Asymptotic approximations for the plasmon resonances of nearly touching spheres

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Excitation of surface-plasmon resonances of closely spaced nanometallic structures is a key technique used in nanoplasmonics to control light on subwavelength scales and generate highly confined electric-field hotspots. In this paper we develop asymptotic approximations in the near-contact limit for the entire set of surface-plasmon modes associated with the prototypical sphere dimer geometry. Starting from the quasi-static plasmonic eigenvalue problem, we employ the method of matched asymptotic expansions between a gap region, where the boundaries are approximately paraboloidal, pole regions within the spheres and close to the gap, and a particle-scale region where the spheres appear to touch at leading order. For those modes that are strongly localised to the gap, relating the gap and pole regions gives a set of effective eigenvalue problems formulated over a half space representing one of the poles. We solve these problems using integral transforms, finding asymptotic approximations, singular in the dimensionless gap width, for the eigenvalues and eigenfunctions. In the special case of modes that are both axisymmetric and odd about the plane bisecting the gap, where matching with the outer region introduces a logarithmic dependence upon the dimensionless gap width, our analysis follows [O. Schnitzer, Physical Review B, 92 235428 2015]. We also analyse the so-called anomalous family of even modes, characterised by field distributions excluded from the gap. We demonstrate excellent agreement between our asymptotic formulae and exact calculations.

Key Words: surface waves, asymptotic analysis, boundary eigenvalue problems

1 Introduction

1.1 The plasmonic eigenvalue problem

The unique optical properties of metal nanoparticles and nanostructures at visible frequencies enable guiding, localisation and enhancement of light on nanometric scales, below the so-called diffraction limit, with applications to bio-sensing, photovoltaics, medical treatment, optical circuitry and metamaterials [1]-[6]. These applications rely on the resonant excitation of localised surface plasmons, namely standing-wave oscillations of the electron-charge distribution at the metal-dielectric boundary and its induced electric field. Resonances are excited by external forcing, e.g., far-field illumination or near-field sources, at a frequency where the metal’s complex permittivity is close to a resonant value. Theoretically, when the metal’s permittivity is exactly equal to a resonant value,
the structure can sustain a localised-plasmon oscillation in the absence of any external forcing. In that case, the forced response could potentially diverge. In reality, however, the resonant values can never be exactly attained, and accordingly the resonance is always damped. In particular, in the quasi-static limit (structures small compared with the wavelength) resonant permittivities are negative real. In comparison, while the permittivity of a metal has a negative real part at frequencies below the plasma frequency, it also has an imaginary part owing to ohmic losses.

The quasi-static surface-plasmon modes of a nanometallic structure are governed by the plasmonic eigenvalue problem, which has recently received a lot of renewed attention in both physics and mathematics \[7 \text{--} 20\]. The problem naturally arises by considering the near-field limit of the macroscopic Maxwell equations governing the time-harmonic electric field in the vicinity of the structure, in the absence of external forcing. In this limit, the electric field is irrotational and can therefore be described by a potential, \( \varphi(\mathbf{x}; \omega) \), where \( \mathbf{x} \) is the position vector and \( \omega \) is the angular frequency. This potential satisfies

\[
\nabla \cdot (\varepsilon(\mathbf{x}; \omega) \nabla \varphi) = 0, \tag{1.1}
\]

where \( \varepsilon(\mathbf{x}; \omega) \equiv \epsilon(\omega) \) within the bounded, possible multiply connected, domain of the structure, while \( \varepsilon(\mathbf{x}; \omega) \equiv 1 \) in the surrounding background; note that \( \epsilon(\omega) \) is the permittivity of the metal nanostructure relative to that of the background. Requiring the field \( -\nabla \varphi \) to attenuate at large distances ensures matching with outward radiating solutions of Maxwell’s equations (considered on the much larger scale of the wavelength). Clearly, a field vanishing for all \( \mathbf{x} \) is always a solution of the above quasi-static problem. For certain special values of \( \epsilon \), however, there exist, in addition, one or more non-trivial solutions. The plasmonic eigenvalue problem is thus to find all such pairs of \( \epsilon \) eigenvalues and corresponding eigen-fields.

The plasmonic eigenvalue problem does not involve the frequency or any material parameters. It is also scale invariant, i.e., the uniform scaling \( \mathbf{x} \to l \mathbf{x} \) leaves the eigenvalues \( \epsilon \) unchanged, while the eigenfunctions transform as \( \varphi(\mathbf{x}) \to \varphi(\mathbf{x}/l) \). Thus the eigenvalue problem is of a purely geometric nature, depending only on the shape of the metallic nanostructure. Inclusions with smooth boundaries possess an infinite discrete set of negative-real \( \epsilon \) eigenvalues accumulating at \( \epsilon = -1 \) (the latter is the condition for quasi-static surface waves at a flat metal-dielectric interface).

Let us assume that the plasmonic eigenvalue problem has been solved for a given shape. Then the optical response of an actual metallic structure having that shape, subject to an arbitrary distribution of external sources, is readily obtained as an explicit combination of the eigenmodes. This spectral representation, which is based on orthogonality and completeness properties of the eigenfunctions, is especially efficient close to resonance where typically one or a few excited surface-plasmon modes dominate the sum \[15\text{--}17\text{,} 20\text{,} 22\]. We emphasise that, in contrast to the permittivity eigenvalues, the dielectric function of the actual metallic structure is frequency dependent and complex valued.
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1.2 Motivation and goals

Surface-plasmon resonance is generally manifested by amplification of the electric near-field, absorption within the metal structure and radiation away from it. It has been widely demonstrated that these features can be greatly enhanced using nanostructure geometries characterised by disparate length scales, e.g., closely spaced particles, particles nearly touching a substrate, as well as elongated particles. In particular, closely spaced structures have been extensively used to generate giant field enhancements in highly confined hotspots at resonant frequencies controlled by the clearance \[5, 23–29\]. This phenomenon is inherent to nanoplasmonic applications based on optical nonlinearities, targeted heating and stimulated emission \[4,30–32\].

In light of their practical importance, closely spaced plasmonic structures have been the subject of numerous theoretical investigations. Many of these studies are based on standard numerical methods such as finite-element simulations, the discrete-dipole method and multipole expansions, that are computationally expensive and often struggle when there is geometric scale disparity. Otherwise, a wide range of analytical techniques have been used, including separation of variables and transformation optics. In three dimensions, however, exact analytical methods are limited to idealised geometries and yield numerical schemes rather than closed-form formulae. While the geometric disparity is not \textit{a priori} encoded in the methods, they have been used to generate robust numerical schemes and in some cases analytical approximations in the near-contact limit \[15,33–38\]. The latter indirect approach of obtaining near-contact approximations is technical and difficult to generalise to non-ideal geometries or more sophisticated physics.

In this paper we adopt an alternative asymptotic approach where the near-contact limit is considered from the outset using matched asymptotic expansions \[39\]. Previously, we applied matched asymptotics to the problem of closely spaced metallic spheres illuminated by a plane wave, the electric field being polarised along the line of centres \[40\]. In particular, asymptotic approximations were obtained for the family of modes excitable in that scenario: axisymmetric modes with polarisation-charge and potential distributions odd about the plane bisecting the gap. Based on these eigensolutions, asymptotic formulae for the resonant field enhancements in the gap were derived and compared with numerical solutions. Our approach was later also applied to a generalised plasmonic description based on the hydrodynamic Drude model \[41, 42\], considering closely spaced cylinders and spheres among other shapes. These works demonstrate, in the context of nanoplasmonics, some of the typical advantages of using matched asymptotics to study singular limits. In particular, the method furnishes asymptotic formulae, e.g., for eigenvalues and field enhancements, in conjunction with a physically descriptive picture that illuminates scalings and dominant physical mechanisms. Furthermore, results are subject to considerable generalisation as the analysis does not rely on the existence of a detailed exact solution.

The axisymmetric odd modes considered in \[40\] constitute just one family of modes among the many comprising the rich spectrum of the sphere-dimer geometry. The modes are usually catalogued into several families based on symmetries, how well they couple with different near- and far-field external sources, as well as their asymptotic behaviour in the near-contact limit \[15,33,37\]. In this paper we will use matched asymptotic expansions
to develop asymptotic approximations in the near-contact limit for the entire set of plasmonic eigenvalues and eigenfunctions of a pair of identical spheres.

In section 2 we formulate the plasmonic eigenvalue problem for a sphere dimer. In §3 we prepare for the use of matched asymptotic expansions in the near-contact limit by describing the three asymptotic regions that take part in the analysis. The analysis is carried out in §4–§7, each section addressing an asymptotically distinct family of modes; for completion we review in §5 the special case of axisymmetric odd modes following [40]. In each section we compare our asymptotic results with an exact semi-analytical scheme based on separation of variables in bi-spherical coordinates. In §8 we compare our approximations for the eigenvalues with approximations obtained by others starting from the latter numerical scheme. Lastly, in §9 we discuss how the present analysis could be generalised to related geometries, limits where our asymptotic results breakdown and an alternative analysis is desirable, and anticipate future applications of these results to excitation scenarios.

