Surface plasmon resonances of an arbitrarily shaped nanoparticle: high-frequency asymptotics via pseudo-differential operators

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Abstract

We study the surface plasmon modes of an arbitrarily shaped nanoparticle in the electrostatic limit. We first deduce an eigenvalue equation for these modes, expressed in terms of the Dirichlet–Neumann operators. We then use the properties of these pseudo-differential operators for deriving the limit of the high-order modes.

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1. Introduction

The interaction between light and metallic nanoparticles can become very strong due to the excitation of surface plasmons. These hybrid modes of the electromagnetic field and the electron gas are confined to the surface of the particle and give rise to an enhancement of the incident field by several orders of magnitude [1–3]. This enhancement enables a variety of applications ranging from the well-established surface-enhanced Raman spectroscopy (SERS), which allows the detection of even a single molecule [4, 5], to the emerging field of plasmonics [6, 7], including, for instance, plasmonic waveguides which effectuate optical energy transfer below the diffraction limit [6, 8, 9].

While an exact analytical description of the optical response of a metallic nanoparticle exists only for very specific geometries such as a sphere or an ellipsoid, numerical methods can be applied for a particle with an arbitrary, realistic shape. There is a wide range of numerical methods for light scattering [10]; the finite difference time-domain approach (FDTD) is a very common one (originally proposed by Yee [11]). The FDTD combined with a suitable discretization of the particle enables one to calculate the response of an almost arbitrary particle to nearly any incident field. Moreover, in the case of a sufficiently small particle, i.e. for particles that are much smaller than the significant wavelengths, for which the dielectric
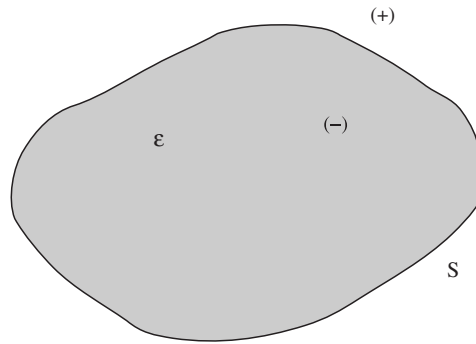
Figure 1. Sketch of an example geometry, with quantities inside the particle being labelled by the index − and outside by +. S denotes the surface of the particle.

function can be taken as constant, the surface plasmon resonances can be determined in the electrostatic limit via the eigenvalues of a surface-integral operator [12–14]. Hohenester and Krenn [14] have shown that this boundary integral approach can be used to calculate the surface plasmon resonances of single and coupled spheres, cylinders and cubic-like nanoparticles.

In this paper, we consider an arbitrarily shaped nanoparticle (see figure 1) and show that the surface plasmon resonances in the electrostatic limit may be obtained as eigenvalues of an operator which may be represented in terms of Dirichlet–Neumann operators. We argue that this reformulation makes the well-developed analytical tools pertaining to the study of such operators available for the study of surface plasmon resonances in cases where exact solution formulae are not available. To support this claim we show here how the asymptotic behaviour of the high-order surface resonances may be analysed. To this end we use the well-known fact that the Dirichlet–Neumann operators are pseudo-differential operators, and use standard properties of such operators.

In section 2, we reformulate the boundary value problem as an eigenvalue problem, and in section 3 we show how one can apply the formalism to a half-space. In section 4, we introduce pseudo-differential operators and prove in rigorous mathematical terms the convergence of the high-order modes.

