Quantum effects and nonlocality in strongly coupled plasmonic nanowire dimers

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Abstract: Using a fully quantum mechanical approach we study the optical response of a strongly coupled metallic nanowire dimer for variable separation widths of the junction between the nanowires. The translational invariance of the system allows to apply the time-dependent density functional theory (TDDFT) for nanowires of diameters up to 10 nm which is the largest size considered so far in quantum modeling of plasmonic dimers. By performing a detailed analysis of the optical extinction, induced charge densities, and near fields, we reveal the major nonlocal quantum effects determining the plasmonic modes and field enhancement in the system. These effects consist mainly of electron tunneling between the nanowires at small junction widths and dynamical screening. The TDDFT results are compared with results from classical electromagnetic calculations based on the local Drude and non-local hydrodynamic descriptions of the nanowire permittivity, as well as with results from a recently developed quantum corrected model. The latter provides a way to include quantum mechanical effects such as electron tunneling in standard classical electromagnetic simulations. We show that the TDDFT results can be thus retrieved semi-quantitatively within a classical framework. We also discuss the shortcomings of classical non-local hydrodynamic approaches. Finally, the implications of the actual position of the screening charge density at the gap interfaces are discussed in connection with plasmon ruler applications at subnanometric distances.

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1. Introduction

In metal nanoparticles, collective excitation of the valence electrons induced by an incident electromagnetic field, the localized plasmon, leads to a plethora of optical phenomena of significant current interest. Strong plasmonic enhancement of the local fields [1–5] opens a route to numerous practical applications such as surface enhanced Raman scattering (SERS) [6–9], and optical nano-antennas [10–13]. In nanoparticle assemblies, the hybridization of plasmonic modes can serve for guiding of the propagating fields [14, 15], as well as offering a path for rational engineering of a desired optical response and local field profile [4]. Not only can light harvesting and sensing properties thus be greatly improved, but the strong geometry dependence of the optical response can also be used as a plasmon ruler to determine the arrangement and nanoscale distances within chemical or biological species [4, 16–21].

Significant advances in fabrication and manipulation techniques nowadays allow for precise control of the geometry of the structure [21–29]. In particular, for nanoparticle assemblies, the width of the gap between adjacent nanoparticles can be brought below one nanometer so that electron tunneling across the junction becomes possible. Thus, plasmonic devices progressively face a quantum regime which represents a significant challenge for current theoretical approaches. Indeed, most of the descriptions of the optical response of metallic nanosystems so far are based on the solution of the classical Maxwell equations where the nanoparticles are modeled with sharp surfaces and the quantum nature of electrons forming the screening charge is neglected. Effects such as the experimentally observed appearance of the charge transfer plasmon for conductively coupled particles prior to direct contact [28, 29], or optical rectification [23, 30] cannot be addressed within a classical framework. As shown in recent quantum mechanical calculations [28, 31–37] the main ingredients missing in classical models are the spill out of conduction electrons outside the nanoparticle surfaces, and the finite spatial profile of the plasmon-induced screening charge. The use of nonlocal dielectric functions [2,35,38–46] can somehow account for the latter effect, introducing a smooth variation of the electron density rather than one infinitely sharp, as assumed in the classical local approach. However, the spill out of electrons outside the nanoparticle surfaces and the associated tunneling across narrow interparticle junctions requires a special treatment that fully accounts for quantum effects.

In this respect, the data available on the coupled nanoparticle dimer are quite revealing. A dimer is a prototypical system for plasmonic nanoparticle coupling, which has been extensively studied [4,47–49]. Theoretical studies based on the solution of the classical Maxwell equations predict a discontinuous transition from the capacitively to conductively coupled particles. For vanishing junction width, the fields in the junction diverge and the plasmon modes experience diverging red shifts as a result of the interaction between the high charge densities induced at the opposite sides of the junction [3-8, 47-49]. The charge transfer plasmon appears abruptly after the conductive contact [48,50]. In an attempt to raise this nonphysical result, nonlocal calculations based on the hydrodynamic model (NLHD) [2,38,39,43–45] have shown that because of the finite spatial profile of the plasmon-induced screening charge, the fields in the junction stay finite albeit large. The number of plasmon resonances and their frequency shift is much reduced compared to local classical predictions. On the other hand, it follows from the quantum treatments [28,31–33,35–37] that for narrow junctions, electron tunneling can short circuit the junction and quench the plasmon-induced field enhancement. The nanoparticles thus appear conductively connected prior to direct contact, and the transition between the non-touching and conductive contact regimes is continuous. In particular, the charge transfer plasmon associated with interparticle charge transfer [51–57] progressively emerges in the optical response of the system, as has been fully confirmed in recent experiments [28, 29]. These quantum effects can be reproduced with the Quantum Corrected Model (QCM) [33] that treats the junction between the nanoparticles as an effective medium mimicking quantum effects within the classical local

Maxwell theory [28, 29].

While quantum calculations provide an *a priori* exact answer to the problem of the optical response of a large amount of interacting electrons, they are extremely heavy numerically, so that to date their application has been limited to rather small coupled plasmonic systems. It is thus of considerable interest to have bench mark quantum results for a plasmonic dimer as large as possible allowing a detailed comparison with the macroscopic theory derived from Maxwell's equations. This would provide the assessment of the role of quantum mechanical effects and of the possibility to account for these effects within classical theory. In this article, which concerns the optical response of a strongly coupled metallic nanowire dimer, we offer such a comparison between full quantum and classical calculations of the optical response. We show that the quantum mechanical results can be quantitatively reproduced with simple models allowing a *local classical* description of quantum mechanical effects such as electron tunneling across narrow plasmonic gaps and dynamical screening.

2. Model and computational aspects

The advantage of the choice of the plasmonic nanowire dimer for the bench mark calculations is that this system is well characterized both from the experimental and theoretical point of view [3, 4]. Full numerical studies based on the solution of the classical Maxwell's equations have been performed [24, 50, 58–62], as well as semi-analytical studies based on transformation optics are available [43, 44, 63]. The system has also been investigated using non-local hydro-dynamic descriptions [35, 43–46], and recently the full quantum studies using time dependent density functional theory (TDDFT) have been reported [35–37].

