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Plasmon Response and Electron Dynamics in Charged Metallic Nanoparticles

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ABSTRACT: Using the time-dependent density functional theory, we perform quantum calculations of the electron dynamics in small charged metallic nanoparticles (clusters) of spherical geometry. We show that the excess charge is accumulated at the surface of the nanoparticle within a narrow layer given by the typical screening distance of the electronic system. As a consequence, for nanoparticles in vacuum, the dipolar plasmon mode displays only a small frequency shift upon charging. We obtain a blue shift for positively charged clusters and a red shift for negatively charged clusters, consistent with the change of the electron spill-out from the nanoparticle boundaries. For negatively charged clusters, the Fermi level is eventually promoted above the vacuum level leading to the decay of the excess charge via resonant electron transfer into the continuum. We show that, depending on the charge, the process of electron loss can be very fast, on the femtosecond time scale. Our results are of great



relevance to correctly interpret the optical response of the nanoparticles obtained in electrochemistry, and demonstrate that the measured shift of the plasmon resonances upon charging of nanoparticles cannot be explained without account for the surface chemistry and the dielectric environment.

INTRODUCTION

In metal nanoparticles, coupling of light with collective electron excitations (plasmons) strongly impacts the optical properties of the system. Along with the far-field response, plasmon resonances allow one to strongly enhance optical near-fields and to obtain hot spots of dimensions well below that of the wavelength of the incident radiation. Light manipulation at subwavelength scales as offered by plasmonics¹⁻⁴ finds numerous practical applications. To cite a few, plasmonic action is relevant in optical nanoantennas,^{5,6} surface enhanced spectroscopies and sensing,⁷⁻¹¹ information transfer,^{12,13} photochemistry,^{14,15} amplification of nonlinear effects,^{16,17} and plasmon rulers.¹⁸ The design and engineering of the corresponding nanostructures with sought optical properties is a subject of continuous effort in the plasmonic community.^{19–24} In this respect, the possibility to actively modify the plasmon modes of a nanosystem would allow fabrication of tunable devices and it is thus of paramount importance.

The strategies for active control proposed in recent works consist in acting on different parameters that determine the plasmon response.²⁵ The sensitivity of the plasmon properties to the screening at the metal/dielectric interface can be exploited using liquid crystal environment,^{26–28} tunable molecular layers,^{29–31} or electrically induced thermal heating.³² The plasmon response of a composite nanoparticle system can

be also modified by directly affecting the strength or nature of the coupling between the plasmon modes of the constituents. Thus, the capacitive coupling between nanoparticles can be changed by using flexible substrates^{33–36} or by changing the geometry due to the applied electromagnetic fields.³⁷ Recently, electrochemical modulation as well as the applied bias has been used in nanoparticle dimers to switch between capacitive and conductive coupling and thus to affect the plasmon modes.^{38,39} Optical excitation of free carriers in the metal allows one to modify the dielectric properties of the later and thus influence the plasmon propagation length at ultrafast fs (10⁻¹⁵ s) time scales;⁴⁰ however, a pump laser of sufficient power is required to produce appreciable effects.

The modulation of the frequencies of plasmon resonances has been also achieved in electrochemistry by applying a bias between the nanoparticles and electrolyte or by adding chemical reductants to a colloidal nanoparticle solution.^{41–51} In some cases a plasmon wavelength shift of 10 nm per eV of applied potential has been reported.⁴⁷ Similar to the 2D planar systems such as graphene,^{52–55} the observed shift of the plasmon frequency has been often interpreted as a result of the

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charge doping of the nanoparticles.⁴¹⁻⁴⁸ The reasoning is as follows, let *n*, *e*, and *m* to be the electron density, electron charge, and electron mass, respectively. The energy of the localized dipolar plasmon (DP) resonance of a small spherical nanoparticle is given by the classical Mie value $\omega_{\rm DP} = \omega_{\rm p}/\sqrt{3}$, where the bulk plasmon frequency is $\omega_{\rm p} = \sqrt{\frac{4\pi n e^2}{m}}$. One would expect that the change in the conduction electron density Δn would lead to the frequency shift of the localized plasmon resonance $\Delta \omega_{\rm DP}/\omega_{\rm DP} \sim \Delta n/2n$. However, such an explanation raises several issues, which we point out in the following: • The bias-induced control of the optical response in 2D

- The blas-induced control of the optical response in 2D materials is limited to date to the THz or mid-IR range because of the low doping concentrations that can be achieved electrically. In metals, the plasmon resonances are in the visible frequency range because of the high density of conduction electrons. For this reason, Δn should also be large to produce a noticeable change, which implies strong charging of the system resulting in high electrostatic potentials.⁵⁵
- Large negative charge Q can render small nanoparticles to be unstable against electron loss as we discuss later in this work. Similarly, large positive charge can lead to, e.g., Coulomb explosion.^{56–58} However, in electrochemical solution, the charged nanoparticle can be stabilized by a dipole layer created by the negative or positive ions around it. This dipole layer should alter the screening and thus the energy of the plasmon mode.
- In virtue of Gauss theorem, in the 3D metallic objects, the volume stays neutral. The screening charges reside at the surface within a narrow layer of width given by the screening length r_s (Wigner-Seitz radius of the metal). It is not obvious that such a narrow layer of surface charge might lead to a noticeable shift in the plasmon frequency.