2. Eigenvalue equation

In the electrostatic limit, the surface plasmon resonances of a particle as sketched in figure 1 are characterized by nontrivial solutions of the Poisson equation without external charges,

$$\Delta\phi_{\pm}(\boldsymbol{r}) = 0 \qquad \text{for} \quad \boldsymbol{r} \notin S, \tag{1}$$

$$\phi_{-}(\boldsymbol{r}) = \phi_{+}(\boldsymbol{r}) \qquad \text{for} \quad \boldsymbol{r} \in S, \tag{2}$$

$$\epsilon\partial_n\phi_{-}(\boldsymbol{r}) = \partial_n\phi_{+}(\boldsymbol{r}) \qquad \text{for} \quad \boldsymbol{r} \in S, \tag{3}$$

with the potential ϕ_{-} and ϕ_{+} inside and outside the particle, respectively; ϵ is the permittivity of the particle, and ∂_n is the outward normal derivative on the surface S of the particle. For convenience, we assumed by stating the boundary condition in equation (3) that the particle surrounded by vacuum is homogeneous, isotropic, local and non-magnetic. Since we restrict ourselves to surface modes, we further assume that the potential vanishes for $r \to \infty$, so that ϕ is determined uniquely. We assume that the surface S is smooth, i.e. has no singularities. So surface resonances are thus given by values of ϵ for which nontrivial solutions of the system (1)–(3) exist.

In order to recast the problem (1)–(3) as an eigenvalue problem, we introduce the Dirichlet–Neumann operators (D_- and D_+) inside and outside the particle. The Dirichlet–Neumann operator inside the particle is defined as

$$D_- : \quad C^\infty(S) \to C^\infty(S) \qquad f \mapsto \partial_n \phi_f,$$

where ϕ_f is the solution of the Dirichlet problem, i.e. it satisfies $\Delta \phi_f(r) = 0$ inside and $\phi_f(r) = f(r)$ on the surface S of the particle. The Dirichlet–Neumann operator outside the particle (D_+) is defined in a similar way.

With the help of the operators D_- and D_+ the problem in equations (1)–(3) can be recast in a compact manner as

$$\epsilon D_- f = D_+ f, \tag{4}$$

where f is the restriction of $\phi_\pm$ to S. Nontrivial solutions of this equation can be found for such ϵ for which

$$\ker(\epsilon D_- - D_+) \neq 0 \quad \Leftrightarrow \quad \ker\left(\epsilon D_- D_+^{-1} - \mathbb{1}\right) \neq 0. \tag{5}$$

Note that D_+ is an invertible operator. Thus, the desired values of ϵ are the inverse eigenvalues of the operator $D_- D_+^{-1}$, i.e.,

$$\epsilon = \frac{1}{\text{eigenvalue}\left\{D_- D_+^{-1}\right\}}. \tag{6}$$

Hence, by means of the Dirichlet–Neumann operators we have reformulated the boundary value problem for the determination of the surface modes as an eigenvalue problem.

As a side remark, note that $D_- D_+^{-1}$ is not self-adjoint with respect to the standard scalar product, although both $D_\pm$ are. This can be remedied either by considering the non-standard scalar product $(f, g) = \int_S (D_+ f)(x) \overline{g(x)} \, dS(x)$ instead or by using $D_+^{-1/2} D_- D_+^{-1/2}$ in (5) instead of $D_- D_+^{-1}$, which is self-adjoint for the standard scalar product and therefore shows the reality and completeness of the spectrum. The discreteness of the spectrum of $D_- D_+^{-1}$ is less obvious and will be shown below for a bounded surface S.

3. Surface modes of a half-space

As an illustration of the method developed above, we determine the surface modes of a half-space. Since the resonances can be found at such ϵ which are equal to the inverse eigenvalues of $D_- D_+^{-1}$ we first derive the Dirichlet–Neumann operators D_- and D_+ for a half-space. The surface S of the material, located at $z < 0$ with the permittivity ϵ, is chosen to be the x–y-plane, so that we have to solve the Laplace equation,

$$\Delta \phi_\mp(x, y, z) = 0, \tag{7}$$

for $z < 0$ and $z > 0$, resp., with the Dirichlet boundary condition

$$\phi_\mp(x, y, 0) = f(x, y), \tag{8}$$

outside the material, for $z > 0$, we assume vacuum. In order to solve equations (7) and (8) we use the Fourier transform in the x- and y-coordinates:

