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Lifetime of electronic excitations in metal nanoparticles

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Abstract. Electronic excitations in metal particles with sizes up to a few nanometers are shown to have a one-electron character when a laser pulse is applied off the plasmon resonance. The calculated lifetimes of these excitations are in the femtosecond timescale but their values are substantially different from those in bulk. This deviation can be explained from the large weight of the excitation wave function in the nanoparticle surface region, where dynamic screening is significantly reduced. The well-known quadratic dependence of the lifetime with the excitation energy in bulk breaks down in these finite-size systems.

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1. Introduction

While the structural properties of materials depend on ground state features, electronic and optical properties are largely determined by their electronic excitations. A large amount of theoretical and experimental work has been devoted to understanding the dynamics and predict the lifetimes of these excitations in metallic solids [1]–[5] and at metal surfaces [6]–[11]. Much less is known about the dynamics of electronic excitations in finite-size systems. In metal nanoparticles, electronic properties are very often size dependent and can be tuned purposely. The modification, at wish, of the electronic properties of metal systems and the subsequent change in the lifetime of electronic excitations have important implications for many technological applications. In photochemistry, for instance, electronically excited states can act as intermediate steps in various chemical processes [12]. Either enhancement or reduction of the reaction rate should thus be possible through a proper design of the intermediate step lifetime.

The difference between the dynamics of hot electrons in nanoparticles and in bulk has to be discussed in terms of two effects. Firstly, the electron lifetime can be enhanced in metal nanoparticles as compared to bulk because of the discretization of levels that reduces the number of final states to which the electronic excitation can decay. Secondly, the lifetime can be shortened in the nanoparticle because of the reduction of dynamic screening for low frequencies. Thus, there are no *a priori* reasons to predict whether the lifetime of electronic excitations in nanoparticles is longer or shorter than in bulk.

From the experimental point of view, laser-based pump–probe techniques have been used to analyze the dependence on size of the electron–electron interaction processes [13]–[16]. Some of the conclusions extracted from these works are puzzling. Measurements of internal thermalization times suggest that the electron–electron scattering rate is increased in Ag nanoparticles of size smaller than 5 nm as compared with the bulk reference value [13]. However, electron lifetimes in supported Ag nanoparticles were measured to be appreciably higher than those obtained for Ag thick films [16]. These apparently contradictory conclusions show the necessity for further research on the subject.

In this work, we combine time-dependent density functional theory (TDDFT) and the self-energy formalism to characterize the electronic excitations in metal nanoparticles and calculate their decay rates in typical pump–probe situations. In section 2.1, we use TDDFT to show that, when a laser pulse is applied off the plasmon resonance, the electronic excitation exhibits a one-electron character. However, TDDFT in the adiabatic local density approximation (ALDA) fails to describe the decay of these states as well as the width of collective electron excitations [17]. For this reason, in section 2.2, we switch to a different methodology and use the self-energy

formalism to calculate the lifetime of the excitation. The GW approximation for the self-energy has already been shown to be an accurate tool to obtain electron lifetimes in metal bulk and surfaces [18]. We show that, for particle sizes up to a few nanometers, the lifetime does not depend much on size. Still, the lifetime value is surprisingly different from the bulk limit. We explain this fact in terms of the partial localization of the electron excitation in the vicinity of the surface.

We restrict our discussion to neutral nanoparticles in closed-shell electronic configurations. The description of the system is simplified by means of the jellium approximation, which allows us to cover a wide range of particle sizes. The spherical jellium model has been widely used in the description of metal clusters and is able to describe many of their experimentally measured electronic properties [19]. The average one-electron radius in the nanoparticle is defined from $r_s = R/N^{1/3}$, where R is the radius of the nanoparticle and N the number of electrons.

