Quantum effects in the plasmon response of bimetallic core-shell nanostructures

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Abstract: We report a quantum mechanical study of the plasmonic response of bimetallic spherical core/shell nanoparticles. The systems comprise up to 10⁴ electrons and their optical response is addressed with Time Dependent Density Functional Theory calculations. These quantum results are compared with classical electromagnetic calculations for core/shell systems formed by Al/Na, Al/Au and Ag/Na, as representative examples of bimetallic systems. We show that for shell widths in the nanometer range, the system cannot be described as a simple stack of two metals. The finite size effect and the transition layer formed between the core and the shell strongly modify the optical properties of the compound nanoparticle. In particular this configuration leads to a frequency shift of the plasmon resonance with shell character and an increased plasmon decay into electron-hole pairs which eventually quenches this resonance for very thin shells. This effect is difficult to capture with a classical theory even upon adjustment of the parameters of a combination of metallic dielectric functions.

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References and links

- J. Lee, P. Hernandez, J. Lee, A. O. Govorov, N. A. Kotov, "Exciton-plasmon interactions in molecular spring assemblies of nanowires and wavelength-based protein detection," Nature Materials 6, 291–295 (2007).
- M. E. Stewart, C. R. Anderton, L. B. Thompson, J. Maria, Stephen K. Gray, J. A. Rogers, and R. G. Nuzzo, "Nanostructured plasmonic sensors," Chem. Rev. 108, 494–521 (2008).
- H. Xu, E. Bjeneld, M. Käll, L. Börjesson, "Spectroscopy of single hemoglobin molecules by surface enhanced Raman scattering," Phys. Rev. Lett. 83, 4357 (1999).
- C. E. Talley, J. B. Jackson, C. Oubre, N. K. Grady, C. W. Hollars, S. M. Lane, T. R. Huser, P. Nordlander, N. J. Halas, "Surface-enhanced Raman scattering from individual Au nanoparticles and nanoparticle dimer substrates," Nano Lett. 5, 1569 (2005).
- J. Theiss, P. Pavaskar, P. M. Echternach, R. E. Muller, S. B. Cronin, "Plasmonic nanoparticle arrays with nanometer separation for high-performance SERS substrates," Nano Lett. 10, 2749 (2010).
- J. Langer, S. M. Novikov, L. M. Liz-Marzán, "Sensing using plasmonic nanostructures and nanoparticles," Nanotechnology 26, 322001 (2015).
- T. H. Taminiau, F. D. Stefani, F. B. Segerink, N. F. van Hulst, "Optical antennas direct single-molecule emission," Nature Photonics 2, 234–237 (2008).
- C. Belacel, B. Habert, F. Bigourdan, F. Marquier, J.-P. Hugonin, S. Michaelis de Vasconcellos, X. Lafosse, L. Coolen, C. Schwob, C. Javaux, B. Dubertret, J.-J. Greffet, P. Senellart, "Controlling spontaneous emission with plasmonic optical patch antennas," A. Maitre, Nano Lett. 13, 1516–1521 (2013).
- 9. L. Novotny, N. van Hulst, "Antennas for light," Nature Photonics 5, 83-90 (2011).
- C. D. Lindstrom, X.-Y. Zhu, "Photoinduced Electron Transfer at Molecule-Metal Interfaces," Chem. Rev. 106, 4281–4300 (2006).
- C. Frischkorn, M. Wolf, "Femtochemistry at Metal Surfaces: Nonadiabatic Reaction Dynamics," Chem. Rev. 106(10), 4207–4233 (2006).
- S. Linic, U. Aslam, C. Boerigter, M. Morabito, "Photochemical transformations on plasmonic metal nanoparticles," Nature Materials 14, 567–576 (2015).

