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Theory of multiharmonic generation and multiphoton electron emission at a metal surface

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The nonlinear-optical processes of multiharmonic generation and multiphoton electron emission at the surface of a metal are studied. Results are derived for arbitrary-order perturbation theory. Application is made to the Sommerfeld model, and estimates of the yields are given for simple free-electron-like metals.

I. INTRODUCTION

In this paper we will study two nonlinear-optical processes of relevance to the field of surface physics: multiphoton electron emission and multiharmonic generation from solid surfaces. In multiphoton electron emission (MPEE) a number of photons are absorbed and the energy is used to promote an electron from some state below the Fermi surface to a state above the vacuum level resulting in the electron leaving the metal. Experimental studies of multiphoton electron emission from a variety of solids have been made by a number of research groups.[1-13] These solids include metals, semiconductors, and insulators. MPEE was observed as a function of laser intensity, work function, and laser frequencies.[5-8] The effect of surface heating was also discussed.[1,2] In insulators[7] resonance enhancement due to the existence of surface states was observed. Theoretical studies of multiphoton electron emission have been reported.[11-13] In multiharmonic generation (MHG), a number of photons are absorbed from the incident laser beam, and a single outgoing photon is created. The energy of the outgoing photon is a multiple of the incident photon energy. Experimental studies of multiharmonic generation have been reported in the literature. These studies include a variety of metals, semiconductors, and insulators as well as adsorbate-covered solids.[14-46] In recent years, theoretical studies of MHG have focused primarily on metals.[14-32] In recent years, a lot of studies have been done on rough surfaces,[33-42] mainly because of the observation of surface-enhanced Raman scattering. Second-harmonic generation (SHG) has been studied extensively due to its utility in probing surface chemistry and structure. It has also been argued[43] that the SHG can give information about the electronic band structure of metal surfaces. More recently,[45] frequency dependence of SHG at simple metal surfaces has been studied using the time-dependent density-functional formalism.

Very little is known about the higher-order MHG or MPEE. In this paper we will develop a perturbation theory valid for any arbitrary order, both for MHG and MPEE. We will restrict our attention to metal surfaces and treat them in a rather primitive way. We will model the metal as a free-electron gas terminated by an abrupt step of finite size. In Sec. II we formulate the perturbation theory for this model. In Sec. III we present calculational results and discuss them.

II. THEORY

Let us start by considering the simplest form of a metal described by the Sommerfeld model in which the metal is taken to be a free-electron gas terminated by an abrupt step in the potential. The electronic states are filled up to the Fermi level and the electromagnetic field appears as a perturbation to the Hamiltonian describing the system.

The form of the potential energy is

$$V(z)=\begin{cases}-V_0 & \text{if } z<0\\ 0 & \text{if } z>0\ ,\end{cases} \tag{2.1}$$

where V_0 is the depth of the inner core potential. It is related to the work function ϕ, and the Fermi energy E_f by

$$V_0=E_f+\phi\ . \tag{2.2}$$

We use atomic units ($\hbar=e=m=1$). The solution to the unperturbed Schrödinger equation

$$\left[\frac{p_z^2}{2}+V(z)-\varepsilon\right]|q\rangle=0 \tag{2.3}$$

is given by

$$u^{(0)}=\begin{cases}\exp(ikz)+r\exp(-ikz) & \text{for } z<0 \quad (2.4a)\\ (1+r)\exp(-\gamma z) & \text{for } z>0\ , \quad (2.4b)\end{cases}$$

where $k=[2(\varepsilon+V_0)]^{1/2}$ and $\gamma=(-2\varepsilon)^{1/2}$ and the reflection coefficient is

$$r=\frac{ik+\gamma}{ik-\gamma} . \tag{2.5}$$

We have let ε represent the net energy associated with the z motion ($\varepsilon=\varepsilon_t-k_\parallel^2/2$). Here ε_t is the total energy.

The perturbed wave function satisfies the differential equation

$$\left[\pm n\omega+\varepsilon+\frac{1}{2}\frac{d^2}{dz^2}-V(z)\right]u_\pm^{(n)}(z)=p_z u_\pm^{(n-1)}(z) . \tag{2.6}$$

The solution will consist of a homogeneous and inhomogeneous part. The homogeneous solution is chosen to correspond to either a wave propagating away from the surface or an evanescent wave decaying away from the surface. This applies both to the vacuum region ($z>0$) as well as the solid itself ($z<0$). For example, let us look at the $n=1$ case:

$$\left[\omega+\varepsilon+\frac{1}{2}\frac{d^2}{dz^2}-V(z)\right]u^{(1)}=p_z u^{(0)} \tag{2.7}$$

so

$$\left[\omega+\varepsilon+\frac{1}{2}\frac{d^2}{dz^2}+V_0\right]u^{(1)}=k\exp(ikz)-rk\exp(-ikz) \quad \text{for } z<0 , \tag{2.8a}$$

$$\left[\omega+\varepsilon+\frac{1}{2}\frac{d^2}{dz^2}\right]u^{(1)}=i\gamma(1+r)\exp(-\gamma z) \quad \text{for } z>0 . \tag{2.8b}$$

