Time-dependent screening of a positive charge distribution in metals: Excitons on an ultra-short time scale

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Abstract

Experiments determining the lifetime of excited electrons in crystalline copper reveal states which cannot be interpreted as Bloch states [S. Ogawa et al., Phys. Rev. B 55, 10869 (1997)]. In this article we propose a model which explains these states as transient excitonic states in metals. The physical background of transient excitons is the finite time a system needs to react to an external perturbation, in other words, the time which is needed to build up a polarization cloud. This process can be probed with modern ultra-short laser pulses. We calculate the time-dependent density-response function within the jellium model and for real Cu. From this knowledge it is possible within linear response theory to calculate the time needed to screen a positive charge distribution and – on top of this – to determine excitonic binding energies. Our results lead to the interpretation of the experimentally detected states as transient excitonic states.

78.47.+p, 72.15.Lh, 71.10.-w, 71.20.Gj
I. INTRODUCTION

Measurements of the lifetime of excited electrons in Cu\(^{1}\) using time-resolved two-photon photoemission (TR-2PPE) spectroscopy\(^{2}\) in connection with very short laser pulses reveal a couple of amazing results. Most stunning is the fact that the data show lifetimes of states along the (100) and (111) direction (\(\Gamma - X\) and \(\Gamma - L\), respectively) with energies between 1 and 4 eV above the Fermi energy \(E_F\). As can be seen from the band structure shown in Fig. 1, Cu has no Bloch states at these energies in these two directions. But also the data for the lifetime of electrons in the remaining direction (110) – the \(\Gamma - K\) direction – are puzzling. \textit{Ab initio} calculations of the lifetime of hot electrons along the (110) direction using the \textit{GW} approximation\(^{3,4}\) reveal a good agreement with the experimental data for electron energies between 2 and 3 eV. For energies lower than 2 eV the results of the \textit{GW} calculation deviate markedly from the experimental data. This is particularly remarkable because typically many-body calculations within the \textit{GW} approximation agree very well with experimental data. This holds for both, the real part of the resulting quasiparticle energies\(^{6,7}\) as well as its imaginary part\(^{4,5,8,9}\) respectively. The imaginary part of the quasiparticle energy of a band state is inverse proportional to the lifetime of this state\(^{10}\). Therefore the discrepancy of the theoretical and experimental results must be due to physics which is not covered by the \textit{GW} approximation. The last point about the experimental data we would like to mention is the fact that the lifetimes in the three directions are very similar\(^{1}\) although the band structure gives no hint for this experimental finding.

The discussion in the preceding paragraph shows that TR-2PPE experiments detect states which are obviously no band states (which are single-particle states). Consequently there has been some speculation in the literature about the origin of these states, most of which violate well established fundamental physical laws. The only explanation which is consistent in this respect and does involve only single-particle states is that electrons which originally had a momentum in the, e.g., (110) direction are scattered from a (110) low-energy electron diffraction (LEED) state into a, say, (100) LEED state. This would explain why
experiments measure the lifetime in this direction. However, the cross section for this process should be small. Moreover, this mechanism would not explain the difference between the results of calculated lifetimes within the GW approximation and the experimental ones. In order to escape these difficulties Cao et al. speculated that “the strongly localized 3d holes generated by photoexcitation of 3d electrons can trap excited electrons through attractive Coulomb interaction”. We picked up this suggestion and outlined the physical mechanism of excitons in metals on a very short time scale, so-called transient excitons. In this article we present a model of how to actually calculate these states.

Now it is common wisdom that excitons exist in semiconductors and rare gases but not in metals. However, in these cases one is thinking of stationary conditions under which the valence electrons of the system have enough time to build up a polarization cloud. For large times the initial Coulomb interaction between the hole and the electron transforms into a Thomas-Fermi-like potential in metals and a Coulomb potential which is screened by the macroscopic dielectric constant in semiconductors. But this polarization needs a final time to be built up and it is during this time that transient excitons can exist. Consequently transient excitons cannot be detected with traditional photoabsorption spectroscopy. It needs modern TR-2PPE spectroscopy combined with the ultra-short laser pulses which are available nowadays.