The main goal of this paper is to study the electron dynamics and plasmon modes of small charged metallic clusters in vacuum. Performing density functional theory (DFT) and timedependent density functional theory (TDDFT) calculations of the electronic structure and dynamics for these well-defined systems allows one to isolate the effects of pure charging with respect to any other external polarization or chemical effects in the optical response of charged metallic nanostructures. In particular, we show that the frequency shift of the plasmon mode is small and has an opposite sign to that expected from the arguments based on the change of electron density. These results can be well understood from the theory of dynamical screening developed in the past to describe the dependence of the dipolar plasmon resonance on the nanoparticle size. We also demonstrate that for negatively charged clusters, as soon as the Fermi level is promoted above the vacuum level, the extra charge decays on femtosecond (fs) time scales. Despite the small size of the systems considered in our model calculations (\sim 5 nm in diameter), our results can be generalized to the case of larger nanoparticles as those commonly treated in electrochemistry. These results reveal that the plasmon energy shifts observed in electrochemical solutions cannot be explained without considering the effect of the dipole layer formed by the ions that screen the nanoparticle charge, and the eventual modification of the surface electronic structure of the metal nanoobject by the chemisorbed species.

The paper is organized as follows. In the Model and Computational Aspects section , we describe the jellium model used in this study for spherical sodium and silver clusters, and we present the ground state properties of the neutral and charged clusters as obtained in DFT calculations. The static DFT results provide an input for the TDDFT study of the electron dynamics and the optical response as a function of the cluster charge, which is detailed in Ground State Properties section. In Absorption Cross Section section we use the TDDFT to address the electron loss by the negatively charged clusters. In the Electron Population Decay in Negatively Charged Clusters section we address the issue of electron losses. Finally, we conclude underlying the consequences that our results might have for the interpretation of electrochemical experiments. Unless otherwise stated, atomic units are used throughout the paper.

MODEL AND COMPUTATIONAL ASPECTS

The sodium and silver spherical nanoparticles studied here are described using the jellium metal (JM) approximation. The positive ion cores are not treated explicitly, but are represented by a uniform positive background charge of density $n_{\perp} = (4\pi r_s^3/r_s^3)$ $3)^{-1}$. The Wigner-Seitz radius (or the screening length of the free electron gas) r_s equals to 4 a_0 for sodium, and 3.02 a_0 for silver (the Bohr radius $a_0 = 0.053$ nm). In the ground state (neutral system) both clusters have a closed shell electronic structure and contain $N_e = 2018$ valence electrons, so that the positive background charge is also $Q_+ = 2018$, which results in a cluster radius $R_{cl} = r_s Q_{+}^{1/3} = 50.6 a_0$ (2.67 nm) for sodium, and $R_{cl} = 38.2 a_0$ (2.06 nm) for silver. R_{cl} defines the jellium edge separating the positive background charge from vacuum. For sodium, which can be considered as a prototype of the free electron metal, the JM performs particularly well to describe the interaction of the optical pulse with nanosized objects. For silver, the contribution of the localized d-electrons to the screening has to be taken into account in order to correctly reproduce the frequencies of the localized plasmon mode(s).⁵⁹⁻⁶² This is achieved by introducing inside the Ag nanoparticle a polarizable background^{62,63} characterized by a nondispersive dielectric constant ε_{∞} = 4.58. For the neutral sodium cluster we obtained the work function $\Phi_{Na} = 3 \text{ eV}$ in good agreement with earlier studies on such systems.^{64–66} For the silver cluster, an additional attractive potential of 3.27 eV is used inside the cluster (the so-called stabilized jellium model^{67,68}), to impose the experimentally measured value of the work function of silver $\Phi_{Ag} = 4.65 \text{ eV}.^{69}$

Despite its simplicity, the JM correctly captures the collective behavior of conduction electrons and allows one to describe many physical properties of metallic nanoparticles including their optical response.^{65,66,70} Since relatively large systems with well-developed plasmon modes can be addressed within the JM, a variety of interesting nanostructures in plasmonics has been treated following this model.^{63,68,70–74} In this context, the studies of plasmonic dimers with narrow gaps^{63,73} have been particularly interesting, leading to the quantitative prediction of quantum tunneling effects. These effects have been experimentally confirmed,^{75–80} and further addressed with the use of full atomistic ab initio quantum calculations.^{81–85}

Prior to the TDDFT studies of the electron dynamics in neutral and charged clusters, their ground state properties are determined with static density functional theory DFT calculations. The Kohn–Sham (KS) scheme of the DFT is used,⁸⁶ where the electron density is given by that of the noninteracting system $n(\vec{r}) = \sum_{j} |\psi_{j}(\vec{r})|^{2}$. The summation runs



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Figure 1. DFT results for the ground state electronic density of neutral and charged sodium (a) and silver (b) clusters. The electronic density (in units of the positive background charge density n_+) is shown as a function of the radial coordinate measured from the center of the cluster. The dashed vertical line indicates the cluster boundary (jellium edge) located at $R_{cl} = 50.6 a_0$ for sodium and $R_{cl} = 38.9 a_0$ for silver cluster. Different colors are used to distinguish the results obtained for different charge of the cluster, Q_i as displayed in the code at the top of the figure. Charge values are given in units of the elementary charge.