We define k_j and γ_j as

$$k_j=[2(j\omega+\varepsilon+V_0)]^{1/2} , \tag{2.9}$$

$$\gamma_j=[-2(j\omega+\varepsilon)]^{1/2} . \tag{2.10}$$

If $\varepsilon+j\omega<0$ then γ_j is the attenuation constant for an electron that has absorbed j photons but still decays into the vacuum. However, if $\varepsilon+j\omega>0$ then

$$\gamma_j=-iq_j , \tag{2.11}$$

where

$$q_j=[2(\varepsilon+j\omega)]^{1/2} . \tag{2.12}$$

This is the propagation vector in vacuum. Thus, for $z>0$

$$u^{(1)}=A_1\exp(iq_1z)+\frac{i\gamma(1+r)}{\omega}\exp(-\gamma z) \tag{2.13}$$

and for $z<0$

$$u^{(1)}=B_1\exp(-ik_1z)+\frac{k}{\omega}[\exp(ikz)-r\exp(-ikz)] . \tag{2.14}$$

These expressions are written as if $\varepsilon+\omega>0$. The constants A_1 and B_1 are determined by matching the wave function and its derivative at $z=0$. We obtain

$$A_1=-\frac{2ik}{\omega}\left[\frac{\gamma+ik}{q+k_1}\right] \tag{2.15}$$

and

$$B_1=-\frac{2ik}{\omega}\left[\frac{\gamma+ik}{q+k_1}\right] . \tag{2.16}$$

For $n=2$, the inhomogeneous differential equations are

$$\left[2\omega+\varepsilon+\frac{1}{2}\frac{d^2}{dz^2}\right]u^{(2)}=-i\frac{du^{(1)}}{dz} \quad \text{for } z>0 , \tag{2.17a}$$

$$\left[2\omega+\varepsilon+V_0+\frac{1}{2}\frac{d^2}{dz^2}\right]u^{(2)}=-i\frac{du^{(1)}}{dz} \quad \text{for } z<0 . \tag{2.17b}$$

Inserting the values of $u^{(1)}$ found before yields

$$u^{(2)}=A_2\exp(iq_2z)+\frac{q_1}{\omega}A_1\exp(iq_1z)-\frac{\gamma^2}{2\omega^2}(1+r)\exp(-\gamma z) \quad \text{for } z>0 , \tag{2.18a}$$

$$u^{(2)}=B_2\exp(-ik_2z)-\frac{k_1}{\omega}B_1\exp(-ik_1z)+\frac{k^2}{2\omega^2}[\exp(ik_zz)+r\exp(-ik_zz)] \quad \text{for } z<0 . \tag{2.18b}$$

The constants A_2 and B_2 are again obtained by matching the wave function and its derivative at $z=0$.

From an examination of the $n=1$ and 2 cases we can conjecture the form of the perturbed wave function for arbitrary n and verify that it indeed is the solution by inserting it into the inhomogeneous differential equation. Thus

$$u^{(n)}=\sum_{j=1}^{n}A_j^{(n)}\exp(iq_jz)+c_n\exp(-\gamma z) \quad \text{for } z>0 \tag{2.19a}$$

and

$$u^{(n)}=\sum_{j=1}^{n}B_j^{(n)}\exp(-ik_jz)+d_n[\exp(ikz)+(-1)^n r\exp(-ikz)] \quad \text{for } z<0 . \tag{2.19b}$$

For $z>0$ the inhomogeneous differential equation becomes

$$n\omega c_n\exp(-\gamma z)+\sum_{j=1}^{n}A_j^{(n)}\left[\frac{q_n^2}{2}-\frac{q_j^2}{2}\right]\exp(iq_jz)=i\gamma c_{n-1}\exp(-\gamma z)+\sum_{j=1}^{n-1}A_j^{(n-1)}q_j\exp(iq_jz) , \tag{2.20}$$

from which it follows that

$$c_n = i\frac{\gamma}{n\omega}c_{n-1} \tag{2.21}$$

and

$$A_j^{(n)}\omega(n-j) = q_j A_j^{(n-1)} . \tag{2.22}$$

The value of c_0 is fixed by the condition that $u^{(0)}$ should equal the unperturbed wave function

$$c_0 = 1 + r . \tag{2.23}$$

Similarly, for $z < 0$,

$$n\omega d_n[\exp(ikz) + (-1)^n r\exp(-ikz)] + \sum_{j=1}^{n} B_j^{(n)}\left[\frac{k_n^2}{2} - \frac{k_j^2}{2}\right]\exp(-ik_j z)$$
$$= kd_{n-1}[\exp(ikz) + (-1)^n\exp(-ikz)] - \sum_{j=1}^{n-1} k_j B_j^{(n-1)}\exp(-ik_j z) \tag{2.24}$$