The article is organized as follows. In Sec. II we present a model that allows us to calculate – and therefore proof the existence of – transient excitonic states. In the two following sections we apply this model to the jellium model and to real copper. We finish with some estimates about the lifetime of electrons in transient excitonic states.

**II. A MODEL FOR TRANSIENT EXCITONS IN METALS**

In this section we present a model for the calculation of transient excitonic states. A complete treatment of the subject implies the solution of the Bethe-Salpeter equation (BSE) using the time-dependent particle-hole potential $v_{eh}(t)$ as interaction. However, it is not our
objective to perform an *ab initio* calculation in order to calculate the excitonic energies to high accuracy. The intent of this article is to show that transient excitonic states in metals do exist. For this, a simple but nevertheless realistic model is very useful.

Starting point of our discussion is the potential due to a localized hole in a 3d band. We obtain it from the density of a 3d-band electron as

$$n^h(r) = \begin{cases} \alpha |\varphi_{3d}(r)|^2 & r \in MT \\ 0 & \text{else} \end{cases}, \quad (1)$$

where the Bloch function $\varphi_{3d}(r)$ is the solution of the Kohn-Sham (KS) equations

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + v_{\text{eff}}(r) \right] \varphi_{q,j}(r) = \epsilon_{q,j} \varphi_{q,j}(r). \quad (2)$$

$q$ and $j$ denote a wave vector in the Brillouin zone (BZ) and a band index, respectively. $v_{\text{eff}}(r)$ is the mean-field potential in which the KS electrons move. Its exchange-correlation potential is treated within the local density approximation (LDA). The wave functions $\varphi_{q,j}(r)$ are expanded with respect to plane waves and the interaction between the ionic cores and the valence electrons is described by an *ab initio* norm-conserving pseudopotential. $\alpha$ has to be chosen in such a way that

$$1 = \int_{MT} d^3r n^h(r). \quad (3)$$

In Cu we use for the radius of the sphere MT a value of 2.3 Bohr. The 3d-hole density $n^h(r)$ is expanded with respect to spherical harmonics and using Poisson’s equation the potential corresponding to $n^h(r)$ is obtained as

$$v^h(r) = \sum_{l,m} \frac{4\pi e}{2l+1} \int_0^{\infty} dr' r'^2 \frac{r'}{r_{\text{\textgreater}}} n_{l,m}^h(r') Y_{l,m}(\hat{r}). \quad (4)$$

$n_{l,m}^h(r)$ are the $(l, m)$ components of $n^h(r)$. $r_<$ and $r_>$ denote the smaller and larger length of $r$ and $r'$, respectively. $\hat{r}$ represents the angular part of $r$. Figure shows the first non-zero components of $v^h(r)$. The by far dominating component is the spherical symmetric part. In the following we approximate $v^h(r)$ by its spherical part and treat this as an external potential switched on at $t = 0$. 

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perturbing the system.

The response of the system to the perturbation $v_{\text{ext}}(r, t)$ is calculated within linear response theory (LRT). In LRT the induced density due to the perturbing potential is given by

$$n_{\text{ind}}(r, t) = \int d^3r' \int_{-\infty}^{\infty} dt' \chi(r, r'; t - t') v_{\text{ext}}(r', t') ,$$

(6)

where $\chi(r, r'; t - t')$ is the (retarded) density-response function. Since we are dealing with a system with translation symmetry it is useful to transform Eq. (6) to Fourier space,

$$n_{\text{ind}}(q + G, \omega) = \sum_{G'} \chi_{G, G'}(q, \omega) v_{\text{ext}}(q + G', \omega) .$$

(7)