The present work continues our earlier study [36] of the energetics and scaling properties of the plasmon resonances in the coupled nanowire dimer illustrated in Fig. 1. Two identical nanowires in vacuum are separated by a junction of variable separation width S, as measured between their surfaces. The nanowires are infinitely extended along the *z*-axis and each nanowire has a circular cross-section of diameter D. The incident light is polarized along the inter-particle axis x.

We focus here on the detailed comparison between full quantum and classical descriptions of the optical response. The extinction cross-section and near field enhancement are calculated within TDDFT, classical Drude, NLHD, and QCM approaches for variable width of the junction *S*. The range of considered *S* extends from large separations down to overlapping nanowires (negative *S*) where conductive contact is established. This allows an analysis of the progressive emergence of the interparticle tunneling, and of its role in the evolution of the plasmonic modes of the system upon reduction of the width of the junction between the nanowires.

For the nanowires we adopt the cylindrical jellium model (JM). Despite its simplicity, this model captures the collective plasmonic modes of the conduction electrons and has demonstrated its predictive power for quantum effects in nanoparticle dimers [28,29]. While obviously not providing chemical accuracy, the JM is well suited for the description of nonlocal effects derived from the conduction electrons such as dynamical screening of the external field and tunneling as we discuss below. Along with the possibility to treat relatively large systems on a full quantum level, the JM model allows for direct comparison between results from quantum and classical approaches. Indeed, the physics underlying the Drude model for the metal response as well as the refinement of the Drude model introduced by the nonlocal hydrodynamic model corresponds best to free electron metals. For noble metals, such as silver and gold, the contribution of the localised d-electrons to the screening would obscure the comparison. The high symmetry of the nanowire dimer with its translational invariance along the *z*-axis allows us to address at the full quantum level cylinders with diameters D = 6.2 nm, and D = 9.8 nm showing fully developed plasmonic modes. To our knowledge this is the largest size of a plas-



Fig. 1. Sketch of the geometry of the nanowire dimer. Two identical cylindrical nanowires are infinite along the *z*-axis and have a diameter D of the circular cross-section in the (x, y)-plane. The nanowires are separated by a junction of separation width S. The incident radiation is linearly polarised with the electric field along the *x*-axis.

monic dimer described so far within a quantum framework. As a matter of comparison, similar TDDFT studies of jellium nanowire dimers have been performed with D = 0.5 nm [37], and D = 4 nm [35] nanowires.

Within the JM, the ionic cores of the nanowire atoms are represented by a uniform background charge density $n_0 = (4\pi r_s^3/3)^{-1}$. The Wigner-Seitz radius r_s is set equal to 4 a_0 (Bohr radius $a_0=0.053$ nm) corresponding to Na metal. Sodium is a prototype system for which the JM performs particularly well in the description of the finite size non-local effects on optical properties [64]. It should be emphasized that the qualitative conclusions drawn in this work are robust and independent of the particular choice of density parameter. Each nanowire is characterised by the number of electrons N_e per unit length. From the charge neutrality the nanowire diameter is then $D = 2\sqrt{4N_e r_s^3/3}$. The circle of diameter D provides the position of the jellium edge separating uniform positive background from the vacuum. The jellium edge is located at half a lattice constant a (a = 4.23 Å for Na) in front of the last atomic plane at the surface. We have performed calculations for $N_e = 40$ and $N_e = 100$ with $D_{40} = 6.2$ nm and $D_{100} = 9.8$ nm respectively. The Fermi energy in both cases is at 2.9 eV below the vacuum level.

The quantum calculations of the absorption cross-section are based on the Kohn-Sham (KS) scheme of the TDDFT [65]. We use the adiabatic local density approximation with the exchange-correlation functional of Gunnarson and Lundqvist [66]. Retardation effects can be neglected for the present polarization due to the small transverse extent of the system. A detailed description of the present numerical implementation can be found in [32]. Here we only discuss specific aspects linked with the present work on interacting nanowires. In brief, the Kohn-Sham orbitals of the ground state of the interacting dimer $\psi_j(x, y)$ are obtained from those of non-interacting distant cylinders by adiabatically reducing the separation *S*. The $\psi_j(x, y)$ -orbitals are discretized on the equidistant mesh in cartesian coordinates as well as the solutions $\Psi_i(x, y, t)$ of the time-dependent Kohn-Sham equations:

$$i\frac{\partial\Psi_j(x,y,t)}{\partial t} = \left(-\frac{\Delta}{2m} + V_{\text{eff}}(x,y,t;[n])\right)\Psi_j(x,y,t),\tag{1}$$

which are solved with initial conditions $\Psi_j(x, y, t = 0) = \psi_j(x, y)$. In Eq. (1) *m* is the free electron mass, and $\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}$. The effective potential of the system V_{eff} depends on the electron density n(x, y, t) given by:

$$n(x, y, t) = 2 \sum_{j \in occ.} \chi_j |\Psi_j(x, y, t)|^2.$$
(2)

The sum runs over the occupied states, the factor 2 is the spin degeneracy, and χ_j is the number of electronic states associated with the *z*-motion along the nanowire.

$$\chi_j = \frac{1}{\pi} \sqrt{2(E_F - E_j)},$$
 (3)

where E_F is the Fermi energy, and E_i is the energy of the $\psi_i(x, y)$ orbital.