Research Article

- A. Stolz, J. Berthelot, M-M Mennemanteuil, G. Colas des Francs, L. Markey, V. Meunier, A. Bouhelier, "Nonlinear Photon-Assisted Tunneling Transport in Optical Gap Antennas," Nano Lett. 14, 2330–2338 (2014).
- 14. J. Berthelot, G. Bachelier, M. Song, P. Rai, G. Colas des Francs, A Dereux, and A Bouhelier, "Silencing and enhancement of second-harmonic generation in optical gap antennas," Opt. Express **20**, 10498 (2012).
- T. Hanke, G. Krauss, D. Träutlein, B. Wild, R. Bratschitsch, and A. Leitenstorfer, "Efficient Nonlinear Light Emission of Single Gold Optical Antennas Driven by Few-Cycle Near-Infrared Pulses," Phys. Rev. Lett. 103, 257404 (2009).
- S. Paloma, M. Danckwerts, and L. Novotny, "Nonlinear plasmonics with gold nanoparticle antennas," J. Opt. A: Pure Appl. Opt. 11, 114030 (2009).
- W. Cai, A. P. Vasudev, M. L. Brongersma, "Electrically Controlled Nonlinear Generation of Light with Plasmonics," Science 333, 1720 (2011).
- A. Bouhelier, M. Beversluis, A. Hartschuh, L. Novotny, "Near-field second-harmonic generation induced by local field enhancement," Phys. Rev. Lett. 90, 013903 (2003).
- 19. Kauranen M., Zayats A.V., "Nonlinear plasmonics," Nature Photonics 6, 737 (2012).
- R. Alvarez-Puebla, L. M. Liz-Marzán, F. J. García de Abajo, "Light Concentration at the Nanometer Scale," J. Phys. Chem. Lett. 1, 2428–2434 (2010).
- J. A. Schuller, E. S. Barnard, W. Cai, Y. C. Jun, J. S. White, M. L. Brongersma, "Plasmonics for extreme light concentration and manipulation," Nature Materials 9, 193–204 (2010).
- N. J. Halas, S. Lal, W.-S. Chang, S. Link, P. Nordlander, "Plasmons in Strongly Coupled Metallic Nanostructures," Chem. Rev. 111, 3913–3961 (2011).
- A. Kuzyk, R. Schreiber, Z. Fan, G. Pardatscher, E.-M. Roller, A. Högele, F. C. Simmel, A. O. Govorov, T. Liedl, "DNA-based self-assembly of chiral plasmonic nanostructures with tailored optical response," Nature 483, 311–314 (2012).
- M. B. Cortie, A. M. McDonagh, "Synthesis and optical properties of hybrid and alloy plasmonic Nanoparticles," Chem. Rev. 111, 3713–3735 (2011).
- M. Mayer, L. Scarabelli, K. March, T. Altantzis, M. Tebbe, M. Kociak, S. Bals, F. J. García de Abajo, A. Fery, L. M. Liz-Marzán, "Controlled living nanowire growth: precise control over the morphology and optical properties of AgAuAg bimetallic nanowires," Nano Lett. 15, 5427–5437 (2015).
- B. Goris, G. Guzzinati, C. Fernández-López, J. Pérez-Juste, L. M. Liz-Marzán, A. Trügler, U. Hohenester, J. Verbeeck, S. Bals, G. Van Tendeloo, "Plasmon mapping in Au@Ag nanocube assemblies," J. Phys. Chem. C 118, 15356–15362 (2014).
- A. K. Samal, L. Polavarapu, S. Rodal-Cedeira, L. M. Liz-Marzán, J. Pérez-Juste, I. Pastoriza-Santos, "Size tunable Au@Ag core-shell nanoparticles: synthesis and surface-enhanced raman scattering properties," Langmuir 29, 15076– 15082 (2013).
- L. Chuntonov, M. Bar-Sadan, L. Houben, G. Haran, "Correlating electron tomography and plasmon spectroscopy of single noble metal core-shell nanoparticles," Nano Lett. 12, 145–150 (2012).
- S. Xing, Y. Feng, Y. Y. Tay, T. Chen, J. Xu, M. Pan, J. He, H. H. Hng, Q. Yan, H. Chen, "Reducing the symmetry of bimetallic Au@Ag nanoparticles by exploiting eccentric polymer shells," J. Am. Chem. Soc. 132, 9537–9539 (2010).
- R. G. Freeman, M. B. Hommer, K. C. Grabar, M. A. Jackson, M. J. Natan, "Ag-Clad Au nanoparticles: novel aggregation, optical, and surface-enhanced Raman scattering properties," J. Phys. Chem. 100, 718–724 (1996).
- S. Li, Y. Zhao, Y. Jiang, Y. Zhang, "Preparation and properties of noble metal core/shell nanostructures prepared by excimer laser ablation in liquid solutions," J. Laser Appl. 26, 022001 (2014).
- 32. R. H. Morris, L. F. Collins, "Optical properties of multilayer colloids," J. Chem. Phys. 41, 3357-3363 (1964).
- J. Sinzig, U. Radtke, M. Quinten, U. Kreibig, "Binary clusters: homogeneous alloys and nucleus-shell structures," Z. Phys. D 26, 242–245 (1993).
- 34. S. Link, S. L. Wang, and M. A. El-Sayed, "Alloy formation of gold-silver nanoparticles and the dependence of the plasmon absorption on their composition," J. Phys. Chem. B 103, 3529–3533 (1999).
- M. Moskovits, I. Srnová-Šloufová, B. Vlčková, "Bimetallic Ag-Au nanoparticles: Extracting meaningful optical constants from the surface-plasmon extinction spectrum," J. Chem. Phys. 116, 10435–10446 (2002).
- P. Mulvaney, M. Giersig, A. Henglein, "Electrochemistry of multilayer colloids: preparation and absorption spectrum of gold-coated silver particles," J. Phys. Chem. 97, 7061–7064 (1993).
- W. Benten, N. Nilius, N. Ernst, H.-J. Freund, "Photoemission spectroscopy of single oxide-supported Ag-Au clusters," Phys. Rev. B 72, 045403 (2005).
- A. L. Aden and M. J. Kerker, "Scattering of electromagnetic waves from two concentric spheres," Appl. Phys. 22, 1242–1246 (1951).
- J. Sinzig, M. Quinten, "Scattering and absorption by spherical multilayer particles," Appl. Phys. A: Mater. Sci. Process. 58, 157–162 (1994).
- H. Xu, "Multilayered metal core-shell nanostructures for inducing a large and tunable local optical field," Phys. Rev. B 72, 073405 (2005).
- C. E. Román-Velázquez, C. Noguez, "Designing the plasmonic response of shell nanoparticles: spectral representation," J. Chem. Phys. 134, 044116 (2011).
- 42. M. Arnold, M. Blaber, and M. Ford, "Local plasmon resonances of metal-in-metal core-shells," Optics Express 22, 3186–3198 (2014).

Research Article

Optics EXPRESS

- M. K. Nayak and S. K. Ghosh, "Optical properties of bimetallic nanospheres: Effect of diffuse electron density profiles at the boundary surfaces," J. Chem. Phys. 130, 204702 (2009).
- S. Bruzzone, G. P. Arrighini, and C. Guidotti, "Theoretical study of the optical absorption behavior of Au/Ag core-shell nanoparticles," Mater. Sci. Eng. C 23, 965–970 (2003).
- C. Yannouleas, P. Jena, and S. N. Khanna, "Optical resonances in bimetallic clusters and their relation to the electronic structure," Phys. Rev. B 46, 9751–9760 (1992).
- 46. G. Toscano, J. Straubel, A. Kwiatkowski, C. Rockstuhl, F. Evers, H. Xu, N. A. Mortensen, and M. Wubs, "Resonance shifts and spill-out effects in self-consistent hydrodynamic nanoplasmonics," Nature Communications 6, 7132 (2015).
- W. Zhu, R. Esteban, A. G. Borisov, J. J. Baumberg, P. Nordlander, H. J. Lezec, J. Aizpurua, and K. B. Crozier, "Quantum mechanical effects in plasmonic structures with subnanometre gaps," Nature Communications 7, 11495 (2016).
- A. Varas, P. García-González, J. Feist, F. J. García-Vidal, and A. Rubio, "Quantum plasmonics: from jellium models to ab initio calculations," Nanophotonics DOI: 10.1515/nanoph-2015-0141 (2016).
- E. Prodan, P. Nordlander, N. J. Halas, "Electronic structure and optical properties of gold nanoshells," Nano Lett. 3, 1411–1415 (2003).
- E. Prodan, P. Nordlander, N. J. Halas, "Effects of dielectric screening on the optical properties of metallic nanoshells," Chem. Phys. Lett. 368, 94–101 (2003).
- A. Kawabata, R. Kubo, "Electronic Properties of Fine Metallic Particles. II. Plasma Resonance Absorption," Journal of the Physical Society of Japan 21, 1765–1772 (1966).
- R. Ruppin, Y. Yatom, "Size an shape effects on the broadening of the plasma resonance absorption in metals," Phys. Status Solidi 74, 647–654 (1976).
- C. Yannouleas, R. A. Broglia, "Landau damping an wall dissipation in large metal clusters," Ann. Phys. 217, 105–141 (1992).
- S. Link and M. A. El-Sayed, "Spectral Properties and Relaxation Dynamics of Surface Plasmon Electronic Oscillations in Gold and Silver Nanodots and Nanorods," J. Phys. Chem. B 103, 8410–8426 (1999).
- J. Lermé, "Size evolution of the surface plasmon resonance damping in silver nanoparticles: confinement and dielectric effects," J. Phys. Chem. C 115, 14098–14110 (2011).
- 56. H. Haberland, "Looking from both sides," Nature 494, E1-E2 (2013).
- R. C. Monreal, T. J. Antosiewicz, P. S. Apell, "Competition between surface screening and size quantization for surface plasmons in nanoparticles," New J. of Physics 15, 083044 (2013).
- P. Apell, Å. Ljungbert, "A general non-local theory for the electromagnetic response of a small metal particle," Physica Scripta 26, 113–118 (1982).
- D. C. Marinica, A. K. Kazansky, P. Nordlander, J. Aizpurua, and A. G. Borisov, "Quantum Plasmonics: Nonlinear Effects in the Field Enhancement of a Plasmonic Nanoparticle Dimer," Nano Lett. 12, 1333 (2012).
- M. A. L. Marques, and E. K. U. Gross, "Time-Dependent Density Functional Theory," Ann. Rev. of Phys. Chem. 55, 427 (2004).
- O. Gunnarson, and B. I. Lundqvist, "Exchange and correlation in atoms, molecules, and solids by the spin-densityfunctional formalism," Phys. Rev. B 13, 4274 (1976).
- E. V. Chulkov, V. M. Silkin, P. M. Echenique, "Image potential states on metal surfaces: binding energies and wave functions," Surf. Sci. 437, 330–352 (1999).
- J. P. Perdew, H. Q. Tran, E. D. Smith, "Stabilized jellium: Structureless pseudopotential model for the cohesive and surface properties of metals," Phys. Rev. B 42, 11627–11636 (1990).
- V. Kulkarni, E. Prodan, and P. Nordlander, "Quantum Plasmonics: Optical Properties of a Nanomatryushka," Nano Lett. 13, 5873 (2013).
- 65. A. Liebsch, "Surface plasmon dispersion of Ag," Phys. Rev. Lett. 71, 145-148 (1993).
- 66. A. Manjavacas, F. J. García de Abajo, "Tunable plasmons in atomically thin gold nanodisks," Nature Communications **5**, 3548 (2014).
- C. Sönnichsen, T. Franzl, T. Wilk, G. von Plessen, J. Feldmann, "Plasmon resonances in large noble metal clusters," New J. of Phys. 4, 93 (2002).
- E. Cottancin, G. Celep, J. Lermé, M. Pellarin, J. R. Huntzinger, J. L. Vialle, M. Broyer, "Optical properties of moble metal clusters as a function of the size: Comparison between experiments and a semi-quantal theory," Theoretical Chemistry Accounts 116, 514–523 (2006).
- J. Zuloaga, E. Prodan, P. Nordlander, "Quantum description of the plasmon resonances of a nanoparticle dimer," Nano Lett. 9, 887 (2009).
- R. Esteban, A. G. Borisov, P. Nordlander, J. Aizpurua, "Bridging quantum and classical plasmonics with a quantumcorrected model," Nature Commun. 3, 825 (2012).
- K. J. Savage, M. M. Hawkeye, R. Esteban,; A. G. Borisov, J. Aizpurua, J. J. Baumberg, "Revealing the quantum regime in tunnelling plasmonics," Nature 491, 574–577 (2012).
- J. A. Scholl, A. García-Etxarri, A. L. Koh, J. A. Dionne, "Observation of Quantum Tunneling between Two Plasmonic Nanoparticles," Nano Lett. 13, 564–569 (2013).
- M. W. Knight, L. Liu, Y. Wang, L. Brown, S. Mukherjee, N. S. King, H. O. Everitt, P. Nordlander, N. J. Halas, "Aluminum Plasmonic Nanoantennas," Nano Lett. 12, 6000–6004 (2012).
- 74. M. W. Knight, N. S. King, L. Liu, H. O. Everitt, P. Nordlander, N. J. Halas, "Aluminum for plasmonics," ACS Nano

