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Long lived electronic states

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Abstract

The deexcitation probability of localized electronic states in metals has been studied regarding the influence of the degree of localization. Results show that localization reduces the probability of deexcitation, thus increasing the lifetime, as a consequence of the mismatch between the momentum spectrum of a highly localized state and the excitation spectrum of the electron gas. The energy dependence of the probability is only slightly affected by the localization of the state. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The development of materials technology, particularly using semiconducting materials, has made it possible today to construct almost any geometrical configuration, or for that matter, material combination with the purpose of controlling different physical parameters. Examples are numerous in fields like nanophysics, photonic materials and scanning microscopies. One of the prime parameters to control the physics is the dimensionality of the space available for free carriers. This is a problem, which both goes long back, like the original proposal on artificial metal or semiconductor superstructures by Esaki [1], as well as has attracted attention more recently, for instance in the work of Kayanuma on the shape and dimensionality effect on excitons in semiconductor microstructures [2]. One way such dimensionality effects would show up in an experiment is when monitoring excited electron lifetimes. Recently there has been a renewed interest in this because the rapid development of new experimental techniques such as Time Resolved Two Photon Photoemission (TR-2PPE) which allows the determination of the deexcitation rates with great accuracy [3–7]. It appears interesting then to study,

which effects could be expected on the lifetimes of excited states, when varying their confinement or dimensionality.

An electron excited above the Fermi energy inside a metal will decay into unoccupied states of lower energy by interaction with the rest of the electrons in the metal. The transition rate, probability per unit time P , of this deexcitation process is a property of the excited state directly related with the imaginary part of its self-energy Σ_2 [8]

$$P(E) = \frac{2}{\hbar} \text{Im} \Sigma_2(E). \quad (1)$$

There are two fundamental factors when calculating the probability for the decay of an excited state. On the one hand we have the phase space available for the transition which is controlled by the energy distance from the energy of the state to the Fermi energy and by the density of states in that region. Experimental confirmation of this fact has been found for example in photoemission experiments on alkali metals where empty d-bands produce anomalously short mean free paths [9]. Penn and coworkers [10,11] also showed that the spin-dependent size of the phase space was the key to understand the spin-dependent lifetimes observed in ferromagnetic materials, which has attracted recent interest [12].

On the other hand, there is the matrix element, which connects the initial and the final state through the screened

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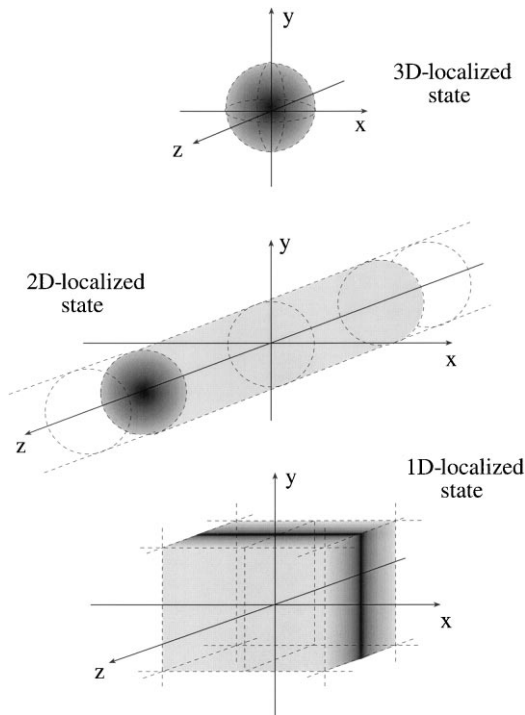


Fig. 1. States with different degrees of localization. The state at the top is localized in three spatial directions and would be confined, e.g. inside a sphere. In the middle, one of the directions is free and the state gets confined inside an infinitely long cylinder. Finally, at the bottom, only one direction remains localized and the state is confined in an infinite slab.

