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Lette

Anisotropy Effects on the Plasmonic Response of Nanoparticle Dimers

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ABSTRACT: We present an ab initio study of the anisotropy and atomic relaxation effects on the optical properties of nanoparticle dimers. Special emphasis is placed on the hybridization process of localized surface plasmons, plasmon-mediated photoinduced currents, and electric-field enhancement in the dimer junction. We show that there is a critical range of separations between the clusters (0.1-0.5 nm) in which the detailed atomic structure in the junction and the relative orientation of the nanoparticles have to be considered to obtain quantitative predictions for realistic nanoplasmonic devices. It is worth noting that this regime is characterized by the emergence of electron tunneling as a response to the



driven electromagnetic field. The orientation of the particles not only modifies the attainable electric field enhancement but can lead to qualitative changes in the optical absorption spectrum of the system.

T he resonant interaction of light with metallic nanostructures is at the heart of the developing field of nanoplasmonics. Recent advances in the fabrication and characterization of nanodevices have opened the possibility of tailoring plasmonic modes and, as a consequence, the response of nanosystems to external radiation.¹⁻³ From these advancements, a number of applications have been realized and/or proposed over the last few years, including optoelectronic hybrid devices,^{4,5} optical nanoantennas,⁶ optical traps,⁷ nanosensors,⁸⁻¹⁰ and broad-band light harvesting devices,¹¹ among others.

Many properties of these nanodevices can be understood perfectly in terms of classical optics.¹² However, if one of the characteristic lengths of the system reaches the subnanometric scale, genuine quantum effects emerge in the optical response,^{2,13} as has been observed over the last few years in a series of breakthrough experiments.^{14–18} In this regime, the theoretical treatment of the electromagnetic response must include the inhomogeneities of valence-electron densities and of photoinduced currents between the constituents of the device. Although there are some recent theoretical attempts aimed at incorporating such effects into the realm of classical optics,^{19,20} in principle, the quantum behavior of both groundstate and light-induced densities should be explicitly treated to obtain reliable theoretical predictions.

A prototypical case is a system made up of two metallic nanoparticles with subnanometric separation. In this metallic nanodimer, the establishment of a photoinduced electric current between the particles dramatically changes the plasmonic modes of the system. $^{21-23}$ The main trends 24,25 can be explained by describing the nanoparticles with the spherical jellium model in which the atomic structure is neglected, and by evaluating the optical response using the quantum mechanical time-dependent density functional theory (TDDFT).²⁶⁻²⁹ The latter provides the necessary accuracy when describing both the inhomogeneity of the electron density and the inherent nonlocality of the electromagnetic response. Thus, the combination of the jellium model and the TDDFT-based quantum treatment of light-matter interactions defines what is now considered to be state of the art in theoretical nanoplasmonics. Consequently, this approach has been applied to analyze the tunable response properties of nanorods,³⁰ plasmonic cavities formed by nanowires,³¹⁻³⁴ nanomatryushkas,³⁵ and more recently, the optical properties of doped semiconductor nanocrystals.³⁶ Furthermore, the predictions of the jellium/TDDFT method can also be used to assess^{31,33} the capabilities of sophisticated refinements of classical optics,^{19,20,37-45} whose range of applicabilities is certainly broader because the numerical implementation of fully quantum methods is limited to systems containing up to thousands of atoms.

Received: March 18, 2015 Accepted: April 29, 2015

The widespread use of the jellium model when analyzing simple sp systems can be easily justified on the basis of the collective character of the plasmonic response. Moreover, the dynamical screening due to d electrons in noble-metal nanostructures can be mimicked by a dielectric background with an appropriate dielectric function.⁴⁶ Then, the atomic structure can be safely neglected in nanostructures made up of weakly interacting compact elements. However, this is not a valid approximation in systems like hybrid nanoclusters,⁴⁷ where the chemical composition of the nanoparticle is essential to understanding its optical properties. For strongly coupled nanostructures, we have recently shown that surface corrugation due to the atomic structure leads to induced near fields with spatial distributions and intensities that are fairly different than the ones obtained from the jellium model.⁴⁸ As mentioned previously, the electromagnetic response of a nanodimer is greatly affected by the induced current between the particles. Therefore, it is expected that the relative orientation of the nanoparticles, which leads to different atomic arrangements around the dimer junction, will have to be taken into account. Thus, a careful analysis is needed to quantify the actual role played by the anisotropy of the atomic structure in the establishment of induced photocurrents and to determine those regimes in which its description is relevant. These are the main objectives of this study.

To achieve this goal, we analyzed the optical response of a prototype sodium nanocluster dimer. Each cluster is made up of 297 atoms in an icosahedral arrangement, which is the most stable configuration for isolated Na nanoparticles of this size.^{49,50} As can be seen in Figure 1, the Na₂₉₇ cluster is almost



Figure 1. Representation of the two different geometrical arrangements of icosahedral Na_{297} dimers considered in the present study. In the edge-to-edge (E2E) relative orientation (upper panel), two 3-atom edges are faced. In the face-to-face (F2F) relative orientation (lower panel), the spacial gap is between two 12-atom faces. The applied electric field is orientated along the dimer axis.

spherical with $2R \simeq 2.61$ nm being its effective diameter. This value corresponds to an average atomic density that is slighty larger than the one corresponding to bulk Na. The distance between the clusters is defined as d = b - 2R, where b is the distance between the central atoms of each cluster. Therefore, this definition does not depend on any atomic rearrangement in the gap region.