2. Theory and results

2.1. Time evolution of electronic excitations

The first goal of our work is the analysis of the electronic excitations produced in the nanoparticle when pumping energy with a laser source. For this purpose, we use TDDFT to describe the dynamical evolution of the electronic density

$$n(\mathbf{r}, t) = \sum_{j \in \text{occ.}} |\varphi_j(\mathbf{r}, t)|^2, \quad (1)$$

where $\varphi_j(\mathbf{r}, t)$ are the Kohn–Sham (KS) wave functions (atomic units will be used unless otherwise stated). The local density approximation (LDA), with the functional form of [20], is used to describe the exchange–correlation potential in the static situation. In the ground state ($t = 0$), the spectrum of KS energy levels ε_j is discrete and each $\varphi_j(\mathbf{r}, t = 0)$ is characterized by the radial quantum number k and the angular momentum l . Dynamical calculations rely on ALDA with the same exchange–correlation functional. Numerical details are similar to those of [21]. In TDDFT, the time evolution of the electron density in response to the external laser field is obtained from the evolution of the occupied KS wave functions:

$$i \frac{\partial \varphi_j(\mathbf{r}, t)}{\partial t} = \{T + V_{\text{eff}}([n], \mathbf{r}, t)\} \varphi_j(\mathbf{r}, t), \quad (2)$$

where T is the kinetic energy operator. The effective KS potential $V_{\text{eff}} = V_{\text{ext}} + V_{\text{H}} + V_{\text{xc}}$ is obtained as the sum of the external potential V_{ext} , the Hartree potential V_{H} and the exchange correlation potential V_{xc} . The external potential is that generated when a Gaussian laser pulse

$$\mathbf{E} = E_0 \cos(\Omega t) \exp\{-(t - t_0)/\Delta\}^2 \mathbf{u}_z \quad (3)$$

is applied. Here, \mathbf{u}_z is a unitary vector along the z -axis, E_0 is the field amplitude, Ω is the laser frequency, t_0 is the time of maximum amplitude, and Δ controls the pulse duration. We choose Δ so that the energy width of the pulse is much lower than the typical energy difference between KS levels in the system. In addition, we selectively tune Ω to a given single-particle excitation (i.e. to the energy difference between two KS levels), making sure that no other single-particle excitations are available for this frequency. During the time evolution, the problem becomes axially symmetric and KS wave functions preserve their quantum number m .