interaction. Several approximations have been used to describe the dielectric response of the electrons in a metal, usually based on different approximations for the dielectric function of a free electron gas or on including dispersion effects in experimental results of the optical response function [13–19]. Inside the matrix element, together with the screened interaction, the wave functions of the initial and the final states are also important. In the case of the calculation of deexcitation probabilities of image states in front of metal surfaces [20,21] the shape of the wave function describing the initial state, particularly its penetration into the solid and the overlap with both bulk and surface states, has been shown to have a fundamental influence on the lifetime [22,23]. These image states are essentially localized in one direction and free-electron-like in the other two directions. However, to the best of our knowledge, there has been no general discussion about effects on the probability due to a general change in the localization character of the wave function in a bulk calculation. In the present work, the deexcitation probability of an excited state with arbitrary spatial extension is calculated inside a free-electron-like metal described by the Lindhard response function. In the limit of complete delocalization the result obtained by Quinn [8] for free

electrons is retrieved while a fully localized state almost lives forever.

2. Lifetime of a 3D localized state

Let us consider the interaction of an arbitrary electronic state $\psi(\mathbf{r})$ with the corresponding states of a metal. If the energy of this electronic state (E_0) is larger than the Fermi energy of the metal ($E_0 > E_F$), the state will have a finite probability to decay, by interaction with the electrons in the metal, to a state with lower energy ($E', E_0 > E' > E_F$). The energy and momentum lost by the electron in the decay process will be absorbed by an excitation in the metal. The probability of this kind of processes can be calculated using the Fermi's Golden Rule. Assuming that a dielectric description is valid for the electrons in the metal, the probability for the state $\psi(\mathbf{r})$ to decay into any of the empty states of the metal will be given by, neglecting exchange processes

$$P = \frac{2}{\hbar V^2} \sum_{\mathbf{p}} \sum_{\mathbf{q}} |c(\mathbf{p} + \mathbf{q})|^2 \frac{4\pi e^2}{q^2} \text{Im}\{-\varepsilon^{-1}(q, \omega)\}, \quad (2)$$

where $c(\mathbf{k})$ are the plane wave components of the state ψ

$$\psi(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{k}} c(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}}. \quad (3)$$

\mathbf{p} is the momentum of the final state of the electron, supposed to be a plane wave. $\varepsilon(\mathbf{q}, \omega)$ is the dielectric function that takes into account both the possible excitations and the screening of the interaction in the metal. \mathbf{q} and $\hbar\omega = E_0 - \hbar p^2/2m$ are, respectively, the momentum and energy transferred to the solid. The description above of occupied and unoccupied states will restrict the \mathbf{q} and \mathbf{p} summations.

In order to study the dependence with localization we are interested in using a wave function $\psi(\mathbf{r})$ which could interpolate between a completely localized state with energy E_0 and a plane wave with the same energy and the appropriate momentum $k_0 = \sqrt{2mE_0}$. In this sense we chose a harmonic oscillator type wave function

$$\psi_{\mathbf{k}_0}^R(\mathbf{r}) = (\sqrt{\pi}R)^{-3/2} e^{-r^2/2R^2} e^{i\mathbf{k}_0\cdot\mathbf{r}}. \quad (4)$$

The direction of \mathbf{k}_0 is arbitrary due to the spherical symmetry of the problem (see Fig. 1). R allows us to control the spatial extension of the state. The Fourier spectrum of this state is

$$c_{\mathbf{k}_0}^R(\mathbf{k}) = (2\sqrt{\pi}R)^{3/2} e^{-(\mathbf{k}-\mathbf{k}_0)^2 R^2/2}. \quad (5)$$

This corresponds to a harmonic oscillator wave packet whose center has been shifted to \mathbf{k}_0 allowing us to retrieve the correct plane wave limit for $R \rightarrow \infty$. Alternatively, the wave function above can be obtained by solving the Schrödinger equation for a standard harmonic oscillator

$$V(\mathbf{r}) = \frac{\hbar^2}{2mR^2} \left[\left(\frac{r}{R} \right)^2 - 3 - 2i\mathbf{k}_0\cdot\mathbf{r} \right], \quad (6)$$

with the addition of complex part in the potential to guarantee the correct plane wave limit.