2 Formulation of the problem

2.1 Plasmonic eigenvalue problem for a sphere dimer

Our interest is in the plasmonic eigenvalues and eigenfunctions of a pair of identical homogeneous spheres surrounded by a homogeneous background medium. The scale invariance of the plasmonic eigenvalue problem naturally lends itself to a dimensionless formulation where lengths are normalised by the radius of the spheres. The scaled geometry, shown in figure 1, is characterised by a single parameter $h$ defined as the ratio of the gap width and the sphere diameter. Since we are not enforcing a certain normalisation of the eigenfunctions, the potentials possess a multiplicative freedom and we can consider them to be dimensionless. Furthermore, an immaterial additive freedom is eliminated by requiring the potentials to attenuate at large distances. It will be convenient to denote the potentials inside and outside the spherical inclusions by $\bar{\varphi}$ and $\varphi$, respectively.

The problem consists of Laplace’s equation inside the spherical inclusions,

$$\nabla^2 \bar{\varphi} = 0,$$

(2.1)
and in the background medium,
\[ \nabla^2 \varphi = 0; \quad (2.2) \]
continuity of potential,
\[ \varphi = \varphi, \quad (2.3) \]
and of electric displacement,
\[ \frac{\partial \tilde{\varphi}}{\partial n} = \frac{\partial \varphi}{\partial n}, \quad (2.4) \]
on the spherical interfaces, where \( \epsilon \) is the eigenvalue and \( \partial / \partial n = \hat{n} \cdot \nabla \), \( \hat{n} \) being the normal unit vector pointing into the background medium; and attenuation,
\[ \varphi \to 0 \quad \text{as} \quad |x| \to \infty, \quad (2.5) \]
where \( x \) is the position vector measured from the centre of the gap, say.

### 2.2 Symmetries

Consider the cylindrical coordinates \((r,z,\phi)\) shown in figure 1. Note that the geometry is symmetric about both the \( z \) axis and the plane \( z = 0 \) bisecting the gap. The axial symmetry implies that the eigenfunctions possess the form
\[
\tilde{\varphi}(r,z,\phi) = \psi(r,z) \begin{cases} \cos(m\phi) \\ \sin(m\phi) \end{cases}, \quad \varphi(r,z,\phi) = \psi(r,z) \begin{cases} \cos(m\phi) \\ \sin(m\phi) \end{cases}, \quad (2.6)
\]
where \( m = 0, 1, 2, \ldots \). Owing to the symmetry about the plane \( z = 0 \), the modes can be further characterised as being either odd or even with respect to that plane. This allows us to consider only the half space \( z > 0 \), with the odd modes satisfying
\[ \psi = 0 \quad \text{at} \quad z = 0 \quad (2.7) \]
and the even modes satisfying
\[ \frac{\partial \psi}{\partial z} = 0 \quad \text{at} \quad z = 0. \quad (2.8) \]

### 2.3 Exact semi-analytical solutions

The above plasmonic eigenvalue problem has been previously studied using separation of variables in bi-spherical coordinates [15, 43] and using transformation optics followed by separation of variables in spherical coordinates [37]. In any case one finds an infinite-tridiagonal-matrix eigenvalue problem that in general must be truncated and solved numerically for the eigenvalues and eigenvectors, the latter being the coefficients in an infinite-series representation of the eigenpotentials. We have implemented this scheme for later comparison with our asymptotic results (see [15] for details).

Computed eigenvalues corresponding to odd modes are shown in figures 4, 5 and 7 for \( m = 1, 2 \) and 0, respectively. Note that the eigenvalues of the odd modes lie below the accumulation point, i.e., \( \epsilon < -1 \), with \( \epsilon \to -\infty \) as \( h \to 0 \). Eigenvalues corresponding to even modes are shown in figures 10–12 for \( m = 0, 1 \) and 2, respectively. Note that there are in general two families of even modes, one with \( \epsilon > -1 \) and the other with
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Figure 2. The gap, pole and outer regions considered in the near-contact analysis.

$\epsilon < -1$. Even modes with $\epsilon > -1$ only exist for $h$ smaller than a critical value, which is different for each mode; these modes are similar to the even modes of a cylindrical dimer in that the eigenvalues satisfy $\epsilon \to 0$ as $h \to 0$, though in the latter case the modes exist for all $h > 0$. Even modes with $\epsilon < -1$, termed “anomalous” in [37], exist for all $h$ and in fact limit to the modes of an isolated sphere as $h \to \infty$. They are anomalous in that the eigenvalues tend to constants as $h \to 0$, which has no analogue in the case of a cylindrical dimer. Moreover, the anomalous modes have their field excluded from the gap in the near-contact limit, whereas all the other modes of a sphere dimer have their field confined to the gap in that limit. Note that for each family of modes, and for each $m$, we use a second integer, $n = 0, 1, 2, \ldots$, to enumerate the eigenvalues with increasing closeness to the accumulation point.

3 The near-contact limit

In what follows our interest is in the limit $h \ll 1$. Note that the limit is taken for a fixed arbitrary mode, which implies $m, n = O(1)$. Since the near-contact limit represents a ratio between two geometric length scales, we anticipate the potentials to have spatially nonuniform asymptotics [44]. We shall accordingly base our analysis on the method of matched asymptotic expansions [39]. In the present section we prepare for this by identifying three distinguished asymptotic regions (see figure 2).

3.1 Outer region

Consider the outer limit: $h \to 0$ with $x$ fixed. The boundary of the sphere in the half space $z > 0$ can be written as $F(r, z; h) = 0$, where

$$F = [z - (1 + h)]^2 + r^2 - 1.$$  \hspace{1cm} (3.1)

In the outer limit, (3.1) gives

$$F(r, z; h) \sim F_0(r, z) + O(h), \quad F_0(r, z) = (z - 1)^2 + r^2 - 1,$$  \hspace{1cm} (3.2)

where the nominal boundary $F_0(r, z) = 0$ is a unit sphere tangent to the symmetry plane. In the outer region, the potentials $\bar{\varphi}$ and $\varphi$ satisfy (2.1)–(2.5), with the interfacial
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conditions mapped to the nominal boundary by use of Taylor expansions. In general, the outer potentials may diverge as the origin is approached \[45\]. Indeed, the asymptotic behaviour in the latter limit is dictated by matching with inner regions describing the gap region and the adjacent region within the inclusion.

We shall see that in most cases a detailed solution of the outer region is not required, at least at leading order. Otherwise, it will be convenient to employ tangent-sphere coordinates \((\xi, \eta, \phi) \[46\], where

\[r = \frac{2\eta}{\xi^2 + \eta^2}, \quad z = \frac{2\xi}{\xi^2 + \eta^2}, \quad (3.3)\]

and \(\phi\) is as before the azimuthal angle. As schematically shown in figure 2, the sphere boundary is \(\xi = 1 + O(h)\), the symmetry plane is \(\xi = 0\), the origin is \(\eta = \infty\) and infinity is approached in the limit \(\xi^2 + \eta^2 \to 0\).

### 3.2 Gap region

Close to the gap the boundaries are approximately paraboloidal, hence the separation between the spheres remains \(O(h)\) over \(O(h^{1/2})\) radial distances. Since the governing equations are linear and homogeneous, and in the absence of additional small parameters, the length scale on which the potential varies is determined by the geometry of the confining boundaries. Thus consider the inner-gap limit: \(h \to 0\) with the stretched coordinates

\[Z = z/h, \quad R = r/h^{1/2} \quad (3.4)\]

fixed. In terms of the gap coordinates \((3.4)\), the sphere boundary follows from \((3.1)\) as

\[Z = H(R; h) \sim H_0(R) + O(h), \quad H_0(R) = 1 + \frac{1}{2} R^2. \quad (3.5)\]

The gap potential, \(\Phi(R, Z) = \psi(r, z)\), satisfies Laplace’s equation \((2.2)\) in the form

\[h^{-1} \frac{\partial^2 \Phi}{\partial Z^2} + \frac{1}{R} \frac{\partial}{\partial R} \left( R \frac{\partial \Phi}{\partial R} \right) - \frac{m^2 R}{R^2} \Phi = 0, \quad (3.6)\]

for \(0 < Z < H(R; h)\). Given \((2.7)\) and \((2.8)\), the odd and even modes respectively satisfy the symmetry conditions

\[\Phi = 0 \quad \text{at} \quad Z = 0 \quad (3.7)\]

and

\[\frac{\partial \Phi}{\partial Z} = 0 \quad \text{at} \quad Z = 0. \quad (3.8)\]

The interfacial conditions satisfied by \(\Phi\) at \(Z = H(R; h)\) will be provided in the next subsection. Furthermore, \(\Phi\) is required to asymptotically match with the outer region in the limit \(R \to \infty\).

