-) \dot{u}_- - (\partial_n u_+) \dot{u}_+) . \end{aligned} \quad (21)$$

Since  $u_- = u_+$  on  $\partial\Omega$ , the l.h.s. becomes

$$\int_{\partial\Omega} d^2S u_- (\epsilon \partial_n \dot{u}_- - \partial_n \dot{u}_+) = \int_{\partial\Omega} d^2S u_- (-\dot{\epsilon} \partial_n u_- + G) . \quad (22)$$

On the other hand, since  $\partial_n u_+ = \epsilon \partial_n u_-$  on  $\partial\Omega$ , the r.h.s. of Eq. (21) takes the form

$$\int_{\partial\Omega} d^2S \epsilon (\partial_n u_-) (\dot{u}_- - \dot{u}_+) = \epsilon \int_{\partial\Omega} d^2S (\partial_n u_-) F . \quad (23)$$

Equating these two expressions (22) and (23), and solving for  $\dot{\epsilon}$ , we obtain

$$\dot{\epsilon} = \frac{\int_{\partial\Omega} d^2S u_- G - \epsilon \int_{\partial\Omega} d^2S (\partial_n u_-) F}{\int_{\partial\Omega} d^2S u_- \partial_n u_-} . \quad (24)$$

Inserting the formulas (17) and (18) for  $F$  and  $G$ , and performing an integration by parts, the numerator reduces to

$$\begin{aligned} & \int_{\partial\Omega} d^2S u_- (\epsilon - 1) \operatorname{div}_{\partial} (a \nabla_{\partial} u_-) \\ & - \epsilon \int_{\partial\Omega} d^2S (\partial_n u_-) (\epsilon - 1) a \partial_n u_- \\ &= (1 - \epsilon) \int_{\partial\Omega} d^2S a ((\nabla_{\partial} u_-)^2 + \epsilon (\partial_n u_-)^2) . \end{aligned} \quad (25)$$

Thus, the desired expression for the first-order change of the plasmonic eigenvalue  $\epsilon$  with the deformation strength  $h$  finally reads

$$\dot{\epsilon} = (1 - \epsilon) \frac{\int_{\partial\Omega} d^2S a ((\nabla_{\partial} u_-)^2 + \epsilon (\partial_n u_-)^2)}{\int_{\partial\Omega} d^2S u_- \partial_n u_-} . \quad (26)$$

This is the principal result of the present work. Observe that  $\Delta u_- = 0$  implies

$$\int_{\partial\Omega} d^2S u_- \partial_n u_- = \int_{\Omega} d^3r (\partial_n u_-)^2 , \quad (27)$$

so that the denominator is positive. Of course,  $\dot{\epsilon}$  can likewise be expressed entirely in terms of  $u_+$ :

$$\dot{\epsilon} = (1 - \epsilon) \frac{\int_{\partial\Omega} d^2S a (\epsilon (\nabla_{\partial} u_+)^2 + (\partial_n u_+)^2)}{\int_{\partial\Omega} d^2S u_+ \partial_n u_+} . \quad (28)$$

### III. APPLICATIONS

Consider an infinite half-space geometry with the dielectric medium filling the volume  $z < 0$ , so that its

boundary is given by the plane  $z = 0$ . Let  $\boldsymbol{\kappa} = (k_x, k_y)$  be a two-dimensional wave vector, with  $\kappa = \sqrt{k_x^2 + k_y^2}$ . Solutions to Laplace's equation (1) which vanish for  $z \rightarrow \pm\infty$  then are given by

$$u_+(\mathbf{r}) = \int \frac{d^2\kappa}{(2\pi)^2} A(\boldsymbol{\kappa}) e^{i\boldsymbol{\kappa}\cdot\mathbf{x} - \kappa z} \quad (29)$$

$$u_-(\mathbf{r}) = \int \frac{d^2\kappa}{(2\pi)^2} B(\boldsymbol{\kappa}) e^{i\boldsymbol{\kappa}\cdot\mathbf{x} + \kappa z} , \quad (30)$$