8,834-840 (2014).

75. D. Gérard, S. K. Gray, "Aluminum plasmonics," J. Phys. D: Appl. Phys. 48, 184001 (2015).

- L. Zhou, Y. Tan, J. Wang, W. Xu, Y. Yuan, W. Cai, S. Zhu, J. Zhu, "3D self-assembly of aluminium nanoparticles for plasmon-enhanced solar desalination," Nature Photonics 10, 393–398 (2016).
- 77. C. F. Bohren, D. R. Huffman, Absorption and Scattering of Light by Small Particles (Wiley, New York, 1983).
- L. Stella, P. Zhang, F. J. García-Vidal, A. Rubio, P. García-González, "Performance of nonlocal optics when applied to plasmonic nanostructures," J. Phys. Chem. C 117, 8941–8949 (2013).
- C. Yannouleas, E. Vigezzi, R. A. Broglia, "Evolution of the optical properties of alkali-metal microclusters towards the bulk: The matrix random-phase-approximation description," Phys. Rev. B 47, 9849–9860 (1993).
- M. Brack, "The physics of simple metal clusters: self consistent jellium model and semiclassical approaches," Rev. Mod. Phys. 65, 677–731 (1993).
- P. Mulvaney, J. Perez-Juste, M. Giersig, L. M. Liz-Marzán, C. Pecharroman, "Drastic surface plasmon modeshifts in gold nanorods due to electron charging," Plasmonics 1, 61–66 (2006).
- L.-H. Shao, M. Ruther, S. Linden, S. Essig, K. Busch, J. Weissmuller, M. Wegener, "Electrochemical modulation of photonic metamaterials," Adv. Mater. 22, 5173–5177 (2010).
- S. K. Dondapati, M. Ludemann, R. Müller, S. Schwieger, A. Schwemer, B. Handel, D. Kwiatkowski, M. Djiango, E. Runge, T. A. Klar, "Voltage-induced adsorbate damping of single gold nanorod plasmons in aqueous solution," Nano Lett. 12, 1247–1252 (2012).
- E. Prodan, C. Radloff, N. J. Halas, P. Nordlander, "A hybridization model for the plasmon response of complex nanostructures," Science. 302, 419–422 (2003).

1. Introduction

The interaction of electromagnetic waves with metal nanoparticles is characterised by strong plasmon resonances which are a result of the excitation of the collective motion of the conduction electrons. Nowadays metal nanoparticle plasmonics is an active field of research because of both the fundamental scientific interest and the potential applications such as in spectroscopy and sensing [1–6], optical nanoantennas [7–9], photochemistry [10–12], non linear optics [13–19], and many others. In this respect, artificially engineered structures such as metal nanoparticle assemblies [6, 20–23] and bimetallic hybrid and alloy plasmonic materials [24] offer a unique opportunity to control light at the nanoscale. Among other systems, bimetallic core-shell nanoparticles provide a remarkable example of wide tunability of the plasmon response as well as near-field enhancements achieved in a geometrically simple structure [25–37].

The technological challenges in the synthesis of core-shell nanoparticles invite for deepening the theoretical understanding of bimetallic structures, so that a particular geometry and composition can be set to achieve the sought plasmonic response. Moreover, the comparison between measured and calculated spectra is often used to disentangle between hybrid or alloy plasmonic nanoparticles obtained as a result of different synthesis procedures [33–37]. So far a few theoretical approaches based on the solution of classical Maxwell's equations have been used to describe the response of bimetallic structures, where the core and the shell are separated by a sharp boundary and the corresponding macroscopic dielectric functions are used within each region [25–28, 38–43]. While this approach might be justified for thick materials, quantum effects play a role for shells of thickness in the nanometer range [44, 45]. A number of recent studies have addressed the importance of quantum effects in setting the optical response of plasmonic structures, demonstrating the importance of tunneling, nonlocal screening, and plasmon coupling to the electron-hole continuum, in situations where the characteristic size of the system (for example the vacuum gap in a plasmonic dimer, cluster size, film thickness, etc.) becomes small [46–50]. In a core-shell system with shells of small thickness one can expect:

(i) Strong broadening of the plasmon resonance because of the decay into electron-hole pairs via scattering at the metal/metal and metal/vacuum interfaces (the so called Landau damping) [51–55].