Figure 2. Electron density change induced by charging is analyzed in panels a and c for sodium, and in panels b and d for silver clusters. Results of the DFT calculations for charged clusters are presented as a function of the radial coordinate *r* measured from the center of the cluster. Panels a and b: change of the number of electrons, $4\pi r^2 \Delta n(r)$, at the surface of the sphere of radius *r*. Panels c and d: change of the number of electrons inside the sphere of radius *r* given by $\Delta N_e(r) = \int_0^r 4\pi r'^2 \Delta n(r') dr'$. Dashed blue vertical lines represent the cluster boundaries. Different colors are used to distinguish the results obtained for different charge of the cluster *Q* as explained in the inset of panel *c*, which is common to all the panels.

over all occupied KS orbitals $\psi_j(\vec{r})$ obtained from the solution of the stationary Schrödinger equations

$$(T + V_{\rm xc}[n](\vec{r}) + V_{\rm H}[n](\vec{r}) + V_{\rm st}(\vec{r}))\psi_{j}(\vec{r}) = E_{j}\psi_{j}(\vec{r})$$
(1)

In eq 1, *T* is the kinetic energy operator, $V_{\rm xc}[n](\vec{r})$ is the exchange-correlation potential derived within the local density approximation (LDA) from the exchange-correlation functional of Gunnarson and Lundqvist,⁸⁷ and $V_{\rm H}[n](\vec{r})$ is the Hartree potential. Finally, $V_{\rm st}(\vec{r})$ is the stabilizing potential used only in case of Ag clusters.

The $\psi_j(\vec{r})$ orbitals obtained in the ground state DFT calculations are used as initial states for the description of the electron density dynamics in the clusters. We use the KS formulation of the TDDFT,^{88,89} where the time-dependent electron density is given by $n(\vec{r},t) = \sum_j |\Psi_j(\vec{r},t)|^2$, and the time-

evolution of the $\Psi_j(\vec{r},t)$ orbitals is determined by the timedependent KS equations

$$i\frac{\partial \Psi_{j}(\vec{r}, t)}{\partial t} = (T + V_{\rm xc}[n](\vec{r}, t) + V_{\rm H}[n](\vec{r}, t) + V_{\rm ext}(\vec{r}, t))\Psi_{j}(\vec{r}, t)$$
(2)

Provided the initial conditions $\Psi_j(\vec{r},t=0) = \psi_j(\vec{r})$, eq 2 is solved on a grid in spherical coordinates using short-time propagation with split-operator technique.⁹⁰ We use the adiabatic local density approximation (ALDA) so that the exchangecorrelation potential $V_{\rm xc}[n]$ has the same functional dependence on the local electron density as in the DFT study. The Hartree potential $V_{\rm H}[n]$ is calculated from $n(\vec{r},t)$ using the nonretarded approximation well suited here because of the small size of the system. Finally, $V_{\rm ext}(\vec{r},t)$ is the external optical perturbation allowing to "probe" the system. Thus, for the impulsive perturbation polarized along the x-axis $V_{\text{ext}} = \epsilon x \,\delta(t)$ (ϵ is a small constant), the frequency-resolved absorption crosssection $\sigma(\omega)$ is obtained from the dynamics of the induced dipole P(t) using the time-to-energy Fourier transform:

$$\sigma(\omega) = \frac{4\pi\omega}{c} \operatorname{Im}\{\alpha(\omega)\}$$
(3)

where $\alpha(\omega) = \frac{1}{\epsilon} \int_0^{\infty} P(t) e^{i\omega t} dt$ is the dipolar polarizability of the cluster, and *c* is the speed of light in vacuum.

GROUND STATE PROPERTIES

In Figure 1 we show the ground state electronic density calculated with DFT for the charged Na and Ag clusters. The results are presented for different values of the cluster charge Q. It is expressed in units of elementary charge so that the change of the number of electrons in the cluster upon charging is $\Delta N_{\rm e}$ = -Q. Within the range of Q displayed in the figure (a maximum of 2% charge variation compared to the total number of electrons in the nanoparticle, N_e), the valence electron density n(r) is not strongly affected by the charging. Generally n(r) is close to the background positive charge density n_{+} , and features Friedel oscillations with radial coordinate r because of the reflection of the electron wave at the nanoparticle boundary. The spill out of the electron density outside the cluster boundary can be also clearly observed in Figure 1. The spatial extension of this effect is slightly larger for Na because of the lower work function and smaller electron confinement in the potential well of the nanoparticle for that case. The spill out effect is also stronger for negatively charged clusters because of the decrease in the electron binding energies (see below).