with  $\mathbf{x} = (x, y)$  and  $\mathbf{r} = (x, y, z)$ , and the continuity condition (2) yields  $B(\boldsymbol{\kappa}) = A(\boldsymbol{\kappa})$ . Moreover, since  $u_{\pm}$  is real, one has  $A^*(\boldsymbol{\kappa}) = A(-\boldsymbol{\kappa})$ . At this point, the amplitudes  $A(\boldsymbol{\kappa})$  describing the excitations at an exactly planar surface are arbitrary. The normal and the in-plane derivatives at  $z = 0$  then are

$$\partial_n u_{\pm} = \mp \int \frac{d^2\kappa}{(2\pi)^2} A(\boldsymbol{\kappa}) \kappa e^{i\boldsymbol{\kappa}\cdot\mathbf{x}} \quad (31)$$

$$\nabla_{\partial} u_{\pm} = \int \frac{d^2\kappa}{(2\pi)^2} A(\boldsymbol{\kappa}) (i\boldsymbol{\kappa}) e^{i\boldsymbol{\kappa}\cdot\mathbf{x}} , \quad (32)$$

respectively, so that the condition (3) immediately provides the well known eigenvalue  $\epsilon = -1$  for this particular geometry. We write

$$(\partial_n u_{\pm})^2 = \int \frac{d^2\kappa}{(2\pi)^2} \int \frac{d^2\kappa'}{(2\pi)^2} A(\boldsymbol{\kappa}) A^*(\boldsymbol{\kappa}') (\kappa \kappa') e^{i(\boldsymbol{\kappa} - \boldsymbol{\kappa}')\cdot\mathbf{x}}$$

$$(\nabla_{\partial} u_{\pm})^2 = \int \frac{d^2\kappa}{(2\pi)^2} \int \frac{d^2\kappa'}{(2\pi)^2} A(\boldsymbol{\kappa}) A^*(\boldsymbol{\kappa}') (\boldsymbol{\kappa} \cdot \boldsymbol{\kappa}') e^{i(\boldsymbol{\kappa} - \boldsymbol{\kappa}')\cdot\mathbf{x}}$$

together with

$$u_{\pm} \partial_n u_{\pm} = \mp \int \frac{d^2\kappa}{(2\pi)^2} \int \frac{d^2\kappa'}{(2\pi)^2} A(\boldsymbol{\kappa}) A^*(\boldsymbol{\kappa}') \kappa' e^{i(\boldsymbol{\kappa} - \boldsymbol{\kappa}')\cdot\mathbf{x}} ,$$

giving

$$\int_{\partial\Omega} d^2S u_{\pm} \partial_n u_{\pm} = \mp \int \frac{d^2\kappa}{(2\pi)^2} |A(\boldsymbol{\kappa})|^2 \kappa . \quad (33)$$

Now we introduce a small deformation of the planar surface, described by some suitable shape function  $a(\mathbf{x})$ . The required amplitudes  $A(\boldsymbol{\kappa})$  consequently are determined by that deformation; the assumption that the exact potential  $u_{\pm}(\mathbf{r})$  can still be written in the form (29) or (30) constitutes the Rayleigh hypothesis<sup>14</sup>. Upon inserting the Fourier transform of the shape function, *i.e.*,

$$a(\mathbf{x}) = \int \frac{d^2\kappa}{(2\pi)^2} \hat{a}(\boldsymbol{\kappa}) e^{i\boldsymbol{\kappa}\cdot\mathbf{x}} , \quad (34)$$

und using  $\epsilon = -1$  for the unperturbed eigenvalue, either Eq. (26) or its variant (28) readily yields