The absorption cross-section per unit length is calculated from the electron density dynamics induced by an impulsive perturbation as: $\sigma_{abs}(\omega) = \frac{4\pi\omega}{c}Im\{\alpha(\omega)\}$, with $\alpha(\omega)$ being the dipolar polarizability (per unit length) of the system, and *c* the speed of light in vacuum. Note that because of the small transverse size of the dimer, the absorption cross-section calculated with TDDFT can be considered equal to the extinction cross-section. In order to analyse the temporal evolution of the induced charges, currents, and fields resulting from the excitation of specific plasmonic resonances, we perform the TDDFT calculations for the nanowire dimer subjected to an incident *x*-polarized laser pulse. The electric field of the pulse is given by $E_L(t) = E_0 \exp\left[-(t-T)^2/\tau^2\right] \cos\Omega t$, where we use $\tau = 0.2T$. The frequency of the pulse Ω is set resonant with the studied plasmonic mode. The duration of the pulse τ (typically 10 fs) allows for the narrow enough spectral width. The amplitude E_0 is sufficiently small for the system to be in the linear response regime [32]. The snapshots of the induced densities, currents, and fields presented in this paper are extracted at $t \sim T/2$.

The classical electromagnetic calculations of the absorption cross-section have been performed with the Comsol Multiphysics package, (version 4.2a, www.comsol.com). Local Drude, nonlocal hydrodynamic (NLHD), and quantum corrected model (QCM) descriptions of the dielectric properties of the system were used. Within the local classical approach the dielectric constant of the nanowires is described with the Drude model, which is a good approximation for a free electron metal such as sodium considered in this work.

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)},\tag{4}$$

where ω_p is the bulk plasma frequency given by $\omega_p = \sqrt{4\pi n_0/m} = 5.89$ eV, and γ (typically of the order of 0.2 eV) accounts for the damping.

Within the NLHD description, the transverse component of the permittivity tensor is given by Eq. (4), and the longitudinal component acquires the wave vector k dependence:

$$\varepsilon_L(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma) - \beta^2 k^2}.$$
(5)

The β parameter is given by $\beta = \sqrt{3/5}v_F$ [2,38,39,43–45]. In the present case, the Fermi velocity of conduction electrons is $v_F = \sqrt[3]{3\pi^2 n_0}/m = 1.05 \times 10^6$ m/s, resulting in $\beta = 0.81 \times 10^6$ m/s. With the transverse and longitudinal components of the permittivity tensor as described above, the absorption cross-section is calculated with the numerical approach as recently implemented by G. Toscano and coworkers within the Comsol Multiphysics package [45].

The recently developed QCM [33] allows for the incorporation of the tunneling effect into the classical Maxwell's equations. We use the local approach where the nanowires are described

with the Drude model given by Eq. (4), and the tunneling across the vacuum gap between the nanowires is accounted for by filling the junction with an effective inhomogeneous dielectric medium. This effective medium is described with the Drude model, similar to Eq. (4), as:

$$\varepsilon_{\rm eff}(x, y, S, \omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma_{\rm eff}(x, y, S))}.$$
(6)

The effective damping γ_{eff} models the transition from resistive (large *S*) to conductive (small *S*) character of the junction. Thus, it acquires a dependence on the junction width *S* and on the *x*-, and *y*-coordinate. For $S \to \infty$ the effective damping $\gamma_{\text{eff}} \to \infty$, and the QCM becomes exactly equivalent to the local classical approach. No tunneling is possible and the vacuum gap limit is retrieved with $\varepsilon_{\text{eff}}(x, y, S, \omega) = 1$. For the overlapping geometry S < 0 the junction is metallic and $\gamma_{\text{eff}}(x, y, S) = \gamma$ within the corresponding (x, y) range. In this work we use exactly the same parametrization of ε_{eff} as in the earlier publication, where the QCM is introduced and described in great detail [33].

3. Results and discussion

3.1. Individual nanowire

We first characterize the linear optical response of an individual nanowire. In Fig. 2 we show the extinction coefficient defined as σ/D where σ is the extinction cross section per unit length calculated with the full quantum TDDFT method and with the classical local Drude and NLHD approaches. The classical local approach with the Drude model given by Eq. (4) for the permittivity of the nanowire leads to the dipole resonance located at a surface plasmon frequency $\omega_{sp} = \omega_p/\sqrt{2} = 4.16 \text{ eV}$ irrespectively of the nanowire diameter. We find that the absolute value of σ and the width of the resonance as calculated with TDDFT is best reproduced with damping parameter $\gamma = 0.2 \text{ eV}$ for the D = 6.2 nm nanowire, and $\gamma = 0.16 \text{ eV}$ for the D = 9.8 nmnanowire. These parameters will be used in all the classical calculations shown in this paper. The smaller damping obtained for the larger nanowire indicates a smaller decay due to surface scattering. Indeed, the surface scattering contribution to the damping can be expressed as $\gamma_S = Av_F/R_{cl}$ [67], where $R_{cl} = D/2$ is the cylinder radius, and A is the system-dependent parameter. The calculated change of the damping is consistent with A = 0.5 in agreement with available experimental and theoretical results for alkali clusters [68, 69].

The dipole resonance calculated with TDDFT is *red shifted* from the classical ω_{sp} value but approaches ω_{sp} for increasing diameter of the nanowire. For the D = 6.2 nm nanowire, the resonance is at $\omega_{res} = 4.027$ eV, and it is at $\omega_{res} = 4.072$ eV for the D = 9.8 nm nanowire. Thus, the present results are in agreement with TDDFT studies of jellium nanowires [35, 36], and show the same trends as those studied in detail for spherical alkali metal clusters [64, 70– 72]. The nonlocal effect at the origin of the red shift of the plasmon resonance is linked with the dynamical screening of the fields produced by conduction electrons. The dipole resonance frequency ω_{res} of the spherical jellium cluster of radius R_{cl} obtained within TDDFT can be related to the classical resonance ω_{sp} from [71–74]:

$$\omega_{\rm res}/\omega_{\rm sp} = 1 - Re[d(\omega_{\rm sp})]/R_{\rm cl} + O(R_{\rm cl}^{-2}). \tag{7}$$

The real part $Re[d(\omega)]$ of the Feibelman's parameter $d(\omega)$ gives the position of the centroid of the induced charge density [75–78] at the interface and determines finite size effects in metal clusters as well as the dispersion of surface plasmons at flat surfaces. When measured from the jellium edge, $Re[d(\omega_{sp})]$ is positive for alkali metals, i.e. the screening charge is shifted into the vacuum because of the spill out of the conduction electrons outside the metal. Following the derivation in [74], Eq. (7) holds for the jellium cylinder and can thus be applied to analyse the



