NONTHERMAL DISTRIBUTION OF HOT ELECTRONS IN METALS

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Abstract. In this paper we give the mathematical background of our kinetic model for the hot electrons nonequilibrium distribution function from our preceding paper [1]. The distribution depends only on energy and time and its deduction includes just the basic phenomena: excitation by light absorption between two levels considered as discrete and de-excitation by electron-electron collisions. We discuss also the limitations and implications of the approximations used in the deduction of the distribution function.

Key words: hot electron, kinetic model, resonant photon absorption, nonequilibrium distribution function.

1. INTRODUCTION

The purpose of this work is to give the mathematical background involved in the deduction of the hot electron nonequilibrium distribution function already published [1]. In our precedent paper we gave the general form of this nonthermal distribution and compared its prediction to the experimental data. Now we present its deduction and discuss the underlying approximations.

Let a laser pulse, of energy $h\nu$ less than the work function of the metal, be incident on a metal and determining a distribution of electrons with kinetic energies $E_F = E_{cin} = E_F + h\nu$. The primary excited electrons can collide with other electrons of the metal, with phonons, defects, impurities or grain boundaries, if the metal has a polycrystalline structure, or may be trapped by surface states. In this model we completely neglect interactions with surface states or defects, impurities and grain boundaries, considering the metal as a perfect single crystal.

In the usual structure of a noble metal, the conduction band is formed by the s and p valence levels of the constituent atoms that, in metal, result in a large *sp* band partially unfilled. The Fermi level (E_F) is situated in this *sp* band. The strong localized *d*-electrons occupy levels situated in a narrower *d* band lying far below the Fermi level and are not excited by the lasers of low energy (about 2 eV) used generally in experiments. The most important transitions are from levels below E_F

to levels above E_F, all these levels being in the *sp* band. So only the *sp* to *sp*, intraband transitions must be considered.

As we are interested mainly in the characterization of the nonthermal distribution of the hot electrons system in short lapse of time after a femtosecond pulse laser irradiation, in the subpicosecond scale, and the electron-phonon collisions have a characteristic time of approximately one picosecond, even if phonons are created by laser excitation, the probability of the electron-phonon interaction is much lower than of electron-electron interaction. So, in the model we completely disregarded the phonons. We also neglected the band dispersion as well as the ballistic transport that determines the spatial electron distribution.

The interaction with the electromagnetic radiation is treated as a resonant dipole transition between two levels E and $E + h\nu$, considered to be discrete. This approximation corresponds to light absorption in an atomic system. It is largely used in the theory of solids for description of the light-solid interaction [2]. Even if in solid crystals one meets continuous bands rather than discrete levels, it is appropriate for electrons in the *sp* band.

We start by deriving a very simple model for the electron distribution depending only on energy and time and including just the basic phenomena: excitation by light absorption between two discrete levels and deexcitation by electron-electron collisions. We will consider only the primary electrons neglecting the secondary ones that come from two sources: electrons excited from the Fermi sea after collision with already excited electrons and relaxation of excited holes, created during the primary excitation process, by means of Auger decay [3, 4].

2. KINETIC MODEL
FOR THE NONEQUILIBRIUM ELECTRON DISTRIBUTION

The kinetic equation that describes the evolution of the distribution function $f(E, t)$ in time contains an excitation and a de-excitation terms:

$$\frac{\mathrm{d}f}{\mathrm{d}t} = P_{ex} - P_{deex} \tag{1}$$

where P_{ex} is the probability of electron transition, in the time unit, from the energy $E_j = E - h\nu \ (\leq E_F)$ to $E \ (\geq E_F)$ and is deduced in the approximation of a dipole transition between two resonant discrete levels using the first order perturbation theory. P_{deex} is the deexcitation probability from level E to any other energy level.

2.1. THE EXCITATION PROBABILITY P_{ex}

We consider the metal and the associated electron sea in the framework of the Fermi liquid theory [5]. Many properties of this system can be described with the

Hartree-Fock approximation in which only the lowest order effects of particle interaction are taken into account. It allows the calculation of the ground state energy and the pair correlation function.