$$\dot{\epsilon} = 2 \frac{\int \frac{d^2\kappa}{(2\pi)^2} \int \frac{d^2\kappa'}{(2\pi)^2} \hat{a}(\boldsymbol{\kappa}' - \boldsymbol{\kappa}) A(\boldsymbol{\kappa}) A^*(\boldsymbol{\kappa}') \kappa \kappa' (\hat{\boldsymbol{\kappa}} \cdot \hat{\boldsymbol{\kappa}}' - 1)}{\int \frac{d^2\kappa}{(2\pi)^2} |A(\boldsymbol{\kappa})|^2 \kappa} , \quad (35)$$

where  $\hat{\boldsymbol{\kappa}}$  denotes the unit vector in the direction of  $\boldsymbol{\kappa}$ . In particular, if  $a(\mathbf{x}) = c$ , one has  $\hat{a}(\boldsymbol{\kappa}) = (2\pi)^2 c \delta(\boldsymbol{\kappa})$ , so that  $\dot{\epsilon} = 0$ : The plasmonic eigenvalue does not change when the entire surface plane is displaced by some amount  $c$ .

There exists an exact integral equation for determining the amplitudes  $A(\boldsymbol{\kappa})$  associated with a given surface deformation, derived by Farias and Maradudin on the basis of the Rayleigh hypothesis<sup>14</sup>:

$$\frac{\epsilon + 1}{\epsilon - 1} A(\boldsymbol{\kappa}') = \int \frac{d^2 \kappa}{(2\pi)^2} J(\boldsymbol{\kappa}' - \kappa | \boldsymbol{\kappa}' - \boldsymbol{\kappa}) (1 - \hat{\boldsymbol{\kappa}} \cdot \hat{\boldsymbol{\kappa}}') \kappa A(\boldsymbol{\kappa}) \quad (36)$$

with

$$J(\alpha | \mathbf{q}) = \frac{1}{\alpha} \int d^2 S e^{-i\mathbf{q} \cdot \mathbf{x}} (\exp(\alpha h a(\mathbf{x})) - 1); \quad (37)$$

this has been applied by Maradudin and Visscher to the study of particular perturbations of planar surfaces<sup>15</sup>. Expanding the latter expression (37) to first order in  $h$  gives

$$J(\alpha | \mathbf{q}) = h \hat{a}(\mathbf{q}) + \mathcal{O}(h^2), \quad (38)$$

so that Eq. (36) becomes

$$\frac{\epsilon + 1}{\epsilon - 1} A(\boldsymbol{\kappa}') = h \int \frac{d^2 \kappa}{(2\pi)^2} \hat{a}(\boldsymbol{\kappa}' - \boldsymbol{\kappa}) (1 - \hat{\boldsymbol{\kappa}} \cdot \hat{\boldsymbol{\kappa}}') \kappa A(\boldsymbol{\kappa}) \quad (39)$$

for sufficiently weak perturbations. Recalling that the unperturbed eigenvalue is  $-1$ , we insert  $\epsilon = -1 + \mathcal{O}(h)$  into the denominator on the l.h.s. Multiplying both sides by  $A^*(\boldsymbol{\kappa}') \boldsymbol{\kappa}'$ , integrating, and rearranging then yields

$$\epsilon = -1 + h \dot{\epsilon} + \mathcal{O}(h^2), \quad (40)$$

with  $\dot{\epsilon}$  indeed formally equal to the previous Eq. (35). Thus, our perturbative result is consistent with the formula (36).

As a second example we consider the deformation of a dielectric sphere of radius  $R$ . In this case the unperturbed potential is written as

$$\begin{aligned} u_+(\mathbf{r}) &= \sum_{\ell=1}^{\infty} A_{\ell} r^{-(\ell+1)} Y_0^{\ell}(\vartheta) \\ u_-(\mathbf{r}) &= \sum_{\ell=0}^{\infty} B_{\ell} r^{\ell} Y_0^{\ell}(\vartheta), \end{aligned} \quad (41)$$

valid for  $r \geq R$  and  $r \leq R$ , respectively. Here  $Y_m^{\ell}$  denote the familiar spherical harmonics. The use of these basis functions with  $m = 0$  only, which do not depend on the azimuthal angle  $\varphi$ , confines us to deformations which preserve the rotation symmetry around the  $z$ -axis. From condition (2) one gets  $B_{\ell} = A_{\ell} R^{-(2\ell+1)}$ , and Eq. (3) then leads to the eigenvalues

$$\epsilon_{\ell} = -\frac{\ell + 1}{\ell}; \quad (42)$$

in particular,  $\epsilon_1 = -2$  characterizes the dipole resonance<sup>16</sup>.