$$\hat{f}(\boldsymbol{\xi}, z) = \int d\boldsymbol{x} \, e^{-i\boldsymbol{x} \cdot \boldsymbol{\xi}} f(\boldsymbol{x}, z), \tag{9}$$

with the two Fourier variables $\boldsymbol{\xi}$ and $\boldsymbol{x} = (x, y)$. Fourier transformation of equations (7) and (8) gives

$$\left(-|\boldsymbol{\xi}|^2 + \partial_z^2\right)\hat{\phi}_\mp(\boldsymbol{\xi}, z) = 0 \qquad \text{and} \qquad \hat{\phi}_\mp(\boldsymbol{\xi}, 0) = \hat{f}(\boldsymbol{\xi}). \tag{10}$$

From this one obtains the solution

$$\hat{\phi}_{\mp}(\boldsymbol{\xi}, z) = \mathrm{e}^{\pm|\xi|z} \hat{f}(\boldsymbol{\xi}) \tag{11}$$

(using the additional boundary condition that ϕ vanishes for $|z| \to \infty$) from which it becomes obvious that the surface modes are confined to a small neighbourhood of the surface of the material.

For the case considered the outward directional derivative is simply given by ∂_z, so that the Dirichlet–Neumann operator D_- can be stated as

$$D_-(f) = \frac{1}{(2\pi)^2} \int \mathrm{d}\boldsymbol{\xi}\, \mathrm{e}^{\mathrm{i}(\boldsymbol{x} \cdot \boldsymbol{\xi})} |\boldsymbol{\xi}| \hat{f}(\boldsymbol{\xi}) \tag{12}$$

and D_+ as

$$D_+(f) = -\frac{1}{(2\pi)^2} \int \mathrm{d}\boldsymbol{\xi}\, \mathrm{e}^{\mathrm{i}(\boldsymbol{x} \cdot \boldsymbol{\xi})} |\boldsymbol{\xi}| \hat{f}(\boldsymbol{\xi}). \tag{13}$$

In particular, for a half-space we have $D_- = -D_+$ and therefore $D_- D_+^{-1} = -\mathbb{1}$. Since the only eigenvalue of the unit operator $\mathbb{1}$ is 1 we obtain the well-known result that $\epsilon = -1$ for the surface modes of a half-space.

4. High-order surface modes

Before we study the convergence of the eigenvalues of the operator $D_- D_+^{-1}$ in rigorous mathematical terms, we briefly discuss the physical expectation. For example, considering a sphere surrounded by vacuum it is well known that the resonances of the surface modes are given by [15]

$$\epsilon_k = -\frac{k+1}{k} \tag{14}$$

for $k = 1, 2, \ldots$. Obviously, for $k = 1$, as corresponding to the dipole mode of the sphere, the resonance can be found at $\epsilon = -2$. On the other hand, in the limiting case of $k \to \infty$, corresponding to the multipole mode of infinite order, the resonance occurs at $\epsilon = -1$, i.e., one retrieves the half-space result deduced above. This convergence property can be understood from the physicist's point of view as follows: the multipole modes of order $k \gg 1$ are related to fields which vary on length scales much smaller than the radius of the sphere; the higher the order k the smaller the length scale. Therefore, these high-order modes cannot distinguish the sphere from a half-space, since the sphere can be considered as locally flat on the length scale of these modes. Hence, the convergence to $\epsilon = -1$ for $k \to \infty$ is not restricted to spheres, but should be expected for arbitrary particles. In the following we prove this property in strict mathematical terms.