from which it follows that

$$d_n = \frac{k}{n\omega}d_{n-1} , \tag{2.25}$$

$$B_j^{(n)} = -\frac{k_j B_j^{(n-1)}}{\omega(n-j)} . \tag{2.26}$$

The value of d_0 is again set by the condition that $u^{(0)}$ should equal the unperturbed wave function

$$d_0 = 1 . \tag{2.27}$$

Iterating the above recurrence formulas leads to the following solutions:

$$A_j^{(n)} = \left[\frac{q_j}{\omega}\right]^{n-j}\frac{1}{(n-j)!}A_j , \tag{2.28}$$

where A_j denotes $A_j^{(j)}$,

$$c_n = \left[i\frac{\gamma}{\omega}\right]^n\frac{1}{n!}(1+r) , \tag{2.29}$$

$$B_j(n) = \left[-\frac{k_j}{\omega}\right]^{n-j}\frac{1}{(n-j)!}B_j , \tag{2.30}$$

where B_j denotes $B_j^{(j)}$ and

$$d_n = \left[\frac{k}{\omega}\right]^n\frac{1}{n!} . \tag{2.31}$$

The constants A_j and B_j are determined from matching the wave function and its derivative at $z = 0$,

$$\sum_{j=1}^{n}(A_j^{(n)} - B_j^{(n)}) = d_n[1 + (-1)^n r] - c_n , \tag{2.32}$$

$$\sum_{j=1}^{n}(q_j A_j^{(n)} + k_j B_j^{(n)}) = d_n kz[1 - (-1)^n r] - i\gamma c_n . \tag{2.33}$$

Let us define the following triangular matrices for $j \le n$:

$$\rho_{nj} = \left[\frac{q_j}{\omega}\right]^{n-j}\frac{q_j}{(n-j)!} , \tag{2.34}$$

$$\sigma_{nj} = \left[-\frac{k_j}{\omega}\right]^{n-j}\frac{k_j}{(n-j)!} , \tag{2.35}$$

$$R_{nj} = \left[\frac{q_j}{\omega}\right]^{n-j}\frac{1}{(n-j)!} , \tag{2.36}$$

$$S_{nj} = \left[-\frac{k_j}{\omega}\right]^{n-j}\frac{1}{(n-j)!} . \tag{2.37}$$

For $n < j$ these are taken to vanish. We also define the vectors

$$T_n = d_n[1 + (-1)^n r] - c_n , \tag{2.38}$$

$$F_n = d_n k[1 - (-1)^n r] - i\gamma c_n . \tag{2.39}$$

There are now four triangular matrices (R, S, ρ, and σ) and four column vectors (A, B, F, and T) in the problem. In order to completely determine the perturbed wave functions we must solve the matrix equations

$$\rho A + \sigma B = F \tag{2.40}$$

and

$$RA - SB = T . \tag{2.41}$$

The solutions to these equations are

$$A = K^{-1}U \tag{2.42}$$

and

$$B = L^{-1}V , \tag{2.43}$$

where

$$K = \rho + \sigma S^{-1}R , \tag{2.44}$$

$$L = \sigma + \rho R^{-1}S , \tag{2.45}$$

$$V = F - \rho R^{-1}T , \tag{2.46}$$

$$U = F + \sigma S^{-1}T . \tag{2.47}$$

Since the K and L matrices are triangular matrices with

vanishing upper components we may solve the equations

$$KA = U \tag{2.48}$$

and

$$LB = V \tag{2.49}$$

directly through the use of simple algebra. The result is

$$A_j = \frac{\det M_j}{\prod_{l=1}^{j} K_{ll}} , \tag{2.50}$$

where

$$M_j = \begin{bmatrix} K_{11} & 0 & \cdots & 0 & U_1 \\ K_{21} & K_{22} & \cdots & 0 & U_2 \\ K_{31} & K_{32} & \cdots & 0 & U_3 \\ \vdots & \vdots & \cdots & 0 & \vdots \\ K_{j-1,1} & K_{j-1,2} & \cdots & K_{j-1,j-1} & U_{j-1} \\ K_{j1} & K_{j2} & \cdots & K_{j,j-1} & U_j \end{bmatrix} . \tag{2.51}$$

Similarly

$$B_j = \frac{\det N_j}{\prod_{l=1}^{j} L_{ll}} , \tag{2.52}$$

where

$$N_j = \begin{bmatrix} L_{11} & 0 & \cdots & 0 & V_1 \\ L_{21} & L_{22} & \cdots & 0 & V_2 \\ L_{31} & L_{32} & \cdots & 0 & V_3 \\ \vdots & \vdots & \cdots & 0 & \vdots \\ L_{j-1,1} & L_{j-1,2} & \cdots & L_{j-1,j-1} & V_{j-1} \\ L_{j1} & L_{j2} & \cdots & L_{j,j-1} & V_j \end{bmatrix} . \tag{2.53}$$

Note that M and N are nonsingular matrices here.

