High-order multiphoton ionization at metal surfaces by laser fields of moderate power

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By considering a laser-induced dipole layer along the surface of a metal and its action on an electron of the metal, it is shown that at moderate laser field intensities of some 10^{10} W cm^{-2} energetic electrons of a few 100 eV can be produced, which explains recent observations of Farkas *et al.* [Phys. Rev. A **41**, 4123 (1990); Opt. Eng. **32**, 2476 (1993)] without necessarily resorting to the mechanism of Coulomb explosion, taking place after the completion of the ionization process. [S1050-2947(98)00601-5]

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With the advent of the laser, the multiphoton photoeffect became of interest and its early investigations are reviewed in a paper by Anisimov *et al.* [1]. As is pointed out in this work, the surface photoeffect becomes dominant, if the laser polarization is perpendicular to the metal surface. This is achieved by grazing incidence of the laser pulse on the surface of the solid. If, in addition, the laser intensity is chosen not too high, of some 10^{10} W/cm^2, and short ps pulses are used, then no plasma will be formed during the ionization process and the surface photoeffect will take place at room temperature. This is the experimental situation envisaged in the following.

In a series of experiments under the above conditions by Farkas and co-workers [2–4], it was shown that energetic electrons of up to 500 eV may be produced that cannot be explained by existing models [5–7]. It was suggested that these energetic electrons have their origin in space-charge effects [8]. However, in most recent experiments by Farkas *et al.* [4] at very low laser field intensities space-charge effects were strongly suppressed and the discreteness of the photoelectron energy spectrum was explicitly discriminated.

Several years ago, it was pointed out by Liebsch and Schaich [9] that for the generation of harmonics at solid surfaces polarization effects play a crucial role. Since harmonic generation and multiphoton ionization are strongly interrelated, we expect that such polarization effects are equally important in the multiphoton photoeffect. It is the purpose of the present work to show by means of a simple model calculation that such polarization effects can be made responsible for the occurrence of energetic electrons in the experiments of Farkas *et al.* [2–4].

First we perform a few preliminary considerations. We take the laser pulse to propagate ideally along the surface of the metal and choose the laser polarization perpendicular to the surface. Farkas *et al.* [2–4] used a Nd:YAG laser emitting 8-ps pulses. Then the photon energy is $\hbar\omega = 1.17$ eV, the frequency $\omega = 2\times10^{15}$ sec^{-1}, and the wavelength $\lambda = 10^{-4}$ cm. The target was a gold surface at $T = 300$ K. For this monovalent metal the effective mass $m^* = m_e$ and the Fermi energy $E_F = 5.53$ eV with Fermi velocity $v_E = 1.4\times10^8$ cm/sec. These data are from Ashcroft and Mermin [10], one of our sources of information. Similarly, we find in Ref. [10] that on one hand the relaxation time of electron-ion collisions $\tau_i = 3\times10^{-14}$ sec and that on the other hand the electron-electron collision time can be estimated from $\tau_e = \hbar E_F/10(k_B T)^2$. Thus for gold at $T = 300$ K $\tau_e = 5.5\times10^{-13}$ sec. Consequently, using the above value of the laser frequency, we get $\tau_i\omega = 60 \gg 1$ and $\tau_e\omega = 11\times10^2 \gg 1$. Hence, in first order of approximation, we can neglect collisional damping effects and electrons near the surface perform on the average 10 free oscillations in the laser field between two collisions. This guarantees a sufficient amount of phase coherence. Next we evaluate the mean free path of electrons due to electron-ion collisions. With the above values for v_F and τ_i we get $l_i = 4.2\times10^{-6}$ cm $= 4.2\times10^{-2}\lambda$. Since the laser pulse was $\tau_p = 8\times10^{-12}$ sec, we find for the number of electron-ion collisions during τ_p, $N = \tau_p/\tau_i = 260$. Hence we can evaluate the average distance that an electron travels during one laser pulse. According to Ashcroft and Mermin [10], this is given by $\overline{l} = \sqrt{N} l_i = 0.67\times10^{-4}$ cm, which is still less than λ. Therefore the use of the dipole approximation for the laser field will be justified.