### 3.3 Pole region

Consider now the region within the spherical inclusion that is adjacent to the gap. The scaling of the gap region, together with the continuity condition \((2.3)\), suggests that \(\psi\)
varies over \(O(h^{1/2})\) distances along the interface. On such a small scale, the spherical domain is effectively unbounded in the transverse direction. Thus, the linearity and symmetry of Laplace’s equation suggest that \(\bar{\psi}\) varies over comparably short distances in that direction. We accordingly introduce the inner-pole limit: \(h \to 0\) with the stretched coordinates

\[
\bar{Z} = z/h^{1/2}, \quad R = r/h^{1/2}
\]

fixed. In terms of the pole coordinates (3.9), the sphere boundary reads as

\[
\bar{Z} = h^{1/2}H(R; h).
\]

Note that since \(H = O(1)\), the boundary is approximately flat in the pole limit. The pole potential, \(\bar{\Phi}(R, \bar{Z}) = \bar{\psi}(r, z)\), satisfies Laplace’s equation (2.1) in the form

\[
\frac{\partial^2 \bar{\Phi}}{\partial \bar{Z}^2} + \frac{1}{R} \frac{\partial}{\partial R} \left( R \frac{\partial \bar{\Phi}}{\partial R} \right) - \frac{m^2}{R^2} \bar{\Phi} = 0,
\]

(3.11) for \(\bar{Z} > h^{1/2}H(R; h)\). The continuity condition (2.3) now reads as

\[
\bar{\Phi} = \Phi \quad \text{on} \quad Z = H(R; h), \quad \bar{Z} = h^{1/2}H(R; h),
\]

(3.12) while the displacement-continuity condition (2.4) reads as

\[
\epsilon h^{1/2} \left( \frac{\partial \bar{\Phi}}{\partial \bar{Z}} - h^{1/2} \frac{dH}{dR} \frac{\partial \bar{\Phi}}{\partial R} \right) = \frac{\partial \Phi}{\partial Z} - h \frac{dH}{dR} \frac{\partial \Phi}{\partial R} \quad \text{at} \quad Z = H(R; h), \quad \bar{Z} = h^{1/2}H(R; h).
\]

(3.13) Lastly, \(\bar{\Phi}\) must asymptotically match with the outer region in the limit \(R^2 + \bar{Z}^2 \to \infty\).

\section*{4 Odd modes}

\subsection*{4.1 Gap region}

We may assume without loss of generality that the potential in the gap is \(O(1)\). We accordingly write

\[
\Phi(R, Z) = \Phi_0(R, Z) + o(1),
\]

(4.1) where the magnitude of the error term is discussed in \(\S\) 4.6. From (3.6), \(\Phi_0\) satisfies

\[
\frac{\partial^2 \Phi_0}{\partial Z^2} = 0,
\]

(4.2) while (3.7) gives the symmetry condition

\[
\Phi_0 = 0 \quad \text{at} \quad Z = 0.
\]

(4.3) It follows that

\[
\Phi_0 = A(R)Z,
\]

(4.4) where \(A(R)\) is an unknown radial distribution. We see that, in the near-contact limit, the odd modes are characterised by a transverse electric field in the gap that varies radially (and azimuthally if \(m \neq 0\)) on a scale large compared with the gap width.
4.2 Pole potential and eigenvalue scaling

Consider next the pole region. The continuity condition (3.12) suggests that the magnitude of the pole potential is comparable to that of the gap potential. We accordingly assume the expansion

$$\Phi(R, \bar{Z}) = \Phi_0(R, \bar{Z}) + o(1).$$  \hspace{1cm} (4.5)

The eigenvalue scaling then follows by inspection of the displacement condition (3.13):

$$\epsilon = O(h^{-1/2}).$$  \hspace{1cm} (4.6)

4.3 Effective eigenvalue problem

We expand the eigenvalue as

$$\epsilon = -\alpha h^{-1/2} + o(h^{-1/2}),$$  \hspace{1cm} (4.7)

where $\alpha$ is a positive constant to be determined from an effective eigenvalue problem governing the leading-order pole potential $\Phi_0$. From (3.11), $\Phi_0$ satisfies Laplace’s equation in the half space $\bar{Z} > 0$,

$$\frac{\partial^2 \Phi_0}{\partial \bar{Z}^2} + \frac{1}{R} \frac{\partial}{\partial R} \left( R \frac{\partial \Phi_0}{\partial R} \right) - \frac{m^2}{R^2} \Phi_0 = 0,$$  \hspace{1cm} (4.8)

while the interfacial conditions (3.12) and (3.13), in conjunction with (4.7), give

$$\Phi_0 = A(R)H_0(R) \text{ at } \bar{Z} = 0,$$  \hspace{1cm} (4.9)

and

$$-\alpha \frac{\partial \Phi_0}{\partial \bar{Z}} = A(R) \text{ at } \bar{Z} = 0.$$  \hspace{1cm} (4.10)

Eliminating $A(R)$ we obtain

$$\Phi_0 + \alpha H_0 \frac{\partial \Phi_0}{\partial \bar{Z}} = 0 \text{ at } \bar{Z} = 0,$$  \hspace{1cm} (4.11)

a self-contained robin-type condition with non-constant coefficients for $\Phi_0$.

To close the problem governing $\Phi_0$ a condition on its behaviour in the limit $R^2 + \bar{Z}^2 \to \infty$ should in principle be deduced from asymptotic matching with the outer region. It is more expedient to assume, subject to verification by matching, that the outer potential within the sphere is asymptotically small compared to the potential in the gap and pole regions. In that case, matching implies the attenuation condition

$$\Phi_0 \to 0 \text{ as } R^2 + \bar{Z}^2 \to \infty.$$  \hspace{1cm} (4.12)

Since $\Phi_0$ satisfies Laplace’s equation, (4.12) can be refined to

$$\Phi_0 = O \left\{ \left( R^2 + \bar{Z}^2 \right)^{-\frac{1+\epsilon}{2}} \right\} \text{ as } R^2 + \bar{Z}^2 \to \infty.$$  \hspace{1cm} (4.13)

Eqs. (4.8), (4.11) and (4.12) then constitute an effective eigenvalue problem governing the leading-order pole potential $\Phi_0$ and scaled eigenvalue $\alpha$. Once $\Phi_0$ is determined, the gap potential can be found using (4.9).
### 4.4 Solution of the effective eigenvalue problem

We look for solutions in the form

\[ \tilde{\Phi}_0(R, \tilde{Z}) = \mathcal{H}_m \hat{\Phi}(s, \tilde{Z}), \tag{4.14} \]

where

\[ \mathcal{H}_m f(s) = \int_0^\infty f(s) J_m(Rs) s \, ds \tag{4.15} \]

is the Hankel transform of order \( m \) and \( J_m \) is the usual Bessel function of order \( m \) [47].

Note that the inverse Hankel transform has the same form as the forward transform.

Substitution of (4.14) into Laplace’s equation (4.8) and using the attenuation condition (4.12) yields

\[ \hat{\Phi}(s, \tilde{Z}) = \frac{1}{s} Y(s) e^{-s \tilde{Z}}, \tag{4.16} \]

where \( Y(s) \) is an unknown function of the transform variable \( s \). In terms of this function, the boundary condition (4.11) reads as

\[ \mathcal{H}_m \left[ \left( \frac{1}{s} - \alpha \right) Y(s) \right] - \frac{\alpha}{2} R^2 \mathcal{H}_m Y(s) = 0. \tag{4.17} \]

Taking the inverse transform of (4.17), using the identity

\[ -R^2 \mathcal{H}_m f(s) = \mathcal{H}_m \left[ \frac{1}{s} \frac{\partial}{\partial s} \left( s \frac{\partial f}{\partial s} \right) - \frac{m^2}{s^2} f \right], \tag{4.18} \]

which is valid if the transform exists and

\[ s \frac{df}{ds} = o(s^{-m}) \quad \text{as} \quad s \to 0 \tag{4.19} \]

(see [47]), yields

\[ \frac{d^2Y}{ds^2} + \frac{1}{s} \frac{dY}{ds} + \left( \frac{2}{\alpha s} - 2 - \frac{m^2}{s^2} \right) Y = 0. \tag{4.20} \]

Analysis of (4.20) for large \( s \) [48] suggests the transformation

\[ Y(s) = s^m e^{-\sqrt{2} s T(p)}, \quad p = 2\sqrt{2}s, \tag{4.21} \]

where \( T(p) \) satisfies the associated Laguerre equation [49]:

\[ p \frac{d^2T}{dp^2} + (1 + \nu - p) \frac{dT}{dp} + nT = 0, \tag{4.22} \]

with parameters

\[ \nu = 2m, \quad n = \frac{\sqrt{2} - (1 + 2m)\alpha}{2\alpha}. \tag{4.23} \]

For non-negative integer \( n \), one solution of (4.22) is the polynomial

\[ L_n^{(\nu)}(x) = \frac{(\nu+1)_n}{n!} {}_1F_1(-n; \nu + 1; x), \tag{4.24} \]

where \((t)_n = \Gamma(t + n)/\Gamma(t)\) is the Pochhammer symbol and \( {}_1F_1 \) the hypergeometric...
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Figure 3. Radial distributions (4.29) and (4.30) of the transverse field in the gap for odd modes with \( m = 0 \) (a) and \( m = 1 \) (b). Thick and thin lines depict modes \( n = 0 \) and \( n = 1 \), respectively. In the case \( m = 0 \) we shall derive more accurate asymptotics in §5.

function, e.g.,

\[
L^{(\nu)}_0(x) = 1, \quad L^{(\nu)}_1(x) = -x + \nu + 1,
\]

\[
L^{(\nu)}_2(x) = \frac{1}{2} [x^2 - 2(\nu + 2)x + (\nu + 1)(\nu + 2)];
\] (4.25)

if \( \nu \) is also an integer, as in the present case where \( \nu = 2m \), these polynomials are termed associated Laguerre polynomials, otherwise they are called the generalised Laguerre function [49]. It can be shown that the second independent solution for non-negative integer \( n \), as well as all solutions for other \( n \) values, are either too singular as \( p \to 0 \) to satisfy (4.19) [and the attenuation rate (4.13)] or grow too fast as \( p \to \infty \) for the transform (4.14) to exist. Thus \( n \) must be a non-negative integer whereby the scaled eigenvalues follow from (4.23) as

\[
\alpha = \frac{\sqrt{2}}{1 + 2n + 2m}, \quad n = 0, 1, 2, \ldots, \quad m = 1, 2, 3, \ldots,
\] (4.26)

with corresponding eigenfunctions

\[
Y(s) = s^m e^{-\sqrt{2}s} L^{(2m)}_n (2\sqrt{2}s), \quad n = 0, 1, 2, \ldots, \quad m = 1, 2, 3, \ldots,
\] (4.27)

where we have set the arbitrary multiplicative constants to unity.