Fig. 2. Extinction coefficient for the single jellium nanowire of diameter D = 6.2 nm (left) and D = 9.8 nm (right). Results are shown as function of the frequency ω of the incident radiation. The incoming field is the *x*-polarised plane wave. The TDDFT calculations are compared with results of the classical electromagnetic calculations using local (Drude) and NLHD. See the legend for definition of the different symbols used in the Fig.

present TDDFT results. From the calculated resonance frequency we obtain $Re[d(\omega_{sp})] = 1$ Å in agreement with earlier calculations and experiments [72, 75, 76]. Importantly, for noble metals such as Au and Ag, finite size effects and surface screening lead to a *blue shift* of the dipole plasmon resonance [29,78,79]. The difference between alkali and noble metals can be explained as due to the contribution of the localised d-electrons to the total screening in noble metals [74, 77, 79–81]. When the d-electron contribution is accounted for, $Re[d(\omega)]$ turns negative indicating that the screening charge is predominantly induced inside the metal [74, 79, 80].

For the small diameter nanowire D = 6.2 nm, the finite size effects manifest themselves in the TDDFT calculations not only in the form of red shifts and line width changes, but also as clearly observable features in the frequency dependent extinction coefficient. These features arise from the strong coupling of collective plasmon- and single electron-hole excitations [35, 82, 83]. For large diameter nanowires, finite size effects become smaller and the plasmon resonance is much better defined. The TDDFT results also show a shallow resonance in the extinction coefficient at $\omega_{mp} = 4.6$ eV associated with a multipole plasmon (MP) [84–86]. For the jellium nanowire this mode is discussed in great detail in [35]. The resonant frequency of the MP obtained here with TDDFT is in good agreement with experimental data [84, 86]. The density oscillations of the MP proceed within the layer of the spilled out charge and obviously can not be captured within the local classical theory.

Finally, the green dotted lines in Fig. 2 show the extinction coefficient calculated with the NLHD model [45]. In contrast to the TDDFT result and experimental data on alkali clusters [71, 72], the NLHD model predicts a blue shift of the dipole plasmon frequency from the ω_{sp} value. The reason for this is that independently of the metal, the plasmon-induced charges in NLHD are localized within a layer of thickness β/ω_p below the metal surface [35,36,44]. Thus, the effective $Re[d_{NLHD}(\omega)]$ is always negative leading to the blue shift of the localised plasmon [77] in contradiction with the spill out effect known for alkali metals. It is worth mentioning that the negative $Re[d_{NLHD}(\omega)]$ inherent to the NLHD description of conduction electrons and so the blue shift of the localised plasmon qualitatively coincides with experimental data of noble metal clusters. However, the agreement in this case is fortuitous as it is not based on solid physical grounds. Indeed, the NLHD ascribes the effect to conduction electrons only, while



Fig. 3. Waterfall plot of the extinction cross section per length for a nanowire dimer in vacuum. The dimer consists of two Na nanowires of diameter D = 6.2 nm (left) and D = 9.8nm (right) separated by a junction of variable width S. The incoming field is an x-polarised plane wave. The centers of the wires are at $x = \pm (D+S)/2$, and S is negative for overlapping cylinders. S = -D would correspond to the limit of a single cylinder. TDDFT results are given as function of the frequency ω of the incident radiation for different separations S between the nanowires. For clarity a vertical shift proportional to the separation distance is introduced for each absorption spectrum. The red curves are used each 5 $a_0 \approx 2.65$ Å of S-change. These are labeled with corresponding S-values each 10 $a_0 \approx 5.3$ Å of S-change. The plasmonic modes responsible for the peaks in the absorption cross-section are labelled. These are: Bonding Dipole Plasmon (DP), Bonding Quadrupole Plasmon (QP), high order hybridised mode close to ω_{sp} (HM), the lowest (dipole) Charge Transfer Plasmon (C1), and the higher energy Charge Transfer Plasmon (C2). On the right panel the blue dotted curve at S = 26.5 Å shows results of the classical Drude calculation with adjusted parameters and the green dotted curve represents results of the NLHD model. Further details are give in the main text.

full quantum calculations show that the blue shift of the plasmon resonance in noble metals is due to the contribution of the localised d-electrons to the dynamical screening of external fields [74–77, 79–81, 84].

3.2. Coupled nanowires

In Fig. 3 we show the TDDFT results for the response of a pair of identical parallel nanowires of the D = 6.2 nm and D = 9.8 nm diameters. The waterfall plots of the extinction cross section are presented as a function of the frequency of the incident radiation for different widths S of the junction. The calculations have been performed for both positive and negative S, where the latter means a geometrical overlap of the nanowires. The S = 0 case corresponds to the kissing cylinders [43, 44] with touching jellium edges where the distance between the topmost atomic planes equals to the interlayer spacing, i.e. a continuous solid is formed at the contact point.

For large positive separations the non-local effects including electron tunneling across the junction are small, and the TDDFT results agree with earlier classical calculations [44, 50, 58, 59]. At S = 26.5 Å the absorption spectrum is dominated by two resonant structures. First, the bonding dipole plasmon (DP) indicated with the blue dotted line in Fig. 3 is formed from the hybridization of the dipole plasmon modes of the individual nanowires. The second resonance indicated with a black dotted line is formed by degenerated higher order modes (HM). This resonance is slightly red shifted with respect to the surface plasmon frequency ω_{sp} . At $S \to \infty$, the DP merges into the HM mode and the spectrum evolves into that of the individual nanowire. As the junction width *S* decreases, the DP shifts to lower frequencies because of the attractive interaction between the charges of opposite sign across the junction. Along with the red shift of the DP, the quadrupolar plasmon (QP indicated in Fig. 3 with an orange dotted line) splits from the degenerate HM mode, and shows a red shift with decreasing *S*.

