Sum rules for surface plasmon frequencies

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Abstract

Surfaces exhibit spatially localized collective electronic excitations. The Mie modes of a particulate is one well-known example. We derive sum rules which (1) relate the surface mode frequencies of complementary systems like a sphere and a void and (2) relate the surface mode frequencies of a system with several interfaces to the ones for the individual surfaces. Our approach is of general nature since the results are based on properties of the Poisson equation and should be of interest for spectroscopies of matter in different fields of physics, in particular for scanning transmission electron microscopy.

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1. Introduction

The electrons in a spherical particulate in vacuum can sustain surface localized collective excitations of frequency \( \omega_p \sqrt{\varepsilon/(2\varepsilon + 1)} \), where \( \varepsilon = 1, 2, \ldots \) numbers the modes and \( \omega_p \) is the corresponding bulk collective excitation frequency for an infinite system. This bulk mode and its relation to similar excitations in different fields of physics is thoroughly discussed in Ref. [1]. For a void the corresponding result to the one above is \( \omega_p \sqrt{\varepsilon/(\varepsilon + 1)/(2\varepsilon + 1)} \). If we add the squared surface mode frequencies of the sphere and the void they thus add up to \( \omega_p^2 \), independent of \( \varepsilon \). See the pictorial representation of this in Fig. 1. We will show that this is a general result for any such complementary division of space into two distinct systems. This is the first sum rule. The second sum rule relates the frequencies of surface modes for a system with several surfaces to those of the individual surfaces.

A lot of insight in physics can be achieved by the use of conserved quantities and sum rules [2–4]. In the first case we have e.g. conservation of energy and momentum and in the second case e.g. the f-sum rule [5,6] which accounts for oscillator strengths; the number of degrees of freedom electrons have in a system. In fact before the invention of quantum mechanics Niels Bohr [7] made an intuitive and impressive guess about oscillator strengths and sum rules [8].
Fig. 1. Collective mode frequencies for a medium with three different geometrical shapes: bulk, a small particulate and a void corresponding to the small particulate. Our first sum rule states that the squared eigenmode frequencies of the particulate \( \omega_1^2 \) and the void \( \omega_2^2 \) add up to the bulk result \( \omega_b^2 \): \( \omega_1^2 + \omega_2^2 = \omega_b^2 \). Thus having calculated one of them the sum rule and the bulk plasma frequency gives the other one automatically.

In optics one uses a large number of integral constraints on optical constants in the form of sum rules. The simpler of these sum rules arise directly from the requirements of causality, inertia and the dynamical laws. These rules may therefore be viewed as the \( \omega \)-space equivalent of the dynamical laws of motion in time space. The sum rules provide a useful means of testing optical measurements against theoretical constraints and independently measured quantities [2,4]. Sum rules are a complement to full calculations, since by integrating out most coordinates they cannot provide detailed information. Instead, however, they can provide expressions for average properties of a system such as mean excitation energies. This is of interest in several different spectroscopies involving both light and charged particles. Through their general nature the sum rules also provide links between different fields of physics and sometimes also different disciplines.

Sum rules have historically played an important role in constraining theoretical approximations in many applications [9,10]. A useful and well-known sum rule is the one for the inverse bulk dielectric function of a homogeneous, isotropic system. It was first given by Nozières and Pines [11] based on the approach of Bethe [12]. This in turn was a generalization to arbitrary wave length of the Kuhn–Reiche–Thomas (f-) sum rule [5,6] mentioned above. The basic physical quantity in this sum rule characterizing the solid is the bulk plasma frequency \( \omega_p \) of the collective electronic motion. One application of this sum rule is in approximating the full response function of solids from their measured long-wavelength response functions [13].