4.5 Eigenfunctions in physical space

The eigenfunctions (4.27) can be inverted to give, for example, the radial distribution of the transverse field in the gap [cf. (4.4) and (4.9)]:

\[
\frac{d\Phi_0}{dZ} = \frac{1}{H_0(R)} \int_0^\infty s^m e^{-\sqrt{2}s} L^{(2m)}_n (2\sqrt{2}s) J_m (Rs) \, ds.
\] (4.28)

It can be shown from (4.28) that \( d\Phi_0/dZ = O(R^{-(m+3)}) \) as \( R \to \infty \). It follows that in that limit \( \Phi_0(R, 0) = O(1/R^{1+m}) \), as anticipated in (4.13), while \( \Phi_0 = O(Z/R^{3+m}) \).
The quadrature (4.28) can be evaluated for given $m$ and $n$. In particular, for $(m,n) = (0, \{0,1\})$:

$$\frac{d\Phi_0}{dZ} = \frac{1}{H_0(R)} \left\{ \frac{1}{(2 + R^2)^{1/2}} \frac{R^2 - 2}{(2 + R^2)^{3/2}} \right\}. \quad (4.29)$$

Similarly,

$$\frac{d\Phi_0}{dZ} = \frac{1}{H_0(R)} \left\{ \frac{R}{(2 + R^2)^{3/2}} \frac{3R(R^2 - 2)}{(2 + R^2)^{5/2}} \right\} \quad (4.30)$$

and

$$\frac{d\Phi_0}{dZ} = \frac{1}{H_0(R)} \left\{ \frac{3R^2}{(2 + R^2)^{5/2}} \frac{15R^2(R^2 - 2)}{(2 + R^2)^{7/2}} \right\} \quad (4.31)$$

for $(m,n) = (1, \{0,1\})$ and $(m,n) = (2, \{0,1\})$, respectively. We plot the transverse gap fields (4.29) and (4.30) in figure 3.

### 4.6 Comparison with exact semi-analytical solutions

Figures 4, 5 present, respectively for $m = 1, 2$, a comparison between the asymptotic prediction (4.7), with $\alpha$ given by (4.26), and the eigenvalues computed using the semi-analytical scheme discussed in §2.3. The agreement is excellent for small $h$, though for reasons discussed in §9 the agreement is delayed to smaller $h$ as $n$ increases. In contrast,

![Figure 4](image.png)

Figure 4. Eigenvalues corresponding to non-axisymmetric ($m = 1$) odd modes as a function of $h$, half the dimensionless gap width. The thick blue lines are the asymptotic predictions (4.7), with $\alpha$ given by (4.26) for $n = 0, 1, 2, 3$. The thin black lines are exact values obtained from the semi-numerical scheme described in §2.3. The thick red line marks the accumulation point $\epsilon = -1$. 
for $m = 0$ the computed eigenvalues are found to converge extremely slowly to the asymptotic result, suggesting that the error in the axisymmetric case is relatively large.

From inspection of the gap-pole equations, one might expect a relative asymptotic error of $O(h^{1/2})$. Recall, however, that the analysis in this section is predicated on the assumption that $\bar{\varphi}$, the outer potential within the sphere, is asymptotically small compared to the potential in the pole and gap regions and accordingly that $\bar{\Phi}_0$ satisfies the attenuation condition (4.12). By analysing the leading-order outer problem, it can be shown that for $m \neq 0$ our naive leading-order solutions are in fact algebraically accurate and that the outer potentials are $\bar{\varphi}, \varphi = O(h^{(m+1)/2})$. For $m = 0$, however, we shall see that $\bar{\varphi}$ is approximately uniform and only $O(1/\ln h)$ smaller than the pole potential. The matching condition (4.12) must accordingly be modified already at that order, leading to logarithmic corrections that are practically important.

5 Axisymmetric odd modes

Our goal in this section is to develop an accurate asymptotic description of the axisymmetric modes. We shall closely follow our analysis in [40] of this case.

5.1 Gap, pole and internal outer regions

We start by generalising expansion (4.7):

$$\epsilon \approx -\alpha (\ln h) h^{-1/2},$$

(5.1)
where the approximation sign will be used to denote an error which is algebraic, i.e., scaling with some power of $h$. In (5.1), and throughout the analysis in this section, we collect together terms that are asymptotically separated by powers of $\ln h$. The leading-order pole and gap potentials are still denoted by $\Phi_0$ and $\Phi_0 = A(R)Z$, respectively, only that by leading order we now mean that the relative error is algebraically small. Hence we allow $\Phi_0$ and $A(R)$ to depend upon $\ln h$. With these conventions, Eqs. (4.8)–(4.11) governing $\Phi_0$ remain in the same form, whereas the attenuation condition (4.12) requires modification.

To see this, consider the outer potential within the sphere $\bar{\varphi}$. The displacement condition (2.4) in conjunction with the largeness of $|\epsilon|$ implies that $\bar{\varphi}$ approximately satisfies a homogeneous Neumann condition on the tangent-sphere boundary. Accordingly, subject to matching with the pole region (in the limit where the origin is approached), we stipulate a uniform leading-order solution, say

$$\bar{\varphi} \approx V,$$

where $V$ is a constant. This, in turn, implies through matching that the pole potential satisfies

$$\bar{\Phi}_0 \to V \quad \text{as} \quad R^2 + \bar{Z}^2 \to \infty$$

instead of the attenuation condition (4.12). From (4.9), the gap potential accordingly satisfies

$$\Phi_0(R, Z) \sim \frac{2V}{R^2} Z \quad \text{as} \quad R \to \infty.$$  

(Note that (5.2) is impossible for $m \neq 0$ and the leading-order outer potential is instead forced by matching with the attenuating pole solutions we found in §4. Conversely, the latter situation leads to a contradiction for $m = 0$, since in that case the attenuating pole solution produces a net flux into the sphere, which is incompatible with the Neumann condition in the outer region. Hence the uniform solution (5.2) holds with $V = o(1)$ yet large compared with $O(h^{1/2})$.)

### 5.2 External outer region

Outside the sphere we expand the outer potential as

$$\varphi \approx \varphi_0(\xi, \eta),$$

where $(\xi, \eta)$ are the tangent-sphere coordinates defined in §3.1. The potential $\varphi_0(\xi, \eta)$ satisfies Laplace’s equation for $0 < \xi < 1$ and $0 < \eta < \infty$; the Dirichlet boundary condition

$$\varphi_0 = V \quad \text{at} \quad \xi = 1,$$

which follows from continuity with the internal outer potential (5.2); the symmetry condition

$$\varphi_0 = 0 \quad \text{at} \quad \xi = 0;$$

attenuation at infinity

$$\varphi_0 \to 0 \quad \text{as} \quad \eta \to \infty;$$
Nearly touching plasmonic spheres

as well as matching with the gap potential. Given (5.4), the latter requirement implies

\[ \varphi_0 \sim V \xi \quad \text{as} \quad \eta \to \infty. \quad (5.9) \]

Thus, the outer potential is the same as if the spheres were perfectly conducting and held at opposite potentials \( \pm V \). The requisite solution is known to be [45]

\[ \varphi_0(\xi, \eta) = V(\xi^2 + \eta^2)^{1/2} H_0 \left( \frac{e^{-s} \sinh(s \xi)}{s \sinh s} \right). \quad (5.10) \]

Note that at large distances from the spheres,

\[ \varphi_0 \sim V \left( \frac{z}{r^2 + z^2} \right)^{3/2} \quad \text{as} \quad r^2 + z^2 \to \infty, \quad (5.11) \]

which relates the dipole moment of the axisymmetric odd modes and the voltage.

5.3 Charge balance

In the electrostatic analogy of the outer solution, where a voltage \( 2V \) is applied between a pair of perfectly conducting spheres, the spheres are oppositely charged. As we shall see, attempting to calculate the charge using the outer solution (5.10) gives a diverging result. Indeed, the overlap with the gap region must be accounted for and the capacitance is accordingly found to be logarithmically large in \( h \) [45].

In contrast, in the plasmonic case it is obvious on physical grounds that the net polarisation charge on each sphere must vanish. Indeed, the problem formulation implies the integral constraint

\[ \int \hat{n} \cdot \nabla \varphi \, dA = 0, \quad (5.12) \]

where the integral is over the surface of the sphere in \( z > 0 \), say. As the outer solution is the same as in the electrostatic problem, we conclude that the excess polarisation charge in the gap must exactly balance the virtual net charge the sphere would have if held at a strictly uniform potential \( V \) (and \( -V \) on the sphere in \( z < 0 \)).