We deform the sphere into a spheroid oriented along the  $z$ -axis, employing the shape function

$$a(\vartheta, \varphi) = R \cos^2(\vartheta). \quad (43)$$

Here the occurrence of the sphere's radius  $R$  as the scale of the deformation is somewhat arbitrary, in view of the additional parameter  $h$ . For estimating the resulting change of  $\epsilon_1$  for small  $h$ , we use

$$u_{1-}(\mathbf{r}) = r Y_0^1(\vartheta) = r \sqrt{\frac{3}{4\pi}} \cos \vartheta, \quad (44)$$

and calculate

$$\begin{aligned} (\partial_n u_{1-})^2 &= \frac{3}{4\pi} \cos^2 \vartheta \\ (\nabla_{\partial} u_{1-})^2 &= \frac{3}{4\pi} \sin^2 \vartheta \\ u_{1-} \partial_n u_{1-} &= \frac{3}{4\pi} R \cos^2 \vartheta \end{aligned}$$

on  $\partial\Omega$ , giving

$$\begin{aligned} \int_{\partial\Omega} d^2 S a (\partial_n u_{1-})^2 &= \frac{3}{5} R^3 \\ \int_{\partial\Omega} d^2 S a (\nabla_{\partial} u_{1-})^2 &= \frac{2}{5} R^3 \\ \int_{\partial\Omega} d^2 S u_{1-} \partial_n u_{1-} &= R^3. \end{aligned} \quad (45)$$

Plugged into Eq. (26), this yields

$$\dot{\epsilon}_1 = -\frac{12}{5}. \quad (46)$$

On the other hand, the plasmonic eigenvalue for the dipole mode of a spheroid is known exactly<sup>16</sup>:

$$\epsilon_1 = 1 - \frac{1}{L}, \quad (47)$$

where  $L$  denotes the so-called depolarization coefficient, given by<sup>17</sup>

$$L(e) = \begin{cases} \frac{1-e^2}{e^3} (\operatorname{artanh}(e) - e), & h > 0 \\ \frac{1+e^2}{e^3} (e - \arctan(e)), & h < 0 \end{cases} \quad (48)$$

with

$$e^2 = \begin{cases} 1 - \frac{1}{(1+h)^2} = 2h + \mathcal{O}(h^2), & h > 0 \\ \frac{1}{(1+h)^2} - 1 = -2h + \mathcal{O}(h^2), & h < 0. \end{cases} \quad (49)$$

Thus,  $e^2$  becomes small with  $h$ , allowing us to expand  $L(e)$  as

$$L(e) = \begin{cases} \frac{1}{3} - \frac{2}{15} e^2 + \mathcal{O}(e^4), & h > 0 \\ \frac{1}{3} + \frac{2}{15} e^2 + \mathcal{O}(e^4), & h < 0. \end{cases} \quad (50)$$

Exploiting Eq. (49) one expresses  $L$  in terms of  $h$ , finding

$$L(h) = \frac{1}{3} - \frac{4}{15}h + \mathcal{O}(h^2). \quad (51)$$

This tells us that  $\epsilon_1$ , as given by Eq. (47), should be expanded in powers of  $(L - 1/3)$ :

$$\epsilon_1 = -2 + 9 \left( L - \frac{1}{3} \right) + \mathcal{O} \left( \left( L - \frac{1}{3} \right)^2 \right). \quad (52)$$

Inserting Eq. (51), we obtain

$$\epsilon_1 = -2 - \frac{12}{5}h + \mathcal{O}(h^2), \quad (53)$$

in accordance with the result (46) of perturbation theory.