$\chi_{G, G'}(q, \omega)$ is obtained from the polarizability \[ P_{G, G'}(q, \omega) = \frac{2}{V} \sum_{k}^{\text{BZ}} \sum_{j, j'} \frac{f_{k, j} - f_{k + q, j'}}{\hbar \omega + \epsilon_{k, j} - \epsilon_{k + q, j'} + i \eta} \]

\[ \langle k, j | e^{-i(q + G)\hat{x}} | k + q, j' > < k + q, j' | e^{i(q + G')\hat{x}} | k, j > \]

by solving the matrix equation \[ \chi_{G, G'}(q, \omega) = P_{G, G'}(q, \omega) \]

\[ + \sum_{G_1, G_2} P_{G_1, G_2}(q, \omega) \left[ \delta_{G_1, G_2} v_{G_1}(q) + f^{xc}(G_1 - G_2) \right] \chi_{G_2, G'}(q, \omega) \]

(9)

for each wave vector $q$ and frequency $\omega$, respectively. In Eq. (8) the $f_{k, j}$ denote the occupation numbers, $\epsilon_{k, j}$ the eigenvalues, and $\langle r | k, j >= \varphi_{k, j}(r)$ the wave functions as obtained from solving the KS equations (2). $V$ is the normalization volume. The sums run over all wave vectors $k$ in the BZ and the band indices $j$ and $j'$, respectively. In Eq. (8) $v_G(q)$ is the Coulomb potential, $v_G(q) = 4\pi e^2/|q + G|^2$, and $f^{xc}(G)$ represents a vertex correction connected to the local-field factor $G$ by $f^{xc}(G) = -v_G(q) G_G(q)$. Within the LDA $f^{xc}(G)$ depends only on the reciprocal lattice vector and not on the wave vector. Setting $f^{xc}(G) = 0$ results in the random phase approximation (RPA) for $\chi$. The time-dependent local density
approximation (TDLDA) is given by $f^{xc}(G) = \int d^3r \ e^{-iGr} dv_{xc}(r)/dn(r)$, where $v_{xc}(r)$ is the exchange-correlation potential used in the KS equations (2).

Having calculated the induced density $n_{ind}(q+G, \omega)$, the induced potential $v_{ind}(q+G, \omega)$ is obtained via Poisson’s equation. Adding the external potential $v_{ext}(q+G, \omega)$ and using the Kramers-Kronig relation a Fourier transform with respect to frequency yields the following expression for the total potential,

$$v_{tot}(q+G, t) = \sum_{G'} \bar{v}_{ext}(q+G') \times$$

$$\left\{ \delta_{G,G'} + \frac{4\pi e^2}{|q+G|^2} \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \frac{1}{\omega} \text{Im} \chi_{G,G'}(q, \omega) \left( 1 - e^{-i\omega t} \right) \right\} \Theta(t), \quad (10)$$

where $\bar{v}_{ext}(q+G)$ is the frequency-independent part of $v_{ext}(q+G, \omega)$. A final Fourier transform leads to the total potential as a function of $r$ and $t$,

$$v_{tot}(r, t) = \frac{1}{V} \sum_{q} \sum_{G} e^{i(q+G)r} v_{tot}(q+G, t). \quad (11)$$

III. THE JELLIUM MODEL

Before we treat real Cu with our model, let us first apply it to the jellium model. Even here it leads to a couple of interesting results. In the jellium model, where there are no $d$ bands, we use for the external potential a bare Coulomb potential

$$v_{ext}(r, t) = -\frac{e^2}{r} \Theta(t), \quad (12)$$

i.e., we calculate the time-dependent screening of a suddenly created point charge in an electron gas. Because of the isotropy assumed in the jellium model the potential, polarizability, and density-response function are simple scalar quantities. Equation (8) reduces to the Lindhard function and Eq. (9) becomes a scalar equation. So Eq. (10) simplifies to

$$v_{tot}(q, t) = \frac{4\pi e^2}{q^2} \left\{ 1 + \frac{4\pi e^2}{q^2} \frac{2}{\pi} \int_{0}^{\infty} d\omega \frac{1}{\omega} \text{Im} \chi(q, \omega) \left( 1 - \cos(\omega t) \right) \right\} \Theta(t), \quad (13)$$

where we used the fact that $\text{Im} \chi(q, \omega)$ is an odd function with respect to $\omega$. Consequently Eq. (11) becomes
\[ v_{\text{tot}}(r,t) = \frac{1}{(2\pi)^3} \int d^3q e^{iqr} v_{\text{tot}}(q,t). \] (14)