(ii) Nonlocal screening effects, where the induced screening charge density is not sharply located at the core/shell and shell/vacuum interfaces but has finite extension in the radial coordinate. As shown for metal clusters [56–58] the nonlocal screening leads to the shift of the

plasmon resonance energy from the classical Mie value.

(iii) Smooth change of the electron density at the core/shell contact. At this region, the difference in the work functions of core and shell should lead to electron transfer between them. The resulting dipole layer formed at the interface [43] allows the alignment of the Fermi levels of the core and the shell.

Here we use the time-dependent density functional theory (TDDFT) to study quantum effects in the optical response of spherical core-shell bimetallic nanoparticles. Particles with a core of several nanometers in diameter, with a relatively large number of valence electrons are addressed so that the plasmonic resonances of the core are well defined. We are particularly interested in revealing the signatures of quantum effects and testing the applicability of the classical electromagnetic approaches to describe the interaction of light with such systems. The finite size effect associated to the spherical metal core is expected to be comparable to that intensively discussed for small metal clusters [55–58]. Therefore, we focus our study on the evolution of the spectroscopic signatures of plasmonic modes in core-shell structures upon progressive increase of the shell thickness, ΔR . The corresponding experimental situation would be that of the growth of the shell material. The comparison between optical absorption cross section calculated with TDDFT and classical electromagnetic theory allows the discussion of the quantum-to-classical transition with increasing ΔR . The paper is organised as follows: the details on the quantum and classical calculations are given in Section 2. Section 3 is devoted to the results and their discussion. The conclusions are drawn in Section 4.

2. Quantum and classical calculations

In the quantum approach, the valence electron dynamics triggered by the electromagnetic plane wave incident on the nanoparticle is calculated using the time-dependent density functional theory (TDDFT). Details of the method are given elsewhere [59]. In brief, the time evolution of the valence electron density $n(\mathbf{r}, t)$ in response to the time dependent external perturbation is calculated *ab initio* within the Kohn-Sham (KS) scheme of the TDDFT [60]. We use the adiabatic local density approximation with the exchange-correlation functional of Gunnarson and Lundqvist [61]. Retardation effects are neglected due to the small size of the system. The frequency-dependent dipolar absorption cross section $\sigma(\omega)$ is then obtained as $\sigma(\omega) = \frac{4\pi\omega}{\sigma}Im[\alpha(\omega)]$, where *c* is the speed of light in vacuum, and $\alpha(\omega)$ is the dynamic polarisability.

The bimetallic core-shell nanoparticle is described with a "two step" spherical jellium model (JM) which has been validated via direct comparison with *ab initio* quantum chemistry calculations [45] of small bimetallic systems. Within the JM, the valence band electrons of the core and shell materials evolve in a uniform spherical positive background charge density $n_{+} = \left(\frac{4\pi}{3} r_{s}^{3}\right)^{-1}$ that occupies the region of space $0 \le r \le R_c$ for the core metal, and $R_c < r \le R_{sh}$ for the shell. Here r is the radial coordinate, and r_s is the Wigner-Seitz radius. R_c and R_{sh} correspond the the external radii of the core and shell, respectively. The width of the shell is then given by $\Delta R = R_{\rm sh} - R_{\rm c}$. In what follows we show the results obtained for an aluminum metal core with $r_{\rm s} = 2.07 a_0$ and silver metal core with $r_{\rm s} = 3.02 a_0$ (Bohr radius $a_0 = 0.053$ nm). Two types of metal shells are considered in this study: sodium ($r_s = 4 a_0$), and gold ($r_s = 3.02 a_0$). The Al core ($R_c = 1.9$ nm) comprises 5108 electrons and its optical response is dominated by the excitation of a strong dipolar plasmon resonance at $\omega_D^{\text{Al}} = 8.83 \text{ eV}$. The Ag core ($R_c = 2.5 \text{ nm}$) comprises 4074 electrons and its dipolar plasmon resonance is at $\omega_D^{\text{Ag}} = 3.62 \text{ eV}$. We vary the number of electrons in the shell up to 3674 (9000) for Na(Au). All the systems considered here posses closed electronic shell structure. To ensure that the work function Φ of the massive material reproduces the empirical data ($\Phi_{Al} = 4.24 \text{ eV}, \Phi_{Na} = 2.9 \text{ eV}, \Phi_{Au} = 5.5 \text{ eV},$ Φ_{Ag} = 4.56 eV) [62] we use the stabilised jellium model [63,64] for aluminum, gold, and silver. A constant attractive pseudopotential (-3.1 eV for Al, -4.4 eV for Au, and -4.3 eV for Ag) is

added to the self-consistent Hartree and exchange-correlation potentials inside the metal. For the case of gold and silver, the contribution of the quasi-bound *d*-electrons to the total screening is accounted for via inclusion of a background dielectric [65] described by a permittivity $\varepsilon_{\infty}^{Au} = 9.5$ for Au [66], and $\varepsilon_{\infty}^{Ag} = 4.58$ for Ag. Indeed, without the polarisable background, the dipolar plasmon of e.g. a small gold nanoparticle has an energy $\tilde{\omega}_D^{Au} = \omega_p / \sqrt{3} = 5.18$ eV, where $\omega_p = \sqrt{\frac{4\pi n e^2}{m}}$ is the bulk plasma frequency (*n*, *e* and *m* are the electron density, electron charge and electron mass, respectively). Inclusion of the polarisable background lowers the dipolar plasmon frequency to $\omega_D^{Au} = \omega_p / \sqrt{2 + \varepsilon_{\infty}^{Au}} = 2.65$ eV, in agreement with experimental results [67, 68]. It is convenient to stress that although the atomistic structure of the metals is not explicitly considered in our current treatment, the TDDFT calculations within the JM correctly capture the collective dynamics of the valence electrons allowing for identification and prediction of quantum effects in plasmonic systems, as corroborated by experiments [47–49, 59, 64, 69–72].

Our choice of the core and shell materials is based on the following reasons:

- The free-electron character of Al and Na metals makes them prototypical systems for the JM description. Moreover, Al structures have recently attracted intense interest for plasmonic applications [73–76]. Equally important, Au remains being the most widely used material in plasmonics.