A. Multiharmonic generation

In developing a perturbation expansion for multiharmonic generation (MHG) we note that for n-harmonic generation, we are dealing with a closed Feynman loop with n absorption vertices and one emission vertex. The intermediate states involve, in general, both electrons and holes. It is possible, however, to write the matrix elements so that all intermediate states are included without the need for Fermi factors. Since there are $n+1$ possible time orderings for the emission and absorption we have $n+1$ independent graphs. We illustrate the case $n=4$ in order to elucidate the general structure of the matrix element. The Feynman diagrams are illustrated in Fig. 1. The matrix element is

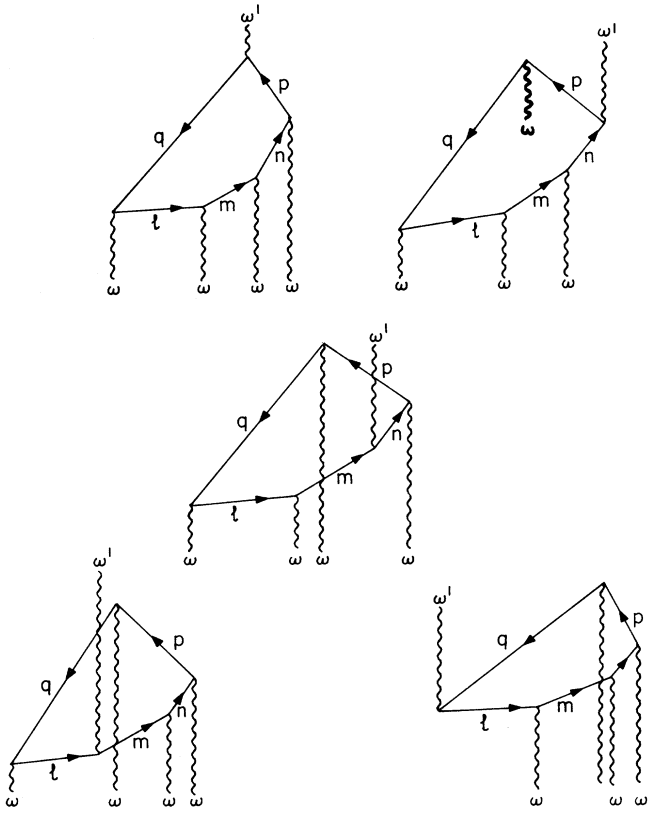

FIG. 1. Feynman diagrams for multiharmonic generation for the case $n=4$. Four photons of frequency ω combine to create one photon of frequency 4ω.

$$M^{(4)} = \sum_{q} \left[\frac{A_0 \hat{\mathbf{e}}_z}{2c} \right]^4 \left[\frac{2\pi}{\omega'} \right]^{1/2} \hat{\mathbf{e}}'_z (M_1 + M_2 + M_3 + M_4 + M_5) f_q^{(-)} , \tag{2.54}$$

where

$$M_1 = \sum_{l,m,n,p} \frac{\langle q|p_z|p\rangle\langle p|p_z|n\rangle\langle n|p_z|m\rangle\langle m|p_z|l\rangle\langle l|p_z|q\rangle}{(4\omega+\varepsilon_q-\varepsilon_p)(3\omega+\varepsilon_q-\varepsilon_n)(2\omega+\varepsilon_q-\varepsilon_m)(\omega+\varepsilon_q-\varepsilon_l)} , \tag{2.55}$$

$$M_2 = \sum_{l,m,n,p} \frac{\langle q|p_z|p\rangle\langle p|p_z|n\rangle\langle n|p_z|m\rangle\langle m|p_z|l\rangle\langle l|p_z|q\rangle}{(-\omega+\varepsilon_q-\varepsilon_p)(3\omega+\varepsilon_q-\varepsilon_n)(2\omega+\varepsilon_q-\varepsilon_m)(\omega+\varepsilon_q-\varepsilon_l)} , \tag{2.56}$$

$$M_3=\sum_{l,m,n,p}\frac{\langle q|p_z|p\rangle\langle p|p_z|n\rangle\langle n|p_z|m\rangle\langle m|p_z|l\rangle\langle l|p_z|q\rangle}{(-\omega+\varepsilon_q-\varepsilon_p)(-2\omega+\varepsilon_q-\varepsilon_n)(2\omega+\varepsilon_q-\varepsilon_m)(\omega+\varepsilon_q-\varepsilon_l)}\ , \tag{2.57}$$

$$M_4=\sum_{l,m,n,p}\frac{\langle q|p_z|p\rangle\langle p|p_z|n\rangle\langle n|p_z|m\rangle\langle m|p_z|l\rangle\langle l|p_z|q\rangle}{(-\omega+\varepsilon_q-\varepsilon_p)(-2\omega+\varepsilon_q-\varepsilon_n)(-3\omega+\varepsilon_q-\varepsilon_m)(\omega+\varepsilon_q-\varepsilon_l)}\ , \tag{2.58}$$

$$M_5=\sum_{l,m,n,p}\frac{\langle q|p_z|p\rangle\langle p|p_z|n\rangle\langle n|p_z|m\rangle\langle m|p_z|l\rangle\langle l|p_z|q\rangle}{(-\omega+\varepsilon_q-\varepsilon_p)(-2\omega+\varepsilon_q-\varepsilon_n)(-3\omega+\varepsilon_q-\varepsilon_m)(-4\omega+\varepsilon_q-\varepsilon_l)}\ . \tag{2.59}$$