To reveal the actual distribution of the extra charges within the cluster we analyze in Figure 2, the DFT results for the change of the ground-state electron density $\Delta n(r) = n_0(r) - c_0(r)$ $n_0(r)$ induced by the charge Q added to the Na and Ag clusters. Here $n_0(r)$ is the ground-state electron density of the cluster with charge Q, $n_0(r)$ is the ground-state electron density of the neutral cluster, and r is the radial coordinate. In panels a and b of the change of the number of electrons $4\pi r^2 \Delta n(r)$ induced at the surface of the sphere of radius r is shown as a function of r. In panels c and d of the same figure, we show the change of the total number of electrons $\Delta N_e(r)$ inside the sphere of radius r defined as $\Delta N_e(r) = \int_0^r 4\pi r'^2 \Delta n(r') dr'$. Provided that an electron charge is $\overline{e} = -1$ (in atomic units), $-\Delta N_{\rm e}(r)$ gives the change of the charge inside the sphere of radius r. The analysis of the induced density clearly demonstrates that the extra charge added to the cluster mainly resides in the surface layer of width given by the screening radius r_s . Indeed, the charge inside the sphere of radius r is almost zero for $r < R_{cl}$, and it quickly reaches the nominal value of Q for $r \simeq R_{\rm cl} + r_{\rm s}$.

This result can be easily understood with the use of the Gauss theorem of electrostatics. If the excess charge were located in some volume inside the bulk of the cluster, this would lead to the presence of electric field across the surface enclosing this volume. In response to such an electric field, the conduction electrons would move until the field is screened, or equivalently until the excess charge is compensated and neutrality is restored. Thus, except for the influence of finite size effects, the electron density in the bulk stays largely unaffected by charging of the cluster and all the excess charge is accumulated in the thin surface layer.

A charge Q located at the surface of the cluster of radius R_{cl} , creates an additional constant potential $V_Q = -Q/R_{cl}$ for the electrons inside the cluster. Thus, adding 20 electrons to the Ag cluster already containing 2018 electrons (1% variation of the total number of electrons), leads to $V_Q = 14$ eV. Based on this simple consideration, we can estimate the energy of the Fermi level $E_{\rm F}$ of the charged cluster as

$$E_{\rm F}^Q = -\Phi - Q/R_{\rm cl} \tag{4}$$

where Φ is the work function of the neutral cluster. As follows from eq 4, the negative charge rises the energy of the Fermi level and decreases the work function of the nanoparticle. Alternatively, positively charged clusters bind valence electrons more strongly.^{64–66} To illustrate the effect of the cluster charge on the electron binding, we show in Figure 3 the Fermi



Figure 3. Energy of the Fermi level E_F (eV) as a function of the cluster charge. The DFT ground state calculations have been performed for Na (red circles) and Ag (black circles) clusters a explained in the text. Straight lines of the corresponding color show the analytical dependence given by eq 4. Zero energy corresponds to the vacuum level.

energies of the charged Na and Ag clusters, obtained in DFT ground state calculations. Equation 4 nicely describes the DFT data, thus allowing for an extrapolation of the same considerations to larger systems, as well as for an analytical description of the population decay in negatively charged clusters, as presented below. It is worth noting that the self-interaction correction $(SIC)^{91-93}$ has not been implemented within the present DFT and TDDFT approaches. Thus, an electron outside of the cluster is subjected to the -Q/rCoulomb potential created by the entire system including selfinteraction. This is while the correct asymptote of the potential at large r should be -(Q+1)/r. As a result, the Fermi energy shift and of the potential barrier confining electrons in the negatively charged clusters are overestimated. However, the corresponding relative error is of the order of 1/Q, so that it is small for large cluster charges, which are of interest here. For the sake of consistency with local density approximation and the choice of the exchange-correlation potential used in our DFT and TDDFT approaches, we have neglected the SIC in deriving equations in this paper.

From the dependence of the Fermi energy on the cluster charge given by eq 4, it follows that negatively charged clusters become unstable for the charge $Q < \tilde{Q}$, where the threshold negative charge is given by

$$Q = -\Phi R_{\rm cl} \tag{5}$$

that corresponds to $E_F^{\tilde{Q}} = 0$. When the cluster charge is $Q = \tilde{Q} + q$ (q < 0), the Fermi level is promoted above the vacuum level, as shown in Figure 3, and Figure 4. The radial dependence of the effective one-electron potential $V_{\text{eff}}[n](\vec{r}) = V_{\text{xc}}[n](\vec{r}) + V_{\text{xc}}[n](\vec{r})$



Figure 4. Effective one-electron potentials (continuous lines) and Fermi level energies (dashed lines) calculated with DFT for the neutral and charged Ag clusters. Zero energy corresponds to the vacuum level. Results are shown as a function of the radial coordinate measured from the center of the cluster. The data for the neutral cluster (Q = 0) is shown with black lines, Q = -10: red lines, and Q = -20: blue lines. The black vertical line indicates the cluster boundary $R_{\rm cl}$. The blue vertical arrow shows the classical turning point of the trajectory of an electron with Fermi energy approaching the Q = -20 cluster from the vacuum. The tunneling barrier separating the cluster potential well from the vacuum region extends along a range of radial coordinates *r* given by $R_{\rm cl} \leq r \leq R_{\rm ext}$.