Despite the overall similarity of the results obtained with smaller and larger diameter nanowires there are some remarkable differences primarily caused by the finite size effect. The resonances are much better defined for the larger D = 9.8 nm nanowire. In this case the width of the resonances is smaller and the spectral features due to the interaction between the plasmon and electron-hole pair excitations disappear. For D = 6.2 nm nanowire, this interaction can even split the single plasmon peak into several spectral lines. The red shift of the DP and QP modes with decreasing S is also more pronounced for the D = 9.8 nm nanowire dimer. This is because of the scale (S/D) invariance of the plasmonic properties of nanostructures in the quasistatic limit. In contrast to the results presented in [35] and [37], we do not observe any noticeable contribution from the bulk plasmons, probably because of the larger nanowire diameters analysed in the present study.

For junction widths below ~ 7 Å, electron tunneling across the junction becomes important. The results obtained here for the nanowire dimer agree with those reported earlier [35, 36], and have much in common with the quantum results for touching nanospheres [31–33], and with recent experimental data [28, 29]. The DP resonance progressively disappears and the charge transfer plasmon mode (C1) emerges prior to the direct contact between the nanoparticles. C1 appears as a broad shallow low-frequency peak at positive $S \simeq 1.5$ Å, and evolves into a well–defined resonance at S < 0. Similarly, because of electron tunneling, the QP mode continuously evolves into a higher order charge transfer plasmon mode C2 before direct contact between the nanowires. Thus, already at positive *S* the nanowires are conductively connected showing characteristic charge transfer plasmon modes [48,51–53,55,56]. For a dimer with a well established conductive contact at negative *S*, the C1 and C2 modes experience a blue shift with increasing overlap as also found in classical calculations [48,63].

To obtain further insights into the effect of electron tunneling across the junction we have calculated the electron density dynamics in the plasmonic dimer subjected to an incident *x*-polarized laser pulse resonant with the lowest (DP or C1) plasmonic modes. The intensity of the pulse is slowly raised and maintained sufficiently small that nonlinear effects [32] can be neglected. Figs. 4(a)-4(j) show snapshots of the induced charge density Δn , the *x*-component of the current density J_x , and the electric field E_x for different junction widths *S*. Results are presented for the case of D = 9.8 nm nanowires. The induced densities are shown at the instant of time corresponding to the maximum dipole moment of the dimer. The currents and fields are shown at the instant of time corresponding to the maximum induced field in the junction.

For large separation S = 7.95 Å the maximum induced dipole corresponds to the in-phase dipole polarisation of each nanocylinder as expected for the DP mode. High charge densities are induced at the surfaces facing the junction resulting in large electric field enhancement $|E_0/E_{in}| \sim 80$. Here, E_{in} is the amplitude of the incident field and E_0 is the amplitude of the field measured at the *x*-axis in the middle of the junction. The structure of the induced charges and



Fig. 4. Panels (a)-(k) Detailed analysis of the plasmon dynamics in the D = 9.8 nm nanowire dimer system. The incident *x*-polarised laser pulse is at resonance with the lowest (DP at S > 0 or C1 at $S \le 0$) plasmon mode. Panels (a)-(j) present snapshots of the induced charge density Δn , current density J_x , and electric field E_x for different junction widths *S* as indicated to the left of each row. The induced currents and fields are measured along the interparticle *x*-axis. Positive (negative) values correspond to the red (blue) color code. The induced densities are shown at the instant of time corresponding to the maximum dipole moment of the dimer. The induced currents and fields are shown at the instants of time when the induced fields in the junction reach the maximum. Panel (k): Conductivity analysis. The current J_x measured on the *x*-axis in the middle of the junction is plotted as a function of the normalized electric field at the same position. Different colors correspond to different junction widths *S* as labeled in the insert.

fields is similar to previous classical results for coupled cylinders [44, 50, 58, 59] and it is also similar to the case of metal sphere dimers [48]. The probability of tunneling between nanowires is negligible and no current flows across the junction. Note that the maximum dipole polarisation corresponds to the instant of time when the maximum charge separation has occurred and the currents inside nanoparticles are minimal. For the reduced junction width S = 2.65 Å, basically the same profiles for induced densities and fields are obtained. Therefore, we do not show E_x but rather focus on the induced current. The junction width is now sufficiently small to allow weak electron tunneling between the nanoparticles. The large optical field in the junction acts as a large BIAS in the scanning tunneling microscope causing tunneling current [33]. Thus, the junction shows a *resistive* character with the maximum current between nanowires reached at the maximum field and consequently at the maximum induced dipole.

Further reduction of the junction width *S* increases the tunneling probability and short circuits the junction. When conductive contact is formed, the DP mode disappears and the C1 mode

emerges in the absorption spectrum. Figs. 4(e) and 4(h) show the induced charges for S = 0 and S = -2.65 Å, respectively. The results are very similar, i.e. already for the S = 0 case of kissing cylinders the charge transfer plasmon mode is well developed (see also Fig. 3, and Fig. 5). The maximum dipole moment of the dimer now corresponds to oppositely charged nanowires. Maximum currents and fields [Figs. 4(f), 4(g), 4(i) and 4(j)] are reached when the total dipole moment of the system is minimum (compare with the S = 2.65 Å case). Precisely, it is this large current flowing trough the entire system that builds the dipole polarisation with opposite charges at the left and right nanowires consistent with the resonant excitation of the C1 mode. The field enhancement is about 30 for both S = 0 and S = -2.65 Å separations. However, the fields are screened at the center of the junction, and the maximum fields are located at its sides [35]. This is similar to the classical result for overlapping cylinders [63].