We introduce a set of perturbed states defined as follows:

$$|u_+^{(1)}\rangle\equiv\sum_l\frac{|l\rangle\langle l|p_z|q\rangle}{\omega+\varepsilon_q-\varepsilon_l}\ , \tag{2.60}$$

$$|u_+^{(2)}\rangle\equiv\sum_{l,m}\frac{|m\rangle\langle m|p_z|l\rangle\langle l|p_z|q\rangle}{(2\omega+\varepsilon_q-\varepsilon_m)(\omega+\varepsilon_q-\varepsilon_l)}=\sum_l\frac{|l\rangle\langle l|p_z|u_+^{(1)}\rangle}{2\omega+\varepsilon_q-\varepsilon_l}\ , \tag{2.61}$$

$$|u_+^{(n)}\rangle\equiv\sum_l\frac{|l\rangle\langle lp_z|u_+^{(n-1)}\rangle}{n\omega+\varepsilon_q-\varepsilon_l}\ . \tag{2.62}$$

Similarly

$$|u_-^{(1)}\rangle\equiv\sum_l\frac{|l\rangle\langle l|p_z|q\rangle}{-\omega+\varepsilon_q-\varepsilon_l}\ , \tag{2.63}$$

$$|u_-^{(n)}\rangle\equiv\sum_l\frac{|l\rangle\langle l|p_z|u_-^{(n-1)}\rangle}{-n\omega+\varepsilon_q-\varepsilon_l}\ . \tag{2.64}$$

It is convenient to define

$$|u_+^{(0)}\rangle=|u_-^{(0)}\rangle=|q\rangle \tag{2.65}$$

so that for $n\geq 1$

$$|u_\pm^{(n)}\rangle=\sum_m\frac{|m\rangle\langle m|p_z|u_\pm^{(n-1)}\rangle}{\pm n\omega+\varepsilon_q-\varepsilon_m}\ . \tag{2.66}$$

In terms of the perturbed states we may write the individual matrix elements as

$$M_1=\langle u_-^{(0)}|p_z|u_+^{(4)}\rangle\ , \tag{2.67}$$

$$M_2=\langle u_-^{(1)}|p_z|u_+^{(3)}\rangle\ , \tag{2.68}$$

$$M_3=\langle u_-^{(2)}|p_z|u_+^{(2)}\rangle\ , \tag{2.69}$$

$$M_4=\langle u_-^{(4)}|p_z|u_+^{(1)}\rangle\ , \tag{2.70}$$

$$M_5=\langle u_-^{(4)}|p_z|u_+^{(0)}\rangle\ . \tag{2.71}$$

The unperturbed states satisfy the inhomogeneous differential equations

$$(\pm j\omega+\varepsilon_q-H_0)|u_\pm^{(j)}\rangle=p_z|u_\pm^{(j-1)}\rangle\ , \tag{2.72}$$

where $j=1,2,3$, etc. From the above example it is clear that for nth-order multiharmonic generation

$$M^{(n)}=\left[\frac{A_0}{2c}\hat{\mathbf{e}}_z\right]^n\left[\frac{2\pi}{\omega'}\right]^{1/2}\hat{\mathbf{e}}'_z\times\sum_{q,s}f_q^{(-)}\sum_{j=0}^{n}\langle u_-^{(j)}|p_z|u_+^{(n-j)}\rangle\ , \tag{2.73}$$

where $\omega'=n\omega$. The notation has been expanded to include spin states.

The previous equations were developed for the case in which we were interested in $u_+^{(n)}$. For $u_-^{(n)}$ we would simply replace ω by $-\omega$ and repeat the calculation. Thus we could write for $z>0$,

$$u_-^{(n)}=\sum_{j=1}^{n}A_j^{(-n)}\exp(iq_{-j}z)+c_n^{(-)}\exp(-\gamma z)\ . \tag{2.74}$$