 $V_{\rm H}[n](\vec{r}) + V_{\rm st}(\vec{r})$ is presented in Figure 4 for the ground-state of the neutral Ag cluster (black lines) and of the Ag clusters charged by adding 10 (Q = -10, red lines) and 20 (Q = -20, blue lines) electrons. In each case, the horizontal dashed lines indicate the corresponding position of the Fermi level. While for the neutral cluster all the electrons are bound in the cluster potential well, for the cluster with charge Q = -10 the Fermi level is promoted above vacuum level along with the entire energy band of the cluster states (originating at the bottom of $V_{\rm eff}$). For the cluster with charge Q= -20 two potential wells can be observed within the radial distance range covered by the figure. The potential well at small r corresponds to the electrons confined inside the cluster, and the potential well at large *r* corresponds to the vacuum region. The electron density of the cluster can thus decay via energy-conserving resonant electron transfer into the continuum of vacuum states through the potential barrier located at $R_{\text{ext}} \leq r \leq R_{\text{cl}}$. This barrier separates the two classically allowed regions of motion, i.e., inside the cluster $r \leq R_{cl'}$ and in vacuum $R_{ext} \leq r$. Here we define R_{ext} as the radial distance where the effective oneelectron potential is equal to Fermi energy.

Assuming that an electron far enough from the charged cluster experiences the Coulomb potential -Q/r, and using eq 4, one can obtain R_{ext} as

$$R_{\rm ext} = \frac{Q}{\Phi + Q/R_{\rm cl}} \tag{6}$$

Obviously, for a cluster charge approaching the critical value \tilde{Q} , $R_{\rm ext} \rightarrow \infty$ so that the potential barrier does not allow electron tunneling and the negative charge is stabilized. On the other hand, for large negative charges, $R_{\rm ext} \rightarrow R_{\rm cl}$. In this situation, the potential barrier which separates the potential well of the cluster and the vacuum region vanishes. The valence electrons can easily escape from the cluster.

As a result of the population decay, the cluster charge would relax to \tilde{Q} , where the Fermi level is brought to the vacuum level and the system becomes stable. Taking into account that the number of electrons already present in the surface layer of width r_s in the neutral cluster is given by $N_s = 3 [R_{cl}/r_s]^2$, the relative variation of the charge allowed before the onset of the electron population decay is given by

$$|\tilde{Q}|/N_{\rm s} = \Phi r_{\rm s}^2/3R_{\rm cl} \tag{7}$$

Thus, the relative number of electrons that can be added to the surface layer of the neutral cluster before the onset of the electron population decay, decreases as $1/R_{\rm cl}$ (note that with respect to the total number of electrons in the cluster $|\tilde{Q}|/N_{\rm e} \propto 1/R_{\rm cl}^2$). The larger the cluster is, the less electrons it can admit in relative terms. For the 2018 electron clusters considered here, \tilde{Q} is -5.6 for Na and -6.5 for Ag. This implies that the system becomes unstable simply with an addition of 6 (7) electrons to the Na(Ag) cluster, which represents less than a 0.4% variation of the total number of electrons in the surface layer of width $r_{\rm s}$.

While we consider in this work charged clusters in vacuum, the situation might be different in electrochemical solution if a dipole layer is formed around the cluster by the positive ions placed at a distance $R_{cl} + d$ from the cluster center, which has the effect of screening the cluster charge.⁴⁷ In this case, and assuming $d \ll R_{cl}$, the change of the energy of the Fermi level can be estimated as

$$E_{\rm F}^Q = -\Phi - Qd/R_{\rm cl}^2 \tag{8}$$

Comparing with eq 4, here the charge Q is replaced by Qd/R_{cl} so that a much larger electron doping is allowed before the Fermi level is promoted to sufficiently high energies producing the population decay. In this case one would expect $|\tilde{Q}|/N_s = \Phi r_s^2/3d$, i.e., a charge variation nearly independent of cluster size. Assuming a realistic effective position of such a dipole layer at a distance $d \simeq 3$ Å, then a silver cluster would be able to admit ~10% variation of the number of electron in the surface layer (~0.2% of the total number of electrons).

It is worth mentioning that, for positively charged clusters, the accumulation of nonscreened ions at the cluster surface leads to the so-called Coulomb explosion where the ions are ejected from the crystal lattice sites into the vacuum.⁵⁶⁻⁵⁸ A description of this process would require to consider the dynamics of the heavy particles, which is not the focus of our attention here.

Since only a limited number of electrons can be added to the cluster before the electron population starts to decay, some approximations have to be done to compute the ground state properties and the electron dynamics of the "overcharged" clusters. To be able to address the properties of the clusters with $Q < \tilde{Q}$ we performed the DFT ground-state calculations using restricted geometry. The zero boundary conditions have been used for the electron orbitals ψ_{ij} and the size of the computational mesh has been set such that the covered range of radial coordinates is $r < R_{ext}$. These constraints are equivalent to the confinement of the system into the box with infinite repulsive potential wells, where the vacuum region available for the electron escape has been removed from the calculations. The electrons are restrained to remain inside the cluster which allows to converge the ground-state calculations even for the negative charges exceeding the threshold value. However, the results have to be considered with caution for Q such that the electron density starts to be non-negligible at R_{ext} . In our

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systems this would typically correspond to charges Q < -60 which we do not address here.

ABSORPTION CROSS SECTION

After addressing the electronic structure of charged clusters in the previous section, we now turn to the TDDFT studies of their optical response. In Figure 5 we present the absorption



Figure 5. TDDFT results of the absorption spectra of charged clusters. Panels a and b show the absorption cross section as a function of the frequency of the incoming plane wave calculated for Ag and Na clusters, respectively. Different colors are used for the results obtained with different cluster charges as indicated in the insets.

spectra calculated for positively and negatively charged Ag (panel a) and Na (panel b) clusters. For clusters with negative charge, $Q < \tilde{Q}$, the computational mesh has been restricted to $r < R_{\text{extr}}$ as in the ground-state DFT calculations. This allows to avoid the decay of the electron population.