The above intuitive reasoning can be made formal. We split the integral in (5.12) at some \( 1 \ll \eta_0 \ll h^{-1/2} \), which corresponds to an inner radial coordinate \( h^{1/2} R_0 = 2/\eta_0 + O(1/\eta_0^3) \). Using the gap expansion for \( R < R_0 \) and the outer expansion for \( \eta > \eta_0 \), (5.12) yields

\[ \int_0^{R_0} A(R) R \, dR + \int_0^{\eta_0} \frac{\partial \varphi_0}{\partial \xi} \bigg|_{\xi=1} \frac{2\eta}{1 + \eta^2} \, d\eta \approx 0. \quad (5.13) \]

Since \( A(R) = O(1/R^2) \) as \( R \to \infty \) [cf. (5.4)], the first integral in (5.13), which represents the leading contribution of the gap region, does not converge as \( R_0 \to \infty \). Indeed, using (4.9) we find

\[ \int_0^{R_0} A(R) R \, dR \sim V \ln \frac{R_0^2}{2} + \int_0^\infty \frac{\Phi(R, 0) - V}{H_0(R)} R \, dR + o(1) \quad \text{as} \quad R_0 \to \infty, \quad (5.14) \]

where the integral on the right hand side now clearly converges and represents the excess gap charge. Next, using the outer solution (5.10) it can be shown that the outer
contribution is
\[
\int_0^{\eta_0} \frac{\partial \varphi_0}{\partial \xi} \left|_{\xi=1} \right. \frac{2\eta}{1 + \eta^2} \, d\eta \sim 2V(\ln \eta_0 + \gamma) + o(1) \quad \text{as} \quad \eta_0 \to \infty, \tag{5.15}
\]
where \(\gamma = 0.5772\ldots\) is the Euler-Gamma constant. Finally, adding (5.14) and (5.15), the singular terms involving the arbitrary values \(R_0\) and \(\eta_0\) cancel out. We thereby derive the integral constraint
\[
V = -\frac{1}{2} \ln(2/h) + 2\gamma \int_0^\infty \frac{\Phi(R,0) - V}{H_0(R)} R \, dR. \tag{5.16}
\]

### 5.4 Integral-differential eigenvalue problem

Consider now the pole problem in terms of the modified potential
\[
\chi(R,\bar{Z}) = \frac{\Phi_0}{V - 1}. \tag{5.17}
\]
Laplace’s equation (4.8) reads as
\[
\frac{\partial^2 \chi}{\partial \bar{Z}^2} + \frac{1}{R} \frac{\partial}{\partial R} \left( R \frac{\partial \chi}{\partial R} \right) = 0, \tag{5.18}
\]
the boundary condition (4.11) reads as
\[
\chi + \alpha H_0 \frac{\partial \chi}{\partial \bar{Z}} = -1 \quad \text{at} \quad \bar{Z} = 0 \tag{5.19}
\]
and the matching condition (5.3) becomes the attenuation condition
\[
\chi \to 0 \quad \text{as} \quad R^2 + \bar{Z}^2 \to \infty. \tag{5.20}
\]
In addition \(\chi\) must satisfy the integral condition (5.16), which becomes
\[
\ln(2/h) + 2\gamma + \int_0^\infty \frac{\chi(R,0)}{H_0(R)} R \, dR = 0. \tag{5.21}
\]

### 5.5 Infinite expansion in inverse logarithmic powers

The above effective eigenvalue problem depends logarithmically upon \(h\) via the integral constraint (5.21). Accordingly, it can be solved perturbatively in inverse logarithmic powers. In particular, the eigenvalue expansion is found as
\[
\alpha \sim \frac{\sqrt{2}}{1 + 2n} \left( 1 - \frac{4}{2n + 1} \ln(1/h) + \cdots \right), \quad n = 0, 1, 2, \ldots \tag{5.22}
\]
The leading order of (5.22) agrees with the approximation obtained in [4] in the case \(m = 0\). We next proceed to solve the effective eigenvalue problem exactly, thus recovering all the terms in the logarithmic expansion in one go.

### 5.6 Algebraically accurate solution

In [40] \(\chi\) was sought in terms of a Hankel transform. A Hankel transform is nothing but the two-dimensional Fourier transform of a radially symmetric function. We shall find
the latter interpretation clearer when transforming the boundary condition (5.19), as the constant term requires carrying out the transform in the sense of distributions [47]. We accordingly write
\[
\hat{\chi}(s, Z) = \frac{1}{2\pi} \int \chi(R, Z) e^{is \cdot R} d^2 R,
\]
(5.23)
where \( R \) is a position vector in the plane \( \bar{Z} = 0 \), whose magnitude is \( R \), and \( s \) is the corresponding transformation variable, whose magnitude is \( s \).

Similar to the analysis in the previous section, Laplace’s equation (5.18) and attenuation (5.20) imply
\[
\hat{\chi}(s, Z) = \frac{1}{s} Y(s) e^{-s \bar{Z}}.
\]
(5.24)
Taking the Fourier transform of the boundary condition (5.19) using (5.24) yields
\[
\nabla_s^2 Y + 2 \left( \frac{1}{\alpha s} - 1 \right) Y = -\frac{4\pi}{\alpha} \delta_{2D}(s)
\]
(5.25)
where \( \delta_{2D}(s) \) is the two-dimensional Dirac delta function. Integrating (5.25) over a small circle of radius \( s' \) and using the divergence law in the plane gives
\[
2\pi s' \left( \frac{dY}{ds} \right)_{s={s'}} + 2 \int_{s<s'} \left( \frac{1}{\alpha s} - 1 \right) Y(s) d^2 s = -\frac{4\pi}{\alpha}
\]
(5.26)
In the limit \( s' \to 0 \), the first and third term in (5.26) balance to give
\[
Y(s) \sim -\frac{2}{\alpha} \log s \quad \text{as} \quad s \to 0,
\]
(5.27)
which \textit{a posteriori} justifies the neglect of the second term in (5.26).

We can now restrict the problem governing \( Y(s) \) to \( s > 0 \), where (5.25) reduces to
\[
\frac{1}{s} \frac{d}{ds} \left( \frac{s}{s} \frac{dY}{ds} \right) + 2 \left( \frac{1}{\alpha s} - 1 \right) Y = 0,
\]
(5.28)
to be considered together with the singular boundary condition (5.27) and the condition that \( Y(s) \) attenuates fast enough for the transform to exist. Following the transformation \( Y(s) = e^{-\sqrt{2}pT(p)} \), where \( p = 2\sqrt{2}s \), the governing equation (5.28) becomes
\[
p \frac{d^2 T}{dp^2} + (1 - p) \frac{dT}{dp} + \tilde{n} T = 0, \quad p > 0,
\]
(5.29)
where the parameter \( \tilde{n} \) is related to the scaled eigenvalue \( \alpha \) through
\[
\alpha = \frac{\sqrt{2}}{2\tilde{n} + 1},
\]
(5.30)
while the asymptotic constraint (5.27) becomes
\[
T(p) \sim -\frac{2}{\alpha} \log p \quad \text{as} \quad p \to 0.
\]
(5.31)
Misleadingly, (5.30) has the exact same form as the leading-order result (4.26) for \( m = 0 \), with \( \tilde{n} \) instead of \( n \). Here, however, \( \tilde{n} \) does not attain integer values. In fact, for any positive non-integer \( \tilde{n} \), a solution that satisfies (5.29), (5.31) and has permissible
Figure 6. First five solution branches of (5.37) as a function of $h$. The equation is solved graphically by plotting $h = (1/8) \exp(-2\Psi(-\tilde{n}))$ as a function of $\tilde{n}$.

behaviour at large $p$ is

$$T(p) = \frac{2}{\alpha} \Gamma(-\tilde{n}) U(-\tilde{n}, 1, p),$$

(5.32)

where $U$ is the confluent hypergeometric function of the second kind; note that

$$U(-\tilde{n}, 1, p) \sim -\frac{1}{\Gamma(-\tilde{n})} \left[ \log p + \Psi(-\tilde{n}) + 2\gamma \right] + o(1) \quad \text{as} \quad p \to 0,$$

(5.33)

$\Gamma(x)$ is the Gamma function and $\Psi(x) = \Gamma'(x)/\Gamma(x)$ is the Digamma function.

At this stage $\tilde{n}$ remains nearly arbitrary, whereas we expect to find a discrete spectrum. Consider however the integral constrain (5.19), rewritten using (5.19) as

$$\ln \frac{2}{h} + 2\gamma = \frac{1}{2\pi} \iint \left( \frac{\alpha}{\partial Z} + \frac{1}{H_0} \right) \delta_{2D}(s) d^2 s.$$

(5.34)

The integral on the right hand side is most easily evaluated using the convolution identity for two-dimensional Fourier transforms [47]. Using (5.24) and noting that the transform of $1/H_0(R)$ is $2K_0(s\sqrt{2})$, where $K_0$ is the modified Bessel function of the second kind, we thereby find

$$\frac{1}{2\pi} \iint \left( \frac{\alpha}{\partial Z} + \frac{1}{H_0} \right) d^2 R = \iint \left( -\alpha Y(s) + 2K_0(s\sqrt{2}) \right) \delta_{2D}(s) d^2 s.$$

(5.35)

Using (5.32), (5.33), and noting that $K_0(x) \sim -\ln(x/2) - \gamma + o(1)$ as $x \to 0$, (5.35) yields

$$\lim_{s \to 0} \left( -\alpha Y(s) + 2K_0(s\sqrt{2}) \right) = 2\ln 4 + 2\Psi(-\tilde{n}) + 2\gamma.$$

(5.36)
Figure 7. Eigenvalues corresponding to axisymmetric ($m = 0$) odd modes as a function of $h$, half the dimensionless gap width. The thick blue lines are the asymptotic predictions (5.1), with $\alpha$ given by (5.38) and $\tilde{n}(n, \ln h)$ determined from (5.37) for $n = 0, 1, 2, 3$. The thin black lines are exact values obtained from the semi-numerical scheme described in §2.3. The thick red line marks the accumulation point $\epsilon = -1$. The inset focuses on the fundamental mode $n = 0$, showing in addition one (dash-dotted line) and two (dashed line) terms of the logarithmic expansion (5.22).