For $z<0$,

$$u_-^{(n)}=\sum_{j=1}^{n}B_j^{(-n)}\exp(-ik_{-j}z)+d_n^{(-)}[\exp(ikz)+(-1)^n r\exp(-ikz)]\ , \tag{2.75}$$

where $C_n^{(-)}$, $A_j^{(-n)}$, q_{-j}, $d_n^{(-)}$, $B_j^{(-n)}$, and k_{-j} are calculated just like the corresponding quantities $C_n,\ldots,k_j$ except that ω is replaced by $-\omega$. The matrix element of Eq. (2.73) is

$$\langle u_-^{(j)}|p_z|u_+^{(n-j)}\rangle=\int_{-\infty}^{0}dz\left[d_j^{(-)*}[\exp(-ikz)+(-1)^j r^*\exp(ikz)]+\sum_{l=1}^{j}B_l^{(-j)*}\exp(ik^*_{-l}z)\right]\times\left[kd_{n-j}[\exp(ikz)-(-1)^{n-j}r\exp(-ikz)]-\sum_{l=1}^{n-j}B_l^{(n-j)}k_l\exp(-ik_lz)\right]+\int_0^{\infty}\left[c_j^{(-)*}\exp(-\gamma z)+\sum_{l=1}^{j}A_l^{(-j)*}\exp(-iq^*_{-l}z)\right]\left[ic_{n-j}\exp(-\gamma z)+\sum_{l=1}^{n-j}A_l^{(n-j)}q_l\exp(iq_lz)\right]\ . \tag{2.76}$$

The individual integrals are readily computed. Thus

$$\langle u_{-}^{(j)}|p_z|u_{+}^{(n-j)}\rangle=\sum_{m=1}^{8} I_m \ , \tag{2.77}$$

where

$$I_1=\frac{1}{2i}d_j^{(-)*}d_{n-j}[(-1)^{n-j}r+(-1)^j r^*] \ , \tag{2.78}$$

$$I_2=-id_j^{(-)*}\sum_{l=1}^{n-j}B_l^{(n-j)}k_l\left[\frac{1}{k+k_l}-(-1)^j\frac{r^*}{k-k_l}\right] \ , \tag{2.79}$$

$$I_3=-i\sum_{l=1}^{j}B_l^{(-j)*}kd_{n-j}\left[\frac{1}{k+k_{-l}^*}+\frac{(-1)^{n-j}r}{k-k_{-l}^*}\right] \ , \tag{2.80}$$

$$I_4=i\sum_{l=1}^{j}\sum_{l'=1}^{n-j}k_{l'}B_l^{(-j)*}B_{l'}^{(n-j)}\frac{1}{k_{-l}^*-k_{l'}} \ , \tag{2.81}$$

$$I_5=\frac{i}{2}C_j^{(-)*}C_{n-j} \ , \tag{2.82}$$

$$I_6=C_j^{(-)*}\sum_{l=1}^{n-j}q_l A_l^{(n-j)}\frac{1}{\gamma-iq_l} \ , \tag{2.83}$$

$$I_7=i\gamma\sum_{l=1}^{j}A_l^{(-j)*}C_{n-j}\frac{1}{\gamma+iq_{-l}^*} \ , \tag{2.84}$$

$$I_8=-i\sum_{l=1}^{j}\sum_{l'=1}^{n-j}q_{l'}A_l^{(-j)*}A_{l'}^{(n-j)}\frac{1}{q_{-l}^*-q_{l'}} \ . \tag{2.85}$$

There is also an L-dependent term

$$I'=kd_j^{(-)*}d_{n-j}L[1-(-1)^n|r|^2]$$

but this term sums to zero when summed over j.

In evaluating the matrix element the sum over spins gives a factor 2. Let S denote the term $\langle u_{-}^{(j)}|p_z|u_{+}^{(n-j)}\rangle$. Then

$$\sum_{sq}f_q^{(-)}\sum_{j=0}^{n}S=2\int\frac{d^3k}{(2\pi)^3}\Theta(k_f^2-k_{\parallel}^2-k_z^2)S \ . \tag{2.86}$$

The three-dimensional integral can be reduced to a one-dimensional integral by integrating out the parallel component. So the matrix element becomes

$$M^{(n)}=\left[\frac{A_0\hat{\mathbf{e}}_z}{2c}\right]^n\left[\frac{2\pi}{\omega'}\right]^{1/2}\hat{\mathbf{e}}_z'\frac{1}{4\pi^2}\times\int_0^{k_f}dk_z(k_f^2-k_z^2)\sum_{j=0}^{n}\langle u_{-}^{(j)}|p_z|u_{+}^{(n-j)}\rangle \ . \tag{2.87}$$

The scattering rate is

$$d\Gamma_n=2\pi\sum_{\mathbf{k}',\lambda}|M^{(n)}|^2\delta(\omega'-n\omega) \ . \tag{2.88}$$