Figure 4(k) provides further analysis of the evolution from resistive to conductive character of the junction with decreasing S. The current $J_x(t)$ on the x-axis at the middle of the junction between the nanowires is shown as a function of the field $E_x(t)$ at the same location. At large separations, the linear relation $J_x(t) = gE_x(t)$ between the current and the local field shows that the junction is resistive. The increase of the slope g (smaller resistance) when S is reduced from S = 5.3 Å to S = 2.65 Å is because of the increase of the tunneling probability. For S = 1.06 Å and S = 0 Å the $E_x(t)$ and $J_x(t)$ acquire a relative phase. Since the field envelope of the incident pulse grows in time for the time interval shown in Fig. 4(k), the anti–clock–wise rotation of the $J_x(t)[E_x(t)]$ curve implies that the current is delayed with respect to the field. The junction thus becomes conductive which is particularly apparent for S = 0.

The TDDFT results show that for small junction widths the optical response is determined by electron tunneling which would be absent in a standard classical description. For a large width of the junction the tunneling is negligible, however the effect of nonlocal screening discussed for the single cylinder should *a priori* influence the optical response of the dimer. The question is then how do quantum results compare to classical Drude, NLHD, and QCM models for different *S*- ranges corresponding to conductively coupled or separated nanowires. The remaining part of the paper is devoted to a comparison of the quantum and classical results with a particular focus on the possibility to account for quantum effects within a classical approach.

3.3. Quantum vs classical approaches

Figure 5 shows the comparison between present TDDFT, QCM, local Drude and NLHD results for the optical response of the dimer system as a function of the junction width S. Since for the individual nanowire TDDFT gives a red shift of the dipole plasmon resonance with respect to the classical ω_{sp} position, while NLHD leads to a blue shift (Fig. 2), we adjust the ω_p parameter of the classical models to obtain an agreement with TDDFT at large separation S = 26.5 Å (see Fig. 3). This allows us to remove the differences due to the different descriptions of the isolated nanowire, and thus focus exclusively on the effects of coupling. Specifically, for the D = 9.8 nm nanowire dimer we have used a plasma frequency $\omega_p = 5.74$ eV in the QCM and classical Drude calculations (5.7 eV for the D = 6.2 nm nanowire dimer), and $\omega_p = 5.5$ eV in the NLHD model. The relatively large correction to the nominal value of 5.89 eV arises in the NLHD case because of the blue shift inherent to this treatment. Adjustment of the nonlocality parameter β is also possible, but then the NLHD model loses its predictive power. Indeed, as far as the adjustment is limited to the ω_p parameter, the finite size effects and also the need for the ω_p correction disappears with increasing size of the nanoparticles as follows from Eq. (7).

The main features of the quantum results have been discussed in connection with Fig. 3 so here we will focus on the comparison between different model approaches. As follows from Fig. 5, the QCM does an excellent job in describing the TDDFT results over the entire range of separations S addressed here. The important features such as the number of resonances, their



Fig. 5. Extinction cross section per length of a nanowire dimer as obtained with the full TDDFT calculations, with the quantum corrected model (QCM), with classical Drude electromagnetic calculations (Drude), and with calculations based on the nonlocal hydrodynamic model (NLHD). The dimer consists of two D = 9.8 nm Na nanowires in vacuum. The incoming plane wave is polarized along the dimer axis *x*. Upper panels: Waterfall plots of the dipole absorption cross-section as a function of the width of the junction *S*. Red curves correspond to S = -5.3 Å, -2.65 Å, 0 Å, 2.65 Å, 5.3 Å, 7.95 Å, and 10.6 Å. For further details see the caption of Fig. 3. Lower panels: Color plots of the local field enhancement at the center of the junction for positive separations. Results are shown as a function of the frequency ω of the incident radiation and junction width *S*. The color code is displayed at the bottom of the corresponding panels. In the Drude case, because of the divergence of the fields, the color scale has been saturated (enhancement > 200) for junction widths below 1.25 Å.

distance dependence and the transition from the separated to conductively coupled regime are well reproduced. In particular, in sheer contrast with local classical theories [44, 48, 50, 58, 59] the change of the spectrum at the moment of contact is progressive. Large charges of opposite sign accumulated at the nanowire surfaces across the junction in the classical model are neutralised by the tunneling current. Thus, the fields at the middle of the junction are quenched in TDDFT and QCM, not diverging with decreasing junction width as in local classical calculations. Besides qualitative aspects, we find that the TDDFT and QCM agree semi-quantitatively as is further stressed in Fig. 6. This Fig. zooms into the most delicate interaction regime corresponding to the transition from the separate to overlapping nanowires.

By construction, the QCM is equivalent to the classical local Drude description for large positive *S* where tunneling is negligible. The good agreement with TDDFT data suggests that the pure local classical description is reasonable for large *S*. At the same time the local classical



Fig. 6. Detailed comparison between TDDFT and QCM calculations. The extinction crosssection per length of the D = 9.8 nm Na nanowire dimer is shown for small separations S. This S-range corresponds to the strong tunneling regime and the transition from separated to conductively coupled nanowires. The frequency range is zoomed at the transition from the bonding dipole (DP) to the lowest charge transfer (C1) plasmon. Waterfall plots of the optical absorption cross-section are shown for the junction widths changing from S = -2.65 Å (lowest blue line) to S = 4.77 Å (upper black line) in steps of 1 a_0 (0.53 Å). For further details see the caption of Fig. 3.

theory fails at small $S \sim 5$ Å, i.e. typically at two lattice constants between surface atomic planes that define the junction [29]. The accumulation of charges at the opposite sides of the junction in the classical description leads to exaggerated coupling between nanowires resulting in diverging fields and too large number of resonances. Similarly, for negative *S*, the sharp edges of the junction, which are otherwise smeared out by the electron tunneling also result in too many hybridized resonances [33].