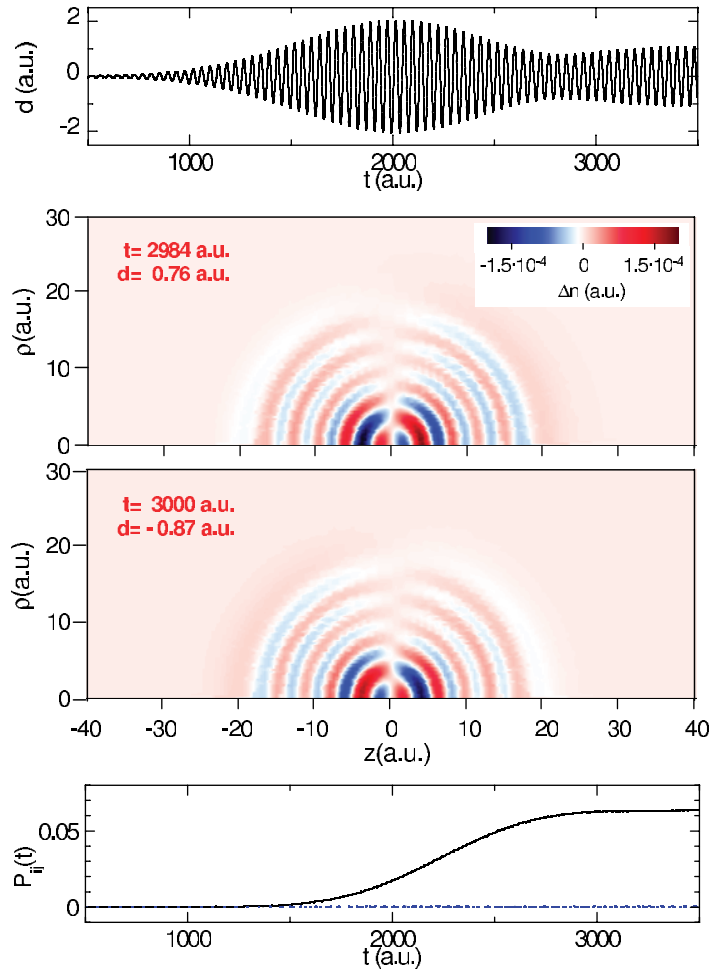


Figure 1. Change in electronic density $\Delta n(\mathbf{r}, t)$ induced in a metal nanoparticle by a laser pulse (central panels). $\Delta n(\mathbf{r}, t)$ is shown over a plane (ρ, z) containing the direction of propagation of the field, for $t = 2984$ and 3000 . The nanoparticle is made of $N = 556$ electrons and $r_s = 2.07$. The laser pulse parameters are $E_0 = 2 \times 10^{-4}$, $t_0 = 2000$, $\Delta = 700$ and $\Omega = 4.12$ eV. The upper panel shows the time evolution of the dipole moment d induced in the nanoparticle. The lower panel shows the projections $P_{ij}(t)$ of an initially occupied level j over an initially unoccupied level i (blue dotted lines). The projection with a maximum value over time is plotted with a black solid line.

Figure 1 shows the dipole moment d induced by the laser pulse in a nanoparticle with $N = 556$ and $r_s = 2.07$ (upper panel). The laser frequency is $\Omega = 4.12$ eV. The change in electronic density $\Delta n(\mathbf{r}, t) = n(\mathbf{r}, t) - n(\mathbf{r}, t = 0)$ is shown at two different times (middle panels), with the induced dipole moments pointing in opposite directions.

We define the projection

$$P_{ij}(t) = \sum_{m_i, m_j} \delta_{m_i m_j} |\langle \varphi_{i \in \text{unocc.}}(\mathbf{r}, t = 0) | \varphi_{j \in \text{occ.}}(\mathbf{r}, t) \rangle|^2 \quad (4)$$

of the time-dependent KS wave functions over those unperturbed KS wave functions that are unoccupied at $t = 0$. The sums over m_i and m_j run over all possible m -values of the energy levels ε_i and ε_j . When the pulse is over, only one projection $P_{ij}(t)$ takes a non-negligible value, as shown in the lower panel. This means that the excitation can be roughly described as a one-electron transition between an initially occupied KS level ε_j and an initially unoccupied KS level ε_i . The excitation energy is close (although not identical) to the energy of the pulse $\varepsilon_i - \varepsilon_j \approx \Omega$. The radial nodes of these two KS wave functions fix the zeros of Δn in the middle panels of figure 1. This result strongly supports the use of unoccupied KS wave functions as final one-electron states in the excitation process.

2.2. Lifetime of electronic excitations

As a second step, we calculate the lifetime of the electronic excitation created by the laser pulse using a different methodology. The wave function of the excited electron is approximated by the corresponding KS one-electron wave function $\varphi_i(\mathbf{r})$ with KS eigenvalue ε_i . This approximation is supported by the TDDFT results of section 2.1 (see lower panel of figure 1). In the framework of many-body theory, the lifetime of this quasiparticle is given by $\tau_i = \Gamma_i^{-1}$, where the decay rate Γ_i can be obtained from the projection of the imaginary part of the electron self-energy $\Sigma(\mathbf{r}, \mathbf{r}', \varepsilon_i)$ over the wave function of the electron. We calculate $\Sigma(\mathbf{r}, \mathbf{r}', \varepsilon_i)$ in the GW approximation [22, 23], widely used in similar problems [10, 11, 24]. If the exact Green function G is replaced by the independent-electrons Green function G^0 , one can show that [25, 26]

$$\Gamma_i = -2 \sum_{f \in \text{unocc.}} \int d\mathbf{r} d\mathbf{r}' \varphi_i^*(\mathbf{r}) \varphi_f^*(\mathbf{r}') \text{Im} W(\mathbf{r}, \mathbf{r}', \omega) \varphi_i(\mathbf{r}') \varphi_f(\mathbf{r}), \quad (5)$$

where $W(\mathbf{r}, \mathbf{r}', \omega)$ is the screened interaction, $\omega = \varepsilon_i - \varepsilon_f$, and the sum over f runs over all unoccupied KS states of energy ε_f below the energy ε_i . The screened interaction $W(\mathbf{r}, \mathbf{r}', \omega)$ is obtained in terms of the bare Coulomb potential $v_C(\mathbf{r}, \mathbf{r}')$ and the density–density response function of the nanoparticle $\chi(\mathbf{r}, \mathbf{r}', \omega)$, the latter calculated in the random phase approximation (RPA).