The Hartree-Fock equations for the motion of an electron in the metal are (see also [6]):

$$E_j \psi_j(\vec{r}) = \frac{-\hbar^2}{2m} \nabla^2 \psi_j(\vec{r}) + U^{ion}(\vec{r}) \psi_j(\vec{r}) + U^{el}(\vec{r}) \psi_j(\vec{r}) -$$
$$\sum_l \int d\vec{r} \frac{e^2}{|\vec{r} - \vec{r}'|} \psi_l^*(\vec{r}') \psi_j(\vec{r}') \psi_l(\vec{r}). \tag{2}$$

Here U^{ion} represents the attractive electrostatic potential of the bare ions and U^{el} represents the Coulomb interaction between electrons. The last term is the exchange between electrons. The above equation is time-independent and can be written in the following compact form:

$$H_0 \psi_i(\vec{r}) = E_i \psi_i(\vec{r}) \tag{3}$$

In the presence of the electromagnetic field, the time-dependent Schrödinger equation may be written as:

$$i\hbar \frac{\partial \Psi(\vec{r},t)}{\partial t} = \left[H_0 + H'(t) \right] \Psi(\vec{r},t) \tag{4}$$

where the time-dependent perturbation Hamiltonian is:

$$H'(\vec{r},t) = -e\vec{E}(t)\vec{r} = -eE_0 \cos(\omega t)\vec{r}. \tag{5}$$

This perturbation depends on time through the electric field vector, considered constant over the dimension of the studied system. The general solution of the time-dependent Schrödinger equation can be expanded as:

$$\Psi(r,t) = \sum_l c_l(t) \psi_l(\vec{r}) e^{-iE_l t / \hbar}, \tag{6}$$

assuming that the unperturbed wave functions $\{\psi_l\}$ form a complete set of orthonormalised solutions of eq. (3). In the first order of the perturbation theory the coefficients $c_l(t)$ satisfy the coupled equations:

$$\dot{c}_k(t) = (i\hbar)^{-1} \sum_l H'_{kl}(t) c_l(t) e^{i\omega_{kl}t}, \tag{7}$$

where $\omega_{kl} = (E_k - E_l)/\hbar$ and

$$H'_{kl}(t) = \left\langle \psi_k \left| H'(\vec{r},t) \right| \psi_l \right\rangle = -e\vec{E}(t) \left\langle \psi_k \left| \vec{r} \right| \psi_l \right\rangle = -e\vec{E}_0 \cos(\omega t) M_{hl}. \tag{8}$$

Here M_{kl} is the dipole transition moment between the levels k and l.

If we suppose that the system is initially in a well-defined stationary bound state of energy E_j described by the wave function ψ_j and that the pulse radiation is switched on at the time $t = 0$, then the initial conditions are given by $c_k(t \leq 0) = \delta_{kj}$ and, to the first order in the perturbation $H'(\vec{r},t)$, the solution is:

$$c_k(t) = (i\hbar)^{-1} \int_0^t H'_{hj}(t') e^{i\omega_{kj}t'} dt'. \tag{9}$$

Introducing in eq. (9) the expression of $H'_{kj}(t)$ from eq. (8) one obtains in the approximation that the laser frequency is fixed to ω:

$$c_k(t) = -e\vec{E}_0 (2i\hbar)^{-1} M_{kj} \left\{ \frac{e^{i(\omega_{kj}-\omega)t} - 1}{i(\omega_{kj} - \omega)} - \frac{e^{i(\omega_{kj}+\omega)t} - 1}{i(\omega_{kj} + \omega)} \right\}. \tag{10}$$

In the above equation the first term corresponds to light absorption and the second term to light emission. If $\omega_{kj} \cong \omega$, then the second term will be negligible and one can deal only with the absorption term. Thus, the probability for the system to be in the state k at time t is:

$$|c_k(t)|^2 = 2e^2 \vec{E}_0^2 (2\hbar)^{-2} M_{kj}^2 \frac{1 - \cos\{(\omega_{kj} - \omega)t\}}{(\omega_{kj} - \omega)^2}. \tag{11}$$