- Within the classical Mie theory, the small isolated nanoparticles of Al are characterised by a dipolar plasmon resonance close to 9 eV, while the resonances for Na, Au, and Ag have frequencies at $\omega_D^{\text{Na}} = 3.4 \text{ eV}$, $\omega_D^{\text{Au}} = 2.65 \text{ eV}$, and $\omega_D^{\text{Ag}} = 3.5 \text{ eV}$, respectively. Thus, the plasmons of the core-shell Al-Na and Al-Au bimetallic systems show either strong core or shell character which simplifies the analysis of the results regarding identification of quantum effects. Additionally, we also consider the Ag-Na core-shell case that allows to consider the situation of near degenerate plasmon modes.

- Owing to the large difference in the valence electron densities of the core and shell materials (8 times for Al-Na, 3 times for Al-Au, and 2 times for Ag-Na) it is expectable to have strong density rearrangements at the interface.

- The differences in work function for different metals allow us to consider the cases of electron transfer from the shell to the core (Al-Na, Ag-Na) as well as from the core to the shell (Al-Au).

The points above are illustrated in Fig. 1 where we show the ground state electronic densities n(r) of the core-shell Al-Na (a) and Al-Au (b) systems. The results obtained for different shell widths ΔR are presented as a function of the cluster radial coordinate r. The evolution of the density profile around $r = R_c$ allows to observe the formation of a transition layer at the interface between the two metals. For shell widths larger than approximately 1 nm, the density profile at the core-shell contact area is converged, as it does not change anymore with increasing the width of the shell. In the case of the Na shell, the electron transfer from the low work function shell to the Al core results in the formation of a positively charged layer at $r \approx 21$ Å where the electron density n(r) is below that of the Na bulk value. On the contrary, for the Al-Au system, the electrons are transferred from the Al core to the large work function Au shell. This is manifested in an increase of n(r) above the Au bulk value, up to $r \approx 22.5$ Å, i.e. within the layer extending by 3 Å from the interface towards inside the shell (see Fig. 1(b)). Because of the *d*-electron contribution to the screening in gold, the charge transfer between Al core and Au shell needed to equilibrate the Fermi levels is much larger than that in the Al-Na case. We calculate that over 100 electrons are transferred into the shell for Al-Au and about 10 electrons are transferred into the core for Al-Na. It is worth mentioning that the formation of the transition layer with the corresponding density rearrangement at the interface between the two metals a priori modifies the confining potential barrier for the core and shell electrons and therefore also the plasmon decay into electron-hole pairs via Landau damping [55].

To better identify quantum effects, along with the quantum study of the optical response of the



Fig. 1. Selfconsistent electron density calculated using density functional theory for the Al-Na (a) and Al-Au (b) core-shell structures. The dashed vertical line indicates the edge of the Al core. Results are shown in units of the bulk Al electron density $\left(\frac{4\pi}{3}r_s^3\right)^{-1}$ as a function of the cluster radial coordinate for different thickness of the shell ΔR . The electron density of the isolated Al sphere ($\Delta R = 0$) is shown with a black line. The bulk valence electron densities of the shell metals are shown with thin horizontal lines. In panel a), we display the results for a width $\Delta R = 1$ Å (0.5 ML) of the Na shell with a dashed black line. The alternating red and blue lines represent the results obtained for $\Delta R = 3.2$ Å (1 ML), $\Delta R = 5.5$ Å (2 ML), $\Delta R = 8.3$ Å (3 ML), $\Delta R = 11.1$ Å (4 ML), $\Delta R = 13.4$ Å (5 ML), $\Delta R = 15.8$ Å (6 ML), correspondingly. For the Au shell in panel b), the alternating red and blue lines represent the results obtained for $\Delta R = 2.3$ Å (1 ML), $\Delta R = 4.8$ Å (2 ML), $\Delta R = 7$ Å (3 ML), $\Delta R = 11.6$ Å (4 ML), $\Delta R = 14.1$ Å (5 ML), $\Delta R = 16.3$ Å (6 ML), correspondingly. The number in parenthesis indicates the approximate number of monolayers (MLs) of the shell material as obtained from previous studies of the surface structure of Na and Au metals [62].

core-shell nanoparticle system, we have also performed classical calculations in the quasistatic approximation. This approach allows direct comparison of the classical results with the TDDFT calculations which also neglect retardation effects. In a core-shell spherical system the absorption cross section can be obtained from the Aden and Kerker theory [38] in the quasistatic limit as [77]:

$$\sigma(\omega) = \frac{4\pi\omega}{c} R_{\rm sh}^3 Im \left[\frac{(\varepsilon_{\rm sh} - 1)(\varepsilon_{\rm c} + 2\varepsilon_{\rm sh}) + g(\varepsilon_{\rm c} - \varepsilon_{\rm sh})(1 + 2\varepsilon_{\rm sh})}{(\varepsilon_{\rm sh} + 2)(\varepsilon_{\rm c} + 2\varepsilon_{\rm sh}) + 2g(\varepsilon_{\rm sh} - 1)(\varepsilon_{\rm c} - \varepsilon_{\rm sh})} \right],\tag{1}$$

where $g = (R_c/R_{sh})^3$ is the volume fraction of the core, and ε_c and ε_{sh} are the dielectric functions of the core and shell materials, respectively. We use the free-electron Drude-like description of the metal permittivity for this classical calculation, consistent with the free-electron JM used in the quantum calculations:

$$\varepsilon(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega(\omega + i\eta)} \tag{2}$$

For Al and Na we use $\varepsilon_{\infty}^{Al} = \varepsilon_{\infty}^{Na} = 1$, and we use $\varepsilon_{\infty}^{Au} = 9.5$ for gold ($\varepsilon_{\infty}^{Ag} = 4.58$ for silver) to account for the *d*-electron contribution to the screening [66]. The choice of the damping parameter η for different materials is discussed below in connection with the computed absorption cross section. To match the TDDFT results η has to account for the effect of Landau damping at the shell/vacuum interface, as well as at the interface between the two metals.

3. Results and discussion

The optical properties of the Al-Na core-shell nanoparticle calculated with TDDFT and with the classical approach are analysed in Fig. 2. Panels a) and b) of the figure show the evolution of the absorption cross-section for increasing thickness of the Na shell, ΔR . The successive ΔR values roughly correspond to the bulk Na interlayer spacing in the (100) direction (2.1 Å) [62] so that the presentation of the data mimics the monolayer (ML) by ML growth. Two absorption resonances emerge in the spectra. The low energy resonance at ω_1 mainly involves the collective electron excitation of the Na shell (Na shell plasmon, NaShP). The high energy resonance at ω_2 has Al core character (Al core plasmon, AlCP). This assignment is supported by the charge density analysis presented in panels (c) and (d) of the figure where we show the induced charge densities calculated with TDDFT at the NaShP and AlCP frequencies. When the NaShP at ω_1 is excited the induced charges of opposite sign are located at the Na/vacuum and Al/Na interfaces [panel (c)] leading to the strong rearrangement of the electron density along the radial coordinate within the shell. Consistent with the simplified sketch of the induced charges given in panel (c) we will also denote this mode as ω_{-+}^{-+} plasmon. When the AlCP at ω_2 is excited, the induced charge is located at the surface of the Al core i.e. at the Al/Na interface [panel (d)]. Since ω_2 is above the bulk plasma frequency of the Na shell, the screening by the shell, and so the electron density rearrangement within the shell, is very small.