In the jellium model \(\text{Im} \chi(q, \omega)\) has a delta-function-like shape for small wave vectors \(q\), representing the plasmon excitation. It is centered at the plasmon frequency \(\omega_p\) with \(\omega_p^2 = 4\pi ne^2/m\), where \(n\) is the electronic density. In order to handle this structure a numerical broadening \(\eta\) has to be introduced. If not said otherwise, we use a broadening of \(\eta = 0.01\) eV, a value corresponding to the real width of the plasmon excitation in alkalines. In order to be sure to sample the plasmon peak properly we used a frequency mesh with a spacing of 0.5 meV (and less) for wave vectors up to 1.5 \(k_F\).

The upper panel of Fig. 3 shows a plot of \(v_{\text{tot}}(q,t)\) as a function of \(t\) for a Wigner-Seitz radius of \(r_s = 2.07\) and a wave vector of \(q = 0.1 k_F\), \(k_F\) being the Fermi wave vector. \(\chi\) was calculated within the RPA. The figure displays \(v_{\text{tot}}(q,t)\) for three different values of \(\eta\) in a time window of just one femtosecond. The solid, dotted, and dashed curve correspond to values of \(\eta\) of 0.01 eV, 0.1 eV, and 0.5 eV, respectively. Even on this short time scale the influence of \(\eta\) can be noticed; \(v_{\text{tot}}(q,t)\) decays at different rates. The frequency of \(v_{\text{tot}}(q,t)\) for the three values is nevertheless the same. It is the plasmon frequency \(\omega_p\). For \(r_s = 2.07\) it is \(\omega_p = 15.83\) eV which corresponds to a period of 0.26 fs. That the potential for small wave vectors oscillates with the plasmon frequency can also be seen if \(\text{Im} \chi(q, \omega)\) is approximated by the plasmon-pole approximation (PPA)

\[ \lim_{q \to 0} \text{Im} \chi(q, \omega) = -\frac{\pi}{2v_q} \omega_p \left\{ \delta(\omega - \omega_p) - \delta(\omega + \omega_p) \right\}, \] (15)

where \(v_q = 4\pi e^2/q^2\). In this case the frequency integral in Eq. (13) can be done analytically leading to

\[ v_{\text{tot}}^{\text{PPA}}(q,t) = \frac{4\pi e^2}{q^2} \Theta(t) \cos(\omega_p t). \] (16)

In the case of small wave vectors the total potential should approach the Thomas-Fermi potential

\[ v^{\text{TF}}(q) = \frac{4\pi e^2}{q^2 + q_{\text{TF}}^2}, \] (17)
for large times. $q_{\text{TF}}$ is the Thomas-Fermi wave vector, $q_{\text{TF}}^2 = 6\pi ne^2/E_F$. Note that Eq. (17) is derived for the limiting case of $q \to 0$ and $\omega \to 0$. Therefore it cannot be expected that $\lim_{t \to \infty} v_{\text{tot}}(q, t) = v_{\text{TF}}(q)$ holds for large wave vectors. For small wave vectors it is fulfilled to a high degree. As an example consider $v_{\text{tot}}(q, t)$ for $q = 0.1 \, k_F$ and $t \to \infty$. For $\eta = 0.01 \, \text{eV}$ the difference to the Thomas-Fermi value of 10.57 a.u. is just 0.8%. The deviation increases for larger broadenings.