For large t values, the function $\varsigma(\omega_{kj} - \omega) = \dfrac{1 - \cos\{(\omega_{kj} - \omega)t\}}{(\omega_{kj} - \omega)^2}$ has a sharp maximum for $\omega_{kj} = \omega$, in other words, transitions that conserve energy are most likely. In the limit $\omega_{kj} \to \omega$

$$\lim_{\omega_{kj} \to \omega} \frac{1 - \cos\{(\omega_{kj} - \omega)t\}}{(\omega_{kj} - \omega)^2} = \lim_{\omega_{kj} \to \omega} \frac{2\sin^2\{(\omega_{kj} - \omega)t/2\}}{(\omega_{kj} - \omega)^2} = \frac{t^2}{2} \tag{12}$$

and consequently (see also [7–9]) the transition probability becomes

$$P_k(t) = |c_k(t)|^2 = e^2 E_0^2 (2\hbar)^{-2} M_{kj}^2 t^2. \tag{13}$$

This result is valid for not too long times in order to have $|c_k(t)|^2 \ll 1$ (otherwise the consideration of the electric field as a perturbation of first order is not valid [8]).

Two approximations were made when deducing the above result: first we considered that the initial and final states are discrete levels when actually they

belong to a continuum of levels and secondly we considered the laser pulse strictly monochromatic but the real pulse has an intrinsic width. In the following we will discuss the influence of these factors on the transition probability.

First, let us suppose that the distribution of one electron states in $\vec{k}$ space is practically a continuum, so that there is a large number of final states with approximately the same wavevector $\vec{k}$ and the same energy [9]. This means that we have to calculate the transition probability between the initial state and a group of very closely spaced final states. We define by $\rho_k(E)$ the density of the final state in energy, so that $\rho_k(E)dE$ is the number of final states having energies in the small interval dE about E_k. The probability that in time t an electron, initially in the level E_j, will make a transition to this group of final states is

$$P_k(t) = e^2 E_0^2 (\hbar)^{-2} \int \rho_k(E) M_{kj}^2 \frac{\sin^2\left\{(\omega_{kj} - \omega)t/2\right\}}{(\omega_{kj} - \omega)^2} dE. \qquad (14)$$

Since the most important contribution comes from a narrow interval about E_k, we may take M_{kj} and $\rho_k(E)$ outside the integral and write eq. (14) as

$$P_k(t) = e^2 E_0^2 (\hbar)^{-1} \rho_k(E) M_{kj}^2 \int_{-\infty}^{\infty} d\omega_{kj} \frac{\sin^2\left\{(\omega_{kj} - \omega)t/2\right\}}{(\omega_{kj} - \omega)^2}. \qquad (15)$$

The integral has the value $\pi t/2$ so that the transition probability becomes

$$P_k(t) = e^2 E_0^2 (\hbar)^{-1} \rho_k(E) M_{kj}^2 \pi t/2. \qquad (16)$$

One sees that taking into account the continuum of states centered on E_k leads to linear time dependence for the transition probability, whereas this dependence is quadratic for a discrete final level.

Now let us comment on the second approximation. Instead of a monochromatic light pulse we shall take into account the finite width of frequencies of the light pulse. A usual light radiation may be considered as a superposition of monochromatic waves of different frequencies with unrelated phases. In this case the total transition probability is the incoherent sum over all the individual transition probabilities associated with each monochromatic wave. In this case one replaces E_0 [8] by

$$\frac{c\varepsilon_0 E_0^2}{2} = \int I(\omega)d\omega, \qquad (17)$$

where c is the speed of light in vacuum and ε_0 is the dielectric permitivity and $I(\omega)$ is the intensity of light per unit of frequency. The transition probability becomes

$$P_k(t) = \frac{2e^2}{c\varepsilon_0(\hbar)^2} M_{kj}^2 \int\limits_{\omega_{kj}-\Delta\omega/2}^{\omega_{kj}+\Delta\omega/2} d\omega \frac{\sin^2\{(\omega_{kj}-\omega)t/2\}}{(\omega_{kj}-\omega)^2} I(\omega). \tag{18}$$