#### IV. CONCLUDING REMARKS

The first-order perturbative expression (26) or (28) for the shift of a plasmonic eigenvalue may have a limited range of applicability, insofar as it is restricted to sufficiently weak deformations, but it stands out because of its generality, and easy use. Together with similar results for higher derivatives<sup>18</sup>, one obtains a formal perturbation series

$$\epsilon(h) \sim \epsilon + h\dot{\epsilon} + \frac{1}{2}h^2\ddot{\epsilon} + \dots \quad (54)$$

Above we have simply assumed the existence of  $\epsilon(h)$  and  $u(\mathbf{r}, h)$ . Given a solution at  $h = 0$ , this existence actually follows from the reformulation of the problem in terms of Dirichlet-to-Neumann operators<sup>13</sup>, and from standard perturbation theory for eigenvalues. If  $\epsilon$  is  $p$ -fold degenerate (as in the case of the sphere), then one has  $p$  branches  $\epsilon_i, u_i; i = 1, \dots, p$ . The analysis then applies to each branch separately, with  $\dot{\epsilon}_i$  being given by Eq. (26) or (28) with  $u = u_i$ , where  $u_1, \dots, u_p$  form a basis of this solution space at  $h = 0$ . How this basis is determined by the perturbation of the volume  $\Omega$  will, in general, have to be deduced from additional considerations.

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#### APPENDIX A: AUXILIARY CALCULATIONS

In this appendix we compute the derivatives entering into the evaluation of Eq. (10) en route to the important result (13). This calculation invokes some notions from differential geometry<sup>12</sup>. We fix a point  $\mathbf{r}_0 \in \partial\Omega = \partial\Omega(0)$

and parametrize  $\partial\Omega$  near  $\mathbf{r}_0$  as  $\mathbf{r} = \mathbf{r}(v, w)$ , with  $\mathbf{r}_0 = \mathbf{r}(0, 0)$ . It is assumed that the parametrization is such that the tangent vectors  $\mathbf{r}_v = \partial_v \mathbf{r}$  and  $\mathbf{r}_w = \partial_w \mathbf{r}$  are orthogonal, and have unit length at  $\mathbf{r}_0$ , and such that the  $v$ -line (*i.e.*,  $v \mapsto \mathbf{r}(v, 0)$ ) and the  $w$ -line through  $\mathbf{r}_0$  have normal vectors parallel to  $\mathbf{n}$  at  $\mathbf{r}_0$  (*i.e.*, have vanishing geodesic curvature).

The curvatures of the  $v$ -line and the  $w$ -line are  $\kappa_v = \mathbf{r}_{vv} \cdot \mathbf{n}$  and  $\kappa_w = \mathbf{r}_{ww} \cdot \mathbf{n}$ , respectively. Considering  $\mathbf{n}$  as a function of  $v, w$ , one has

$$\mathbf{r}_v \cdot \mathbf{n} = 0 \quad (A1)$$

and hence

$$\mathbf{r}_{vv} \cdot \mathbf{n} + \mathbf{r}_v \cdot \mathbf{n}_v = 0, \quad (A2)$$

giving

$$\kappa_v = -\mathbf{r}_v \cdot \mathbf{n}_v; \quad (A3)$$

analogously,  $\kappa_w = -\mathbf{r}_w \cdot \mathbf{n}_w$ .

Note that orthonormality of  $\mathbf{r}_v$  and  $\mathbf{r}_w$  holds only at  $\mathbf{r}_0$ , not at nearby points. In the following calculations we always evaluate at  $h = 0$  after differentiating in  $h$ , and at  $\mathbf{r} = \mathbf{r}_0$  after differentiating in  $v, w$ .