Either the incident or outgoing photon may be polarized parallel to or perpendicular to the scattering plane. The four possibilities are depicted in Fig. 2. Since M is proportional to a power of $\hat{\mathbf{e}}_z$ it is clear that those states in which the incident polarization vector is perpendicular to the scattering plane will not contribute to the MHG signal. This rules out situations 1 and 2 in Fig. 2. Likewise, situation 3 will also not contribute because the matrix element also is proportional to $\hat{\mathbf{e}}_z'$. Only situation 4 will contribute and we may replace $\hat{\mathbf{e}}_z$ by $-\sin\theta$ and $\hat{\mathbf{e}}_z'$ by $-\sin\theta'$ giving us

$$d\Gamma_n=2\pi\int\frac{d\mathbf{k}'}{(2\pi)^3}\frac{1}{16\pi^4}\left[\frac{A_0}{2c}\right]^{2n}\times\sin^{2n}\theta\frac{2\pi}{n\omega}\sin^2\theta'\delta(\omega'-n\omega)\times\left[\int_0^{q_f}dq_z(q_f^2-q_z^2)\times\sum_{j=0}^{n}\langle u_{-}^{(j)}|p_z|u_{+}^{(n-j)}\rangle\right]^2 . \tag{2.89}$$

If the initial light beam is unpolarized then we must divide this expression by 2. If we introduce an element of solid angle, $d\Omega'$, and use the dispersion relation $\omega'=k'c$ we obtain

$$\frac{d^2\Gamma}{d\omega' d\Omega'}=\frac{1}{64\pi^5}\left[\frac{E_0}{2\omega}\right]^{2n}\frac{\omega'}{c^3}\sin^2\theta'\sin^{2n}\theta\delta(\omega'-n\omega)\times\left[\int_0^{q_f}dq_z(q_f^2-q_z^2)\sum_{j=0}^{n}\langle u_{-}^{(j)}|p_z|u_{+}^{(n-j)}\rangle\right]^2 , \tag{2.90}$$

where we have replaced the amplitude of the vector potential by the amplitude of the electric field using the re-

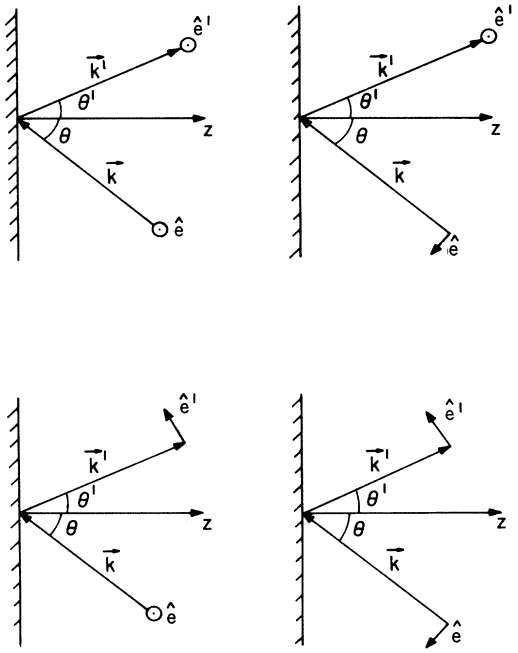

FIG. 2. The four states of polarization. The propagation vectors are denoted by $\mathbf{k}$ and $\mathbf{k}'$ and their respective polarization vectors by $\hat{\mathbf{e}}$ and $\hat{\mathbf{e}}'$.

lationship $E_0 = i\omega A_0/c$.

From the above expression it is clear that emission in directions nearly parallel to the surface are favored. The differential scattering cross section is

$$\frac{d^2\Gamma}{d\omega' d\Omega'} = \frac{\omega'}{c^3}\frac{1}{64\pi^5}\left[\frac{E_0}{2\omega}\right]^{2n}\sin^{2n}\theta\sin^2\theta'\delta(\omega'-n\omega) \times\left|\int_0^{k_f} dk_z(k_f^2-k_z^2) \times\sum_{j=0}^{n}\langle u_-^{(j)}|p_z|u_+^{(j)}\rangle\right|^2, \quad (2.91)$$

where $k_f=(2\varepsilon_f)^{1/2}$ and $E_z=k_z^2/2-V_0$ and $\phi+k_f^2/2=V_0$.

The total radiation emitted into the half space $0\le\theta'\le\pi/2$ is obtained by integrating over solid angles. The integration over ω' can be used to eliminate the delta function. Finally, dividing the rate by the incident flux provides us with a formula for the total scattering yield for MHG:

$$Y=\frac{n}{24\pi^3}\left[\frac{e^2}{\hbar c}\right]^4\left[\frac{eE_0\hbar}{2m\omega e^2}\right]^{2n-2}\sin^{2n}\theta T, \quad (2.92)$$

where

$$T=\left|\int_0^{k_f} dk_z(k_f^2-k_z^2)\sum_{j=0}^{n}\langle u_-^{(j)}|p_z|u_+^{(j)}\rangle\right|^2. \quad (2.93)$$

Note that the units have been restored.

B. Multiphoton electron emission

Multiphoton photoexcitation of a solid is the process in which n photons are absorbed and the electronic energy is elevated by $n\hbar\omega$. If the electronic energy is high enough to overcome the work function then photoemission can occur. We will refer to this latter process as multiphoton photoemission. The process results in a hole being created in some state $|q\rangle$ and the electron transferring to some excited state $|f\rangle$. Diagrams for the first-, second-, and third-order processes are shown in Figs. 3, 4, and 5, respectively. These diagrams show electrons and/or holes in the intermediate states.