Once the distance d is fixed, there are two main features to consider: the relative orientation of the clusters and the atomic relaxation due to the mutual interaction. Concerning the relative orientation, in the present work, we treat the two cases depicted in Figure 1. The first leads to a spatial gap that is limited by two 12-atom faces (F2F orientation), whereas the second corresponds to a spatial gap between two 3-atom edges (E2E orientation). Thus, in the F2F geometry, we maximize the width of the dimer junction whereas the E2E configuration corresponds to a smaller separation between atoms. That is, there are two distinct effects (the distance between the nearestneighbor atoms and the contact width) that tend to cancel out. Thus, we performed energy-optimized relaxation of the atomic positions in the E2E geometry, which is required due to the smaller distance between atoms. Such a relaxation obviously has to be restricted to the region around the spacial gap because the dimer itself is metastable: full relaxation would lead to coalescence of the two clusters.

Both energy optimization and ground-state calculations are performed under a real-space prescription of the density functional theory (DFT) Kohn–Sham equations⁵¹ using the OCTOPUS package.^{52–55} The explicit treatment of the 3s conduction electrons using norm-conserving pseudopotentials⁵⁶ suffices for the purposes of the present work. The relaxation is performed using the FIRE algorithm⁵⁷ recently implemented in OCTOPUS⁵⁵ under a semilocal approximation to the exchange-correlation (XC) functional. Once the equilibrium geometries were obtained, ground-state electron densities, $n_0(\mathbf{r})$, were evaluated using the same prescription.

The TDDFT optical response was also calculated with OCTOPUS following the Yabana–Bertsch time-propagation recipe, ⁵⁸ which is very efficient in systems containing hundreds of atoms. At t = 0, the electron system was perturbed by a delta-kick electric field $\mathbf{E}(\mathbf{r}, t) = (\hbar \kappa_0/e) \delta(t) \mathbf{e}_x$, where e is the absolute value of the electron charge, \mathbf{e}_x is the direction of the dimer axis (i.e., the external field is oriented along the dimer junction), and $\kappa_0 = 0.005$ a.u. Then, all of the E1 selection-rule transitions were excited, and the induced density of a transition of frequency ω was directly related to the time-dependent density of the system after the kick, $n(\mathbf{r},t)$, though a Fourier transform

$$\delta n(\mathbf{r}, \omega) = \int_{0}^{\infty} \delta n(\mathbf{r}, t) e^{(i\omega - \gamma)t}$$
$$\simeq \int_{0}^{T_{\text{max}}} \delta n(\mathbf{r}, t) e^{(i\omega - \gamma)t} dt$$
(1)

where $\delta n(\mathbf{r}, t) = n(\mathbf{r},t) - n_0(\mathbf{r})$. Here, $\gamma = 0.1 \text{ eV}/\hbar$ is a damping frequency that accounts for absorption spectra broadening due to nonelectronic losses, and T_{max} is the actual propagation time in the calculations. The absortion cross-section is then given by $\sigma_{\text{abs}}(\omega) = (\omega/c \epsilon_0) \text{Im}\alpha(\omega)$, where the dynamical polarizability $\alpha(\omega)$ is

$$\alpha(\omega) = -\frac{e^2}{\hbar\kappa_0} \int x \delta n(\mathbf{r}, \, \omega) \, \mathrm{d}\mathbf{r}$$
⁽²⁾

In practice, $\alpha(\omega)$ is evaluated from the Fourier transform of the kick-induced time-dependent dipole moment. Well-converged results are achieved using $T_{\text{max}} = 20$ fs, a propagation-time step of $\Delta t = 10^{-4} T_{\text{max}}$ and grid spacing of 0.026 nm.

The dipole optical absorption of Na₂₉₇ dimers in the $0 \le d \le$ 0.6 nm range of separations is presented in Figure 2 for unrelaxed F2F and relaxed E2E geometries. For completeness,



Figure 2. Optical absorption of Na₂₉₇ dimers vs the distance *d* as defined in the text. Upper panels: contour plots of the photoabsorption cross sections, $\sigma_{abs}(\omega)$. The vertical dashed line indicates the approximate distance of where the hybridized Q mode becomes the main spectral feature in the spectrum. Lower panel: waterfall plot of the absorption cross sections. The red [blue] lines correspond to the F2F [relaxed E2E] relative orientations. For each distance, the separation in nm between faces [edges] is indicated in parentheses. The spectral peaks corresponding to coupled D, charge-transfer D and Q₄ and hybridized Q modes are indicated as well.

we have also included the optical absorption for the E2E overlapping clusters (d = -0.1 nm), where a major reconstruction of the junction occurs. We can define three distinct regimes: (a) $d \ge 0.6 \text{ nm}$, where the interaction between clusters is mainly electromagnetic and the photoinduced charge transfer (CT) is very small; (b) $d \le 0.1 \text{ nm}$, where there is a direct overlap of the ground-state densities of each cluster because the Fermi level of the system is above the potential barrier in the dimer junction; and (c) 0.1 nm < d <0.6 nm, where tunnelling CT between the clusters appears as a result of a photoinduced voltage bias between the clusters.