As mentioned, in the case of total delocalization ($R \rightarrow \infty$) the Fourier spectrum in Eq. (5) reduces to a delta function, and the state becomes a plane wave with momentum \mathbf{k}_0 , and the probability for free electrons is retrieved from Eq. (2) [8]:

$$P_{R \rightarrow \infty}^{3D}(E_0) = \frac{1}{2\pi^2 \hbar k_0} \int_{p_F}^{k_0} dp p \int_{q^-}^{q^+} dq q \frac{4\pi e^2}{q^2} \times \text{Im}\{-\varepsilon^{-1}(q, \omega)\}. \quad (7)$$

p_F is the Fermi momentum and $q^\pm = k_0 \pm p$ are, respectively, the maximum and minimum momentum transfers allowed in the deexcitation process and $\hbar\omega$ is the energy transfer as defined above.

In the other limiting case ($R \rightarrow 0$) all the plane wave components of the state will have the same weight, which corresponds to a delta-like function in real space describing a state with zero extension. In this limit, the probability is:

$$P_{R \rightarrow 0}^{3D}(E_0) = \frac{4\sqrt{\pi}R^3}{\pi^3 \hbar} \int_{p_F}^{k_0} dp p^2 \int_0^\infty dq q^2 \frac{4\pi e^2}{q^2} \times \text{Im}\{-\varepsilon^{-1}(q, \omega)\}. \quad (8)$$

Observe that this probability will go to zero when decreasing the radius ($P_{R \rightarrow 0}^{3D} \propto |c_{\mathbf{k}_0, R \rightarrow 0}^{3D}|^2 \propto R^3$) independently of the initial energy of the state. Notice that, in contrast with the case of the deexcitation of a free electron (plane wave), there is no restriction on the transferred momentum. This is because in the Fourier representation of a state being completely localized, all momentum values are represented and momentum conservation is automatically fulfilled.

Finally, the probability for arbitrary R is given by

$$P_R^{3D}(E_0) = \frac{\sqrt{\pi}R}{2\pi^4 \hbar} \int_{p > p_F}^{p < k_0} d\mathbf{p} \int_0^\infty dq q \frac{e^{-R^2(|\mathbf{p} - \mathbf{k}_0| + q^2)}}{|\mathbf{p} - \mathbf{k}_0|} \times \sinh(2R^2|\mathbf{p} - \mathbf{k}_0|q) \frac{4\pi e^2}{q^2} \text{Im}\{-\varepsilon^{-1}(q, \omega)\}. \quad (9)$$

These integrals can be carried out numerically once the dielectric response function of the metal is specified, as we will do below.

3. 2D and 1D localized states

Using appropriate wave functions, it is possible, following exactly the same procedure as shown above, to calculate the deexcitation probability of partially localized states. These are states that are localized in one or two directions being free-electron-like states (plane waves) in the other directions. Although the absence of symmetry makes the calculation harder, these states are more similar to the electronic states existing at surfaces, interfaces or in quantum well structures.

In order to construct a state which is localized in two directions, for instance x and y , but free to travel along the z axis, that is, localized inside an infinite cylinder of radius $\sim R$ and length $L \rightarrow \infty$ (Fig. 1), we can use a wave function given by

$$\psi_{\mathbf{k}_0}^R(\mathbf{r}) = \frac{1}{\sqrt{\pi}R} e^{-x^2/2R^2} \frac{1}{\sqrt{L}} e^{i\mathbf{k}_0 \cdot \mathbf{r}}, \quad (10)$$

where $\mathbf{r} = (\mathbf{X}, z)$ and $\mathbf{k}_0 = (\mathbf{K}_0, k_{0z})$. In momentum representation

$$c_{\mathbf{k}_0}^R(\mathbf{k}) = \sqrt{L} \delta_{k_z, k_{0z}} 2\sqrt{\pi}R e^{-(\mathbf{K} - \mathbf{K}_0)^2 R^2/2}. \quad (11)$$