For thin shells quantum and classical results differ qualitatively. Indeed, the classical theory predicts that the well-resolved plasmon peak with Na shell character, NaShP at ω_1 , is always present irrespective of the shell thickness. However, in the quantum calculations the low energy mode is only formed for ΔR larger than 0.8-1 nm (2-3 ML). Below this shell thickness, the rearrangement of the electron density within the shell cannot be performed to built the ω_{-+}^{-+} plasmon mode which breaks into a broad structure with discrete features due to the one-particle electron-hole pair excitations [48–50, 78]. For shell thickness above 3 ML the NaShP emerges. With increasing ΔR , the width Γ of the corresponding absorption peak decreases and the mode becomes better defined. This behaviour is similar to the one generally found in metal nanoparticles [54] and reflects the evolution with size of the collective plasmon resonance decay into one particle electron-hole pair excitations by scattering at the metal/vacuum and metal/metal interfaces (Landau damping) [55]. In the phenomenological picture, the change of Γ with $\Delta R \gtrsim 3$ ML can be described by the dependence $\Gamma = \Gamma_0 + Av_F/\Delta R$, where v_F is the Fermi velocity of the electrons, and Γ_0 and A are parameters [51–55].

It is worth noting that there is no clear definition of the threshold shell size at which the NaShP emerges. Indeed, even a very ill-defined structure obtained from a 2 ML shell can be still viewed as a plasmon resonance albeit extremely broadened. Here, we use the criterium that the quasistationary state is defined when its decay rate Γ (width of the resonance) is such that $\Gamma \ll \omega_1$. Otherwise the collective mode is not distinguishable from the continuum of electron-hole pair excitations.

Overall, for a shell thicknesses above 3 ML the agreement between the quantum [panel a)] and classical [panel b)] results for the optical response of the bimetallic system becomes semiquantitative. In this range of shell widths, the intensity of the NaShP excitation (ω_1) grows with increasing ΔR and the energy red shifts. Obviously, for large ΔR , the limit of the nonretarded dipolar plasmon of a massive Na nanoparticle is reached. The AlCP excitation (ω_2) blue shifts with increasing ΔR and its intensity decreases because of the screening by the shell. All the classical calculations reported in panel (b) of the figure were performed with a damping parameter of $\eta_{Na} = 0.5$ eV which allows to retrieve the TDDFT result at the NaShP resonance for the largest shell width considered, $\Delta R = 15.8$ Å (6 ML). Because of the presence of two interfaces, this value of the damping parameter is larger than typical values deduced from experimental data, and from calculations of the dipole plasmon broadening in isolated Na nanoparticles of similar size [59, 79].

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Fig. 2. Optical response of the Al-Na core-shell bimetallic nanoparticle. Panels (a) and (b): absorption cross section calculated with TDDFT and classical electromagnetic approaches, respectively. The results are presented as a function of the frequency of the incoming radiation for shells of variable thickness ΔR . The absorption cross section of the isolated Al sphere ($\Delta R = 0$) is shown with a black line. The dashed line is used for the results obtained for $\Delta R = 1$ Å (0.5 ML). The alternating red and blue lines represent the results obtained for increasingly large shell widths, as indicated in the figure. For the sake of clarity a vertical offset of 20 nm² is applied upon each 1 ML change of the shell width. The plasmon resonances with shell and core character are labelled as ω_1 and ω_2 , respectively. Panels (c) and (d): snapshots of the charge density induced by a linearly polarised incident plane wave resonant with ω_1 , NaShP (c) and ω_2 , AICP (d). Results are shown in the plane containing the nanoparticle centre and the incident electric field vector. The instant of time when the charge density is calculated corresponds to the maximum dipolar polarization of the nanoparticle. Dashed lines indicate the outer surfaces of the core and the shell. The simplified sketch of the distribution of induced charges is also shown.

Regarding the AlCP resonance at ω_2 for the individual Al nanoparticle, the TDDFT results can be quantitatively reproduced by classical calculations with the use of a damping parameter of $\eta_{AI} = 0.7$ eV which closely matches the empirical data [73,74]. It should be noted though that the dipolar absorption resonance obtained in quantum calculations is red-shifted with respect to the classical Mie position $\omega_p/\sqrt{3}$ because of the effect of non-local screening [79, 80]. The damping parameter η_{AI} has been also used for the classical calculations of the absorption cross section of the Al-Au bimetallic nanoparticle shown in Fig. 2(b). When the Al core is covered by Na, the TDDFT results predict that the AlCP resonance is always present in the absorption spectra irrespective of the Na coverage. However, the modification of the potential from the Al/Vacuum to the Al/Na interface leads to an increased Landau damping and the resonance width increases. Similar results have been obtained in noble metal clusters embedded into a dielectric matrix [55]. Because of the broadening, discrete features due to electron-hole pair excitations emerge in the AlCP peaks. We have found that for $\Delta R = 15.8$ Å (6 ML), the TDDFT results can be retrieved with classical calculations assuming $\eta_{Na} = 0.5$ eV, and $\eta_{AI} = 1.2$ eV (70 % value increase compared to that of an individual nanoparticle). Note that the independent adjustment of η_{Na} and η_{AI} is possible in our core/shell system because of the well separated frequencies of the plasmons with core or shell character.

The plasmon modes of the Al-Au core-shell nanoparticle are analysed in Fig. 3 as a function of the shell width. The successive ΔR values addressed in our calculations roughly correspond to the bulk Al interlayer spacing in the (111) direction (2.4 Å). Similar to the Al-Na case, the TDDFT [panel a)] and classical [panel b)] results reveal absorption resonances with Au shell (AuShP, ω_1) and Al core (AlCP, ω_2) character. The assignment of the modes can be done based on the distribution of the radial component of the induced electric field [panel c), classical calculation] and on the induced charge density [panel d), TDDFT] extracted at the corresponding frequencies ω_1 and ω_2 . The induced electric field maps are used here because the assignment of modes exclusively based on the induced electron density is less straightforward here compared to the Al-Na case [see Fig. 2 c), d)]. The AuShP excitation is characterized by enhanced fields inside the shell region, as well as by large induced charges of opposite sign at the inner and outer surfaces of the shell. The strong rearrangement of the induced charge density along the radial coordinate within the shell is a signature of the ω_{-+}^{-+} mode introduced earlier. When the AlCP is excited at ω_2 , the induced charges mainly reside at the core-shell interface. In this case the charge rearrangement along the radial coordinate within the shell is smaller than that for the AuShP.