As seen in Figure 2, there are marginal differences between the E2E and F2F optical spectra for the (a) and (b) separation regimes. The irrelevance of the relative orientation of the clusters in regime (a) is not at all a surprise because there are minor differences between the F2F absorption and the spherical jellium model even when d = 0.5 nm.⁴⁸ Furthermore, this is the regime in which the optical absorption can be explained well in classical terms, and it is also possible to have a quantitative agreement with the quantum predictions as long as the nonlocality of the electromagnetic response and the inhomogeneity associated with the electron-density spill-out in each nanoparticle are properly addressed. As is wellknown,^{21,39,59-61} the optical absorption in this regime is dominated by coupling between the Mie dipole-localized surface plasmon resonances (LSPRs) of the individual clusters. This coupled mode, in what follows labeled as D, is red-shifted with respect to the value $\omega_{\rm M} = 3.13 \text{ eV}/\hbar$ of the main Mie

resonance of the isolated Na_{297} cluster.⁴⁸ In addition, a weak but discernible spectral feature appears at higher frequency. This is the signature of hybridized plasmon resonance (Q) due to excitation of the quadrupole LSPR of each cluster by the induced near field of the other.

As mentioned above, regime (b) corresponds to direct overlap of ground-state densities. In this limit, the two clusters cannot be consider as individual entities anymore and the system is actually a single "peanut-like" nanoparticle. The atomic arrangements in the junction and at the surfaces are very different in the F2F and E2E geometries, but such differences are blurred in the valence-electron density. As a consequence, the classically predicted sensitivity of the propagation of surface modes with respect to the surface inhomogeneities⁶² is no longer relevant. In this case, the spectrum is dominated by two LSPRs, labeled as D(CT) and Q(CT). In both resonances, there is a capacitive charge transfer between the two clusters (actually, between the two lobes of the peanut-shaped nanoparticle). In turn, these modes can also be characterized using classical optics if the actual ground-state density of the system is properly modeled.^{61,63}

On the contrary, the importance of the relative orientation between the nanoparticles is manifested in regime (c), where the optical absorption of the dimer is the result of a delicate interplay of the electromagnetic interaction mediated by near fields and the appearance of a tunneling CT between the clusters. When $d \ge 0.4$ nm, the splitting of the D and Q modes in the F2F geometry is clearly visible. Furthermore, the frequency of the D mode decreases when approaching the clusters. Thus, the behavior of the F2F response can be described by classical electromagnetism despite the fact that there is charge transfer between the clusters as we will show below. For the E2E geometry, the value of the frequency of the D mode is already locked in this range of separations, and the transfer of spectral weight from the D mode to the hybridized Q mode is clearly reflected in the spectrum. Interestingly, the intensity of the tunneling current, I_{CT}, when the D mode is excited is very similar in the F2F and E2E configurations. However, because the junction in the E2E orientation is substantially narrower than in the F2F one, the CT current density across the spatial gap is greater in the E2E case. As a consequence, propagation of the plasmonic density waves over the surface of the clusters is slightly altered by the tunneling CT in the F2F geometry, and the hybridization process follows the classically predicted trends. In fact, the quantum effects are only discernible in the F2F spectrum when the distance d is less than 0.4 nm. However, the E2E optical response is more sensitive to the establishment of an induced current, and we can say that the onset of quantum behavior due to tunneling is above d =0.5 nm.

Within regime (c), the differences are more dramatic at smaller separations. In the F2F orientation at d = 0.3 nm, the D mode still dominates the spectrum, but the corresponding mode in the E2E geometry has already been quenched, and the main spectral feature comes from the hybridized Q mode. Nevertheless, this interpretation cannot be taken literally because, unlike the well-defined classical plasmon modes, quantum collective excitations are the result of a coherent superposition of multiple electron—hole transitions, which cannot be isolated from other surrounding electron—hole pairs. In fact, the broad absorption range that characterizes both spectra at d = 0.3 nm is an admixture of the quantum collective excitations to the classical D and Q modes,

electron-hole transitions, and likely other many-body collective excitations.⁶⁴ In any case, at d = 0.3 nm, the two spectra are qualitatively different, and such a difference will be even more evident when analyzing the driven-induced densities and currents. The spectral feature corresponding to the D mode in the F2F orientation finally vanishes when the separation is smaller than 0.3 nm, and the maximum absorption at d = 0.2 nm corresponds to the excitation of a Q mode for both geometries. Note that there is still reminiscence of the D mode excitation in the F2F spectrum around $\omega = 2.3 \text{ eV}/\hbar$.

We will now analyze the impact of atomic relaxation in the optical absorption. The corresponding reconstruction in the junction is negligible if the distance between nearest-neighbor atoms is >0.6 nm and hardly noticeable in the range 0.5-0.6nm, which means that relaxation effects are expected to be significant if $d \leq 0.4$ nm for the E2E geometry and ≤ 0.25 nm for the F2F configuration. For shorter distances, when the atomic densities of both clusters overlap, the atomic reconstruction itself will be noticeable. However, we have seen that, in this regime, the specific atomic arrangement is not a fundamental issue. Therefore, the atomic relaxation will play a role only in the range of critical distances in which there is a transition from a dominant D mode to a Q mode. To confirm and quantify this prediction, we compared the relaxed-E2E optical absorption considered so far with that of unrelaxed-E2E at d = 0.1 and 0.3 nm. This comparison is depicted in Figure 3



Figure 3. Impact of the atomic relaxation on the absorption cross sections for E2E Na₂₉₇ dimers at separations of d = 0.1 and 0.3 nm. Optical absorption for relaxed geometries are the solid blue lines, and absorption for unrelaxed geometries are the dashed lines. For the sake of comparsion, the corresponding F2F spectra are also depicted (red solid lines).

where, as expected, we see that atomic relaxation has a marginal impact on the optical response when d = 0.1 nm. At the critical distance d = 0.3 nm, the separation between the atoms is slightly greater in the unrelaxed configuration than in the relaxed one (0.51 and 0.48 nm, respectively). This small rearrangement does affect the absorption spectrum, because the intensity of the tunneling CT is weaker in the unrelaxed configuration. In any case, the changes are merely quantitative and less important than those related to the relative orientation, albeit they illustrate the sensitivity of the plasmonic response to the CT current intensity.