Now we perform the following elementary calculations. In a monovalent metal to each Wigner-Seitz cell, containing one ion, at any instant of time a quasifree conduction electron can be associated. Along a surface layer of the metal we denote the positions of the ions by $\mathbf{x}_j$ and the positions of the electrons by $\mathbf{x}_j(t)$. Then the potential of a test charge $-e$ at position $\mathbf{x}$ near the surface is given by

$$V = \sum_j \left(\frac{e^2}{|\mathbf{x} - \mathbf{x}_j(t)|} - \frac{e^2}{|\mathbf{x} - \mathbf{x}_j|} \right). \tag{1}$$

If at $t = 0$ the electrons are at the positions $\mathbf{x}_j$ and for $t > 0$ move essentially with constant velocities into arbitrary directions, we can write $\mathbf{x}_j(t) = \mathbf{x}_j + \mathbf{v}_j t + \boldsymbol{\xi}(t)$ where $|\mathbf{v}_j| \cong v_F$ and $\boldsymbol{\xi}(t) = \xi(t)\boldsymbol{\varepsilon}$ describes the laser-induced oscillations of the electrons near the surface. $\boldsymbol{\varepsilon}$ is the unit vector of linear polarization, pointing into the positive z direction, and the surface is located in the (x,y) plane such that $z > 0$ is the exterior region. Making in Eq. (1) a multipole expansion and retaining the dipole terms only we get

$$V=\sum_j \frac{e^2[\mathbf{v}_j(t)+\boldsymbol{\xi}(t)](\mathbf{x}-\mathbf{x}_j)}{|\mathbf{x}-\mathbf{x}_j|^3}+\cdots=V_s+V_d. \quad (2)$$

Going over to continuous variables $\mathbf{x}_j,\mathbf{v}_j\rightarrow\mathbf{x}',\mathbf{v}(\mathbf{x}')$ and introducing the corresponding integrations we find

$$V_s=e^2n_e\int d^3x' \frac{\mathbf{v}(x')t(\mathbf{x}-\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|^3},$$
$$V_d=e^2n_e\int d^3x' \frac{\xi(z',t)(z-z')}{|\mathbf{x}-\mathbf{x}'|^3}. \quad (3)$$

V_s is the static dipole potential layer at the surface of the metal, also present in the absence of the laser field, and V_d is the dynamic part, induced by the laser, where we observed that $\boldsymbol{\xi}(t)$ is perpendicular to the metal surface. n_e is the density of electrons.

We first consider V_s. According to the classic book of Seitz [11], along the surface of the metal the electrons can move freely in the (x,y) directions but they are confined in the z direction to within a short distance of the order of magnitude of the Bohr radius a_0. Thus we decompose V_s into its components parallel and perpendicular to the surface. Introducing plane polar coordinates (ρ',φ') in the (x,y) plane and observing that in this plane $|\mathbf{v}(\mathbf{x}')|\cong v_F$ we get

$$V_s=e^2n_e\int_0^{2\pi}d\varphi'\int_0^{\infty}\rho'\,d\rho'\int_{-a_0}^{0}dz' \times\frac{v_Ft\rho'\cos\varphi'+z'(z-z')}{[\rho'^2+(z-z')^2]^{3/2}}$$
$$=2\pi e^2n_e\int_{-a_0}^{0}z'\,dz'\frac{z-z'}{|z-z'|}=\pm 2\pi e^2n_ea_0^2/2, \quad (4)$$

where in the last expression $(+)$ holds for $z>0$ and $(-)$ for $z<-a_0$. Hence the total potential jump due to this dipole barrier is $D=4\pi e^2n_ea_0^2/2$. Taking the values $n_e=5.9\times10^{22}$ cm^{-3} and $a_0=0.53\times10^{-8}$ cm we find $D=1.4$ eV in reasonable agreement with results of much more sophisticated quantum mechanical calculations [12]. This static dipole barrier potential is a contribution to the work function W of the metal. Since later on we shall describe the static part of the metal surface by Sommerfeld's step potential of depth $V_0=E_F+W$, we do not need to consider D any further.