Having discussed the total potential as a function of wave vector we now turn to $v_{\text{tot}}(r, t)$. In order to perform a good quadrature of the integral in Eq. (14) we calculated $v_{\text{tot}}(q, t)$ on a wave vector mesh which is dense enough to sample the oscillations of $v_{\text{tot}}(q, t)$ with respect to $q$. They are shown in the lower panel of Fig. 3 where we plot $v_{\text{tot}}(q, t)$ as a function of wave vector at an intermediate time. In general the frequency of the oscillations increases with increasing $t$ and with increasing $q$. At the same time the amplitude of the oscillations die out quicker so that at large times the asymptotic potential is approached. The plot shows another feature which holds for all times; the oscillations stop between 0.7 and 0.8 $k_F$, i.e., they stop in the wave vector range where the plasmon excitation is destroyed by particle-hole transitions (Landau damping) and the density-response function becomes dominated by single-particle transitions.

Figure 4 shows snapshots of $v_{\text{tot}}(r, t)$ as a function of $r$ for fixed times calculated for $r_s = 5$ (upper row) and $r_s = 2.07$ (lower row). At $t = 0$, $v_{\text{tot}}(r, t)$ is just the Coulomb potential (upper left plot). The horizontal lines are the first four eigenvalues for this potential calculated using a reduced mass of $\mu = 0.5$ due to the equal masses of the hole and the electron, respectively. The next plot shows $v_{\text{tot}}(r, t)$ at a larger time. The potential is already narrower and consequently the eigenvalues are shifted upwards. This trend continues and at $t = 0.25$ fs $v_{\text{tot}}(r, t)$ crosses the Thomas-Fermi potential [Fourier transform of Eq. (17)]

$$v_{\text{TF}}(r) = -\frac{e^2}{r} e^{-q_{\text{TF}} r}, \quad \text{(18)}$$

(dashed line) for the first time. At this time the potential has no bound states any more. The system is now overscreening the perturbation which leads to a decaying oscillation of
\( v_{\text{tot}}(r, t) \) around its asymptotic form which lasts for 10 to 20 fs, the exact value depending on \( r_s \). This is shown for \( r_s = 2.07 \) in the lower panel of Fig. 4. At \( t = 20 \) fs the potential has reached its asymptotic value. As can be seen from the last plot, the difference between this potential and the Thomas-Fermi potential is rather small.

Before we close the discussion about the jellium model we want to discuss the influence of the vertex correction \( f^{xc} \). We discuss this for \( r_s = 5 \) since \( f^{xc} \) for this Wigner-Seitz radius is more than eight times larger than the \( f^{xc} \) for \( r_s = 2.07 \) (-24.443 a.u. and -3.917 a.u., respectively). We use the parametrization of the exchange-correlation potential due to Perdew and Zunger.\(^{26}\) The upper panel of Fig. 5 shows a comparison of \( v_{\text{tot}}(q, t) \) calculated with (dot-dashed line) and without (solid line) the use of vertex corrections, respectively. The figure shows that for wave vectors smaller than \( 2.2 \) \( k_F \) the two curves start to differ. For small wave vectors the difference is quite remarkable. After the Fourier transform the difference in the resulting \( v_{\text{tot}}(r, t) \) is much smaller. This is because the difference for small \( q \) in \( v_{\text{tot}}(q, t) \) is reflected in a difference for large \( r \) in \( v_{\text{tot}}(r, t) \). For our considerations this range is not of importance.