To gain further insights concerning the optical properties of the nanocluster dimers, we analyzed the electron dynamics at different resonant frequencies. Specifically, we looked at the induced densities, the current intensities between the clusters, and the total electric field (external plus induced) at the middle of the junction, $\mathbf{r} = 0$. To carry out this study, we applied a weak uniform quasi-monochromatic laser pulse of mean frequency ω_{ext} over the system with duration $\tau = 20 \pi/\omega_{ext}$ given by

$$\mathbf{E}(t) = -E_0 \sin(\pi t/\tau) \cos(\omega_{\text{ext}} t) \mathbf{e}_x$$
(3)

where $E_0 = 10^{-6}$ a.u. $\simeq 0.51 \times 10^6$ V m⁻¹ is the maximum amplitude of the incident electric field. The maximum intensity of the laser pulse is 34.5 kW cm⁻², which is well below the onset of nonlinear effects.²⁵

In Figure 4, we depicted snapshots of the photoinduced densities in a plane containing the dimer axis for the following selected cases: (a) D mode at d = 0.5 nm (E2E, $\omega_{ext} = 2.83 \text{ eV}/\hbar$), (b) D and Q modes at d = 0.1 nm (E2E, $\omega_{ext} = 2.01 \text{ eV}/\hbar$ and $\omega_{ext} = 3.05 \text{ eV}/\hbar$, respectively), (c) D mode (F2F, $\omega_{ext} = 2.79 \text{ eV}/\hbar$) and Q mode (E2E, $\omega_{ext} = 3.00 \text{ eV}/\hbar$) at d = 0.3 nm. In all of these cases, the relaxed atomic geometries were used for the E2E relative orientation. The snapshots were collected at times where the induced current is maximum (i.e., when the two clusters have the same charge) and where the induced current is close to a minimum (i.e., when the net charge of each cluster reaches its maximum absolute value).

Case (a) is representative of a coupled D mode (albeit very slightly altered by the appearance of a tunneling CT). The coupling between the dipole resonances of each cluster is reflected by a high concentration of oscillating-induced charges of opposite sign in the sides of the junction. As has been extensively analyzed using classical and quantum prescriptions, this distribution of charge is the primary reason for the high electric field enhancements that appear in this plasmonic cavity.

In case (b), we show direct CT modes. Although the overall shape of the driven densities are partially obscured by the atomic corrugation, the different nature of the D and Q modes is evident. Also note that the induced densities are practically zero in the junction, which is in fair correspondence with the single-nanoparticle character of the system at this separation.

Finally, case (c) illustrates the sensitivity of the dynamical response to the atomic configuration in the critical regime in which the optical absorption is affected by photoinduced electron tunneling. The most relevant aspect is the difference between the E2E and F2F driven densities. The first can be assigned to a Q mode (compare with the corresponding Q mode at 0.1 nm), whereas the second has a shape closer to a D mode. Also note the different distributions of the induced densities around the spacial gap between the clusters.

In Figure 5, we display the time-evolution of the induced current, $I_{\rm CT}$, and the total electric field at the middle of the junction ($\mathbf{r} = 0$) for the three cases discussed above. We have also included the induced current and field for the F2F configuration at d = 0.5 nm (D mode, $\omega_{\rm ext} = 2.78 \, {\rm eV}/\hbar$). It is worth emphasizing the overall delay in the response with respect to the applied field and the persistence of the induced currents and fields even when the external field has vanished, which are obvious signatures of resonant coupling. Non-electronic losses are not included in this calculation and, therefore, the decay of the driven modes can only occur via Landau fragmentation (i.e, though the formation of electron-hole pairs).⁶⁴⁻⁶⁶ Also note that the generation of hot electrons



Figure 4. Snapshots of the induced electron densities at different resonant frequencies, as indicated in each panel. The top panels depict the induced densities when the current between the clusters reaches a maximum, whereas the second line corresponds to induced densities when the charge difference between clusters is maximum (zero intensity). The scale range is $-\rho \le \delta n \le +\rho$, where $\rho = 0.5 \times 10^{-6}$ a.u. for d = 0.1 and 0.3 nm, whereas $\rho = 10^{-6}$ a.u. for d = 0.5 nm. A sketch of the corresponding ground-state electron densities is also shown to illustrate the different contact regimes.



Figure 5. Time evolution of induced currents (solid green lines) and total electric fields (dotted blue lines) at the middle of the dimer junction (**r** = 0) due to the resonant coupling of selected modes of the nanoparticle dimer with an applied external field (depicted in the upper panel) of frequency ω_{ext} . In each panel, we indicate the maximum value of the induced intensity, I_{CT} , corresponding to an incident electric field with maximum amplitude $E_0 = 10^{-6}$ a.u.

mediated by plasmon resonances is a very efficient mechanism that has important implications in heterogeneous catalysis, for instance.⁶⁷ In any case, the excitation of electron-hole pairs is the main damping mechanism of plasmons in nanoparticles of this size.