Now we consider in Eq. (3) the laser-induced dipole-layer potential V_d. Using again plane polar coordinates (ρ',φ'), the final integration will depend on the form of $\xi(z',t)$. For $z'<0$, we take the field strength of the laser pulse along the surface to have the form $F(t)=F_0\exp(z'/\delta)\sin\omega t$, where δ is the penetration depth. We have shown above that the laser pulse can be safely described in the dipole approximation, in particular, since the laser beam propagates along the surface (for example, in the x direction) while the integration is along z' and we shall see below that $\delta\ll\lambda$. Then, solving the equation of motion of an electron of the metal in this field, we find $\xi(z',t)=\alpha_0\exp(z'/\delta)\sin\omega t$ with $\alpha_0=eF_0/m\omega^2$ for $z'<0$. Hence the final integration in the expression for V_d (from now on simply V) yields

$$V=\begin{cases}2\pi n_ee^2\delta\alpha_0\sin\omega t, & z>0 \quad (5a)\\ 2\pi n_ee^2\delta(2\exp(z/\delta)-1)\alpha_0\sin\omega t, & z<0. \quad (5b)\end{cases}$$

We introduce the amplitude

$$V_1=2\pi n_ee^2\delta\alpha_0=(1/2)(\omega_p/\omega)^2(\delta/\lambda)\mu mc^2, \quad (6)$$

where $\omega_p^2=4\pi n_ee^2/m$ is the plasma frequency and $\mu=eF_0/m\omega c=10^{-9}\sqrt{I}/\hbar\omega$ is the intensity parameter in which the intensity I is measured in W/cm^2 and the photon energy in eV. In our case, the plasma frequency of gold [10] $\omega_p=1.38\times10^{16}$ sec$^{-1}\gg\omega$. Then the penetration depth is roughly given by $\delta\cong c/\omega_p$ [11] and we get $V_1=\frac{1}{2}(\omega_p/\omega)\mu mc^2$. To estimate the order of magnitude of V_1 we use $\hbar\omega_p=10.5$ eV, $\hbar\omega=1.17$ eV, and $I=2.5\times10^{10}$ W/cm^2. We find $V_1=304$ eV. Why this potential is so much larger than D, discussed before, can be seen as follows. While D depends on $a_0^2=2.8\times10^{-17}$ cm^2 the corresponding parameter in Eq. (6) is $\delta\alpha_0$. Using from above the value for ω_p, we get $\delta=2.17\times10^{-6}$ cm$\cong10^3a_0$. On the other hand, one finds from our values for I and ω, $\alpha_0=1.6\times10^{-9}$ cm. Hence, although the amplitude of the electron oscillations is so small, still $\delta\alpha_0=3.4\times10^{-15}$ cm$^2\cong10^2a_0^2$ evaluated before. Therefore, the comparatively large penetration depth of the laser field into the metal is responsible for the surprisingly large laser-induced dipole-layer potential.

To simplify the following analysis, we take in Eq. (5b) the asymptotic value for $z\rightarrow-\infty$. Thus we get an idealized double-layer potential that oscillates at frequency ω between $-V_1$ and $+V_1$ at a phase difference of π between $z>0$ and $z<0$. Moreover, we describe the static potential exerted on an electron by the metal surface by Sommerfeld's step function $V_0[\Theta(z)-1]$ where V_0 is the depth of the potential well. Consequently, the wave function of an electron will have to obey the two Schrödinger equations

$$(\hat{p}^2/2m-V_0-V_1\sin\omega t)\Psi_I=i\hbar\partial_t\Psi_I \quad (z<0) \quad (7a)$$

$$(\hat{p}^2/2m+V_1\sin\omega t)\Psi_{II}=i\hbar\partial_t\Psi_{II} \quad (z>0) \quad (7b)$$

where I refers to the interior region and II to the exterior region, respectively.