**IV. TRANSIENT EXCITONS IN COPPER**

The heart of the calculation of the total potential Eq. (10) is the calculation of the polarizability given by Eq. (8) for all wave vectors in the BZ and a sufficient number of \( G \) vectors needed to obtain a reliable density-response function Eq. (9). In Fig. 6 we show the imaginary part of \( \chi_{G,G'}(q, \omega) \) for \( G = G' \) and three wave vectors \( q + G \). The upper panel of Fig. 6 shows the imaginary part of the density-response function for a small wave vector. It displays clearly the characteristic double peak structure\(^{27}\) around 20 and 29 eV sitting on top of a broad structureless hump which decays only very slowly. The calculations of the polarizability were done using 200 bands, i.e., considering transitions up to 355 – 390 eV above the Fermi energy (the exact number depends on the wave vector). This energy cutoff is the reason for the sudden decline of \( \text{Im} \chi_{G,G'}(q, \omega) \) between 360 and 380 eV which can be
observed in all of the three plots. The middle panel shows \( \text{Im} \chi_{G, G'}(q, \omega) \) for a wave vector on the edge of the BZ and the lower panel the imaginary part of the density-response function for a wave vector \( q + G \) in the third zone. In all cases \( \chi_{G, G'}(q, \omega) \) was calculated within the RPA using a numerical broadening of \( \eta = 0.4 \) eV in the calculation of the polarizability. It is obvious from the plots that this value is small compared to the broad structures of the density-response functions of Cu.

In the jellium model the screening process was completely determined by the plasmon excitation. The plots in Fig. 6 make clear that this is not the case for Cu. The density-response function of Cu is dominated by single-particle transitions and the already mentioned dispersionless double-peak structure caused by collective excitations of the \( d \) electrons.

As was already mentioned, the external potential Eq. (5) is spherical symmetric. Although the full matrix of \( \chi_{G, G'}(q, \omega) \) was used in the calculation of the total potential \( v_{\text{tot}}(q + G, t) \) (we used the first two shells of reciprocal lattice vectors, i.e., 15 \( G \) vectors) this leads to a nearly spherical symmetric total potential. Therefore the Fourier transform to real space could be done replacing the sum in Eq. (11) by an integral and performing the angular part of the integration analytically. Figure 7 shows the total potential in Cu as a function of \( r \) for four different times. The plot in the upper left corner shows the potential at \( t = 0 \) fs, i.e., the external potential. For finite times the potentials quickly becomes shallower. This behavior is the pendant to the time dependence within the jellium model where the potential became narrower. As in jellium model the total potential is overscreening (see lower left panel in Fig. 7) and oscillating around the equilibrium potential. However, compared to the jellium model this process is faster in Cu. The oscillations are completely died out at 2 fs. At this time \( v_{\text{tot}}(r, t) \) has reached its asymptotic value.

We are now in the position to apply the textbook approach for the estimate of excitonic binding energies in semiconductors to copper. We chose a high lying \( d \) band and (typically) the lowest unoccupied band for a given direction in the BZ and calculated the effective masses for each of the bands (\( m_h^* \) and \( m_e^* \) for the effective mass of the hole in the \( d \) band and the effective mass of the electron in the conduction band, respectively). A typical case is
given by the two bands drawn as thick lines in the $L - \Gamma$ panel of Fig. 8. From the knowledge of $m_h^*$ and $m_e^*$ the reduced mass $\mu$ for each wave vector is determined. Then the Schrödinger equation for $v_{\text{tot}}(r, t)$ at a given time $t$ is solved for each $\mu$. $t$ has to be chosen in such a way that $v_{\text{tot}}(r, t)$ still possesses bound states. The resulting lowest eigenvalue is plotted with respect to the eigenvalue of the unoccupied band. This is the excitonic binding energy.