The electric fields at $\mathbf{r} = 0$ for the two coupled D modes at d = 0.5 nm considered here (EFE and F2F) are very similar, although the field corresponding to the E2E geometry is slightly more intense. We can attribute this effect to the shorter atom—atom distance and also to the more angular profile of the induced density in the E2E configuration. On the other hand, fields and intensities practically oscillate in phase, corresponding to a resistive character of the junction. This behavior agrees with that obtained for the jellium nanocluster²⁵ and nanowire dimers.³³ Note the weak charge-transfer intensity (on the order of 100 nA) for the incident laser pulse given in eq 3.

Focusing on the direct CT regime, d = 0.1 nm, we must first note the different phase shifts of the oscillations of both the Q and D modes with respect to the applied field. Moreover, for both resonances, there is a relative phase between the induced current and the electric field in the center of the dimer with the intensity being delayed with respect to the total electric field. Again, this capacitive character of the resonance is in full agreement with previous findings for jellium systems.^{25,33} Although the optical absorption at the D mode is weaker than at the Q resonance (see Figure 1), the E field intensity is stronger in the D mode. Nevertheless, once the applied field fades out, the amplitudes of the D mode oscillations are quickly damped as expected from the wider corresponding peak in the absorption spectrum. Finally, in this regime, the charge-transfer intensity is approximately one order of magnitude larger than in the tunneling regime previously described (at touching distance, d = 0, the maximum charge-transfer intensity is 1600 nA).

In line with the previous discussion, there are quantitative differences between the E2E and F2F orientations in the intermediate distance regime d = 0.3 nm. The intensities of the driven currents are rather similar up to a small relative phase. However, the electric field in the E2E geometry is weaker than in the F2F orientation. This is not surprising because the dominant mode in the E2E geometry is the Q resonance. Remarkably, the intensity and the total E field oscillate in phase in the F2F dimer, thus indicating that the charge flows across a resistive junction. On the contrary, the E field and the current do not oscillate completely in phase in the E2E geometry. This is consistent with a weak capacitive behavior, which again can be traced back to the different atomic configurations in the junction.

In summary, we have presented a detailed study of the impact of the atomic configuration on the electromagnetic modes of prototypical metallic nanodimers when a charge transfer is established between the constituent clusters. Effects like atomic relaxation and different relative orientations, to date unexplored in quantum implementations of ab initio nanoplasmonics, have been explicitly addressed. Our findings confirm the accuracy of the jellium model, either in combination with quantum mechanical calculations or classical theories, except in the subnanometric separation regime in which the photoinduced tunnel current leads to changes in the optical properties of the system. This is precisely the regime where the most complicated processes occur. Thus, we have shown that accounting for the atomic structure of the junction (mainly the relative orientations between the faces) for very close nanoparticles is necessary to obtain theoretical results with enough predicitive power.

Although quantum TDDFT simulations can be applied to systems containing thousands of atoms, this is still too small for the sizes of many nanoparticles of technological interest. In these cases, the theoretical analyses aimed at helping in the design and characterization of novel nanodevices must necessarily be performed using either advanced prescriptions of the well-established classical electromagnetic theory^{19,20} or simplified TDDFT methods.^{68,69} However, even in simple systems like the one analyzed in this work, there is a subtle interplay between induced near fields (which can be perfectly described classically using nonlocal optics) and induced tunnel charge transfers (which can be approximately accounted for using effective dielectric media²⁰). Therefore, the present work provides a stringent playfield for the assessment of future refinements of semiclassical theories which, as we have noted, are much more amenable for the analysis of very complex structures than quantum ab initio methods. From a different perspective, the conclusions raised in this study pave the way for further explorations concerning fieldlike optoelectronics, nanosensing, and photoinduced catalysis in which the complexity of the light-matter interactions at the nano scale opens the possibility of a panoply of applications.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thankfully acknowledge financial support by the European Research Council (ERC-2010-AdG Proposal No. 267374 and ERC-2011-AdG Proposal No. 290891), the Spanish Government (Grants MAT2011-28581-C02-01, FIS2013-46159-C3-1-P, and MAT2014-53432-C5-5-R), and the Basque Country Government (Grupos Consolidados IT-578-13). We also appreciate technical support by Joseba Alberdi-Rodríguez and fruitful discussions with Prof. Javier Aizpurua, Prof. Andrei G. Borisov, Prof. Juan Carlos Cuevas, Dr. Johannes Feist, Dr. Antonio Fernández-Domínguez, and Dr. Pu Zhang.

REFERENCES

(1) Schuller, J. A.; Barnard, E. S.; Cai, W.; Jun, Y. C.; White, J. S.; Brongersma, M. L. Plasmonics for Extreme Light Concentration and Manipulation. *Nat. Mater.* **2010**, *9*, 193–204.

(2) Halas, N. J.; Lal, S.; Chang, W.-S.; Link, S.; Nordlander, P. Plasmons in Strongly Coupled Metallic Nanostructures. *Chem. Rev.* **2011**, *111*, 3913–3961.

(3) Gray, S. K. Theory and Modeling of Plasmonic Structures. J. Phys. Chem. C 2013, 117, 1983–1994.

(4) Ward, D. R.; Hüser, F.; Pauly, F.; Cuevas, J. C.; Natelson, D. Optical Rectification and Field Enhancement in a Plasmonic Nanogap. *Nat. Nanotechnol.* **2010**, *5*, 732–736.

(5) Galperin, M.; Nitzan, A. Molecular Optoelectronics: the Interaction of Molecular Conduction Junctions with Light. *Phys. Chem. Chem. Phys.* **2012**, *14*, 9421–9438.

(6) Mühlschlegel, P.; Eisler, H.-J.; Martin, O. J. F.; Hecht, B.; Pohl, D. W. Resonant Optical Antennas. *Science* **2005**, *308*, 1607–1609.