To fulfill the continuity conditions of the scattering problem at the surface at $z=0$, we make Floquet ansätze in terms of fundamental solutions of Eqs. (7a) and (7b)

$$\Psi_I=\left[\chi_0^{(+)}-\chi_0^{(-)}+\sum_n R_n\chi_n^{(-)}\right]\exp[i(V_1/\hbar\omega)\cos\omega t], \quad (8a)$$

$$\Psi_{II}=\sum_k T_k\varphi_k^{(+)}\exp[i(V_1/\hbar\omega)\cos\omega t], \quad (8b)$$

where $\chi_n^{(\pm)}=\exp[\pm iq_nz/\hbar-i(E_0+n\hbar\omega)t/\hbar]$ with $q_n=[2m(V_0+E_0+n\hbar\omega)]^{1/2}$ and, correspondingly, $\varphi_k^{(+)}=\exp[ip_kz/\hbar-i(E_0+k\hbar\omega)t/\hbar]$ with $p_k=[2m(E_0+k\hbar\omega)]^{1/2}$. The unknown reflection and transmission coefficients R_n and

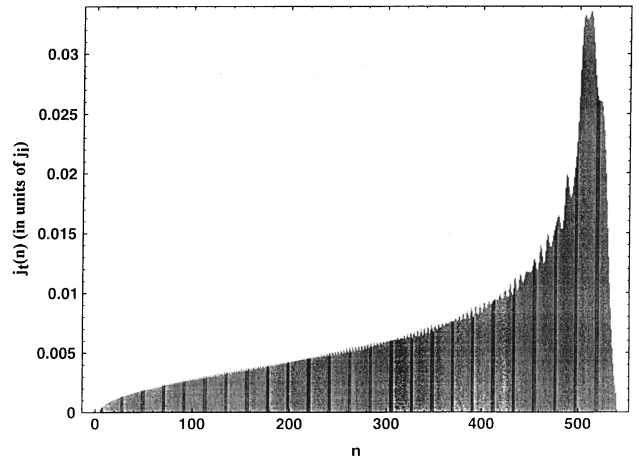

FIG. 1. Photoelectric currents $j_t(n)$ (normalized) as a function of the nonlinear order n for laser intensity $I=2.5\times10^{10}$ W/cm^2 at which the parameter $a=520$. Maximum current predicted near 500 eV electron energies.

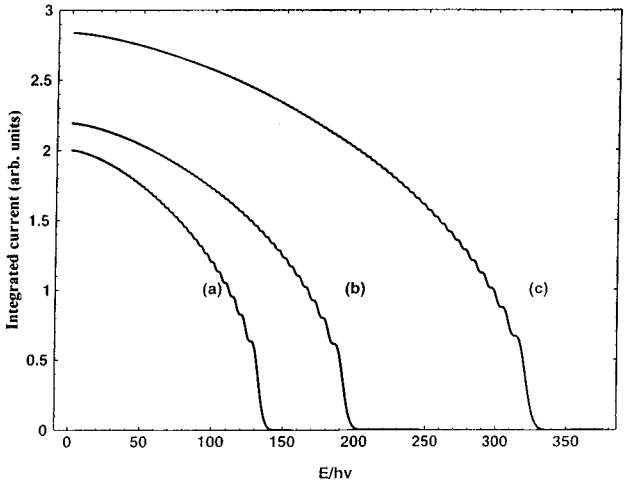

FIG. 2. Integrated photoelectric currents in arbitrary units for (a) $I=3.1\times10^9$ W/cm^2 with $a=140$, for (b) $I=3.7\times10^9$ W/cm^2 with $a=200$, and for (c) $I=10^{10}$ W/cm^2 with $a=330$. The general shapes of these curves agree very well with observation.