With the development of electron energy loss spectroscopy (EELS), scanning transmission electron microscopy (STEM) and scanning tunneling microscopy (STM) one probes both bulk and surface properties of matter. This means that not only bulk modes but also surface modes are probed [14,15]. Energy losses will appear at characteristic surface mode frequencies. In this way one can today do spatially resolved spectroscopies on samples to study impact parameter dependence and complexity introduced due to geometrical effects, in effect leading to a new field of microprobe spectroscopy. Furthermore the parallel development of materials technology has made it possible to construct almost any geometrical configuration. Our interest in this paper is to express the connection between geometrical shape and characteristic loss energies. The classical dielectric theory has proved to be a good tool to analyze energy loss of e.g. STEM electrons [16–20]. Solutions have been worked out for a number of geometries. A challenge in the future is to move towards more complicated geometries and microstructures [21] still using classical dielectric theory. Such a theoretical development will benefit from knowing the normal modes and sum rules like the ones worked out in this paper. However, the notion of a collective motion is not only confined to solid state physics alone; it also appears in other fields such as nuclear physics where sum rule techniques have been developed substantially [22,23] as well as in cluster physics [24]. Our results in what follows have therefore a larger applicability going beyond electrodynamics in their implications.

2. Rewriting the Poisson equation

A medium subjected to an external electro-magnetic disturbance (photon, electron, ion, . . .) will respond and develop an induced screening charge. In what follows we will present an equation of motion
for this screening charge. This yields the superficial collective excitation frequencies of the medium.

If we have no external charges to a system we can solve for the normal modes associated with surface excitations using one of the Maxwell equations:

\[ \nabla \cdot \mathbf{D} = 0. \]  

(1)

The displacement field \( \mathbf{D}(\mathbf{x}, \omega) \) (time is Fourier transformed with respect to \( \omega \)) is within linear response related to the electric field \( \mathbf{E}(\mathbf{x}, \omega) \) through the dielectric tensor \( \varepsilon_{ij}(\mathbf{x}, \mathbf{x}', \omega) \) according to:

\[ D_i(\mathbf{x}, \omega) = \sum_j \int d^3x' \varepsilon_{ij}(\mathbf{x}, \mathbf{x}', \omega) E_j(\mathbf{x}', \omega). \]  

(2)

To make our presentation as simple as possible we let \( \varepsilon_{ij} \) be diagonal and connect \( \mathbf{D} \) and \( \mathbf{E} \) locally, viz. \( \mathbf{D}(\mathbf{x}, \omega) = \varepsilon(\mathbf{x}, \omega) \mathbf{E}(\mathbf{x}, \omega) \). This form is still general enough to contain the necessary surface information through the \( x \)-dependence of \( \varepsilon \). Combining Eq. (1) and the local version of Eq. (2) we now get

\[ \varepsilon(\mathbf{x}, \omega) \nabla \cdot \mathbf{E} + \mathbf{E} \cdot \nabla \varepsilon(\mathbf{x}, \omega) = 0. \]  

(3)

In bulk we would not have any spatial dependence on \( \mathbf{x} \) in \( \varepsilon \). Possible modes are then given by \( \varepsilon(\omega) = 0 \); the well-known bulk plasmon condition. However close to a surface \( \varepsilon(\mathbf{x}, \omega) \) will go between the solid’s bulk value \( \varepsilon_s(\omega) \) and the bulk dielectric function of the surrounding medium \( \varepsilon_r(\omega) \). We therefore write:

\[ \varepsilon(\mathbf{x}, \omega) = f_0(\mathbf{x}) \varepsilon_s(\omega) + [1 - f_0(\mathbf{x})] \varepsilon_r(\omega), \]

where \( f_0(\mathbf{x}) \) is a function which is unity in one medium (0) and zero in the complementary medium. In a classical situation \( f \) switches between unity and zero in a step-wise manner at the surface but in a more general situation it can have a smooth transition in between. Hence \( f_0(\mathbf{x}) \) defines the shape of the surface.

Combining Eqs. (1)–(3), and the division of \( \varepsilon(\mathbf{x}, \omega) \) given above, with Poisson’s equation \( \nabla \cdot \mathbf{E} = \rho_{\text{ind}}(\mathbf{x}, \omega) \) we get the following equation of motion for the induced screening charge \( \rho_{\text{ind}}(\mathbf{x}, \omega) \):

\[
\Lambda(\omega) \rho_{\text{ind}}(\mathbf{x}, \omega) = -\frac{1}{4\pi} \nabla \cdot \left[ f_0(\mathbf{x}) \nabla \int d^3x' \frac{\rho_{\text{ind}}(\mathbf{x}', \omega)}{|\mathbf{x} - \mathbf{x}'|} \right]
\equiv \hat{\Lambda}\rho_{\text{ind}}(\mathbf{x}, \omega),
\]  