In Fig. 8 the excitonic binding energies in the three main crystallographic directions are drawn as horizontal bars. The bands which were used in the calculation are indicated by thick solid lines. Since in the $\Gamma - K$ direction there are two unoccupied bands close together, the calculation was done for both bands. Figure 8 shows that excitonic states in the $L - \Gamma$ direction exist in an energy range where there are no band states. The energetic positions of the excitonic states are in agreement with the experimental data (see Ref. 1). The excitonic energy levels were determined from the eigenvalues of a time-dependent potential at a fixed time. They therefore shift with time. However, in order to study the effects of this shifting in more detail one needs to solve the Bethe-Salpeter equation\textsuperscript{16}–\textsuperscript{18} which describes the dynamics of the correlated electron-hole pairs. This is beyond the scope of our model calculation which is intended to proof and explain the existence of transient excitonic states in Cu. In the $\Gamma - K$ direction exists a $sp$-like band which crosses the Fermi energy. In addition to these single-particle states there are also a wealth of excitonic states. Assuming that the lifetime of excitonic states is longer than the electronic lifetime of band states (see Sec. V) this explains the experimental finding that the lifetime of electrons in these two directions are very similar. It also explains why $GW$ calculations – which only address electron-electron scattering of excited band states with valence states – reveal shorter lifetimes as compared with experiment. For both directions the eigenvalues were calculated using the total potential $v_{\text{tot}}(r, t)$ at $t = 0.01$ fs. In the $\Gamma - X$ direction the excitonic energies are a little bit higher due to the high energies of the lowest unoccupied band (7.5 eV at the $X$ point). The excitonic energies in this direction were calculated at $t = 0.002$ fs. Due to the large slope of the lowest unoccupied bands the transient excitonic states which can be probed by experiment are all in the vicinity of the high symmetry points $X, L,$ and $K$. 

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V. LIFETIME OF ELECTRONS IN TRANSIENT EXCITONIC STATES

Having shown the possibility of transient excitons in metals we want to close with some comments about the lifetime of electrons in these states. The dominating process which determines the lifetime of excited electrons in band states is electron-electron scattering. Due to collisions with electrons of the valence band the excited electron is scattered out of its state, creating an electron-hole pair. This process – which diagram is shown in Fig. 9.a) – and exchange scattering are the two processes which are considered in GW calculations. However, only diagram 9.a) contributes to a final lifetime. Experience shows that the lifetime due to this process is proportional to the density of states of the final states. In metals this is therefore a rather efficient process. The bound states as described by transient excitons on the other hand can only decay via pair annihilation - pair creation, i.e., via an Auger process. The decay process is displayed in Fig. 9.b). As a consequence of the bound-state character of electrons trapped in a transient excitonic state we conclude that the lifetime of these states is longer than in band states. This reasoning would explain the disagreement between ab initio GW calculations for the lifetime of excited electrons along the Γ − K direction and the experimental data.

VI. CONCLUSIONS

In this article we presented a model which allowed us to calculate transient excitonic states in metals. The model was applied to jellium and to real Cu. The results obtained within the jellium model describe how a (nearly) free electron system screens a localized positive charge. An analysis of the time-dependent total potential shows that the complete screening of the external charge takes 10 to 20 fs. This is the time needed until the polarizability is fully built up and in equilibrium. At this time the potential is nearly identical to the Thomas-Fermi potential. This near identity is caused by the fact that the screening process is completely determined by the plasmon excitations of the system. The contribu-
tions from single-particle transitions – which are always present in the response function for finite wave vectors – are negligible. The potential possesses bound states for the first 0.2 fs.

The situation in Cu is different since the imaginary part of the density-response function (which is proportional to the loss function) has no distinct plasmon peak. Instead the density-response function of Cu shows plasmon-like excitations originating from the $d$ electrons. This double peak sits on top of a broad structure caused by single-particle transitions. The screening of a localized charge distribution is therefore faster. Nevertheless, the total potential possesses bound states for small times. In our model calculation for the determination of excitonic energies these eigenvalues are plotted with respect to the lowest unoccupied band. We find that the excitonic energies are in the energetic region of states detected in the measurements of the lifetime of hot electrons in crystalline Cu using TR-2PPE spectroscopy. It is important to stress that only experiments with very short laser pulses allow the detection of these states.

Our calculations explain thus the puzzling experimental fact of states which are no band states. We interpret them as transient excitons. With the coarse estimate of the lifetime of these states we are also able to explain the difference between the experimentally determined lifetime of hot electrons in the (110) direction with respect to the results of GW calculations; we think that the states probed in this direction are not band states but excitonic states.