If $I(\omega)$ is taken to have a constant value $I(\omega_{kj})$ over the range $\Delta\omega$ then in eq. (18) $I(\omega_{kj})$ can be taken out of the integral and the remaining integral has the limiting values: Int $= t^2 \Delta\omega/4$ for $t\Delta\omega \ll 1$ but, Int $= \pi t/2$ for t $\Delta\omega \gg 1$ [10]. For a usual femtosecond laser pulse, the frequency width is actually given by $t_{pulse} \Delta\omega = \pi/4$. So, we are in an intermediate situation between the limiting cases $t\Delta\omega \ll 1$ or $t\Delta\omega \gg 1$. But the function $\varsigma(\omega_{kj}-\omega)$ can still be approximated by

$$\zeta(\Delta\omega) = \frac{2\sin^2(\Delta\omega t/2)}{(\Delta\omega)^2} \cong \frac{t^2}{2}. \tag{19}$$

Consequently, eq. (13) that gives a quadratic dependence of the transition probability on t is valid and we consider it the starting point of our derivation.

In the following we shall deduce the hot electron kinetic equation neglecting the continuum of levels in the metal. The transition probability discussed above was deduced under the assumption that the initial level j is fully occupied at $t = 0$. Actually its occupancy is $f_{FD}(E_j)$, the Fermi-Dirac function for E_j in the unperturbed metal. The probability that the level E_k be free before the transition takes place is $(1 - f(E_k, t))$ where $f(E_k, t)$ is the nonequilibrium distribution at the excitation instant. The excitation probability is function of the transition probability discussed above, of the population of the initial state j and of the probability that the final state is unoccupied.

Using eq. (13), the excitation probability in unit time of the level E_k is:

$$P_{ex} = \frac{\partial c_k(t)^2}{\partial t} f_{FD}(E_j)(1 - f(E_k,t)) = t\frac{e^2 E_0^2 M_{kj}^2}{2\hbar^2} f_{FD}(E_j)(1 - f(E_k,t)) =$$
$$= p_0 t(1 - f(E_k,t)) \tag{20}$$

2.2. THE DEEXCITATION PROBABILITY P_{deex}

An electron inside a solid, with energy E_k above Fermi energy, tends to decay to states with lower energy due to the interaction with the rest of electrons in the solid. The time the electron remains in the state depends strongly on the energy E_k and grows when E_k approaches to Fermi energy because the closer to Fermi energy the electron is, the smaller the phase space where it can decay [11, 5]. When $(E - \mu) \gg kT$ the theory of a degenerate Fermi liquid of Landau-Silin (that provides a formal description of the influence of Coulomb interaction on electron motion in metals) gives for the excited electron lifetime [5]:

$$\tau_e = \tau_0 \frac{E_F^2}{(E_k - E_F)^2} \tag{21}$$

where τ_0 is the proportionality constant. The above formula shows that the electron lifetime gets longer as its energy gets closer to the Fermi level.

In the macroscopic theory of Landau and Silin τ_0 cannot be calculated. An appropriate formula for τ_0 may be deduced only in a microscopic theory. For example, τ_0 can be only approximately calculated using the Linhard dielectric function under random phase approximation (RPA) that is not quite valid for the region of metallic densities but rather for the high density limit. In the Linhard description, the proportionality constant τ_0 of eq. (21) is: $\tau_0 = 128/\left(\pi^2 \omega_p \sqrt{3}\right)$ where ω_p is the plasma frequency.

Quinn [12] proposed to use a dielectric function different from the Linhard's one that must be composed of two contributions: a free electron part (excitations that occur inside the *sp* band) and an interband part (transitions between the d-band and the *sp*-band). Due to virtual interband transitions that give rise to additional screening, the resulting dielectric function will have greater values than the Linhard function. Consequently, τ_0 will be larger than the Linhard's value by roughly a factor of $(1 + \delta\varepsilon_1)^{-1/2}$, where $\delta\varepsilon_1$ is the change of the real part of the dielectric function due to virtual interband transitions. Recent debates on τ_0 may be seen in [4, 13]. τ_0 may also be extracted from the experiments performed on metals [4, 14–17] that provide a wealth of information about electron relaxation in metals.

We take the probability of deexcitation in time unit inversely proportional to the electron lifetime τ given by the Fermi liquid theory:

$$P_{deex} = \frac{f(E_k,t)}{\tau} = \frac{f(E_k,t)(E_k - E_F)^2}{\tau_0 E_F^2}. \tag{22}$$

In the following we shall replace E_k with E.