(7) Tsuboi, Y.; Shoji, T.; Kitamura, N.; Takase, M.; Murakoshi, K.; Mizumoto, Y.; Ishihara, H. Optical Trapping of Quantum Dots Based on Gap-Mode-Excitation of Localized Surface Plasmon. *J. Phys. Chem. Lett.* **2010**, *1*, 2327–2333.

(8) Xu, H.; Bjeneld, E. J.; Käll, M.; Börjesson, L. Spectroscopy of Single Hemoglobin Molecules by Surface Enhanced Raman Scattering. *Phys. Rev. Lett.* **1999**, *83*, 4357–4360.

(9) Stewart, M. E.; Anderton, C. R.; Thompson, L. B.; Maria, J.; Gray, S. K.; Rogers, J. A.; Nuzzo, R. G. Nanostructured Plasmonic Sensors. *Chem. Rev.* **2008**, *108*, 494–521.

(10) Vo-Dinh, T.; Dhawan, A.; Norton, S. J.; Khoury, C. G.; Wang, H.-N.; Misra, V.; Gerhold, M. D. Plasmonic Nanoparticles and Nanowires: Design, Fabrication and Application in Sensing. *J. Phys. Chem. C* **2010**, *114*, 7480–7488.

(11) Aubry, A.; Lei, D. Y.; Fernández-Domínguez, A. I.; Sonnefraud, Y.; Maier, S. A.; Pendry, J. B. Plasmonic Light-Harvesting Devices over the Whole Visible Spectrum. *Nano Lett.* **2010**, *10*, 2574–2579.

(12) Maier, S. A. Plasmonics: Fundamentals and Applications; Springer: New York, 2007.

(13) Tame, M. S.; McEnery, K. R.; Özdemir, S. K.; Lee, J.; Maier, S. A.; Kim, M. S. Quantum Plasmonics. *Nat. Phys.* **2013**, *9*, 329–340.

(14) Arielly, R.; Ofarim, A.; Noy, G.; Selzer, Y. Accurate Determination of Plasmonic Fields in Molecular Junctions by Current Rectification at Optical Frequencies. *Nano Lett.* **2011**, *11*, 2968–2972.

(15) Savage, K. J.; Hawkeye, M. M.; Esteban, R.; Borisov, A. G.; Aizpurua, J.; Baumberg, J. J. Revealing the Quantum Regime in Tunneling Plasmonics. *Nature* **2012**, *491*, 574–577.

(16) Scholl, J. A.; García-Etxarri, A.; Koh, A. L.; Dionne, J. A. Observation of Quantum Tunneling between Two Plasmonic Nanoparticles. *Nano Lett.* **2013**, *13*, 564–569.

(17) Tan, S. F.; Wu, L.; Yang, J. K. W.; Bai, P.; Bosman, M.; Nijhuis, C. A. Quantum Plasmon Resonances Controlled by Molecular Tunnel Junctions. *Science* **2014**, *343*, 1496–1499.

(18) Zhu, W.; Crozier, K. B. Quantum Mechanical Limit to Plasmonic Enhancement as Observed by Surface-Enhanced Raman Scattering. *Nature Commun.* **2014**, *5*, 5228.

(19) Toscano, G., Rockstuhl, C., Evers, F., Xu, H., Mortensen, N. A. Self-consistent Hydrodynamic Approach to Nanoplasmonics: Resonance Shifts and Spill-out effects. arXiv:1048:5862 [physics.optics] preprint.

(20) Esteban, R.; Borisov, A. G.; Nordlander, P.; Aizpurua, J. Bridging Quantum and Classical Plasmonics with a Quantum-Corrected Model. *Nature Commun.* **2012**, *3*, 825.

(21) Atay, T.; Song, J.-H.; Nurmikko, A. V. Strongly Interacting Plasmon Nanoparticle Pairs: From Dipole-Dipole Interaction to Conductively Coupled Regime. *Nano Lett.* **2004**, *4*, 1627–1631.

(22) Marhaba, S.; Bachelier, G.; Bonnet, C.; Broyer, M.; Cottancin, E.; Grillet, N.; Lermé, J.; Vialle, J.-L.; Pellarin, M. Surface Plasmon Resonance of Single Gold Nanodimers near the Conductive Contact Limit. *J. Phys. Chem. C* **2009**, *113*, 4349–4356.

(23) Pérez-González, O.; Zabala, N.; Borisov, A. G.; Halas, N. J.; Nordlander, P. Optical Spectroscopy of Conductive Junctions in Plasmonic Cavities. *Nano Lett.* **2010**, *10*, 3090–3095.

(24) Zuloaga, J.; Prodan, E.; Nordlander, P. Quantum Description of the Plasmon Resonances of a Nanoparticle Dimer. *Nano Lett.* **2009**, *9*, 887–891.

(25) Marinica, D. C.; Kazansky, A. K.; Nordlander, P.; Aizpurua, J.; Borisov, A. G. Quantum Plasmonics: Nonlinear Effects in the Field Enhancement of a Plasmonic Nanoparticle Dimer. Nano Lett. 2012, 12, 1333–1339.

(26) Runge, E.; Gross, E. K. U. Density-Functional Theory for Time-Dependent Systems. *Phys. Rev. Lett.* **1984**, *52*, 997–1000.

(27) Onida, G.; Reining, L.; Rubio, A. Electronic Excitations: Density-Functional Versus Many-Body Green's-Function Approaches. *Rev. Mod. Phys.* **2002**, *74*, 601–659.