Thus we find from (5.34) a transcendental equation for $\tilde{n}$:

$$2\Psi(-\tilde{n}) = \ln \frac{1}{8h}.$$  

(5.37)

Clearly $\tilde{n}$ depends logarithmically upon $h$, with $\tilde{n} \to n$ as $h \to 0$, where $n$ is a non-negative integer. The first few roots of (5.37) are shown in figure 6 as a function of $h$. From (5.30), the scaled eigenvalues are

$$\alpha = \frac{\sqrt{2}}{2\tilde{n}(n, \ln h) + 1}, \quad n = 0, 1, 2, \ldots,$$

(5.38)

where for each $n$, $\tilde{n}$ is defined as the solution of (5.37) that tends to $n$ as $h \to 0$. We note that using the asymptotic behaviour of the Digamma function close to its poles it is easy to retrieve the first two terms in the logarithmic expansion (5.22), as well as higher-order ones.
Figure 8. Axisymmetric odd eigenfunctions from the asymptotic analysis of §5. (a) The outer potential corresponds to nearly touching perfectly conducting spheres at opposite uniform potentials [cf. (5.2) and (5.10)]. The outer potential is independent of the mode number \( n \) and the small parameter \( h \). (b) The transverse-field distribution in the gap region varies radially and depends on \( n \) and \( \ln h \) (here \( h = 0.001 \)); thick, thin and dashed lines depict modes \( n = 0, 1 \) and \( n = 2 \), respectively [cf. (5.40)].

5.7 Comparison with exact semi-analytical solutions

Figure 7 compares the asymptotic prediction (5.38) for the axisymmetric odd modes against the corresponding eigenvalues computed using the semi-analytical scheme discussed in §§2.3. The agreement is excellent for small \( h \) and on par with the agreement found for \( m \neq 0 \) in §4.

5.8 Eigenfunctions in physical space

The internal and external outer potentials (5.2) and (5.10), which are independent of the mode number and \( h \), are plotted in figure 8(a). In contrast, the gap and pole potentials depend on the mode number \( n \) and \( \ln h \) via the parameter \( \tilde{n} \). Note that when inverting (5.23) we may treat the two-dimensional Fourier transform as a Hankel transform:

\[
\chi(R, \bar{Z}) = \mathcal{H}_0 \left( s^{-1} Y(s) e^{-s\bar{Z}} \right). \tag{5.39}
\]

The field in the gap then follows from \( A(R)H_0(R) = V\chi(R,0) + 1 \) as

\[
\frac{d\Phi_0}{dZ} = \frac{V}{H_0(R)} \left( 1 + \sqrt{2}(1 + 2\tilde{n})\Gamma(-\tilde{n}) \right. \int_0^\infty e^{-\sqrt{2}sU(-\tilde{n},1,2\sqrt{2}s)J_0(Rs)} ds \bigg). \tag{5.40}
\]

The first three field profiles are plotted in figure 8(b).
6 Even modes

6.1 Gap region

Consider now the eigenfunctions that are even about the plane $z = 0$. In the gap region we pose the expansion

$$
\Phi \sim \Phi_0(R, Z) + h^{1/2}\Phi_{1/2}(R, Z) + h\Phi_1(R, Z) + \cdots.
$$

(6.1)

As we shall see, in the even case a leading-order solution entails consideration of the above three leading terms. The $O(1)$, $O(h^{1/2})$ and $O(h)$ balances of Laplace’s equation (3.6) respectively give

$$
\frac{\partial^2 \Phi_0}{\partial Z^2} = 0, \quad \frac{\partial^2 \Phi_{1/2}}{\partial Z^2} = 0, \quad \frac{\partial^2 \Phi_1}{\partial Z^2} = -\frac{1}{R} \frac{\partial}{\partial R} \left(R \frac{\partial \Phi_0}{\partial R}\right) + \frac{m^2}{R^2} \Phi_0,
$$

(6.2)

whereas (3.8) yields at these orders the symmetry conditions

$$
\frac{\partial \Phi_0}{\partial Z} = 0, \quad \frac{\partial \Phi_{1/2}}{\partial Z} = 0, \quad \frac{\partial \Phi_1}{\partial Z} = 0 \text{ at } Z = 0.
$$

(6.3)

It readily follows from (6.2) and (6.3) that $\Phi_0$ and $\Phi_{1/2}$ are independent of $Z$, i.e., $\Phi_0 = \Phi_0(R)$ and $\Phi_{1/2} = \Phi_{1/2}(R)$; furthermore, integrating the equation for $\Phi_1$ with respect to $Z$ and using (6.3) yields

$$
\frac{1}{H_0} \left(\frac{\partial \Phi_1}{\partial Z}\right)_{Z=H_0(R)} = -\frac{1}{R} \frac{d}{dR} \left(R \frac{\partial \Phi_0}{dR}\right) + \frac{m^2}{R^2} \Phi_0.
$$

(6.4)

6.2 Pole and outer regions and eigenvalue scaling

Continuity of potential (3.12) suggests expanding the pole potential as

$$
\Phi(R, \bar{Z}) \sim \Phi_0(R, \bar{Z}) + O(h^{1/2}).
$$

(6.5)

The scaling of the eigenvalue $\epsilon$ can now be extracted by considering the leading-order balance of the displacement-continuity condition (3.13):

$$
-\epsilon h^{-1/2} \frac{\partial \Phi_0}{\partial Z} \sim \frac{dH_0}{dR} \frac{d\Phi_0}{dR} - \frac{\partial \Phi_1}{\partial Z} \text{ at } Z = H_0(R), \quad \bar{Z} = 0.
$$

(6.6)

(Note that the independence of $\Phi_0$ upon $Z$ eliminates a potentially leading-order term proportional to $H_1(R)$.)

The scaling

$$
\epsilon = O(h^{1/2})
$$

(6.7)

allows balancing the left-hand and right-hand sides of (6.6). In this case, the projection of the radial field on the nearly transverse direction of the boundary normal, together with the comparably weak transverse field, balances the displacement associated with the strong transverse field in the pole region. Small $\epsilon$ implies that to leading order the external outer potential satisfies a homogeneous Neumann boundary condition on the tangent-sphere boundary and hence must diverge as the gap is approached. The gap and pole potentials are therefore asymptotically large in comparison to the outer potential.

Before proceeding with the analysis of the strongly localised even modes we note that
is not the only possible scaling. Indeed, the regular scaling $\epsilon = O(1)$ leads to the anomalous even modes, which we will study in §. Note that if $\epsilon$ is regular then (6.6) degenerates into a Neumann condition on $\tilde{\Phi}_0$.

### 6.3 Effective eigenvalue problem

In light of the above discussion, the eigenvalue is expanded as

$$\epsilon \sim -\alpha h^{1/2} + o(h^{1/2}), \quad (6.8)$$

where $\alpha$ is a positive constant. As in the odd case, we shall develop an effective eigenvalue problem governing the prefactor $\alpha$ and the pole potential $\tilde{\Phi}_0$. From (3.11), the latter satisfies

$$\partial^2 \tilde{\Phi}_0 + \frac{1}{R} \frac{\partial}{\partial R} \left( R \frac{\partial \tilde{\Phi}_0}{\partial R} \right) - \frac{m^2}{R^2} \tilde{\Phi}_0 = 0 \quad (6.9)$$

in the half space $\tilde{Z} > 0$, while (3.12) and (3.13) respectively yield the boundary conditions

$$\tilde{\Phi}_0(R, 0) = \Phi_0(R) \quad (6.10)$$

and

$$\alpha \frac{\partial \tilde{\Phi}_0}{\partial \tilde{Z}} = \frac{dH_0}{dR} \frac{\partial \tilde{\Phi}_0}{\partial R} \quad \text{at} \quad \tilde{Z} = 0, \quad Z = H_0(R). \quad (6.11)$$

Using (6.4), (6.9), (6.10) and (6.11) are combined to give

$$\alpha \frac{\partial \tilde{\Phi}_0}{\partial \tilde{Z}} + H_0 \frac{\partial^2 \tilde{\Phi}_0}{\partial Z^2} = \frac{R}{2} \frac{\partial \tilde{\Phi}_0}{\partial R} \quad \text{at} \quad \tilde{Z} = 0, \quad (6.12)$$

a boundary condition involving only $\tilde{\Phi}_0$. Lastly, since the outer potential is asymptotically smaller than the pole potential, the latter satisfies the attenuation condition

$$\tilde{\Phi}_0 \to 0 \quad \text{as} \quad R^2 + \tilde{Z}^2 \to \infty. \quad (6.13)$$