2.3. THE TOTAL DISTRIBUTION FUNCTION

Using eq. (20) and eq. (22), one can write the kinetic equation (1) explicitly in terms of $f(E, t)$:

$$\frac{\mathrm{d}f(E,t)}{\mathrm{d}t} = p_0 t - \left(p_0 t + \frac{1}{\tau}\right) f(E,t) \tag{23}$$

This differential equation has the integral analytical solution already presented in a preceding paper [1]:

$$f(E,t) = 1 - \exp\left[-\left(\frac{p_0 t^2}{2} + \frac{t}{\tau}\right)\right]\left[1 - f_{FD}(E) + \frac{1}{\tau}\int_0^t dt_1\left(\frac{p_0 t_1^2}{2} + \frac{t_1}{\tau}\right)\right]. \qquad (24)$$

The above solution verifies the initial condition $f(E, t = 0) = f_{FD}(E)$.

Equations (23, 24) are effective only during the laser action. After laser extinction at time t_f, the equation (23) simplifies to:

$$\frac{df(E,t)}{dt} = -\frac{f(E,t)}{\tau} \qquad (25)$$

that can be integrated to give the laser off solution:

$$f(E,t) = \exp\left(-\frac{(t-t_f)}{\tau}\right)f(E,t_f). \qquad (26)$$

This electronic distribution goes exponentially to zero. Actually, a physical result must imply the thermalization to an equilibrium distribution $f_{FD}(E)$ corresponding to an electronic temperature slightly greater than the initial one and characterizing the mean energy of the electronic population excited above E_F. But for levels far enough from the Fermi level, $f_{FD}(E)$ is almost zero, so this error is not important.

3. RESULTS AND DISCUSSION

The above nonequilibrium electron distribution function eq. (24, 26) was already calculated and compared with the experimental data of Fann *et al.* [18] for a gold film of 300 A°. The hot electrons were excited with a laser having an energy of 1.84 eV and a duration of 180 fs. We found a good agreement between our results and the experimental data [1].

Here we will present, only the global dependence of the distribution function on time and energy, calculated using eqs. (24) and (26). In our calculations we used the following constants deduced from the characteristics of the Fann *et al.* [18] experiment: $F = 300$ μJ/cm^2, $E_0 = 3.3\cdot10^8$ V/m, $E_F = 5.53$ eV, $t_f = 180$ fs, $\tau_0 = 5$ fs. We calculated E_0 using $E_0 = \sqrt{(2F/(\varepsilon_0 c t_f))}$ and considering that the laser pulse has a rectangular temporal form. For $|M_{kj}|^2$, we used a value of 10^{-19} m^2 [1]. With the above values, the initial probability is $p_0 = 5\cdot10^{24}$ s^{-2}.

One sees from Fig. 1 that the distribution rises clearly in time for all the energies but this rise is more evident for low energies (close to the Fermi level) than for higher energies. This fact may be explained by the lower rate of deexcitation for electrons close to Fermi level. After laser extinction, when only the

Fig. 1 – Time and energy dependence of the electron distribution function calculated for a rectangular laser pulse of 1.84 eV, 180 fs, 300 μJ/cm² absorbed fluence.
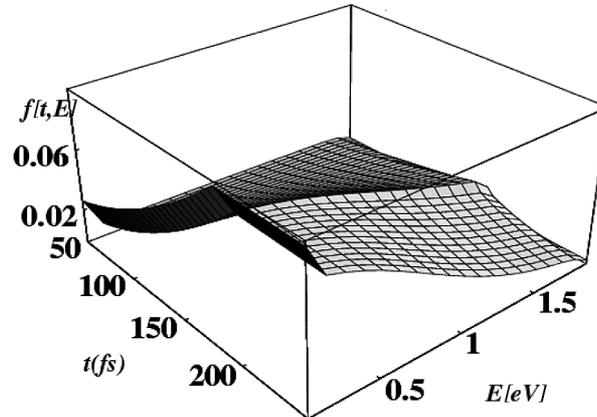
deexcitation process is active, the distribution function decays to lower values. This time, the decay is more evident for higher energies than for lower energies because of the difference in the lifetime of the electrons. An electron at a higher energy lives less than one at a lower energy.