In the case of large radius R , this state tends to a plane wave and Eq. (7) is re-obtained for the probability. Further, in the complete localization limit, the probability will go to zero as $P_{R \rightarrow 0}^{2D} \propto R^2$. The probability for arbitrary R is given by

$$P_R^{2D}(K_0, k_{0z}) = \frac{4R^2}{(2\pi)^3 \hbar} \int_{p > p_F}^{p < k_0} d\mathbf{p} \int dQ Q I_0(2R^2|\mathbf{P} - \mathbf{K}_0|Q) \times e^{-R^2(|\mathbf{P} - \mathbf{K}_0| + Q^2)} \frac{4\pi e^2}{q^2} \text{Im}\{-\varepsilon^{-1}(q, \omega)\}, \quad (12)$$

where $\mathbf{p} = (\mathbf{P}, p_z)$, and $\mathbf{q} = (\mathbf{Q}, k_{0z} - p_z)$ is the transferred momentum. $\hbar\omega$ is again the energy transfer as defined above. I_0 is a zero order Bessel function of imaginary argument. Notice that, due to the limited symmetry, the probability depends not only on the energy E_0 (on the modulus of the momentum \mathbf{k}_0), but also on the direction of the momentum of the state.

In the case that the localization takes place in only one direction, chosen as z without any loss of generality, remaining two free directions where the state will be described by plane waves, the state could be viewed as confined in an infinite slab of thickness $\sim R$ (Fig. 1). The ground state corresponding to this potential will be

$$\psi_{\mathbf{k}_0}^R(\mathbf{r}) = (\sqrt{\pi}R)^{-1/2} e^{-z^2/2R^2} \frac{1}{L} e^{i\mathbf{k}_0 \cdot \mathbf{r}}. \quad (13)$$

Again $\mathbf{r} = (\mathbf{X}, z)$. Equivalently, in Fourier space

$$c_{\mathbf{k}_0}^R(\mathbf{k}) = L \delta_{\mathbf{K}, \mathbf{K}_0} c_{k_{0z}}^R(k_z) = L \delta_{\mathbf{K}, \mathbf{K}_0} (2\sqrt{\pi}R)^{1/2} e^{-(k_z - k_{0z})^2 R^2/2}. \quad (14)$$

The plane wave limit is again re-obtained for a large localization radius, while for a small radius the probability will go to zero linearly as, $P_{R \rightarrow 0}^{1D} \propto R$. For an arbitrary radius, the probability in the 1D case is

$$P_R^{1D}(K_0, k_{0z}) = \frac{2}{(2\pi)^4 \hbar} \int_{p > p_F}^{p < k_0} d\mathbf{p} \int_{-\infty}^\infty dq_z |c_{k_{0z}}^R(p_z + q_z)|^2 \times \frac{4\pi e^2}{q^2} \text{Im}\{-\varepsilon^{-1}(q, \omega)\}. \quad (15)$$

$\mathbf{p} = (\mathbf{P}, p_z)$, $\mathbf{q} = (\mathbf{K}_0 - \mathbf{P}, q_z)$ is the transferred momentum, and $\hbar\omega$ is the energy transfer as before. Again the probability

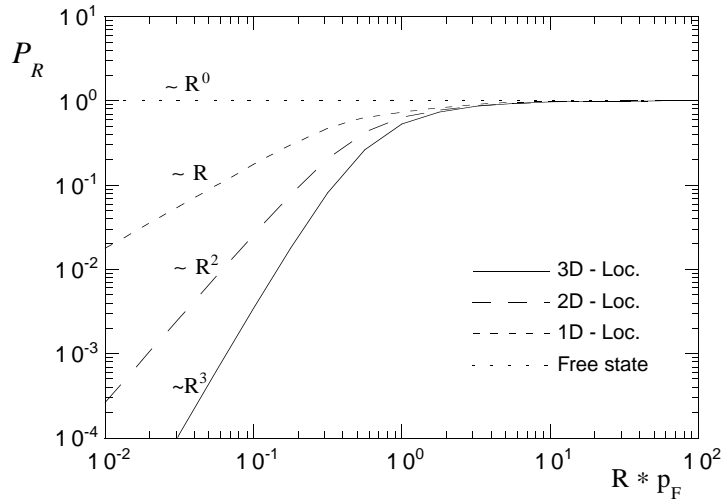


Fig. 2. Dependence of deexcitation probability with localization radius for states localized in one, two and three directions. p_F is the Fermi momentum. The energy of the states is 1 eV above the Fermi energy. The Lindhard's response function has been used with $r_s = 2.67$ corresponding to copper. Results are normalized to the probability obtained for a free electron of the same energy ($P_{\text{free}}(1 \text{ eV}) = 3.86 \times 10^{-2} \text{ fs}^{-1}$).

will depend on the particular orientation of the momentum \mathbf{k}_0 and not only on its modulus.