The numerical procedure can be found in [25] and is only summarized here. We build one-electron Green functions for every ω and use them to calculate the multipole components of $\chi^0(\mathbf{r}, \mathbf{r}', \omega)$. The RPA-type integral equation is solved in real space after matrix inversion for every polar component l . An imaginary damping η is added to the value of ω in the numerical calculation of $\chi^0(\mathbf{r}, \mathbf{r}', \omega + i\eta)$. Without a certain indeterminacy in the energy value, Γ would be strictly zero for transitions between discrete states. In real systems, physical effects such as temperature and finite duration of the laser pulse account for this indeterminacy. We have checked that the results do not vary more than 3% for values of the damping between $\eta = 10^{-3}$ and $\eta = 10^{-2}$. We choose a value $\eta = 0.005$ for all calculations presented here.

In figure 2, we show the decay rate Γ as a function of $\varepsilon_i - \varepsilon_F$, where ε_F is the highest occupied state energy. We choose values of $r_s = 2$ ($N = 1314$) and $r_s = 4$ ($N = 912$), representing Al and Na nanoparticles, respectively. The present results are compared with the decay rates of electronic excitations in an infinite homogeneous free electron gas (FEG) calculated in the same approximation [27]. Our results show that the values of Γ in a nanoparticle are still in the femtosecond timescale, but are significantly larger than the values of Γ in an FEG.

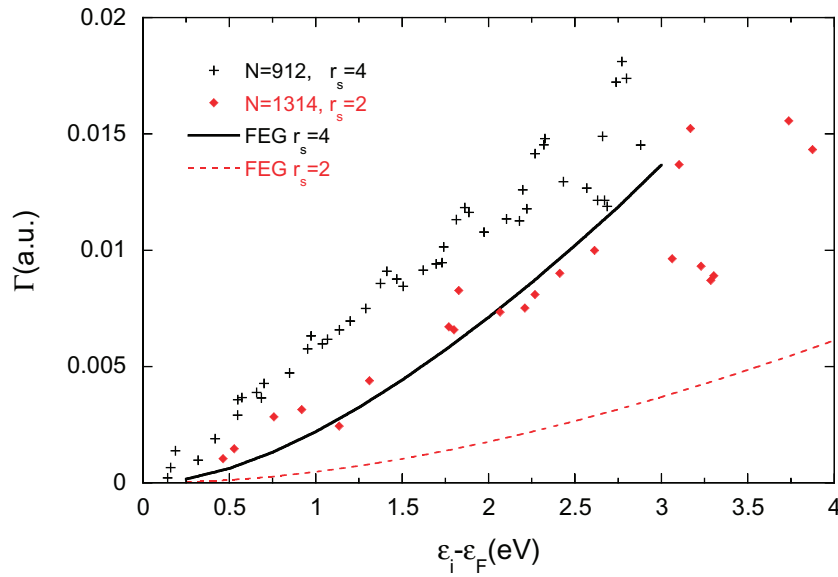


Figure 2. Decay rate $\Gamma = \tau^{-1}$ for electronic excitations in nanoparticles as a function of the excitation energy $\varepsilon_i - \varepsilon_F$. (Red) diamonds refer to a nanoparticle of $N = 1314$ and $r_s = 2$ ($R = 1.1$ nm). (Black) crosses refer to a nanoparticle of $N = 912$ and $r_s = 4$ ($R = 1.9$ nm). The dashed (red) line and the solid (black) line show the values of Γ in an infinite electron gas of $r_s = 2$ and $r_s = 4$, respectively.

In an FEG and for small values of $\varepsilon_i - \varepsilon_F$, the decay rate is known to depend on the excitation energy ε_i through a quadratic function $\Gamma \propto (\varepsilon_i - \varepsilon_F)^2$ [28]. This scaling law arises from the phase space available for the electronic excitation to decay [29]. Figure 2 shows that the quadratic dependence breaks down in a nanoparticle. The discrete spectrum of excitation energies in a finite system modifies the available phase space and thus the dependence on the energy. In addition, the dependence of Γ on r_s is also smoother in a nanoparticle, as can be seen in figure 2. In other words and according to our calculation, lifetimes of electronic excitations in nanoparticles are less material dependent than those in bulk. Further experimental evidence would be useful to gain insight into these points.