Our distribution function was deduced under several approximations. The interaction with the electromagnetic radiation was treated as a resonant dipole transition between two discrete levels in the first order of the perturbation theory. As we already discussed, this approximation is valid if $|c_k(t)|^2 << 1$ is fully respected for the considered domain of laser fluences and duration. In particular, for the experimental data used in my calculations $|c_k(t)|^2 = p_0 t_f^2 / 2 = 8.1 \cdot 10^{-2}$, thus the approximation of the radiation field as a first order perturbation is valid.

The model does not apply to interaction of metals with intense lasers pulses (intensity greater than 10^{13} W/cm²) where plasma is created and other microscopic processes, neglected here, take place.

The model includes only the effect of the pump laser. This is equivalent to consider that all the emitted electrons, obtained by probe laser excitation have an equal probability to leave the metal. The electron population obtained by photoemission is in fact the result of the population of the excited electrons in a metal submitted to the pump and probe laser. A complete model should take into account the effect of the second laser pulse and a realistic transition probability of the excited electrons towards the vacuum.

4. CONCLUSION

We presented the mathematical deduction of a simple, phenomenological, microscopic model for the nonequilibrium electron distribution that arises in metals submitted to short laser pulses of moderate intensity. The model includes only

primary electrons and two basic phenomena: excitation by light absorption between two discrete levels and de-excitation by electron-electron collisions. Even if it is limited by several approximations, the model fulfills some necessary conditions and is in a full agreement with the experimental results of Fann *et al.* [18].

A necessary extension of the model will be the inclusion of the phonons and of the secondary electrons. Another extension of the model is the inclusion of the dispersion band structure and the excitation of the *d*-band electrons. Then the model could be applied to the description of the dynamic occupancy of the image states of low index (the image states are located near the vacuum level arising from the long rang image potential experienced by an electron in front of a metal surface) that are usually investigated in two-photon photoemission experiments.

REFERENCES

1. D. Bejan and G. Raseev, Phys. Rev. **B 55**, 4250 (1997).
2. J. M. Ziman, *Principles of the Theory of Solids*, Univ. Press, Cambridge, 1969.
3. M. Bauer, S. Paulik, M. Aeschlimann, Proc. **SPIE 3272**, 201 (1998).
4. M. Bauer, A. Aeschlimann, J. El. Spec. **124**, 225 (2002).
5. D. Pines and P. Nozieres, *The Theory of Quantum Liquids*, chap. 5.4, Benjamin Press, New York, 1966.
6. N. W. Aschroft and N. D. Mermin, *Solid State Physics*, p. 332, Holt-Saunders LTD, Japan, 1981.
7. A. Messiah, *Mécanique quantique*, chap. 17, Dunod, Paris, 1964.
8. C. Cohen-Tannoudji, B. Diu, F. Laloe, *Mécanique quantique*, chap. 13, Hermann, Paris, 1980.
9. S. Raimes, *The Wave Mechanics of Electrons in Metal,* North-Holland, Amsterdam, 1961.
10. R. Loudon, *Quantum Theory of Light*, chap. 2.3, Clarendon Press, Oxford, 1988.
11. Ch. Kittel, *Introduction to Solid State Physics*, chap. 7–8, John Wiley and Sons, Inc., New York, 1971.
12. J. J. Quinn, Appl. Phys. Lett. **2**, 167 (1963).
13. L. Vitali, P. Wahl, M. A. Schneider, K. Kern, V. M. Silkin, E. Chulkov, P. M. Echenique, Surf. Sci. **523**, L47 (2003).
14. C. A. Schmuttenmaer, M. Aeschlimann, H. E. Elsayed-Ali, R. D. Miller, D. A. Mantell, J. Cao, and Y. Gao, Phys. Rev., **B 50**, 8957 (1994).
15. S. Ogawa and H. Petek, Surf. Sci., **357–358**, 585 (1996).
16. H. Petek, H. Nagano, S. Ogawa, Appl. Phys., **B 68**, 369 (1999).
17. M. A. Aeschlimann, M. Bauer, S. Paulik, Chem. Phys., **205**, 127 (1996).
18. W. S. Fann, R. Storz, H. W. K. Tom, and J. Bokor, Phys. Rev., **B 46**, 13592 (1992).