Overall, for large junction width *S*, the NLHD description does not perform better than the local Drude approach. The comparison with the TDDFT result is even worse for NLHD regarding the relative intensities of the modes (in particular HM). This lack of accuracy of the NLHD treatment has been already pointed out by Stella et al [35]. For small *S*, the NLHD description avoids the S = 0 divergence problem [43,44] inherent to the local Drude model. The number of resonances remains limited and the fields in the middle of the junction stay finite albeit too large as compared to TDDFT. These results for the narrow junction can be easily understood thanks to the elegant transformation optics approach developed for interacting cylinders by Fernández-Domínguez and coworkers [44]. At positive *S* an analytic solution is found which depends on the effective junction width \tilde{S} given by $\tilde{S} \simeq S + 2\delta$, where $\delta \simeq \beta/\omega_p$ (1 Å in the present case). The renormalisation of the width of the junction is because in the NLHD approach the plasmon induced screening charges are located inside the geometrical surface of the nanowires. Indeed,

the induced charges across the junction determine the coupling between plasmonic modes localised on each nanowire and thus the energies of the hybridized plasmonic modes of the entire system as well as the plasmon induced field enhancement. As discussed above for the isolated cylinder, in terms of the dynamical screening theory, δ can be associated with an effective Feibelman parameter $\delta = -Re[d_{\text{NLHD}}(\omega)]$. Thus, even for S = 0, the induced charges at the opposite sides of the junction are actually separated by a finite distance 2δ so that the interaction between them does not diverge. However, the improvement as compared to the local Drude approach is only superficial because the model does not reflect the actual physical situation in the junction. From the analysis of the TDDFT result, the tunneling current through the narrow junction neutralises the screening charges at its opposite sides, thus removing divergences, and determining the optical response of the dimer. The tunneling effect is not accounted for in the NLHD approach. As a consequence the NLHD treatment maintains finite screening charges at $S \rightarrow 0$, and therefore fails to reproduce the quenching of the field enhancement at the middle of the junction for small positive S. The NLHD also fails to smoothen out the transition from separated to overlapping regimes and gives an abrupt nonphysical transition between both situations. The number of modes is smaller than in the classical Drude description, but still larger than what is obtained in TDDFT or QCM calculations.

Our final remark concerns the QP plasmon that evolves into the C2 charge transfer mode for negative S. The associated resonances are much less pronounced in the TDDFT cross section as compared to model approaches. One possible reason is the finite size effect: the system size is not large enough for the corresponding density oscillations to be completely formed. However, the similarity between the TDDFT results for D = 6.2 nm and D = 9.8 nm nanowire dimers as shown in Fig. 3 suggests that quantum size effects play only a minor role. We thus tentatively attribute the weaker high order resonances as obtained in TDDFT to the nonlocal effect of the smearing of the induced surface charge densities. This *a priori* reduces the coupling between the dipolar and higher order modes and so the intensity of the QP resonance.

3.4. Dynamic screening

From the results presented in the previous subsection, we can conclude that tunneling determines the optical properties of the system at small junction widths. For large widths S > 7 Å tunneling is absent and nonlocal dynamic screening influences the optical properties. While all calculations agree on the overall red shift of the modes with decreasing *S* because of the interaction between the screening charges across the junction, the detailed analysis presented in Fig. 7 shows systematic differences between the different approaches. For a fixed *S*, similar to the case of the individual nanowire, the frequency of the DP obtained with TDDFT appears red shifted with respect to the classical prediction given by the Drude model. The NLHD gives a blue shifted DP. This difference is increasing with decreasing *S*. Since we have applied a frequency correction so that the plasmon modes for infinite separations are the same, it is clear that the interaction between the screening charges across the junction is underestimated in the classical Drude calculations and this underestimate is even more pronounced in the NLHD treatment.

Figure 7 presents the analysis of the role of the dynamic screening in determining the frequency of the bonding dipole plasmon. The nature of the dynamic screening effect is illustrated in Fig. 7(a). The time dependent charge density Δn induced at the surface of the left nanowire by the *x*-polarised plane wave is shown as a function of the *x*-coordinate along the axis of the D = 9.8 nm dimer. The junction width is S = 13.25 Å, and x = 0 corresponds to the center of the junction. For the right cylinder Δn is antisymmetric with respect to x = 0. The vertical solid line at x = -6.625 Å marks the jellium edge of the metallic cylinder and the metal extends in negative *x*-direction. Different curves correspond to instants of time spanning 1/2 optical period starting from t_0 (black line). The frequency of the incoming radiation $\omega = 3.16$ eV is in



Fig. 7. Dynamic screening. (a) Time evolution of the density Δn induced by the $\omega = 3.16$ eV laser pulse at the surface of the left cylinder facing the S = 13.25 Å wide junction. The data is shown as a function of the x-coordinate along the dimer axis for the D = 9.8 nm dimer. x = 0 corresponds to the center of the junction. Different curves correspond to instants of time spanning 1/2 optical period starting from t_0 . For further details see the text. (b) Schematic representation of the location of the plasmon induced screening charges in the junction. Within the local classical approach the screening charges are at the geometrical surfaces of the cylinders (here equivalent to the jellium edges) separated by the junction of width S. Within the TDDFT, the centroids of the screening charges (red areas) are located at $Re[d(\omega)]$ in front of the jellium edges so that the effective separation is $S - 2Re[d(\omega)]$. In the NLHD approach the centroids of the screening charges (blue areas) are located at a distance δ below the geometrical surface so that the effective separation is $S + 2\delta$. (c) Energy of the dipole plasmon resonance as function of the junction width S. Dots: TDDFT results obtained for the D = 9.8 nm nanowire dimer. Dashed red (gray) lines show results of classical Drude (NLHD) calculations where the separation S is measured between the jellium edges. The solid red line shows the results of the classical Drude calculations performed for an effective separation $S - 2Re[d(\omega)]$. The dotted gray line shows the results of the NLHD calculations performed for an effective separation $S - 2Re[d(\omega)] - 2\delta$. (d) Energy of the dipole plasmon resonance as function of the junction width S. Dots: TDDFT results obtained for nanowire dimers formed by D = 6.2 nm and D = 9.8 nm nanowires (see the legend). Solid and dashed lines show results of classical Drude calculations for D = 6.2 nm (blue) and D = 9.8 nm (red) dimers. Dashed lines: calculations performed for the junction width S measured between the jellium edges. Solid lines: calculations performed for a corrected effective separation $S - 2Re[d(\omega)]$.

resonance with the DP. As follows from the Fig., not only the induced density strongly spills out into the vacuum part of the junction, but its spatial profile shows a pronounced time dependence. It has been shown that in this case the screening is characterized by the centroid of the induced charge density $d(\omega)$. In particular, $Re[d(\omega)]$ shows the average position of the induced charge with respect to the jellium edge [74–77, 80, 84]. For the density parameter of Na ($r_s = 4$ a₀), $Re[d(\omega)] \approx 0.9$ Å in the frequency range of interest [76], which means that the screening charge is shifted by ≈ 0.9 Å into the vacuum.