(4)

where we have defined

\[
\Lambda(\omega) \equiv \frac{\varepsilon_s(\omega)}{\varepsilon_s(\omega) - \varepsilon_r(\omega)}.
\]  

(5)

Eq. (4) introduces the definition of an operator \( \hat{\Lambda} \) whose eigenvalues are \( \Lambda(\omega) \). This yields possible surface mode frequencies through Eq. (5) and eigenvectors \( \rho_{\text{ind}}(\mathbf{x}, \omega) \). For the case of a metal, with plasma frequency \( \omega_p(\varepsilon_s(\omega) = 1 - \omega_p^2/\omega^2) \), next to vacuum \( (\varepsilon_s(\omega) = 1) \), \( \Lambda(\omega) = (\omega/\omega_p)^2 \). In this case \( f_0(\mathbf{x}) \) is nothing but the electron density profile of the metal normalized to unity inside the bulk. Eq. (4) has been obtained earlier in terms of the induced potential instead, expressed as surface integrals [25,26] and converted to an eigenvalue problem in a very neat manner in [27–29]. We focus here on the induced charge density instead, as the important physical variable, and keep the full three-dimensional nature of the problem to start with. Before that we should just mention that the so called spectral representation of Bergman [27], for the effective dielectric function of a two-component material, is a sum over bulk and surface plasmon eigenmode terms having poles when \( \Lambda \), as defined in Eq. (5), equals the so called depolarization factor [30] of the set-up. These surface and bulk terms fulfill sum rules [31–33] which are analogous of the f-sum rule.

We see from Eq. (4) that in a homogenous medium where there are no gradients we only have the bulk plasmon \( \omega_p \) as a solution \( (\Lambda = 1) \), defined by \( \varepsilon_s(\omega_p) = 0 \). The presence of a surface, and hence density gradients, provides surface information which determines the actual frequencies of the possible surface modes. In the classical case, which is of most interest in e.g. STEM applications, where \( f_0(\mathbf{x}) \) makes a jump at the surface the induced density becomes localized right at the interface since it is proportional to \( \nabla f \). For a smooth transition a non-vanishing \( \nabla f_0(\mathbf{x}) \) defines the extension of \( \rho_{\text{ind}}(\mathbf{x}, \omega) \) and hence the extension of the surface or interface region.

3. Surface modes’ sum rules

After this mathematical formulation of the physics we are ready to derive two geometrical sum rules.
3.1. First sum rule

Let the surface for one medium (\(\omega\)) have a unit normal vector \(\hat{s}\) at the position \(x\). Then from Eq. (4) we have

\[
\hat{\rho}_o = \left[ f_o(x) - \frac{1}{4\pi} \frac{\partial f_o}{\partial s} \int d^3x' \frac{1}{|x - x'|} \right].
\]  

(6)

The complementary system (c) has a structure function \(f_c \equiv 1 - f_o\). Using this in Eq. (6) we see immediately that \(\hat{\rho}_c = 1 - \hat{\rho}_o\). Thus if \(\hat{\rho}_o\) has the eigenvalue \(\Lambda(\omega_o)\) then \(\hat{\rho}_c\) has the same eigenvalue \(\Lambda(\omega_c)\). Provided the induced density \(\rho_{\text{ind}}\) is the same in both systems we then get the first sum rule:

\[
\Lambda(\omega_o) + \Lambda(\omega_c) = 1,
\]  

(7)

for the surface mode eigenvalues of a complementary system: \(f_o(x) + f_c(x) = 1\). Eq. (7) has its greatest virtue for systems where \(\rho_c\) makes a very sharp jump. Now for instance having STEM applications in mind where classical interfaces and local dielectric functions are sufficient, with present resolution, the conditions for the full use of Eq. (7) are really at hand. As remarked above the eigenmode frequencies are found when \(\Lambda = n\), where \(n\) is the so called depolarization factor of the medium [30]. Needle like structures would have small (positive) values of \(n\) and plate like objects would have large values (< 1) of \(n\). For a sphere \(n = 1/3\) leading to the well-known surface mode condition \(\varepsilon_s(\omega_o) + 2\varepsilon_c(\omega_c) = 0\). If we denote by \(n_o\) the depolarization factor of the ordinary medium and by \(n_c\) that of the complementary medium another way of stating our sum rule in Eq. (7) is to say

\[
n_o + n_c = 1.
\]  

(8)

This sum rule should not be confused with the internal one for a single body where \(\Sigma_{i=x,y,z} n_i = 1\) [30].