An interesting question for confined systems is always the size for which the properties merge into those of bulk. We analyze the dependence of the decay rate $\Gamma = \tau^{-1}$ on the particle radius R in figure 3. Values of Γ are plotted for three different excitation energies ε_i in nanoparticles with $r_s = 4$. An exact matching in energy is not possible because of the discretization of energy levels in finite-size systems. For the largest sizes considered in this work (≈ 5 nm diameter), there is still a significant difference between the lifetime of electronic excitations in nanoparticles and bulk, even if the density of final states in the decay can be considered roughly as a continuum. The first reason for this deviation is that the dynamic screening between electrons in a nanoparticle of this size is still different from the one in bulk, even in the inner regions of the nanoparticle. The second and most important reason for the difference is the localization in space of the electronic excitation. In an infinite homogeneous system, the initial states of the excitation can be considered as plane waves, extended all over the space. In a nanoparticle, we have shown above that unoccupied KS wave functions appropriately

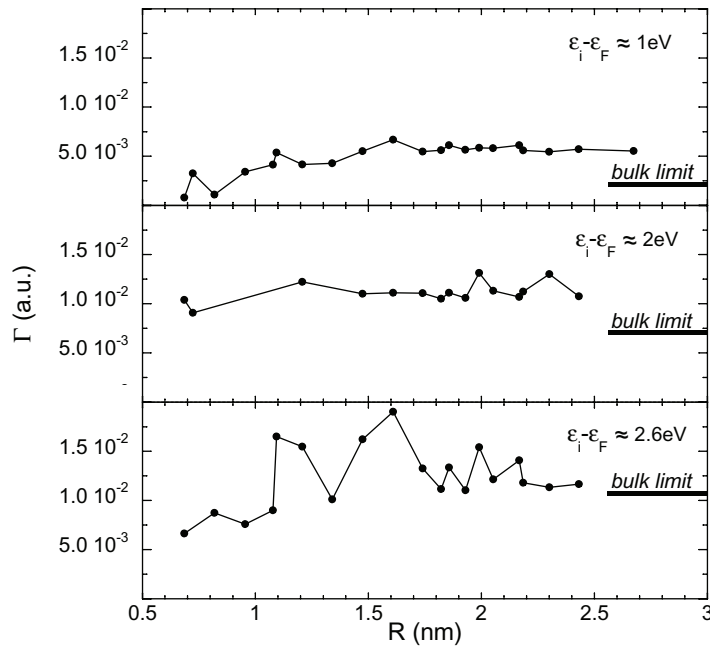


Figure 3. Decay rate $\Gamma = \tau^{-1}$ for electronic excitations in nanoparticles of $r_s = 4$ as a function of their radius R . Three different excitation energies are shown. The values for the FEG are also shown (bulk limit).

describe the excited state after laser excitation. Figure 4 shows that the unoccupied KS wave functions have a large weight near the surface. Dynamic screening in the vicinity of the surface is less effective than in bulk, making the electron–electron interaction stronger. Significant overlap between the initial and final wave functions in the surface region modifies the decay probability as compared to the bulk case.

Let us finally discuss our results in connection with the aforementioned experimental evidence. The decay rates calculated above for nanoparticles correspond to lifetimes τ between 1 and 100 fs. Experimental results for Ag nanoparticles [16] are in between these values. Our theoretical results also show that the decay rate is larger in nanoparticles than in bulk. This is in agreement with the conclusions extracted from the measurements of thermalization times in Ag nanoparticles [13], but it does not help us to understand the opposite behavior obtained in supported Ag nanoparticles [16]. Further research is thus needed to clarify this point.