(28) Pitarke, J. M.; Silkin, V. M.; Chulkov, E. V.; Echenique, P. M. Theory of Surface Plasmons and Surface-Plasmon Polaritons. *Rep. Prog. Phys.* **2007**, *70*, 1–87.

(29) Marques, M. A. L., Maitra, N. T., Nogueira, F. M. S., Gross, E. K. U., Rubio, A., Eds. Fundamentals of Time-Dependent Density Functional Theory; Springer: Berlin, 2012.

(30) Zuloaga, J.; Prodan, E.; Nordlander, P. Optical Properties and Tunability of Metallic Nanorods. *ACS Nano* **2010**, *4*, 5269–5276.

(31) Stella, L.; Zhang, P.; García-Vidal, F. J.; Rubio, A.; García-González, P. Performance of Nonlocal Optics when Applied to Plasmonic Nanostructures. *J. Phys. Chem. C* 2013, *117*, 8941–8949.

(32) Teperik, T. V.; Nordlander, P.; Aizpurua, J.; Borisov, A. G. Robust Subnanometric Plasmon Ruler by Rescaling of the Nonlocal Optical Response. *Phys. Rev. Lett.* **2013**, *110*, 263901.

(33) Teperik, T. V.; Nordlander, P.; Aizpurua, J.; Borisov, A. G. Quantum Effects and nonlocality in Strongly Coupled Plasmonic Nanowire Dimers. *Opt. Express* **2013**, *21*, 27306–27325.

(34) Andersen, K.; Jensen, K. L.; Mortensen, N. A.; Thygesen, K. S. Visualizing Hybridized Quantum Plasmons in Coupled Nanowires: From Classical to Tunneling Regime. *Phys. Rev. B* **2013**, *87*, 235433.

(35) Kulkarni, V.; Prodan, E.; Nordlander, P. Quantum Plasmonics:
 Optical Properties of a Nanomatryushka. *Nano Lett.* 2013, 13, 5873–5879.

(36) Zhang, H.; Kulkarni, V.; Prodan, E.; Nordlander, P.; Gorovov, O. Theory of Quantum Plasmon Resonances in Doped Seminconductor Nanocrystals. J. Phys. Chem. C 2014, 118, 16035–16042.

(37) McMahon, J. M.; Gray, S. K.; Schatz, G. C. Nonlocal Optical Response of Metal Nanostructures with Arbitrary Shape. *Phys. Rev. Lett.* **2009**, *103*, 097403.

(38) McMahon, J. M.; Gray, S. K.; Schatz, G. C. Optical Properties of Nanowire Dimers with a Spatially Nonlocal Dielectric Function. *Nano Lett.* **2010**, *10*, 3473–3481.

(39) David, C.; García de Abajo, F. J. Spatial Nonlocality in the Optical Response of Metal Nanoparticles. *J. Phys. Chem. C* 2011, *115*, 19470–19475.

(40) Raza, S.; Toscano, G.; Jauho, A.-P.; Wubs, M.; Mortensen, N. A. Unusual Resonances in Nanoplasmonic Structures Due to Nonlocal Response. *Phys. Rev. B* 2011, *84*, 121412(R).

(41) Toscano, G.; Raza, S.; Jauho, A.-P.; Mortensen, N. A.; Wubs, M. Modified Field Enhancement in Plasmonic Nanowire Dimers Due to Nonlocal Response. *Opt. Express* **2012**, *20*, 4176–4188.

(42) Fernández-Domínguez, A. I.; Wiener, A.; García-Vidal, F. J.; Maier, S. A.; Pendry, J. B. Transformation-Optics Description of Nonlocal Effects in Plasmonic Nanostructures. *Phys. Rev. Lett.* **2012**, *108*, 106802.

(43) Fernández-Domínguez, A. I.; Zhang, P.; Luo, Y.; Maier, S. A.; García-Vidal, F. J.; Pendry, J. B. Transformation-Optics Insight into Nonlocal Effects in Separated Nanowires. *Phys. Rev. B* 2012, *84*, 241110(R).

(44) Dong, T.; Ma, X.; Mittra, R. Optical Response in Subnanometer Gaps due to Nonlocal Response and Quantum Tunneling. *Appl. Phys. Lett.* **2012**, *101*, 233111.

(45) Christensen, T.; Yan, W.; Raza, S.; Jauho, A.-P.; Mortensen, N. A.; Wubs, M. Nonlocal Response of Metallic Nanospheres Probed by Light, Electrons, and Atoms. *ACS Nano* **2014**, *8*, 1745–1758.

(46) Liebsch, A. Surface-plasmon Dispersion and Size Dependence of Mie Resonance: Silver versus Simple Metals. *Phys. Rev. B* **1993**, *48*, 11317–11328.

(47) Weissker, H.-Ch.; Barron Escobar, H.; Thanthirige, V. D.; Kwak, K.; Lee, D.; Ramakrishna, G.; Whetten, R. L.; López-Lozano, X. Information on Quantum States Pervades the Visible Spectrum of the

Ubiquitous $Au_{144}(SR)_{60}$ Gold Nanocluster. Nat. Commun. 2014, 5, 3785.

(48) Zhang, P.; Feist, J.; Rubio, A.; García-González, P.; García-Vidal, F. J. Ab Initio Nanoplasmonics: The Impact of Atomic Structure. *Phys. Rev. B* **2014**, *90*, 161407(R).