The results in Figure 5 point out that the charging of the cluster affects both the energy and the width of the plasmon resonance, albeit in a very moderate way, as has been also reported in ref.55 A more pronounced modification of the optical response is produced for the Na cluster as compared to Ag, due to lower work function and thus larger electron density spill out into the vacuum. As well, stronger effects are noticeable for negatively charged clusters in both cases. In general, the removal of electrons from the cluster (positively charged clusters) leads to the blue shift of the plasmon resonance frequency, with the resonance becoming narrower and better defined. Adding electrons to the cluster (negatively charged clusters) leads to the red shift of the plasmon resonance. These findings are in full agreement with earlier experimental and theoretical data reported in cluster physics,^{91,94-100} and can be explained within the theory of dynamical screening at surfaces. Neglecting retardation effects,

the dipolar plasmon frequency of the nanoparticle is given by $\omega_{\rm DP} = \frac{\omega_{\rm p}}{\sqrt{3}} [1 - \delta/R_{\rm cl}]$, where δ is the position of the dynamically induced screening charges measured with respect to the jellium edge.^{101–103} For positively charged clusters, the electrons are tighter bound in the strong attractive potential well. The spill out of the electron density outside the cluster boundaries decreases leading to a smaller δ and thus to the blue shift of the dipolar plasmon frequency, as compared to that of the neutral cluster. On the contrary, for the negatively charged clusters, the electron density protrudes further away from the cluster boundaries because of the reduced binding so that δ increases and the dipolar plasmon redshifts.^{95,96,99}

Our results show that charged cluster with excess of electron density located in the surface layer cannot be modeled assuming a bimetallic core—shell nanoparticle with different electron densities and thus different optical response of the core and of the shell. Indeed, in the case of core—shell bimetallic structures, the plasmon modes of the system result from the coupling between the core-localized and shell-localized plasmons.^{104–109} These plasmon modes of individual core and shell nanoparticles correspond to an electron cloud oscillation around its own ionic background of the corresponding density. In the case of the negatively charged cluster the electron density oscillates around a unique positive background corresponding to the cluster ions as a whole.

It is worth stressing that the frequency shifts of the dipolar plasmon resonance with the cluster charge, as calculated here and also measured for clusters in gas phase show the behavior that is opposite to the experimental data obtained in electrochemistry.⁴¹⁻⁵¹ In electrochemical experiments, the blue/red shift of the localized plasmon resonance has been measured for negative/positive charging of nanoparticles. Those results have been often interpreted in terms of the corresponding change of the valence electron density. However, the situation of the individual nanoparticle in vacuum, as considered in our study, accounts for all charging effects evoked so far in explanation of electrochemical data. Since our TDDFT study shows opposite frequency shifts, we conjecture that additional screening effects due to the electrochemical environment (in particular the dipole layer formed around the nanoparticle), and the eventual modification of the surface electronic structure due to chemisorption must be responsible for the plasmon energy shifts measured with electrochemical charge doping.

The broadening of the resonance for the negatively charged clusters as seen in the optical absorption cross section in Figure 5a,b reflects a faster decay of the underlying plasmon mode. The increase of the decay rate is associated with an increased coupling between the collective plasmon and the continuum of the single particle electron-hole excitations, where the hot electron produced by the plasmon decay can be emitted from the cluster.^{91,94,100,110} In this context, we ascribe the features in the absorption spectra for Q = -20 and Q = -30 Na clusters to this coupling as has been observed in TDDFT calculations on various systems.^{111,112} Considering the work function of silver $(\Phi_{Ag} = 4.65 \text{ eV})$ and sodium $(\Phi_{Na} = 3 \text{ eV})$ clusters addressed in this work, the decay of the dipolar plasmon with electron emission is impossible for the silver cluster, and concerns only the electrons within an energy range of \sim 0.2 eV from the Fermi level for the sodium cluster. However, the Fermi level $E_{\rm F}^Q$ of the negatively charged cluster (Q < 0) approaches the vacuum level, as expressed with eq 4. For $Q < \tilde{Q}$, $E_{\rm F}$ is promoted above



Figure 6. TDDFT results for the electron population decay in small sodium (panels a and c) and silver (panels b and d) negatively charged clusters. Panels a and b: time-evolution of the number of excess electrons in the cluster, $\Delta N_e(t) = -Q(t)$, where Q(t) is the time-dependent cluster charge. Different colors are used to display the results obtained with different initial charge Q(t = 0), as explained in the insets. t = 0 is the instant of time when the computational constraints are released and the system is allowed to decay. Panels c and d: time-dependence of the population decay rates as extracted from the data presented in panels a and b of this figure. For further details, see the main text.

the vacuum level and the height of the potential barrier that confines the electrons inside the cluster decreases (see Figure 4). As a result, the probability of the plasmon decay with electron emission increases. Alternatively, for positively charged clusters (Q > 0), the overall binding energy of the electrons in the cluster increases and the confining potential becomes sharper, leading to a smaller plasmon damping.¹¹³