Our model does not yet include the possibility to determine the exact lifetime of electrons in transient excitonic states. The model is only applicable up to the moment at which the electron is trapped in a bound state and an exciton is formed. Work along this line, i.e., the evaluation of diagram b) in Fig. 9 is in progress.

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FIG. 1. The band structure of Cu calculated using a plane-wave code. For the energy range between 1 and 4 eV above $E_F$, Cu possesses no band states in the $\Gamma - L$ and the $\Gamma - X$ directions. There is a $sp$-like band in the $\Gamma - K$ direction.
FIG. 2. The first four non-zero components of the hole potential $v^h(r)$ calculated from the density distribution of a $d$ electron at the X point in Cu. The solid line is the spherical symmetric component ($l=0$, $m=0$). The dotted, dashed, and dot-dashed lines denote the components ($l=2$, $m=0$), ($l=2$, $m=1$), and ($l=4$, $m=4$), respectively. The long-dashed line shows the Coulomb potential multiplied by $\sqrt{4\pi}$. 
FIG. 3. The total potential $v_{\text{tot}}(q,t)$ for $r_s = 2.07$ in atomic units. The upper panel shows $v_{\text{tot}}(q,t)$ for $q = 0.1 \, k_F$ plotted as a function of time for different values of $\eta$ in a small time window. The broadenings used are 0.01 eV, 0.1 eV, and 0.5 eV (solid, dotted, and dashed line, respectively). The oscillations with the frequency $\omega_p$ can be clearly seen. In the lower panel $v_{\text{tot}}(q,t)$ is plotted as a function of $q$ in units of the Fermi wave vector for $t = 10$ fs.
FIG. 4. Snapshots of the total potential $v_{\text{tot}}(r,t)$ as a function of $r$ for different times. The upper row shows the potential for small times calculated using $r_s = 5$. The horizontal lines denote the eigenvalues of the potential calculated with a reduced mass of $\mu = 0.5$. In the lower row $v_{\text{tot}}(r,t)$ is shown for larger times and $r_s = 2.07$. It can be nicely seen how the system overscreens the perturbing potential which results in a decaying oscillation around the asymptotic form of the total potential. Note that the times shown cannot be used as a measure for the frequency of the oscillations which is much larger (see Fig. 3). The dashed lines denote the Thomas-Fermi potentials for the two Wigner-Seitz radii.
FIG. 5. Influence of the vertex correction $f_{xc}$ on the total potential. The upper panel shows $v_{tot}(q,t)$ calculated with and without the vertex correction (dot-dashed and solid line, respectively). In the lower panel $v_{tot}(r,t)$ is displayed. The solid line shows again the result of the calculation with $f_{xc} = 0$ and the dot-dashed line the result of a calculation with a vertex correction. In both plots the dashed line denotes the Thomas-Fermi potential. The calculations were done for $r_s = 5$ and $t = 1000$ fs.
FIG. 6. The imaginary part of the density-response function $\chi_{G,G'}(q, \omega)$ of Cu calculated for three wave vectors $q + G$. The underlying calculation of the polarizability was done including 200 bands.
FIG. 7. Four snapshots of the total potential in Cu. The total potential was calculated using a polarizability which includes 200 bands. Note the different scales in the upper and lower row.
FIG. 8.  Band structure of Cu in the three main crystallographic directions (solid lines). In addition to the single-particle states the transient excitonic states at $t = 0.01$ fs ($L - \Gamma$ and $\Gamma - K$ directions) and $t = 0.002$ fs ($\Gamma - X$ direction) are plotted as horizontal bars.
FIG. 9. Diagrams for the possible decay mechanism of electrons in a band state and a transient excitonic state. In a) the diagram for the decay of a band state is shown. This diagram determines the lifetime of excited electrons in $GW$ calculations. Diagram b) is the annihilation process involved in the decay of a transient excitonic state.