3. Summary

In summary, our results show that the lifetimes of electronic excitations in nanoparticles are in the femtosecond time scale. We also show that the well-known quadratic dependence of the lifetime on the excitation energy in bulk $\tau \propto (\varepsilon - \varepsilon_F)^{-2}$ breaks down in metal nanoparticles. This peculiar quasilinear behavior has also been predicted in other low-dimensional systems [30] and would require experimental evidence to be confirmed. Finally, substantial quantitative variations are seen between the lifetimes of electronic excitations in metal nanoparticles and bulk. Electron excitations have a significant weight in the nanoparticle surface region, where

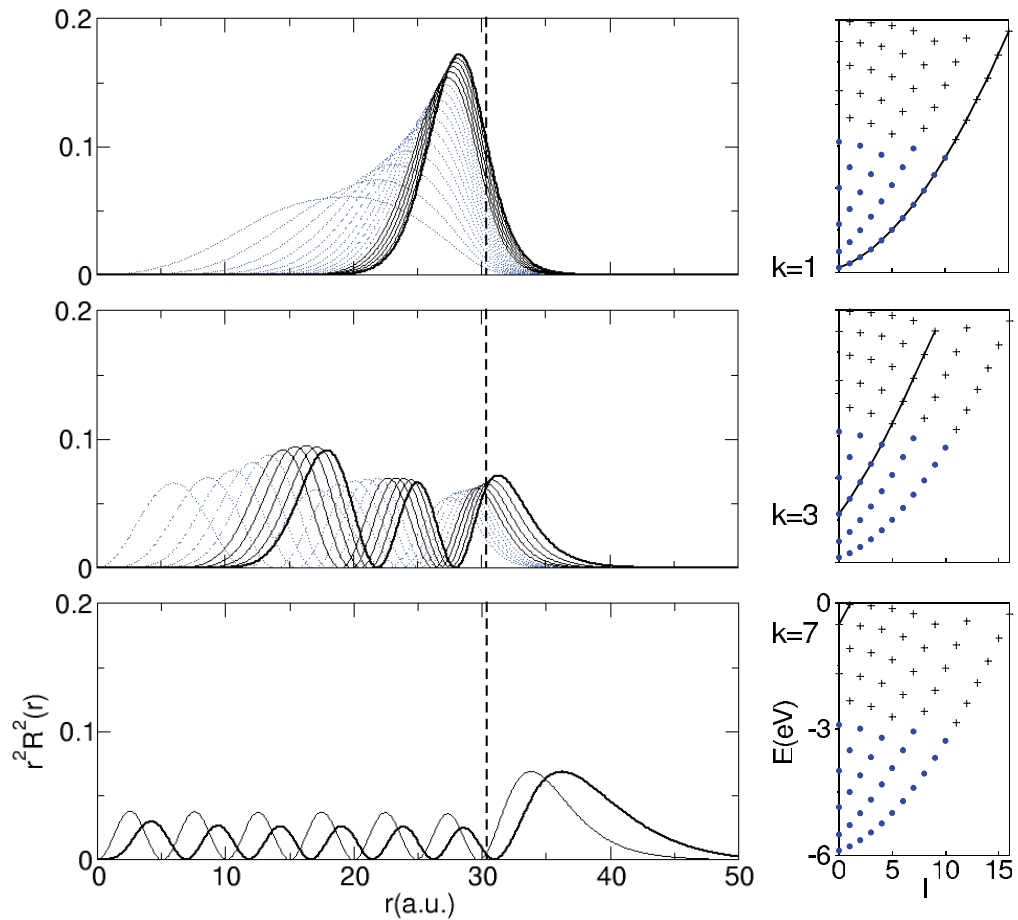


Figure 4. Left panels: radial distributions for the wave functions in a nanoparticle with $N = 440$ and $r_s = 4$ ($R = 1.6$ nm). Blue dotted (black solid) lines represent occupied (unoccupied) states. The unoccupied state of highest energy is represented with a thick solid line. The nanoparticle surface is indicated with a dashed line. Right panels: energy levels as a function of angular momenta. Blue circles (black crosses) indicate occupied (unoccupied) states. Lines are plotted joining the energy levels for which radial distributions are shown on the left panels.

dynamic screening is largely reduced, and the lifetime of these excitations is subsequently shortened. Finite-size effects thus play a major role in the decay of electronic excitations in metal nanoparticles.

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