We analyse now the similarities and differences between the classical and quantum results which resemble those discussed for the Al-Na system. In particular, the TDDFT absorption spectra are only reproduced with the classical calculations for shell widths above 2 ML. Indeed, in the classical calculations, the well resolved AuShP resonance exists for any shell thickness ΔR . However, in the TDDFT results for small ΔR , only a broad structure with features given by one-particle electron-hole pair excitations can be observed. The AuShP is well-formed for shell thickness starting from $\Delta R \gtrsim 7$ Å (3 ML). With further increasing the shell thickness, the Landau damping by scattering at Au/Vacuum and Al/Au interfaces is progressively reduced, and the resonance in the absorption spectra narrows. The AlCP excitation is also broadened by the Landau damping at the Al/Au interface, and the features due to electron-hole pair excitations are clearly visible in the corresponding resonance absorption peak. We found that for the maximum shell width considered here, the absolute value of the resonant absorption cross section, as well as the width of the resonances calculated with TDDFT can be reproduced within the classical theory assuming a damping of $\eta_{AI} = 0.9$ eV and $\eta_{Au} = 0.3$ eV. We thus used these parameters in the classical calculations presented in Fig. 3b). Since these effective parameters incorporate the decay via the interface scattering, they are larger than the typical empirical values for the individual materials [67, 68, 73]. We emphasize however that for the case of very thin shells



Fig. 3. Optical response of the Al-Au core-shell bimetallic nanoparticle. Panels (a) and (b): absorption cross section calculated with TDDFT and classical electromagnetic approaches, respectively. Results are presented as a function of the frequency of the incoming radiation for shells of variable thickness ΔR . The alternating red and blue lines represent results obtained for shells that increase their width in 1 ML, as indicated in the figure. For the sake of clarity a vertical offset of 5 nm² is applied to each curve. The plasmon resonances with shell and core character are labelled as ω_1 and ω_2 , respectively. The vertical green line shows the position of the AuShP $[\omega_1]$ as obtained in classical calculations for thick shells. Panel (c): 2D maps of the radial component of the induced field obtained in classical calculations for the ω_1 AuShP and ω_2 AlCP resonances in the case of the 5 ML thick shell. Results are shown in the plane containing the nanoparticle centre and the incident electric field vector. Panel (d): snapshots of the TDDFT charge density induced by an incident plane wave linearly polarised along the horizontal axis, at the resonance frequencies ω_1 , AuShP, and ω_2 , AlCP, respectively. The instant of time corresponds to the maximum induced dipole. Results are shown in the plane containing the nanoparticle centre and the incident electric field vector. Dashed lines indicate the outer surfaces of the core and the 5 ML thick shell.

one can not define effective damping parameters that allow to classically reproduce the TDDFT results simultaneously for both core and shell resonances in the absorption cross section.

Already for the thinnest Au shell considered here with $\Delta R = 2.3$ Å (1 ML), classical and quantum calculations predict a strong redshift of the Al core plasmon primarily because of the screening by the *d*-electrons of the Au shell. The redshift of the AlCP is further increased for increasing shell widths. This is in contrast with Al-Na core-shell system, where the AlCP blueshifts with increasing ΔR (see Fig. 2). This difference can be understood from the asymptotic value of ω_2 obtained for an Al nanoparticle inside a metallic (M) shell when neglecting attenuation: $\omega_2 \rightarrow \sqrt{(\omega_p^2(Al) + 2\omega_p^2(M))/(1 + 2\varepsilon_{\infty})}$ Here $\omega_p(Al)$, and $\omega_p(M)$ are the corresponding bulk

plasma frequencies, and $\varepsilon_{\infty} = 1$ for sodium and 9.5 for gold. With increasing shell width, the AlCP looses intensity since the core becomes screened by the Au shell. In such a situation, the AuShP gains intensity, consistent with the evolution of the system towards the limit of the pristine Au nanoparticle.

As far as the energy of the AuShP is concerned, we obtain qualitative differences between quantum and classical results over the entire range of ΔR considered here. While the classical theory predicts nearly the same energy of the resonance irrespective of the shell thickness, the quantum results display a strong blueshift of the AuShP with decreasing shell width. It is tempting to explain this behaviour as a result of the charge donation from the Al core to the Au shell so that the shell becomes negatively charged. The smaller the shell width is the larger the mean increase of the electron density n [see Fig. 1 b)]. As a consequence, the bulk plasmon frequency ω_p of the shell increases leading to the blueshift of the AuShP, as has been often evoked to explain the frequency shift of the dipolar plasmon in charged metal clusters [81–83]. We performed classical calculations using a modified Drude model to describe the gold shell, where the plasma frequency, ω_p , is determined from the local electron density. These simulations fail to reproduce the TDDFT results. Indeed, the increased electron density in the shell region, close to the core, screens the positive charge of the latter. The dipole layer formed in this way in the transition region allows the Fermi levels of the core and the shell to be aligned. Therefore, being bound by the positive charge of the Al core, the extra electrons transferred to the Au shell are not available to participate in the collective density oscillations forming the plasmon.

In clusters research, the blueshift of the dipolar plasmon mode of individual metal clusters with decreasing cluster size has been consistently explained as due to the effect of non-local dynamical screening [46, 56–58]. The plasmon frequency shift $\Delta \omega$ depends linearly on the inverse of the cluster radius, and this dependency arises because the induced charges do not



Fig. 4. Energy of the ω_1 AuShP resonance obtained with TDDFT calculations as a function of the inverse of the width of the shell for Al-Au core-shell bimetallic nanoparticles. The red curve shows the line fit to the results with the explicit $\omega_1 \left(\frac{1}{\Delta R}\right)$ dependence given in the insert.



Fig. 5. Optical response of a Na shell in vacuum. The absorption cross section calculated with TDDFT is presented as a function of the frequency of the incoming radiation for shells of variable thickness ΔR . The dashed line represents results obtained for $\Delta R = 1$ Å (0.5 ML). The alternating red and blue lines represent the results obtained for increasingly large shell widths, as indicated in the figure. For the sake of clarity a vertical offset is applied upon each 1 ML change of shell width. The plasmon resonances with bonding and antibonding character are labelled as ω_{BD} and ω_{AB} , respectively. The insert of the figure zooms into the evolution of the ω_{AB} resonance. A simplified sketch of the distribution of induced charges for each plasmon mode is shown to the left.

reside at the geometrical surface of the nanoparticle, but are spatially shifted inside the metal. Comparing panels (c) of Fig. 2 and (d) of Fig. 3, we can clearly observe that at the resonance with shell character, ω_1 , the induced free-electron charge density in the Al-Au system is localised inside the shell for both metal/metal and metal/vacuum interfaces. Interestingly, the blueshift of the AuShP resonance frequency shows a linear dependence with the inverse of the shell width, $1/\Delta R$, as we demonstrate in Fig. 4. For metal clusters, the non-local screening effects can be captured by the classical theory upon redefinition of an effective dielectric constant [58] which becomes explicitly dependent on the cluster radius and the position of the centroid of the induced plasmon charge density (Feibelman parameter) [57]. Elaboration of a similar approach for a bimetallic core-shell system is beyond the scope of this work.