T_k respectively are then obtained from the matching equations $\Psi_I(0,t)=\Psi_{II}(0,t)$ and $\Psi_I'(0,t)=\Psi_{II}'(0,t)$, where $\Psi'=\partial_z\Psi$. Using the generating function of ordinary Bessel functions $J_n(z)$ to Fourier decompose the time-dependent exponentials, the matching equations yield the following relations:

$$R_n=\sum_k J_{n-k}(a)i^{n-k}T_k \tag{9a}$$

$$\delta_{n,0}=\sum_k J_{n-k}(a)i^{n-k}[(q_n+p_k)/2q_0]T_k, \tag{9b}$$

where we have introduced the dimensionless parameter $a=2V_1/\hbar\omega$ in which $2V_1$ is the total maximum jump of the oscillating dipole-layer potential.

The time-averaged outgoing electron current components (for which p_n is real), corresponding to n-photon absorption, can be obtained from Ψ_{II}. We normalize these current components with respect to the incoming current, j_i, and get

$$j_t(n)=(p_n/q_0)|T_n|^2 \quad (n\geqslant n_0), \tag{10a}$$

where n_0 is the minimum number of photons to be absorbed in order to yield true free running outgoing waves (i.e., ionization). The corresponding normalized reflected currents are

$$j_r(n)=(q_n/q_0)|R_n-\delta_{n,0}|^2 \quad (n\geqslant n_1), \tag{10b}$$

with a similar meaning for n_1 as for n_0. Conservation of probability requires $\Sigma_n[j_t(n)+j_r(n)]=1$, which can be used to check the accuracy of numerical solutions of the matching equations.

In general Eq. (9b) cannot be solved analytically. The numerical solution requires the truncation of the kernel matrix. The size of the truncated set of equations depends, however, crucially on the parameter ''a'' for which we get from our above example for V_1 the value 520. Hence, we expect a truncated set of matrix equations of the order 1000×1000 to achieve a reliable accuracy. Fortunately, for very large ''a'' an approximate analytic solution of Eq. (9b) can be found, which is particularly accurate for large values of n. Multiplying Eq. (9b) by $J_{s-n}(-a)$ and summing over n we get, putting $n-k=\lambda$,

$$J_s(-a)=\sum_{k,\lambda} J_{s-k-\lambda}(-a)J_\lambda(a)[(q_{\lambda+k}+p_k)/2q_0]T_k i^{-k}. \tag{11}$$

If we approximate $(q_{\lambda+k}+p_k)/2q_0$ by unity, then the summation over λ can be performed exactly by means of the addition theorem of Bessel functions and we obtain the approximation $T_n\cong J_n(-a)i^n$ so that

$$j_t(n)\cong(p_n/q_0)J_n^2(-a). \tag{12}$$

Hence it follows from Eq. (9a) that in this approximation $R_n=\delta_{n,0}$ and there are no reflected currents. Nonetheless, we do not get the sum rule $\Sigma_n j_t(n)=1$, since our approximation is very crude for small values of n.

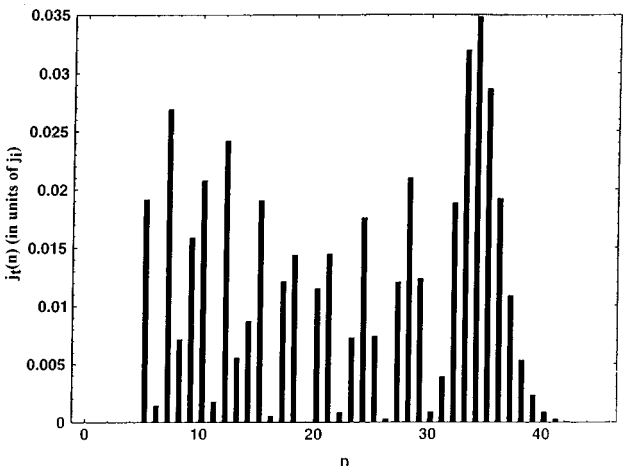

FIG. 3. Photoelectric currents $j_t(n)$ (normalized) as a function of n for laser intensity 120 MW/cm^2 for which $a=36.5$. At these low intensities space-charge effects alone cannot be made responsible for the observed photoelectron currents.