The schematic representation of the location of the plasmon induced screening charges in the junction of width *S* is shown in Fig. 7(b). Within the local classical approach, the screening charges are localised at geometrical surfaces of the cylinders separated by *S*. We recall that we use the definition of the geometrical surface such that it coincides with the jellium edge. Within TDDFT, the screening charge is shifted by 0.9 Å into the vacuum and located at ≈ 3 Å outside the surface atomic plane of the nanoparticle. The separation between the centroids of plasmon induced screening charge densities across the junction is thus $S_{\text{TDDFT}} = S - 2Re[d(\omega)]$. For the NLHD approach, with the present choice of the non–locality parameter β , the screening charges are induced at $\delta = 1$ Å inside the geometrical surface. Thus, within the NLHD approach the centroids of the screening charges are separated by a larger distance $S_{\text{NLHD}} = S + 2\delta$. This insight provides an explanation for the junction width dependence of the dispersion of the DP modes shown in Figs. 7(c) and 7(d) for two different nanowire dimers. The effective junction width is smaller in the TDDFT calculations and larger in the NLHD approach explains the corresponding red and blue shift of the DP energy with respect to the classical Drude value.

In our previous work we have shown that a physically sound definition of the junction width can be based on the separation between the centroids of screening charge densities induced at the facing surfaces across the junction [36]. This provides a universal model–independent dispersion of the DP energy as follows from the results presented in Figs. 7(c) and 7(d) which show an excellent agreement between corresponding TDDFT, classical Drude and NLHD calculations: $\omega_{\text{TDDFT}}(S) \approx \omega_{\text{Drude}}(S - 2Re[d(\omega)]) \approx \omega_{\text{NLHD}}(S - 2Re[d(\omega)] - 2\delta)$. For Na metal, the NLHD approach requires the largest redefinition of the junction width.

Thus, the TDDFT dispersion of the DP can be fully retrieved with local classical calculations. The main issue here is the size of the junction for which the calculations have to be performed. Given geometry of our nanostructure, it seems convenient to define the surfaces of the objects as given by the jellium edges. In this case the width S = 0 of the junction would correspond to a continuous solid formed at the contact point. On the other hand, classical calculations have to be performed for the effective junction width given by the actual separation between centroids of the screening charge. Several remarks are necessary with respect to the universal character of the junction width scaling. First, once the curvature radii of the typical nanoplasmonic structures is provided, the position of the centroid of the screening charge is simply a material dependent quantity. It does not depend on the geometry therefore it has to be defined only once for the frequency range of interest using e.g. Eq. (7) and the data on plasmon resonances in small clusters, or, alternatively the plasmon dispersion on flat metal surfaces [71–77]. Second, the rescaling of the junction width is only valid for large enough S, where electron tunneling can be neglected. When electron tunneling is efficient the electron densities of the nanoobjects start to overlap in the junction, and the centroids of the screening charges at opposite surfaces become ill defined. Third, at present we deliberately limit the discussion to the DP mode. Higher order modes exhibit a nontrivial nodal structure along the nanowire surface [35,37] which may alter the simple physical picture proposed above. Further investigations of these effects are in progress.

4. Summary and conclusions

In conclusion, we have presented a fully quantum mechanical study of the optical response of a plasmonic dimer formed by parallel cylindrical Sodium nanowires in vacuum. This system is also representative of interacting nanorods and is of relevance for SERS, plasmon rulers, and plasmon transport applications. The translational invariance of this system makes it possible to apply the time–dependent density functional theory to structures of the largest size attained so far in quantum calculations.

The free-electron character of the Na valence electrons implies that the material permittivity can be well described with the Drude model, as well as it is consistent with approximations behind the hydrodynamic approach to model the nonlocal character of the dielectric function. Thus, this is the system of choice where we could set the full quantum TDDFT benchmark results. We then used these results to test different theoretical approaches addressing the plasmonic response of strongly coupled objects. This was one of the central goals of the present work.

We have found that for small junction widths, the optical response is determined by quantum tunneling of conduction electrons across the potential barrier separating the nanowires. A decreasing junction width leads to progressive attenuation of the plasmon modes of separated nanowires and the emergence of charge transfer plasmon modes of the conductively coupled dimer. As this happens, the fields in the middle of the junction are screened. The maximal field enhancement moves from the middle to the external regions of the junction. In this junction widths range the classical local Drude and NLHD model descriptions fail since they do not account for tunneling. In contrast, the QCM results are found to be in excellent agreement with the full quantum calculations.

For large junction widths, electron tunneling is negligible and the overall agreement between TDDFT, classical Drude, and the QCM results is good. Thus, the QCM performs well over the entire range of separations studied here. The agreement between the classical and TDDFT results can be further improved by taking into account the shift of the plasmon-induced charge density with respect to the geometrical surface of the nanoparticle. The latter can be defined as the jellium edge as in the present work, or as a last atomic layer at the surface. The effective junction width is then given by the separation of centroids of plasmon induced charges at the opposite sides of the junction. Introducing a simple distance correction into the classical Drude calculations allows for fully accounting of this non-local effect so that the quantum TDDFT results are retrieved. This finding has implications in the concept of plasmon ruler [20, 21], and it shows that care should be taken with respect to the definition of the separation in gaps which is commonly measured by matching calculated and experimental results of the optical response.

Finally, we hope that results presented here contribute to the understanding of the role of quantum nonlocal effects in strongly coupled plasmonic systems, and help in elaborating efficient theoretical approaches with value for prediction.

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