Notice that \(\Lambda\) in itself is a function of the frequencies we are looking for (cf. Eq. (5)). For the special case of a metal/vacuum interface where \(\Lambda(\omega) = \frac{\omega}{\omega_p}\), or for that matter any interface combination leading to a \(\Lambda\) being quadratic in \(\omega\), Eq. (7) reads:

\[
\omega_o^2 + \omega_c^2 = \omega_p^2,
\]  

(9)

independent of the actual form of the surface profile functions \(f_o,c(x)\) in directions perpendicular to \(\hat{s}\), the surface normal. \(\omega_p\) is the bulk plasma frequency of the metal in question. This relation was first introduced by Ronveaux et al. using a different approach [34].

A small sphere and the void was an example given in the introduction. Another example is an infinite space divided into two distinct halves (see Fig. 2). By symmetry \(\omega_o^2 = \omega_c^2 = \omega_p^2/2\) yielding the well-known factor 1/2 for the squared surface plasmon frequency of a semi-infinite metal adjacent to vacuum compared to the squared bulk plasma frequency. For semi-infinite dielectrics the symmetry of Eq. (7) gives right away \(\Lambda(\omega_o) = 1/2\) or \(\varepsilon_o(\omega_o) + \varepsilon_c(\omega_c) = 0\) which is the well-known so called surface plasmon condition in this case. A beautiful illustration of Eq. (9) is found in Ref. [35] where the frequencies squared of the modes of a ridge on a surface and that of the complementary channel geometry add up to \(\omega_p^2\).

3.2. Second sum rule

Fig. 2. Surface plasmon oscillation frequency for a semi-infinite metal. The symmetry of the problem and our first sum rule immediately yield that the squared frequency of the semi-infinite medium is 1/2 that of the bulk medium \((\omega_p^2)\). Thick lines denote surfaces.

So far we have considered a situation which is best characterized as having only one interface. The simplest example of the opposite is a thin film of thickness \(L\) having two surfaces. Let \(\rho_o(x,\omega)\) be the screening charge at one surface and \(\rho_c(x,\omega)\) the screening charge at the other one. The total induced density is a superposition of \(\rho_1\) and \(\rho_2\). It is then
convenient to define the following matrix elements of \( \mathcal{O} \) in Eq. (4) in the \((\rho_1, \rho_2)\)-basis:

\[
O_{ij} = \frac{\int dV \rho_i(x, \omega) \left( \mathcal{O} \rho_j(x, \omega) \right)}{\left[ \int dV \rho_i^2(x, \omega) \right]^{1/2}} \left[ \int dV \rho_j^2(x, \omega) \right]^{1/2},
\]

\((i,j = 1, 2)\). Notice that \( \rho_j \) is not an eigenfunction of the whole operator \( \mathcal{O} \) since \( \mathcal{O} \) contains information about both surfaces. In fact the electrostatic coupling between \( \rho_1 \) and \( \rho_2 \) (present in \( \mathcal{O}_{12} \)) leads to the change in frequencies of the individual surfaces (\( \mathcal{O}_{11} \) and \( \mathcal{O}_{22} \)). Thus \( \mathcal{O}_{12} \to 0 \) when \( L \to \infty \) since then we are back in the bulk situation.

We will only consider a situation where the induced screening charges are not overlapping: \( \int dV \rho_1 \rho_2 = 0 \) or very small. In fact if \( \rho_1 \) and \( \rho_2 \) were overlapping there is no point in speaking about two separate quantities and our method is of little use. Thus the constraint of no overlap is not a real deficiency in what follows. Finding the eigenvalues of the \( 2 \times 2 \) matrix \( \mathcal{O}_{ij} \) gives us two surface mode eigenvalues \( \Lambda(\alpha) \) and \( \Lambda(\beta) \), for the thin film \((\alpha(\beta) = \text{anti(bonding)})\). They are out-of-phase and in-phase linear combinations of the induced screening charges \( \rho_1 \) and \( \rho_2 \). Now we let \( \mathcal{O}_{11} = \Lambda(\alpha) \) and \( \mathcal{O}_{22} = \Lambda(\beta) \). \( \Lambda(\alpha) \) and \( \Lambda(\beta) \) are the original eigenvalues characterizing respectively the individual surfaces making up the thin film. Then since the trace of a matrix does not depend on the basis set (interaction) we get immediately our next sum rule for a system with two surfaces:

\[
\Lambda(\alpha) + \Lambda(\beta) = \Lambda(\alpha) + \Lambda(\beta) = 1,
\]

where the last line follows from Eq. (7). For the metal/vacuum situation Eq. (11) reads \( \omega_{\alpha}^2 + \omega_{\beta}^2 = \omega_p^2 \) and \( \omega_{\alpha}^2 + \omega_{\beta}^2 = \omega_p^2 \). It can be generalized to more than two interfaces in a straightforward manner. Notice that the individual values for \( \Lambda(\alpha, \beta) \) depend strongly on the surface/surface coupling while \( \Lambda(\alpha, \beta) \) are a characteristic feature of each individual surface when neglecting the change in \( \rho_{1,2} \) due to the interaction as well as any overlap between them. For a metal film with equal and abrupt surfaces \( \omega_{\alpha}^2 = \omega_{\beta}^2 = \omega_p^2 / 2 \) and hence \( \omega_{\alpha}^2 + \omega_{\beta}^2 = \omega_p^2 \). The actual values of \( \omega_{\alpha}^2 \) and \( \omega_{\beta}^2 \) were derived many years ago by one of us [14]: \( \omega_{\alpha, \beta}^2 = (\omega_p^2 / 2)(1 \pm e^{-\kappa L}) \). \( \kappa \) is the conserved wave vector parallel to the surface and \( L \) is the film thickness. The exponential factor is a direct consequence of the interaction. For a film surrounded by a dielectric \( \varepsilon_s \), \( \Lambda \) is not proportional to \( \omega^2 \), and the meaning of Eq. (11) is perhaps less clear. However in this case \( \omega_{\alpha, \beta}^2 = \omega_p^2 / [1 + \varepsilon_s(\coth \kappa L / 2, \tanh \kappa L / 2)] \) and inserting this in \( \Lambda \equiv \varepsilon_s / (\varepsilon_s - 1 + \omega_p^2 / \omega^2) \) one readily finds, as should be the case, that \( \Lambda(\alpha) + \Lambda(\beta) = 1 \) for any value of \( \kappa L \).

4. Examples

We have already in connection with formulating the two sum rules discussed a number of well-known cases for surface plasmons. In this section we will give three more extended examples showing the use of the sum rule to get an increased insight into a problem or as a check on the convergence of a numerical calculation. We will also connect different areas of physics through those examples. The first, for example, connects surface, atomic and stopping power physics [36–38].

4.1. Collective modes in fullerenes

The new form of carbon, as expressed so beautifully in the \( C_{60} \) molecule [36], opens up new frontiers of research and connects different subfields of physics. The 60 carbon atoms form a thin hollow almost spherical shell with radius 3.6 Å and thickness corresponding to approximately one carbon atom. Based on an earlier treatment of possible collective modes in one of the shells of the \( Xe \) atom [37] we found the following frequencies for the in-phase and out-of-phase modes of a spherical fullerene molecule [38]:

\[
\omega_{\alpha, \beta}^2 = \left[ \frac{1}{2} \left( 1 \pm \frac{1}{2\ell + 1} \right) \right] \left[ \frac{1}{2} \left( 1 + 4\ell(\ell + 1) \left( \frac{r_1}{r_2} \right)^{2\ell + 1} \right) \right],
\]