ELECTRON POPULATION DECAY IN NEGATIVELY CHARGED CLUSTERS

Analytical Expressions. As discussed in connection with the shift of the Fermi level, when the cluster charge is $Q = -\Phi R_{\rm cl} + q$, with q < 0, the Fermi level of the cluster is promoted above the vacuum level. The electron population of the cluster associated with the extra charge, q, above the threshold value, $\tilde{Q} = -\Phi R_{\rm cb}$ decays because of the electron escape into the continuum. Prior to the discussion of the results obtained in the TDDFT study of this effect, let us outline some simple theoretical considerations, which facilitates understanding of the numerical data. Within the Wentzel–Kramers–Brillouin (WKB) approximation, the decay rate, Γ , of the excess of electron population is given by

$$\Gamma = \Gamma_0 \exp(-2\gamma) \tag{9}$$

where $\Gamma_0 \propto v_F/R_{cl}$ is a parameter proportional to the frequency at which the Fermi electron with speed v_F collides with cluster boundary, and $\exp(-2\gamma)$ is the probability of electron tunneling through the potential barrier, with

$$\gamma = \int_{R_{\rm cl}}^{R_{\rm ext}} \sqrt{2 \left[\frac{|Q|}{r} - E_{\rm F}^{Q} \right]} \mathrm{d}r \tag{10}$$

Eq 10 corresponds to an electron at the Fermi energy $E_{\rm F}^Q = |Q|/R_{\rm ext}$ that tunnels through the potential barrier located at $R_{\rm cl} \leq r \leq R_{\rm ext}$ as shown in Figure 4. The effective one-electron potential is approximated by the -Q/r dependence, so that the theory of alpha-decay¹¹⁴ can be used, resulting in

$$\gamma = \sqrt{2|Q|R_{\text{ext}}} \left[\arccos(\sqrt{R_{\text{cl}}/R_{\text{ext}}}) - \sqrt{R_{\text{cl}}/R_{\text{ext}}} \sqrt{1 - R_{\text{cl}}/R_{\text{ext}}} \right]$$
(11)

It is convenient to rewrite eq 11 in terms of the cluster charge. Using $R_{\text{ext}} = \frac{Q}{a}R_{\text{cl}}$, which can be obtained from eq 6, leads to

$$\gamma = |Q|\sqrt{2R_{\rm cl}/|q|} \left[\arccos(\sqrt{q/Q}) - \sqrt{q/Q}\sqrt{1 - q/Q}\right]$$
(12)

The analytical expression given by eq 12 allows the discussion of the threshold behavior of the population decay for $E_F^Q \rightarrow 0^+$, where the decay rate is small and can not be calculated with TDDFT. In this case, the cluster charge is given by $Q = \tilde{Q} + q (q \rightarrow 0^-)$, and $R_{\rm cl}/R_{\rm ext} \ll 1$. Using the asymptotic expansion we obtain for γ :

$$\gamma = \frac{\pi}{\sqrt{2}} |\tilde{Q}| \sqrt{2R_{\rm cl}/|q|} \tag{13}$$

Therefore, the decay rate of the excess of electron population (excess-charge q) is given by

$$\Gamma = \Gamma_0 \exp\left[-\sqrt{2} \pi \Phi \sqrt{R_{\rm cl}^3/|q|}\right]$$
(14)

With these analytical results at hand, we now turn to the numerical TDDFT study of the electron escape from the negatively charged clusters.

TDDFT Results. In the TDDFT study of the electron population decay in negatively charged clusters, the $\psi_i(\vec{r})$



Figure 7. Analysis of the decay of the negative charge in small sodium (panels a and c) and silver (panels b and d) clusters, based on the TDDFT results. Different colors represent the results obtained with different initial cluster charges, as defined in the insets of panels c and d. Panels a and b: electron population decay rates $\Gamma(t)$ extracted from the TDDFT calculations using eq 15. Results are shown as a function of the instantaneous negative charge Q(t). Panels c and d: validity check of the analytical approach given by eq 12. The logarithm of the instantaneous decay rate $\ln(\Gamma)$ is shown as a function of charge-varying parameter γ .

orbitals obtained in the DFT ground-state calculations on a restricted-size mesh are used as initial states for the time propagation. However, different from the calculation of the absorption cross-section, the confinement constraint has been lifted off at an instant of time t = 0. This is achieved by providing the radial mesh that extends to $r \gg R_{\text{ext}}$. The negative charge of the cluster can then decay via electron escape into the vacuum.

In Figure 6a,b, we show the time evolution of the number of excess electrons in Na and Ag clusters, $\Delta N_e(t) = -Q(t)$, calculated with TDDFT for different initial cluster charges Q(t = 0). For highly charged clusters $(Q \sim -40, -50)$, about 10 to 20 electrons are lost in less than 2000 au of time (50 fs). The cluster charge drops, and the electron population decay slows down approaching time constants characteristic of low initial charges. Indeed, the smaller is the cluster charge Q(t), the higher is the potential barrier separating the potential well inside the cluster from the vacuum region. This results in a lower population decay rate Γ . We can introduce the instantaneous decay rate $\Gamma(t)$ via the equation:

$$\frac{\mathrm{d}Q(t)}{\mathrm{d}t} = -\Gamma(t)(Q(t) - \tilde{Q}) = -\Gamma(t)q \tag{15}$$

which describes the relaxation of the cluster charge toward the threshold value \tilde{Q} . In panels c and d of Figure 6, we display the decay rate $\Gamma(t)$ obtained from the charge dynamics shown in panels a and b of the same figure, with use of eq 15. Overall, the decay rate is smaller for low initial charges, and it decreases at longer times as soon as the cluster becomes less charged.