### 6.4 Solution of the effective eigenvalue problem

Consider the eigenvalue problem consisting of (6.9), (6.12) and (6.13). Following the analysis in the odd case, we look for solutions in the form

$$\tilde{\Phi}_0(R, \tilde{Z}) = \mathcal{H}_m \tilde{\Phi}(s, \tilde{Z}). \quad (6.14)$$

Given (6.14) and (6.13) we again write

$$\tilde{\Phi} = \frac{1}{s} Y(s) e^{-s\tilde{Z}} \quad (6.15)$$

with $Y(s)$ to be determined. To this end, transforming condition (6.12) gives

$$\alpha Y(s) + \mathcal{H}_m R \to s \left( \frac{R}{2} \frac{\partial \tilde{\Phi}}{\partial R} \right)_{Z=0} = s Y(s) + \frac{1}{2} \mathcal{H}_m \left( R^2 \frac{\partial^2 \tilde{\Phi}}{\partial Z^2} \right)_{Z=0} \quad (6.16)$$

Assuming that $\tilde{\Phi}_0(R, 0) = o(1/R^2)$ as $R \to \infty$ we find by integrating by parts

$$\mathcal{H}_m \left( \frac{R}{2} \frac{\partial \tilde{\Phi}}{\partial R} \right)_{Z=0} = \frac{Y}{s} - \frac{dY}{ds} \quad (6.17)$$
Nearly touching plasmonic spheres

and

$$\mathcal{H}_m \left( \frac{R^2 \partial^2 \Phi}{\partial \bar{Z}^2} \right)_{\bar{Z}=0} = -s \frac{d^2 Y}{ds^2} - 3 \frac{dY}{ds} - \frac{Y}{s} + \frac{m^2}{s} Y. \quad (6.18)$$

By substituting (6.17) and (6.18) into (6.16) we find

$$s \frac{d^2 Y}{ds^2} + \frac{dY}{ds} - \left( \frac{1 + m^2}{s} + 2s - 2\alpha \right) Y = 0. \quad (6.19)$$

Making the substitution

$$Y(s) = s^{1+m^2} e^{-\sqrt{2}s T(p)}, \quad (6.20)$$

where $p = 2\sqrt{2}s$, transforms (6.19) into the associated Laguerre equation (4.22) with parameters

$$\nu = 2\sqrt{1+m^2}, \quad n = \frac{\alpha}{\sqrt{2}} - \frac{1}{2} = \sqrt{1+m^2}. \quad (6.21)$$

Similar to the odd case, we conclude that $n$ must be a non-negative integer for the transform (6.14) to exist and for $\Phi_0(R, 0)$ to have the assumed attenuation rate as $R \to \infty$. The scaled eigenvalues are thus obtained as

$$\alpha = \sqrt{2} \left(n + \frac{1}{2} + \sqrt{1+m^2}\right), \quad n = 0, 1, 2, \ldots, \quad (6.22)$$

with associated eigenfunctions

$$Y(s) = s^{1+m^2} l_n^{(2\sqrt{1+m^2})}(2\sqrt{2}s), \quad (6.23)$$

where we have chosen the multiplicative factor to be unity.

### 6.5 Eigenfunctions in physical space

The eigenfunctions are readily inverted to give, for example, the radial distribution of the gap potential:

$$\Phi_0(R) = \int_0^\infty s^{1+m^2} e^{-s\sqrt{2} L_n^{(2\sqrt{1+m^2})}(2\sqrt{2}s)} J_m(Rs) ds. \quad (6.24)$$

It can be shown from (6.24) that $\Phi_0 = O(1/R^{1+\sqrt{1+m^2}})$ as $R \to \infty$, except for $m = 0$ in which case $\Phi_0 = O(1/R^3)$. These attenuation rates are compatible with our assumption $\Phi_0 = o(1/R^2)$ and imply that the outer potential is $O(h^{3/2})$ for $m = 0$ and $O(h^{(1+\sqrt{1+m^2})/2})$ for $m \neq 0$.

The quadrature (6.24) can be evaluated exactly for given $m$ and $n$. For example, for $(m, n) = (0, \{0, 1, 2\})$:

$$\Phi_0(R) = \left\{ \frac{\sqrt{2}}{(2 + R^2)^{3/2}}, \frac{\sqrt{2}(-2 + 5R^2)}{(2 + R^2)^{5/2}}, \frac{2\sqrt{2}(4 + 7R^2(R^2 - 2))}{(2 + R^2)^{7/2}} \right\}. \quad (6.25)$$
Figure 9. Radial distributions (6.25) and (6.26) of the gap potentials for even modes with $m = 0$ (a) and $m = 1$ (b). Thick, thin and dashed lines depict modes $n = 0, 1$ and $n = 2$, respectively.

Similarly, for $(m, n) = (1, \{0, 1\})$:

$$
\Phi_0(R) = \left\{ 2^{-2 - \frac{1}{2} \Gamma(\sqrt{2} + 2)} R_2 F_1 \left( 1 + \frac{1}{\sqrt{2}}, \frac{3}{2} + \frac{1}{\sqrt{2}}, -\frac{R^2}{2} \right),
\right.
$$

$$
2^{-\frac{1}{2} - \frac{1}{2} \Gamma(\sqrt{2} + 2)} R \left[ (4 + \sqrt{2})_2 F_1 \left( 1 + \frac{1}{\sqrt{2}}, \frac{3}{2} + \frac{1}{\sqrt{2}}, -\frac{R^2}{2} \right)
\right.
$$

$$
-4(1 + \sqrt{2})_2 F_1 \left( \frac{3}{2} + \frac{1}{\sqrt{2}}, 2 + \frac{1}{\sqrt{2}}, -\frac{R^2}{2} \right) \right\}. \quad (6.26)
$$

We plot the gap potentials (6.25) and (6.26) in figure 9.

6.6 Comparison with exact semi-analytical solutions

Figures 10–12 present, respectively for $m = 0, 1$ and 2, a comparison between the asymptotic prediction (6.8), with $\alpha$ given by (6.22), and the eigenvalues computed using the semi-analytical scheme discussed in § 2.3.

7 Anomalous even modes

7.1 Scaling and outer eigenvalue problem

We finally consider the anomalous even modes, for which

$$
\epsilon \sim \epsilon_0 + o(1) \quad \text{as} \quad h \to 0,
$$

with $0 > \epsilon_0 = O(1)$. In this case, the leading-order eigenvalues and eigenfunctions will be determined by an effective problem confined to the outer region.

Without loss of generality we now assume that the potentials are $O(1)$ in the outer
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Figure 10. Eigenvalues corresponding to axisymmetric \((m = 0)\) even modes as a function of \(h\), half the dimensionless gap width. The thick blue lines are the asymptotic predictions: localised gap modes \((-\epsilon < 1)\) — (6.8) and (6.22) for \(n = 0, 1, \ldots, 5\); anomalous modes \((-\epsilon > 1)\) — (7.1) and (7.15). The thin black lines are exact values obtained from the semi-numerical scheme described in §2.3. The thick red line marks the accumulation point \(\epsilon = -1\).

region. We accordingly pose the expansions

\[
\tilde{\psi} \sim \tilde{\psi}_0(\xi, \eta) + o(1), \quad \psi \sim \psi_0(\xi, \eta) + o(1),
\]

(7.2)

where \((\xi, \eta)\) are the tangent-sphere coordinates introduced in §3.1. The leading-order potentials satisfy Laplace’s equation

\[
\nabla^2 \tilde{\psi}_0 = 0 \quad \text{for} \quad 0 < \xi < 1; \quad \nabla^2 \psi_0 = 0 \quad \text{for} \quad \xi > 1;
\]

(7.3)

the continuity condition

\[
\tilde{\psi}_0 = \psi_0 \quad \text{at} \quad \xi = 1;
\]

(7.4)

and displacement condition,

\[
\epsilon_0 \frac{\partial \tilde{\psi}_0}{\partial \xi} = \frac{\partial \psi_0}{\partial \xi} \quad \text{at} \quad \xi = 1;
\]

(7.5)

the symmetry condition

\[
\frac{\partial \psi_0}{\partial \xi} = 0 \quad \text{at} \quad \xi = 0;
\]

(7.6)

and attenuation

\[
\psi_0 = 0 \quad \text{as} \quad \xi^2 + \eta^2 \to 0.
\]

(7.7)

The above eigenvalue problem is closed by matching considerations in the limit \(\eta \to \infty\). For \(\epsilon = O(1)\) the pole potential approximately satisfies a homogeneous Neumann
Figure 11. Same as figure [10] but for non-axisymmetric even modes with $m = 1$.

condition at $\bar{Z} = 0$ (see §§6.2) and thus forced solely by matching with the internal outer potential. For $m = 0$, these conditions are consistent with a uniform leading-order pole (and gap) potential. The requisite matching condition for $m = 0$ is thus

$$\psi_0 \to \text{const. as } \eta \to \infty. \quad (7.8)$$

A uniform pole potential is obviously impossible for $m \neq 0$. Instead, the leading-order pole solution must grow as $R^2 \to R^2 \to \infty$; hence the outer solution is asymptotically large compared to the potentials in the gap and pole regions. The requisite matching condition for $m \neq 0$ is thus

$$\psi_0 \to 0 \text{ as } \eta \to \infty. \quad (7.9)$$

7.2 Solution of the outer eigenvalue problem

A general solution that satisfies Laplace’s equations (7.3), the continuity condition (7.4), the symmetry condition (7.6), and attenuation (7.7) can be obtained by superposing solutions of Laplace’s equation in tangent-sphere co-ordinates [46].

$$\bar{\psi}_0(\xi, \eta) = (\xi^2 + \eta^2)^{1/2} \mathcal{H}_m[B(s)s^{-1} e^s \cosh(s) e^{-s}], \quad (7.10)$$

$$\psi_0(\xi, \eta) = (\xi^2 + \eta^2)^{1/2} \mathcal{H}_m[B(s)s^{-1} \cosh(s)], \quad (7.11)$$

where $B(s)$ is to be determined subject to the remaining conditions and existence of the transforms.