with \( \ell = 1, 2, ..., \) and \( r_1 \) and \( r_2 \) are the radius of the inner and outer surfaces respectively. The plasma frequency is related to the effective number of \( \pi \)-electrons responding [38].
We first observe that $\omega_1^2 + \omega_2^2 = \omega_2^2$, independent of $\ell$ and $r_1/r_2$; fulfilling the second sum rule. For $r_1 = 0$, Eq. (12) gives the void and sphere frequencies as it should. For $C_{70}$ and other more deformed shells a similar treatment can be made [39], again the modes found conform to our sum rules. Apart from generating the frequencies Eq. (4) also yields the eigenvectors so one can calculate a spectral distribution of mode strengths. Denote by $S_a$ and $S_b$ the weights of $\omega_a$ and $\omega_b$ so found. With the f-sum rule yielding $S_a + S_b = 1$, the $\omega^2$-sum rule [10] giving $\omega_a^2 S_a + \omega_b^2 S_b = 1/3$ and our new sum rule demanding $\omega_f^2 + \omega_2^2 = 1$ (all frequencies normalized in units of $\omega_p$) there is little room for the four quantities to change a lot. They are more or less constrained by the different sum rules. This is important for instance in Stopping theory where one needs to calculate the average excitation energy $I_o$ of a system [8]. For the fullerene molecule our treatment yields $I_o = \omega_a^2 + \omega_b^2$, which with the three constraints above gives very little variation in $I_o$, and hence we will expect little variation in stopping power between the different forms of fullerenes as well as the different forms of carbon; at least within our framework here, where we exhaust the f-sum rule by only considering collective excitations.

With all the different forms of fullerenes appearing; tubes, onions, doped etc this will be an interesting field of research for years to come where effects of geometry can be studied first hand.

4.2. Scanning tunneling microscope light emission

One of the major advances in surface science the last decade has been the development of the Scanning Tunneling Microscope [40]. Though originally made to measure the current passing between the scanning tip and a sample many different types and modes of operation have been explored. Recently several groups have detected photons emitted in inelastic tunneling events [41]. The yield is very small and if it were not for a field enhancement in the cavity formed between the tip and sample one would hardly detect any light at all. This field enhancement is related to that the near-field of the emitting electron can couple to and excite the surface modes in the system. For a real working situation, with tip and sample very close, the tip and sample modes couple strongly and change frequencies. However our sum rule states that the sum of these (squared) frequencies stays the same and equals the sum of squared surface plasmon frequencies for the isolated tip and isolated sample, independent of the strength of the interaction. We will see in the next section how this can be used to monitor the accuracy of such strong coupling calculations. Here we will briefly deal with the modes of the isolated tip. Experiments on light emission from a scanning tunneling microscope have been rather successfully explained [41,42] in a model where the tip is replaced by a sphere. In order to see the order of approximation made one has to look into different shapes of the tip – especially such which can sustain a non-zero charge density (remember that the isolated sphere, being charge neutral, has only the dipolar mode as the lowest one). We are not here going to give the full calculation instead we will give the expression for the possible modes of a more realistic model of the tip. In this respect prolate spheroidal coordinates are very useful since they describe a hyperboloid of revolution characterized by a parameter $\eta$. $\eta = \cos \theta$, where $2 \theta$ is the opening angle of the cone which is asymptotic to the hyperboloid, $\eta = 0$ corresponds to a planar surface which should facilitate a description of the sample surface when calculating the change in mode frequencies when tip and a planar sample interact. In this coordinate system the surface modes are solutions to [43]:

$$\epsilon(\omega) = - \frac{P_r(\eta_0) P_r(\eta_0)}{P_r(-\eta_0) P_r(-\eta_0)}.$$

where $\eta_0$ characterizes the particular geometry chosen and $P_r$ is a Legendre function where $-1/2 < \nu < 1$. The spectrum is thus continuous compared to the discrete spectrum of the model with a sphere over a plane.

The first sum rule can be used to check if Eq. (13) has the right symmetry. Solving Eq. (13) we get modes $\omega_{\nu,0}$. The complementary body is one having a hyperboloid hole which by symmetry is nothing but the $\eta \rightarrow -\eta_0$ body. Under this change Eq. (13) shows that $\epsilon(\omega_{\nu,0}) \cdot \epsilon(\omega_{\nu,c}) = 1$ which for a Drude dielectric function implies that $\omega_{\nu,0}^2 + \omega_{\nu,c}^2 = \omega_0^2$. as our first sum rule states. Thus Eq. (13) is consistent with the first sum rule. When doing the full coupled
Fig. 3. The figure shows a check on a numerical calculation for the interaction between two equal spheres as a function of \( \gamma \) (sphere diameter/center-center distance) for different sizes of the interaction matrix. The size of the matrix \( \ell_{\text{max}} \) depends on how many modes are included in the calculation. We use our second sum rule which implies that independent of the distance \( \gamma \) the sum over squared eigenfrequencies of the non-interacting system should match the corresponding sum for the interacting system. We define the ratio of these as \( Q_m = 0 \) (see Eq. (14)). For \( \gamma \) approaching unity we clearly see the need for including more modes (increasing \( \ell_{\text{max}} \)) since then the spheres are very close to each other. Typically \( \ell_{\text{max}} \approx 1/(1 - \gamma) \) to obtain a good accuracy at a given distance \( \gamma \).