According to the analytical approach (see eq 9 and eq 12) the potential barrier for electron tunneling and therefore the decay rate is determined by the cluster charge Q(t). Indeed, as shown in panels a and b of Figure 7, when the decay rate Γ is displayed as a function of the instantaneous charge, the results obtained for different initial cluster charges Q(t = 0) fall into a

universal curve. The features at short propagation times arise because the exponential decay needs some time to set in as known from the studies of the decay of quasi-stationary states.¹¹⁵

The TDDFT results can be used to further test the analytical approach for the negative cluster population decay. In Figure 7c,d, the logarithm of the instantaneous decay rate $ln(\Gamma)$ is shown as a function of parameter γ given by eq 12. Note that γ is time-dependent through the time-dependence of the cluster charge. We observe that the same linear dependence with a slope close to -2 (see eq 9) is obtained irrespective from the initial cluster charge. With the validity of the semiclassical approach established by this comparison with the TDDFT results, we can use eq 14 to analyze the evolution of the population decay rates for clusters of varying size. The population decay rate can be expected to be similar for charged clusters with $|q| \propto R_{\rm cl}^3$. Since the number of electrons in the cluster, N_{e} , is also proportional to the cluster volume, we obtain that clusters characterized by the condition q/N_e = const should have similar time scales for the population relaxation. Using the results shown in Figure 6a,b, we conclude that half of the excess-charge, representing 2% of the total number of electrons, will be lost in 50 fs following the charging event. Thus, the addition of small amount of electrons representing some percents of the total amount of the valence electrons can only lead to a transitory negative charge, unless the metal/ vacuum interface is replaced by the a dipole layer as for instance in an electrochemical solution.

SUMMARY AND CONCLUSSIONS

Using TDDFT calculations for Na and Ag clusters, we have demonstrated that the surface plasmon modes of small spherical clusters in vacuum are only mildly sensitive to the positive/negative charging and do not present significant resonance frequency shifts. We show that the negative charging

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leads to a red shift of the plasmon frequency and the positive charging leads to a blue shift of the plasmon frequency. This behavior is opposite to the one reported in electrochemical experiments. Present TDDFT results can be understood within the theory of dynamical screening considering that (i) the electron density in the cluster volume cannot be modified, which means that the excess charge is accumulated at the surface of the cluster in a thin layer of width given by the screening radius of the corresponding metal, and (ii) the electron density spill-out from the cluster boundaries is larger for negative clusters and smaller for positive clusters.

We have also shown that even small (relative to the total number of electrons in the system) negative charge might raise the Fermi level of the cluster above the vacuum level, which renders the system unstable. In such a case, an electron population (or, equivalently, the cluster charge) decays via resonant energy-conserving electron tunneling into the freeelectron continuum of propagating states above the vacuum level. The characteristic time scales for the decay of the cluster charge are of the order of some tens of femtoseconds that can be fully understood using an analytical study based on the WKB method. This limits the possibility to charge the system. The larger the cluster is, the smaller the amount of negative charge Q it can admit relative to the number of electrons present in the surface layer, or, equivalently, relative to the total number of electrons in the cluster $N_{\rm e}$. Our results indicate that $|Q|/N_{\rm e}$ < 1%.

While present calculations have been performed for spherical clusters, the results obtained in this study stem from robust physical phenomena such as nonlocal screening in metal nanoparticles and rise of the repulsive electrostatic potential upon negative charging. We thus expect that the qualitative conclusions obtained in this work apply for nanoparticles of other 3D geometries.

Our findings for the charged clusters in vacuum shed light on the relevant role played by the chemisorbed species and by the dipole layer formed around charged nanoparticles as the actual sources for the frequency shift of plasmon resonances obtained in electrochemical experiments. Indeed, we show that the electron density in the volume of the nanoparticle is not affected by charging effects, and that the change of the freeelectron density at the surface leads to a plasmon frequency shift opposite to that observed with electrochemical charge doping.^{41–51}

The calculations presented in this work do not account for the effects of screening and chemisorption at the nanoparticle surface, but rather serve to explicitly point out their relevance by noting the difference in the optical response between the "charged" metal/vacuum interface considered here and the surfaces of metal nanoparticles in electrochemical solution. The importance of the screening due to the electrochemical environment and the change of the surface electronic structure by chemisorbed species has been indeed pointed out in works such as those in refs.⁴⁹⁻⁵¹ At this point, it is worth stressing that a large electron donation to a metallic nanoparticle necessarily requires a screening charge around it in order to avoid the decay of the electron population. The resulting dipole layer created around the nanoparticle would affect the screening of electromagnetic fields and thus the frequency of the localized plasmon modes. Thus, a consistent explanation of the experimental data in electrochemistry should evoke these effects, which paves a way for further theoretical studies.

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Notes

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