(49) Noya, E. G.; Doye, J. P. K.; Wales, D. J.; Aguado, A. Geometric Magic Numbers of Sodium Clusters: Interpretation of the Melting Behaviour. *Eur. Phys. J. D* **2007**, *43*, 57–60.

(50) The relaxed atomic structure of the Na₂₉₇ cluster is taken from the Cambridge Cluster Database, http://www-wales.ch.cam.ac.uk/CCD.html.

(51) Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **1965**, *140*, A1133–A1138.

(52) Marques, M. A. L.; Castro, A.; Bertsch, G. F.; Rubio, A. octopus: a First-Principles Tool for Excited Electron-Ion Dynamics. *Comput. Phys. Commun.* **2003**, *151*, 60–78.

(53) Castro, A.; Appel, H.; Oliveira, M.; Rozzi, C. A.; Andrade, X.; Lorenzen, F.; Marques, M. A. L.; Gross, E. K. U.; Rubio, A. octopus: a Tool for the Application of Time-Dependent Density Functional Theory. *Phys. Status Solidi B* **2006**, *243*, 2465–2488.

(54) Andrade, X.; Alberdi-Rodríguez, J.; Strubbe, D. A.; Oliveira, M. J. T.; Nogueira, F.; Castro, A.; Muguerza, J.; Arruabarrena, A.; Louie, S. G.; Aspuru-Guzik, A.; Rubio, A.; Marques, M. A. L. Time-Dependent Density-Functional Theory in Massively Parallel Computer Architectures: the octopus Project. *J. Phys.: Condens. Matter* **2012**, *24*, 233202.

(55) Andrade, X.; Strubbe, D.; de Giovannini, U.; Larsen, A. H.; Oliveira, M. J. T.; Alberdi-Rodríguez, J.; Varas, A.; Theophilou, I.; Helbig, N.; Verstraete, M. J.; Stella, L.; Nogueira, F.; Aspuru-Guzik, A.; Castro, A.; Marques, M. A. L.; Rubio, A. Real-Space Grids and the Octopus Code as Tools for the Development of New Simulation Approaches for Electronic Systems. *Phys. Chem. Chem. Phys.* **2015**, DOI: 10.1039/C5CP00351B.

(56) Troullier, N.; Martins, J. L. Efficient Pseudopotentials for Plane-Wave Calculations. *Phys. Rev. B* **1991**, *43*, 1993–2006.

(57) Bitzek, E.; Koskinen, P.; Gähler, F.; Moseler, M.; Gumbsch, P. Structural Relaxation Made Simple. *Phys. Rev. Lett.* **2006**, *97*, 170201. (58) Yabana, K.; Bertsch, G. F. Time-Dependent Local-Density

Approximation in Real Time. *Phys. Rev. B* **1996**, *54*, 4484–4487. (59) Prodan, E.; Radloff, C.; Halas, N. J.; Nordlander, P. A

Hybridization Model for the Plasmon Response of Complex Nanostructures. *Science* **2003**, *302*, 419–422. (60) Nordlander, P.; Oubre, C.; Prodan, E.; Li, K.; Stockman, M. I.

Plasmon Hybridization of Nanoparticle Dimers. *Nano Lett.* **2004**, *4*, 899–903.

(61) Romero, I.; Aizpurua, J.; Bryant, G. W.; García de Abajo, F. J. Plasmons in Nearly Touching Metallic Nanoparticles: Singular Response in the Limit of Touching Dimers. *Opt. Express* **2006**, *14*, 9988–9999.

(62) Luo, Y.; Lei, D. Y.; Maier, S. A.; Pendry, J. B. Transformation-Optics Description of Plasmonics Nanostructures Containing Blunt Edges/Corners:From Symmetric to Asymmetric Edge Rounding. *ACS Nano* **2012**, *6*, 6492–6506.

(63) Lei, D. Y.; Aubry, A.; Luo, Y.; Maier, S. A.; Pendry, J. B. Plasmonic Interaction between Overlapping Nanowires. *ACS Nano* **2011**, *5*, 597–607.

(64) Townsend, E.; Bryant, G. W. Plasmonic Properties of Metallic Nanoparticles: The Effects of Size Quantization. *Nano Lett.* **2012**, *12*, 429–434.

(65) Yannouleas, C.; Vigezzi, E.; Broglia, R. A. Evolution of the Optical Properties of Alkali-Metal Microclusters Towards the Bulk: The Matrix Random-Phase-Approximation Description. *Phys. Rev. B* **1993**, 47, 9849–9861.

(66) Li, J.-H.; Hayashi, M.; Guo, G.-Y. Plasmonic Excitations in Quantum-Sized Sodium Nanoparticles Studied by Time-Dependent Density Functional Calculations. *Phys. Rev. B* 2013, *88*, 155437.

(67) Mukherjee, S.; Libisch, F.; Large, N.; Neumann, O.; Brown, L. V.; Cheng, J.; Lassiter, J. B.; Carter, E. A.; Nordlander, P.; Halas, N. J. Hot Electrons Do the Impossible: Plasmon-Induced Dissociation of H_2 on Au. Nano Lett. 2013, 13, 240–247.

(68) Banerjee, A.; Harbola, M. K. Hydrodynamic Approach to Time-Dependent Density Functional Theory; Response Properties of Metal Clusters. J. Chem. Phys. **2000**, 113, 5614–5623.

(69) Xiang, H.; Zhang, X.; Neuhauser, D.; Lu, G. Size-Dependent Plasmonics Resonances from Large-Scale Quantum Simulations. *J. Phys. Chem. Lett.* **2014**, *5*, 1163–1169.