To this end, we first briefly introduce the concept of pseudo-differential operators, for a more detailed introduction to this topic we refer the reader to [16]. The definition of a general pseudo-differential operator P with *symbol* $p(\boldsymbol{x}, \boldsymbol{\xi})$ operating on the function $u(\boldsymbol{x})$ can be stated as (with $\boldsymbol{x}, \boldsymbol{\xi} \in \mathbb{R}^n$)

$$[Pu](\boldsymbol{x}) = \frac{1}{(2\pi)^n} \int \mathrm{d}\boldsymbol{\xi}\, \mathrm{e}^{\mathrm{i}\boldsymbol{x} \cdot \boldsymbol{\xi}} p(\boldsymbol{x}, \boldsymbol{\xi}) \hat{u}(\boldsymbol{\xi}). \tag{15}$$

From this definition it can be seen that if the symbol $p(\boldsymbol{x}, \boldsymbol{\xi})$ is a polynomial in $\boldsymbol{\xi}$ the operator P is a conventional differential operator, which has constant coefficients if p is independent of $\boldsymbol{x}$. However, for pseudo-differential operators one admits more general symbols: the smooth function p is required to have an asymptotic expansion as $\xi \to \infty$ of the form $p(\boldsymbol{x}, \boldsymbol{\xi}) \sim p_m(\boldsymbol{x}, \boldsymbol{\xi}) + p_{m-1}(\boldsymbol{x}, \boldsymbol{\xi}) + p_{m-2}(\boldsymbol{x}, \boldsymbol{\xi}) + \cdots$, where each p_{m-i} is positively

homogeneous in $\boldsymbol{\xi}$ of degree $m - i$, i.e. satisfies $p_{m-i}(\boldsymbol{x}, \boldsymbol{\xi}) = |\boldsymbol{\xi}|^{m-i} p_{m-i}(\boldsymbol{x}, \hat{\boldsymbol{\xi}})$ for $\boldsymbol{\xi} \neq 0$, where $\hat{\boldsymbol{\xi}} = \boldsymbol{\xi}/|\boldsymbol{\xi}|$.[3] The number m can be an arbitrary real number and is called the *order* of P. The leading term p_m is called the *principal symbol* of P and denoted as $\sigma_m(P)$. In the case of a differential operator with $p(\boldsymbol{x}, \boldsymbol{\xi}) = \sum_{|\beta| \leqslant m} \alpha_\beta(\boldsymbol{x}) \boldsymbol{\xi}^\beta$ (where $\beta \in \mathbb{N}_0^n$ is a multi-index), the principal symbol is $\sigma_m(P) = \sum_{|\beta|=m} \alpha_\beta(\boldsymbol{x}) \boldsymbol{\xi}^\beta$.

We defined pseudo-differential operators as acting on functions of $\boldsymbol{x} \in \mathbb{R}^n$, which seems essential since the Fourier transform was used in the definition. However, by means of local coordinates one may define pseudo-differential operators on a manifold (for example, the surface S), and then the principal symbol is independent of the choice of coordinates if $\boldsymbol{\xi}$ is interpreted as a covector.

A basic (albeit non-obvious) property of pseudo-differential operators is that if P and Q are pseudo-differential operators of orders m, l, respectively, then their composition PQ is a pseudo-differential operator of order $m + l$, with the principal symbol $\sigma_{m+l}(PQ) = \sigma_m(P)\sigma_l(Q)$. The identity operator has order 0 with the principal symbol $\sigma_0(\mathbb{1}) = 1$, therefore if P is invertible then the principal symbol of its inverse is $\sigma_{-m}(P^{-1}) = (\sigma_m(P))^{-1}$.