From the results reported so far, we have concluded that the main qualitative difference between quantum and classical calculations concerns the ω_{-+}^{-+} plasmon mode with shell character. In particular, classical theory predicts that this shell resonance is always present in the absorption spectra, while TDDFT studies show that a finite threshold width of the shell is required for this mode to be developed. The origin of this quantum effect can be associated to the strong rearrangement of the induced charges along the radial coordinate within the shell at the ω_{-+}^{-+} resonance. The charge configuration with opposite charges at the inner and outer surface of the shell requires hybridization of several electron orbitals with shell character and different nodal structure (radial quantization) within the shell. Thus, not too small ΔR is required so that

 $k_F \Delta R \approx n\pi$ can be fulfilled, with *n* an integer, and k_F the Fermi wavevector. This interpretation is further supported by the calculations of the absorption spectra for an individual shell in vacuum (no core metal). In Fig. 5 we show the TDDFT results for Na shells of various widths spanning the same variation of ΔR as that reported in Fig. 2. Thick shells feature two resonances associated to the bonding ω_{BD} and antibonding ω_{AB} plasmon modes [22, 49, 50, 84]. The bonding (BD) plasmon mode is characterised by a nodal structure of the induced density along the angle Θ , and it requires angular hybridization of the electronic orbitals. This bonding plasmon is thus always present in the absorption spectra irrespective of the width of the shell. The antibonding (AB) plasmon mode has a charge configuration denoted in this work as ω_{-+}^{-+} resonance. The corresponding induced charge density requires both angular and radial hybridization. The orbitals with different nodal structure in the radial coordinate need to be localized within the shell. Because of this quantum confinement, the emergence of this mode is only possible for shell thickness ΔR larger than 2–3 ML (6–9 Å), as follows from the calculated one-particle Kohn-Sham orbitals.



Fig. 6. Optical response of a Ag-Na core-shell bimetallic nanoparticle. Panels (a) and (b): absorption spectra for shells of variable thickness ΔR calculated with TDDFT and classical electromagnetic approaches, respectively. The results are normalised to the geometrical cross section of the shell $\sigma(\omega)/R_{\rm sh}^2$. The absorption cross section of the isolated Ag sphere ($\Delta R = 0$) is shown with a black line. The dashed line shows the results obtained for $\Delta R = 1$ Å (0.5 ML). The alternating red and blue lines represent the results obtained for increasingly large shell widths, as indicated in the figure. For the sake of clarity a vertical offset is applied upon each change of the shell width. The hybridised plasmon resonance with core-shell character is labelled as ω_1 . The plasmon resonance with shell character is labelled as ω_2 . Panels (c) and (d): 2D maps of the radial component of the induced field obtained in classical calculations for the ω_1 and ω_2 resonances in the case of the 5 ML thick shell. Results are shown in the plane containing the nanoparticle centre and the incident electric field vector.

Thus, the antibonding ω_{AB} excitation is only formed in the absorption spectra for shells thicker than this critical value.

The analysis above is further supported by the results of a different type of core-shell nanoparticle formed by Ag-Na, shown in Fig. 6. In this case, and differently to the Al core structures, the dipolar plasmon resonances of the core and shell metals have similar frequencies and strongly hybridize. In this situation, as follows from the induced field distribution shown in panel (c) of the figure, the low-energy ω_1 excitation corresponds to the core-shell nanostructure which responds nearly as an homogeneous nanoparticle as a whole. Adding shell material to this homogenous structure has the effect of extending the core, and therefore the ω_1 resonance is always present in the absorption spectra both in quantum and classical calculations. Note that in the TDDFT results, because of the finite size effect, the dipolar plasmon resonance of the Ag core is slightly blue shifted with respect to the classical value [57]. As a result, as ΔR the ω_1 increases, the low-energy resonance redshifts evolving from the dipolar plasmon of the Ag core to that of the Na sphere with radius $R_{\rm sh}$.

The high-energy resonance, ω_2 , is located at an energy slightly below the bulk plasmon of Na. As follows from the analysis of the induced electric field in panel (d), this resonance has a well defined shell character with induced charges of opposite signs located at the Na/vacuum and Ag/Na interfaces. Thus, the induced charge configuration is that of the ω_{-+}^{-+} mode, with electron density rearrangement along the radial coordinate within the shell. Consistent with all the results presented above, due to the finite size effect, this mode is only present in the TDDFT calculations for shell widths above the critical thickness $\Delta R \gtrsim 3$ ML. This behaviour is not captured by the classical theory that features the ω_2 resonance in absorption spectra even for very thin shells.

As a final remark, we would like to point out that the TDDFT study using the jellium model for silver and gold only accounts for the excitation of quasi-free s-p electrons. The losses in gold for frequencies above 2.5 eV (4 eV for silver) are underestimated because the d-electron excitation is not accounted for. The same holds for the classical Drude model used here for the sake of consistency with TDDFT. Above these critical frequencies one would expect the experimentally measured resonances, such as for instance the AlCP, to be essentially broader and less intense than the results reported in Fig. 3(a), (b). However, this should not alter the main conclusions presented here for the low-energy range of the spectra, which are a consequence of finite size effects, electron rearrangement at the bimetallic interface, and nonlocal screening in the system, all of them pure quantum effects.

4. Conclusions

In conclusion, using time dependent density functional theory and classical electromagnetic calculations performed in the quasistatic limit, we have studied the role of quantum effects in the plasmonic response of core-shell bimetallic nanoparticles. From our results, it follows that the classical picture of the simple stack of two materials can be applied only for thick enough shells (typically above 3-5 ML). We showed that the quantum confinement, the formation of a transition region with electronic density rearrangement at the interface between the two materials, and the nonlocal screening strongly affect the optical properties of bimetallic nanoparticles with thin shells (below 3 ML).

In particular, because of the quantum confinement effects, shell widths larger than approximately 1 nm are needed for the plasmon resonance with shell character to be formed. Classical calculations, however, miss this effect and predict that the shell mode exists for any arbitrarily small shell width. For shells with thickness below ≈ 1 nm, the plasmon mode with shell character is strongly broadened because of Landau damping at the metal/metal and metal/vacuum interfaces. This broadening decreases with increasing shell width. The resonance with core character is also broadened by interface effects.

In some cases quantum effects can be accounted for phenomenologically within a classical

approach by adjustment of the corresponding dielectric function of the core and shell materials separated by the sharp boundary. However, nonlocal screening and the formation of the transition layer in the metal/metal interface might lead to the presence of effects that exceed the capacity of simple classical descriptions.

Despite the fact that we used a jellium model to describe the valence electrons of the shell and core materials, and that the feasibility of quantum calculations restricts the size of the systems to be tackled to a few nanometers, we believe that our conclusions hold with generality for bimetallic nanoparticles currently synthesised for plasmonic applications. Indeed, the jellium models used in this work have proven their predictive power for isolated nanoparticles and plasmonic dimers. More importantly, the physics behind our results is based on the presence of robust quantum phenomena which emerge at the junction between two different materials due to the electron density rearrangement.

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