We now derive an expression for  $\dot{\mathbf{n}}$ . The surface  $\partial\Omega(h)$  is parametrized by

$$\mathbf{r}(v, w, h) = \mathbf{r}(v, w) + ha(v, w)\mathbf{n}(v, w), \quad (A4)$$

where we abuse notation by considering  $a$  and  $\mathbf{n}$  as functions of  $v, w$ . Its unit normal is  $\mathbf{n} = \mathbf{N}/\|\mathbf{N}\|$ , where  $\mathbf{N} = \mathbf{r}_v \times \mathbf{r}_w$ . At  $\mathbf{r}_0$  one has  $\mathbf{n} = \mathbf{N}$  by assumption. Differentiating, one gets

$$\begin{aligned} \dot{\mathbf{n}} &= \frac{\dot{\mathbf{N}}}{\|\mathbf{N}\|} - \frac{\mathbf{N}}{\|\mathbf{N}\|^2} \left( \frac{\mathbf{N}}{\|\mathbf{N}\|} \cdot \dot{\mathbf{N}} \right) \\ &= \frac{1}{\|\mathbf{N}\|} \left( \dot{\mathbf{N}} - \mathbf{n}(\mathbf{n} \cdot \dot{\mathbf{N}}) \right), \end{aligned} \quad (A5)$$

which states that  $\dot{\mathbf{n}}$  is determined by the tangential part of  $\dot{\mathbf{N}}$ . Moreover,

$$\dot{\mathbf{N}} = \dot{\mathbf{r}}_v \times \mathbf{r}_w + \mathbf{r}_v \times \dot{\mathbf{r}}_w. \quad (A6)$$

Since  $\dot{\mathbf{r}} = a\mathbf{n}$ , one has

$$\dot{\mathbf{r}}_v = a_v \mathbf{n} + a \mathbf{n}_v. \quad (A7)$$

At  $\mathbf{r}_0$ , the identity  $\mathbf{n} = \mathbf{r}_v \times \mathbf{r}_w$  implies  $\mathbf{n} \times \mathbf{r}_w = -\mathbf{r}_v$  and  $\mathbf{r}_v \times \mathbf{n} = -\mathbf{r}_w$ . In addition,  $\mathbf{n}_v \times \mathbf{r}_w = (\mathbf{n}_v \cdot \mathbf{r}_v)\mathbf{r}_v \times \mathbf{r}_w$ , because the component of  $\mathbf{n}_v$  parallel to  $\mathbf{r}_w$  drops out of the vectorial product. (Observe that  $\mathbf{n} \cdot \mathbf{n} = 1$  implies  $\mathbf{n}_v \cdot \mathbf{n} = 0$ , so that  $\mathbf{n}_v$  lies in the span of  $\mathbf{r}_v$  and  $\mathbf{r}_w$ .) Putting this together and using Eq. (A3), one finds

$$\begin{aligned} \dot{\mathbf{r}}_v \times \mathbf{r}_w &= (a_v \mathbf{n} + a \mathbf{n}_v) \times \mathbf{r}_w \\ &= -a_v \mathbf{r}_v + a(\mathbf{n}_v \cdot \mathbf{r}_v)\mathbf{n} \\ &= -a_v \mathbf{r}_v - a\kappa_v \mathbf{n}; \end{aligned} \quad (A8)$$

analogously,

$$\mathbf{r}_v \times \dot{\mathbf{r}}_w = -a_w \mathbf{r}_v - a \kappa_w \mathbf{n}. \quad (\text{A9})$$

Inserting Eqs. (A8) and (A9) into Eq. (A6), we arrive at

$$\dot{\mathbf{N}} = -(a_v \mathbf{r}_v + a_w \mathbf{r}_w) - a(\kappa_v + \kappa_w) \mathbf{n}. \quad (\text{A10})$$