Transforming the displacement condition (7.5) in conjunction with (7.10) and (7.11),
followed by application of identity (4.18), yields:

\[ s^2 (\epsilon_0 \cosh s + \sinh s) \frac{d^2 B}{ds^2} + s (2\epsilon_0 \sinh s + (2s + \epsilon_0) \cosh s + \sinh s) \frac{dB}{ds} \\
+ [\epsilon_0 (s - m^2) \cosh s + (s\epsilon_0 - m^2) \sinh s] B = 0. \] (7.12)

In the limit \( s \to 0 \) solutions of (7.12) with \( m = 0 \) are easily shown to be \( O(1) \) or \( O(\log s) \), whereas for \( m \neq 0 \) the solutions are \( O(s^m) \) or \( O(s^{-m}) \). Only the regular solutions are compatible with our use of identity (4.18), which suggests rejecting the singular ones. The same conclusion also follows from the respective matching conditions (7.8) and (7.9).

Indeed, by inverting (7.11) it can be shown that

\[ B(s) \sim \int_0^\infty \frac{\psi_0(\xi, \tau/s)}{(s^2/\tau^2 + \tau^2)^{1/2}} J_m(\tau) \tau d\tau \quad \text{as} \quad s \to 0, \] (7.13)

whereby using (7.8) and (7.9) we find that \( B(s) = O(1) \) for \( m = 0 \) and \( B(s) = o(1) \) for \( m \neq 0 \).

In light of the above, a higher-order analysis of (7.12) in the limit \( s \to 0 \) shows that

\[ B \sim \text{const.} \times \left( s^m - \frac{2m + \epsilon_0}{(1 + 2m)\epsilon_0} s^{m+1} + \ldots \right) \quad \text{as} \quad s \to 0 \] (7.14)

for any positive integer \( m \), where given the multiplicative freedom the constant prefactor can be chosen arbitrarily. For any given \( \epsilon_0 \), the small-s behaviour (7.14) determines the solution to (7.12). An asymptotic analysis of (7.12) in the latter limit (48), however, yields solutions attenuating like \( s^{-1/(1+\epsilon)} \exp(-2s) \) and \( s^{-\epsilon/(1+\epsilon)} \) and clearly only the former is acceptable. Thus \( B(s) \) must satisfy both (7.14) and exponentially decay, which
is only possible for special values of $\epsilon_0$. We solve this eigenvalue problem using a shooting method, where we integrate backwards starting from the exponentially decaying solution at large $s$, choosing $\epsilon_0$ such that (7.14) is satisfied as $s \to 0$. Using this scheme we calculated the following eigenvalues:

\begin{align*}
    m = 0 : \quad & \epsilon \sim \{-1.6964, -1.3553, -1.2412, -1.1837, \ldots\}; \\
    m = 1 : \quad & \epsilon \sim \{-1.7999, -1.3862, -1.2562, -1.1926, \ldots\}; \\
    m = 2 : \quad & \epsilon \sim \{-1.4582, -1.2918, -1.2138, -1.1689, \ldots\},
\end{align*}

and corresponding eigenfunctions $B(s)$, where as usual for each $m$ the eigenvalues are ordered with increasing closeness to the accumulation point.

Excellent agreement between (7.15) and the eigenvalues computed using the semi-analytical scheme discussed in §§2.3 is presented in figure 10-12. Figure 13 depicts the first four modes for $m = 0$ and $m = 1$.

\section{Approximations in the literature}

As already noted, the sphere-dimer geometry has been extensively studied using the infinite algebraic system obtained from separation of variables in bi-spherical coordinates, or using transformation optics followed by separation of variables in spherical coordinates. In particular, this exact formulation has been used as a starting point for deriving approx-
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Approximations in the near-contact limit. It is useful to note in which cases these approximations coincide with the ones derived here using matched asymptotic expansions.

Consider first the odd modes. Our leading-order approximation for the eigenvalues (4.26) is equivalent to the approximation obtained by Klimov and coworkers [15,33,34]. As we have seen, this approximation is only accurate for the non-axisymmetric odd modes \((m \neq 0)\). The fact that there is a logarithmic error in the axisymmetric case \(m = 0\) was first noted by Lebedev et al. [35,36]. Our algebraically accurate approximation for \(m = 0\) (5.38) includes all the terms in an infinite expansion in inverse logarithmic powers. Incidentally, (5.22) reveals that the leading logarithmic correction given in [36] is off by a factor of two. Consider next the gap-localised even modes. Our approximation for the eigenvalues (6.22) is equivalent to the approximation obtained by Klimov and coworkers [15,34], only that their result is given in terms of an infinite series. We now see that the latter series is nothing but the expansion of \(\sqrt{1 + m^2} - m\) about \(m = \infty\).

Finally, we note that we have not found analytical approximations in the literature for the anomalous even modes. Pendry et al. provide a heuristic formula that in the axisymmetric case can be fitted to give good agreement with computed eigenvalues [37].

9 Concluding remarks

We have obtained asymptotic approximations for all the plasmonic eigenvalues and eigenfunctions of a sphere dimer in the near-contact limit. Using the spectral decomposition method for localised-surface-plasmon resonance, these results could be used to study the resonant response of a pair of closely spaced nanometallic spheres to arbitrary external forcing and for arbitrary material parameters (with ohmic losses accounted for). While this is outside the scope of this paper, we note that calculating the response in this way entails normalising the eigenmodes and evaluating the overlap between the excited eigenmodes and the external radiation. The description of the eigenmodes in the form of matched asymptotic expansions is particularly suitable for this purpose. Indeed, in many cases the associated integrals would be confined to the gap and pole regions, where the geometry and form of the solution are greatly simplified; in fact, the integration could be carried out directly in Hankel space by using the Plancherel theorem [47] (for an example, see [40]). Even without carrying out detailed calculations, the scalings and asymptotic structure we found could be used to rapidly estimate scattering cross sections, localisation and field enhancements, thus providing significant insight to plasmonic resonance with nearly touching particles.

Our approach could be generalised to related closely spaced geometries, such as dissimilar spherical particles, a particle close to a plane substrate, and in contrast to other analytical approaches, also non-spherical particle pairs. For modes strongly localised to the gap and pole regions, it is clear that the geometry would only come in through the curvatures at the point of minimum separation. For modes that involve the outer region to leading order, the outer problem could be reduced via matching to a regularised problem that is amenable to a straightforward numerical solution. Further generalisations of interest would be clusters of more than two closely spaced plasmonic particles [34,50] and periodic arrangements of nearly touching particles [15,51]. Matched asymptotic ex-
expansions could also be used to study other types of nearly singular geometries such as elongated nanorods \[29\].

It is important to emphasise that in this paper we analysed the near-contact limit with the mode numbers \(m\) and \(n\) fixed. It is evident that the near-contact and high-mode-number limits do not commute: in the former limit the eigenvalues tend to either negative infinity, zero or constants smaller than \(-1\), whereas in the latter all of the eigenvalues approach the accumulation point \(-1\). Intuitively, a high mode number implies fast oscillations along and exponential decay away from boundaries. When taking that limit with the sphere-dimer geometry fixed, the modes approach the high-mode-number modes of isolated spheres and accordingly \(\epsilon \sim -1 - 1/n\). A more interesting distinguished limit is \(n, m = O(1/h^{1/2})\), where the interaction between the spheres is important yet our present analysis breaks down. Approximations have been suggested in the limit of high azimuthal number \(m\) based on the bi-spherical scheme \[15\]: it has been shown that these modes are important when calculating the van der Waals attraction between spheres \[37, 52\]. It would be interesting to consider limits where either or both \(n\) and \(m\) are large using singular perturbation techniques. This will necessarily involve not only matched asymptotic expansions but also WKBJ theory \[39\], as the plasmon wavelength will be small compared with local radii of curvature.

We finally recall that our analysis is based on a quasi-static formulation valid in the limit where the structure is small compared to the wavelength. This is often the preferable scenario in nanoplasmonics, since for larger particles plasmon resonances are usually damped by radiation losses. Nevertheless, radiation corrections are often large enough to be of practical interest. Moreover, the singular near-contact and quasi-static limits probably do not commute, suggesting that in some cases retardation may play a role even for small structures. Remarkably, the plasmonic eigenvalue problem and its concomitant spectral theory can be generalised to the full Maxwell equations with a Silver–Müller radiation condition applied at large distances \[15, 53–57\]. In this formulation, which has several advantages \[54, 57\] over expansions in quasi-normal modes \[58\], the resonant permittivity values become frequency dependent and, owing to radiation losses, complex valued.

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**References**


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