In order to prove the shape-independent convergence of the high-order surface modes we need one more well-known result (see [16]): the Dirichlet–Neumann operators $D_\pm$ are pseudo-differential operators on S whose principal symbols are the same as in the case of a half-space (12) and (13):

$$\sigma_1(D_-) = |\boldsymbol{\xi}|, \qquad \sigma_1(D_+) = -|\boldsymbol{\xi}|. \tag{16}$$

From this we get $\sigma_{-1}(D_+^{-1}) = -\frac{1}{|\boldsymbol{\xi}|}$ and then

$$\sigma_0(D_- D_+^{-1}) = -1. \tag{17}$$

This implies that the zeroth-order operator, $R := D_- D_+^{-1} + \mathbb{1}$, has the principal symbol $\sigma_0(R) = -1 + 1 = 0$, hence is in fact a pseudo-differential operator of order -1. Now any pseudo-differential operator of negative order on a bounded surface is a compact operator, and the spectral theory of compact operators implies that the eigenvalues r_k of R form a sequence converging to zero as $k \to \infty$. The eigenvalues of $D_- D_+^{-1} = -\mathbb{1} + R$ are $-1 + r_k$, so the resonances obey

$$\epsilon_k = (-1 + r_k)^{-1} \to -1 \qquad \text{as} \quad k \to \infty. \tag{18}$$

We emphasize that this limit is independent of the shape of the particle and equal to the result for the half-space. The physical expectation based on our consideration of curvature becoming invisible to leading order at small scales is reflected in this argument by the fact that the principal symbol of the Dirichlet–Neumann operator is independent of the shape.

We remark that with more refined methods of spectral asymptotics for pseudo-differential operators a more precise asymptotic result can be obtained which explains the correction $-\frac{1}{k}$ in the formula $\epsilon_k = -1 - \frac{1}{k}$ for the sphere, (14).

Finally, we mention a different reduction of the plasmonic eigenvalue problem (1)–(3) to an eigenvalue problem on the surface S, derived by the method of layer potentials in [12, 13]. For $\boldsymbol{r}, \boldsymbol{r}'$ on S let

$$F(\boldsymbol{r}, \boldsymbol{r}') = -\frac{1}{2\pi} \frac{n(\boldsymbol{r}) \cdot (\boldsymbol{r} - \boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|^3},$$

where $n(\boldsymbol{r})$ is the outer unit normal. Then $\epsilon = \frac{\lambda-1}{\lambda+1}$ for the eigenvalues λ in the equation

$$\int_S F(\boldsymbol{r}, \boldsymbol{r}') \sigma(\boldsymbol{r}') d^2\boldsymbol{r}' = \lambda \sigma(\boldsymbol{r}), \qquad \boldsymbol{r} \in S.$$

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[3] Sometimes one considers even more general symbols, and then those we defined are called classical symbols of type (1, 0); see [16].

Here σ is the outward normal derivative $\partial_n \phi$ (which is proportional to the induced surface charge density). The operator on the left is compact (in fact, a pseudo-differential operator of order -1), hence $\lambda_k \to 0$, and this shows $\epsilon_k \to -1$ again. For a proof of this fact, see [16] where also the relation of this operator and the Dirichlet–Neumann operators is discussed.

5. Conclusion

In this paper, we have applied methods of microlocal analysis to the study of plasmon resonances of arbitrarily shaped nanoparticles. We have first reformulated the boundary value problem for such resonances as an eigenvalue problem on the particle's surface. The fact that the Dirichlet–Neumann operators, which occur naturally in this context, are pseudo-differential operators then allows one to take advantage of the rich amount of knowledge available for these objects, and thereby to analyse the properties of the surface modes in rigorous mathematical terms. The remarkable ease with which the well-known result $\epsilon = -1$ for the surface modes of a half-space has been recovered here is a clear indication for the power of this approach. Moreover, we have used the eigenvalue equation for proving that the limit of the high-order modes is independent of the shape of the particle. As expected on the grounds of intuitive physical arguments, the high-order modes converge locally to the half-space modes. While this result itself appears natural, what matters here is the mathematical toolbox by which it has been obtained, which may be still somewhat unfamiliar to physicists, but which offers great conceptual clarity and flexibility. Thus, we hope that the approach suggested in this paper will prove useful for obtaining further insight into mathematical problems occurring in plasmonics.

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