Eq. (15) also provides a simple expression to study the decay of surface or image states to free-electron-like bulk states and its dependence with the details of the wave function describing the initial state. Although in Eq. (15) the screening does not correspond to a surface configuration it can provide a rough estimation of the localization effects. Moreover, it has been shown that the main contribution is precisely this bulk contribution [23,24].

4. Numerical results and discussion

Using the Lindhard response function [25] to describe the metal response, probabilities have been calculated in the three cases of localization described above. The energies of all the excited states are chosen to be 1 eV above the Fermi energy since these are the typical energies studied in TR-2PPE experiments. The results of these calculations are shown in Fig. 2. In the case of 1D and 2D localized states, as mentioned above, the probability depends on the particular choice of the direction of the momentum but this dependence has been found to be very small and it can be assumed that $P_R^{\text{1D,2D}}(K_0, k_{0z}) \approx P_R^{\text{1D,2D}}(E_0)$, as in the case for $P_R^{\text{3D}}(E_0)$. There are two clearly distinguishable limits in the three curves as described by the typical length scale $1/p_F$ of the screening electron gas. Firstly, for extended states ($R \gg 1/p_F$) the results converge to the free electron value calculated by Quinn [8] independent of the degree of localization. Secondly, for highly localized states ($R \ll 1/p_F$) the

probability decreases with the degree of localization

$$P_R^{\text{nD}} \propto R^n, \quad (16)$$

i.e. the logarithm of P is directly proportional to the dimensionality. This decay of the probability is related to the Fourier components necessary to describe the localized state. As we increase localization, Fourier components of larger momentum are involved in the description of the state. The Fourier components of momenta much larger than the typical momentum of the electron gas, this being the Fermi momentum p_F , cannot overlap with the electron states in the solid and thus are unable to decay creating an excitation in the solid. In the limit of total localization ($R \rightarrow 0$) an infinite range of Fourier components is necessary to describe the state and, as a consequence, it will have virtually zero probability to decay due to the small overlap of these large Fourier components with the solid's states. In this sense, the localized state becomes invisible to the electron gas.

Regarding the energy dependence of the probability, the $(E - E_F)^2$ dependence predicted by the Fermi Liquid theory for energies close to the Fermi energy ($E \rightarrow E_F$) is found to be valid for any radius of the state. In fact, this is a general result as a consequence of the reduction of the available phase space for the deexcitation when the energy of the state gets closer to the Fermi energy, independent of the particular wave function being used. Once the energy of the state moves away from the Fermi energy, corrections to the $(E - E_F)^2$ scaling are expected. Quinn showed that for plane wave states and low energies $P_{R \rightarrow \infty}(E_0) \propto k_0^{-1} \cdot (E_0 - E_F)^2$, a result which we reproduce in the $R \rightarrow \infty$ limit. However, we found that in the high localization limit,

deviations from the simple quadratic behavior, are much smaller than in the case of plane waves. This can be understood if we look at the origin of the momentum dependence in the free electron result. This dependence arises from the restriction imposed by the momentum conservation on the phase space which reduces its size. However, when the state gets localized, more momentum components are included in the description of the state, and the restrictions in the phase space due to momentum conservation are weakened. In the limit of complete localization, all momentum values are present with equal weight and momentum conservation is no longer a problem.

5. Summary

The effect of the localization on the deexcitation probability of excited electronic states has been studied using a dielectric approach and a model wave function that can interpolate between a plane wave and a completely localized state. Results show that localization decreases the probability of the deexcitation process due to the incapability of the electron gas to interact with the high momentum components implied in the description of the localized states in one, two and three dimensions. The rate with which the probability goes to zero depends directly on the number of localized directions of the state. The energy dependence of the probability is only slightly affected by the localization of the state.

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