tip–sample calculation the isolated tip modes from Eq. (13) and the surface modes (actually corresponding to \( \eta_0 = 0 \) where \( \varepsilon(\omega) = -1 \) as it should) should satisfy the second sum rule. For more details about this geometry see Ref. [44].

4.3. Convergence check for a bispherical system

In this section we will use the sum rule in Eq. (11) to consider the accuracy of a calculation of the interaction between two spheres, which at close distances is an elaborate problem because of the strong coupling [45–47]. Eq. (11) can then be used to estimate the accuracy of the calculation in the following way. Assume for simplicity two identical metallic spheres (with diameter \( D \)) in vacuum, their centers a distance \( d \) apart. Let \( \gamma = D/d \) be the normalized length variable (\( \gamma = 1 \) corresponds to touching spheres). Our second sum rule states that summing all squared eigenfrequencies \( \omega^2(\gamma) \) for the interacting spheres (symmetric (s) and antisymmetric (as) modes), for a given \( m \) (rotational symmetry) should be equivalent to the sum over the non-interacting modes. Form a ratio \( Q_m \) between these two summations:

\[
Q_m = \left[ \frac{2 \sum_{\ell = m}^{\ell_{\text{max}}} \frac{\ell \omega_p^2}{2\ell + 1}}{\sum_{\ell = m, s&as}^{\ell_{\text{max}}} \omega^2(\gamma)} \right].
\]

\( \omega_p^2 \) is the squared surface plasmon resonance frequency of an individual sphere and \( \ell_{\text{max}} \) is the upper \( \ell \)-value used in the actual numerical calculation. Deviations of \( Q_m \) from unity indicates mistakes or numerical problems in the calculations.

In Fig. 3 we show the result of such a calculation of \( Q_0 \) for three different maximum sizes of the interaction matrix (the number of modes included). We see that when \( \gamma \rightarrow 0.95 \) clear deviations from fulfilling the sum rule are at hand. This indicates insufficient number of modes included, when the interaction strength increases. Our results show that a choice of \( \ell_{\text{max}} \approx 1/(1 - \gamma) \) will give reasonable results. We find the same scaling in a different convergence check employed in Ref. [46]. We leave for the future, however, a more thorough analysis of this numerical problem for the two-sphere problem which has attracted attention recently [47,48].

5. Conclusions

Through a simple equation of motion for the screening charge at solid surfaces we have derived two useful sum rules. The first one relates bodies which have complementary shapes, i.e. together they fill up all space. The second relates the interacting modes set up in one system with two or more interfaces. In both situations our sum rules tell us that the sum of eigenvalues of the collective surface modes add up to unity when properly normalized. These sum rules could be used to understand the response of more complex structures. They can also give a check on numerical calculations as well as approximations done within a certain calculational scheme as we have demonstrated in our three examples.

The existence of sum rules makes possible intelligent guesses on unknown systems before one endeavours on large-scale computations. They make it
possible to approximate complicated situations and they have the potential of reducing the amount of work needed in a given situation. Having found the modes for a sphere over a plane e.g. we also get for free the surface mode frequencies for a void hidden in a material. Another example is a set of interacting spheres of material A embedded in a medium B. A recent example of this would be C_{60} molecules in a matrix. The second sum rule implies a spread of the interface modes which depends on the relative position (interaction) of the spheres. Such spreading of modes is not included in effective medium approaches such as the Maxwell–Garnett theory since such a theory can only give a single interface loss depending on the composition. As has been pointed out by Walls and Howie there exists experimental results which cannot be explained in terms of any available effective medium theory [21]. We thus foresee that the sum rules discussed in this paper will be helpful in further analysis of such results and others.

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