Now we observe that

$$a_v \mathbf{r}_v + a_w \mathbf{r}_w = \nabla_{\partial} a \quad (\text{A11})$$

is the gradient of  $a$  as a function in the surface  $\partial\Omega$ . Since according to Eq. (A5) the desired derivative  $\dot{\mathbf{n}}$  is the tangential component of  $\dot{\mathbf{N}}$ , we have the compact result

$$\dot{\mathbf{n}} = -\nabla_{\partial} a. \quad (\text{A12})$$

Next we calculate  $\mathbf{n} \cdot (\nabla u)$  for  $u = u_+$  or  $u = u_-$  at  $\mathbf{r}_0$ . Starting from

$$\begin{aligned} (\nabla u)'(\mathbf{r}) &= \left. \frac{\partial}{\partial h} \right|_{h=0} (\nabla u)(\mathbf{r} + h a(\mathbf{r}) \mathbf{n}(\mathbf{r}), h) \\ &= a(\mathbf{n} \cdot \nabla) \nabla u(\mathbf{r}) + \nabla \dot{u}(\mathbf{r}) \end{aligned} \quad (\text{A13})$$

one finds

$$\mathbf{n} \cdot (\nabla u)' = a(\mathbf{n} \cdot \nabla)^2 u + \partial_n \dot{u}. \quad (\text{A14})$$

To simplify notation we assume that coordinates in  $\mathbb{R}^3$  are chosen such that  $\mathbf{n} = (0, 0, 1)$  at  $\mathbf{r}_0$ , reducing the first term on the r.h.s. to  $a \partial_{x_3}^2 u$  at  $\mathbf{r}_0$ . Because  $\Delta u = 0$ , we then have, at  $\mathbf{r}_0$ ,

$$\mathbf{n} \cdot (\nabla u)' = -a(\partial_{x_1}^2 + \partial_{x_2}^2) u + \partial_n \dot{u}. \quad (\text{A15})$$

This has to be expressed in terms of derivatives of  $u$  inside the surface. We choose the surface coordinates as  $v = x_1$ ,  $w = x_2$ , but still write  $\mathbf{r} = \mathbf{r}(v, w)$ . Differentiating  $u$  twice with respect to  $v$ ,

$$\begin{aligned} \partial_v u(\mathbf{r}(v, w)) &= (\mathbf{r}_v \cdot \nabla) u(\mathbf{r}(v, w)) \\ \partial_v^2 u(\mathbf{r}(v, w)) &= (\mathbf{r}_v \cdot \nabla)^2 u(\mathbf{r}(v, w)) \\ &\quad + (\mathbf{r}_{vv} \cdot \nabla) u(\mathbf{r}(v, w)), \end{aligned} \quad (\text{A16})$$

and observing  $\mathbf{r}_v \cdot \nabla = \partial_{x_1}$  and  $\mathbf{r}_{vv} = \kappa_v \mathbf{n}$ , we get

$$\partial_v^2 u = \partial_{x_1}^2 u + \kappa_v \partial_n u. \quad (\text{A17})$$

Combining this with the analogous equation for  $x_2$  gives

$$(\partial_{x_1}^2 + \partial_{x_2}^2) u = (\partial_v^2 + \partial_w^2) u - (\kappa_v + \kappa_w) \partial_n u. \quad (\text{A18})$$

Introducing the mean curvature  $H$  of  $\partial\Omega$ ,

$$H = \frac{1}{2}(\kappa_v + \kappa_w), \quad (\text{A19})$$

and identifying

$$\Delta_{\partial} u = (\partial_v^2 + \partial_w^2) u \quad (\text{A20})$$

as the Laplace-Beltrami operator of the surface  $\partial\Omega$ , Eq. (A15) takes the final form

$$\mathbf{n} \cdot (\nabla u)' = -a \Delta_{\partial} u + 2aH \partial_n u + \partial_n \dot{u}. \quad (\text{A21})$$

While we had used a special coordinate system for simplifying the derivation, the Laplace-Beltrami operator is defined independent of the choice of coordinates as  $\Delta_{\partial} = \text{div}_{\partial} \nabla_{\partial}$ . Here  $\text{div}_{\partial}$  is the divergence inside the surface, given by the negative adjoint of the gradient with respect to the surface volume element. This is exploited in Eq. (11).

The fact that the two results (A12) and (A21) obtained in this appendix are expressed invariantly, that is, without reference to coordinates, is essential for their use in Sec. II.

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