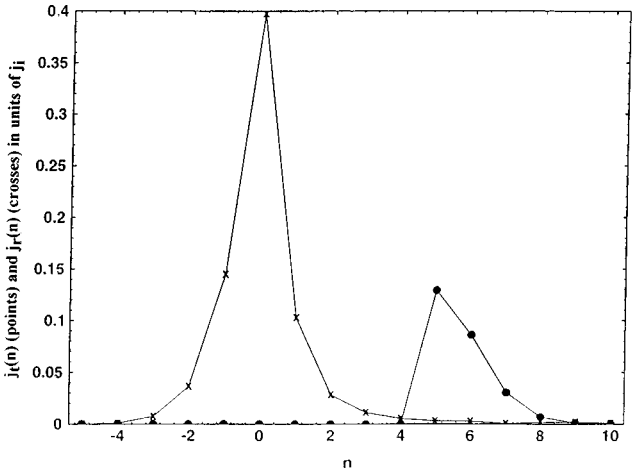

FIG. 4. Photoelectric currents $j_t(n)$ and $j_r(n)$ (normalized) for $I=3.8\times10^6$ W/cm^2 for which $a=6.5$. At these very low intensities, standard models yield negligible effects contrary to observation.

Our above approximation relies on the assumption that the average energy of the emitted electrons is much larger than the binding energy V_0. It can be shown that this approximation is equivalent to solving the scattering problem, defined by Eqs. (7a) and (7b), in the Born approximation, disregarding the boundary conditions at $z=0$.

For the numerical examples, presented below, we choose the parameter values of the experiments of Farkas *et al.* [2–4]. For gold as target material $E_F=5.51$ eV, $A=4.68$ eV, thus $V_0=10.2$ eV, and with $n_e=5.9\times10^{22}$ cm^{-3}, $\hbar\omega_p=10.53$ eV. All experiments were done with a Nd:YAG laser with $\hbar\omega=1.17$ eV. The initial experiments were performed with laser intensities of about 10^{10} W/cm^2, but later experiments were done with much lower intensities of about 100 MW/cm^2 to reduce the space charge effects which can lead to Coulomb explosion.

In Fig. 1 we show the normalized transmitted currents $j_t(n)$ as a function of n for $I=2.5\times10^{10}$ W/cm^2 in which case the parameter $a=520$. In agreement with the experimental findings, energetic electrons of about 500 eV are predicted by our theory.

In Fig. 2 we present in arbitrary units the integrated currents for three different intensities: (a) 3.1×10^9 W/cm^2 with the parameter $a=140$, (b) 3.7×10^9 W/cm^2 with $a=200$, and (c) 10^{10} W/cm^2 with $a=330$. These predicted current distributions agree very well with the results of Fig. 3 of Ref. [3].

In Fig. 3 we plot the normalized transmitted current $j_t(n)$ for a much lower intensity $I=120$ MW/cm^2 for which $a=36.5$. As one can see, the largest currents are predicted in the vicinity of $n=35$, which considerably overestimates the experimentally observed photoelectron energy spectrum that ends near $n=9$ [4]. It should be stressed, however, that the penetration depth δ and thus the parameter a are only defined up to a factor of 2 [11,13].

Finally, in Fig. 4 we show the normalized transmitted (points) and reflected (crosses) currents for a very much lower intensity $I=3.8\times10^6$ W/cm^2 for which $a=6.5$. Even at this low intensity, the transmitted currents are still appreciable and in accord with experiments [4] while standard model calculations [5–7] yield at these laser intensities negligible effects.

Summarizing, we have shown that surface polarization effects can be made responsible for the appearance of energetic electrons in the observation of the high-order multiphoton photoeffect at metal surfaces at comparatively low laser field intensities. These effects cannot be explained by the existing model calculations [5–7]. It is true that space-charge effects will play an appreciable role in the interpretation of the high-energy photoelectrons [8], however, the discreteness of the energy spectrum, observed by Farkas *et al.* [4] in their latest experiment, cannot be ascribed to Coulomb explosion since this mechanism could only yield a continuous spectrum.

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