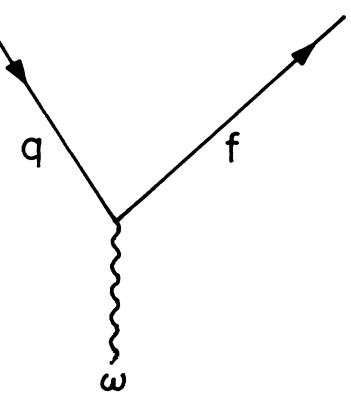

FIG. 3. First-order photoemission.

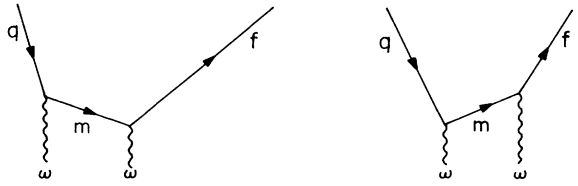

FIG. 4. Second-order photoemission.

The matrix element for the first-order process is

$$M^{(1)}=\frac{A_0\hat{\mathbf{e}}_z}{2c}\langle f|p_z|q\rangle = \frac{A_0\hat{\mathbf{e}}_z}{2c}\langle f|p_z|u_+^{(0)}\rangle . \quad (2.94)$$

For the second-order process it is

$$M^{(2)}=\left[\frac{A_0\hat{\mathbf{e}}_z}{2c}\right]^2\sum_m\frac{\langle f|p_z|m\rangle\langle m|p_z|q\rangle}{\omega+\varepsilon_q-\varepsilon_m} = \left[\frac{A_0\hat{\mathbf{e}}_z}{2c}\right]^2\langle f|p_z|u_+^{(1)}\rangle . \quad (2.95)$$

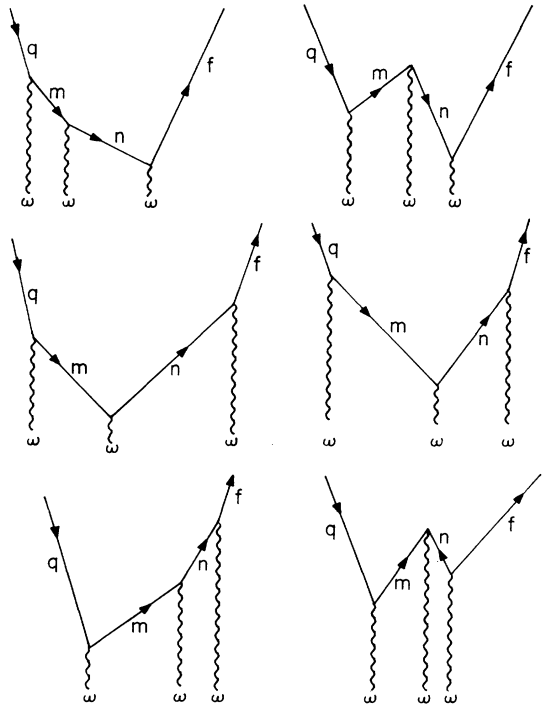

FIG. 5. Third-order photoemission.

For the third-order process it is

$$M^{(3)}=\left[\frac{A_0\hat{\mathbf{e}}_z}{2c}\right]^3\sum_{mn}\frac{\langle f|p_z|m\rangle\langle m|p_z|n\rangle\langle n|p_z|q\rangle}{(2\omega+\varepsilon_q-\varepsilon_m)(\omega+\varepsilon_q-\varepsilon_n)}$$
$$=\left[\frac{A_0\hat{\mathbf{e}}_z}{2c}\right]^3\langle f|p_z|u_+^{(2)}\rangle\ . \tag{2.96}$$

In deriving these concise formulas we have shown that the diagrams involving intermediate electrons and holes may be replaced by a single diagram in which all intermediate states are included.

The nth-order process results in the matrix element

$$\overline{M}^{(n')}=\left[\frac{A_0\hat{\mathbf{e}}_z}{2c}\right]^n\langle f|p_z|u_+^{(n-1)}\rangle(2\pi)^2\delta(\mathbf{q}'_\parallel-\mathbf{q}_\parallel)\ . \tag{2.97}$$

Here we have included the integration over transverse momentum states. The transition rate is obtained from Fermi's golden rule:

$$\Gamma^{(n)}=2\pi\sum_s\sum_{fq}|\overline{M}^{(n)}|^2\delta(\varepsilon_q+n\omega-\varepsilon_f)f_q^{(-)}f_f^{(+)}\ . \tag{2.98}$$

Here s denotes the electron spin projection. Since multiphoton excitation preserves spin projection there is only a single spin common to both the initial and final state. In the δ function ε_q and ε_f should actually refer to the total energy including the kinetic energy associated with motion parallel to the surface, $q_\parallel^2/2$ and $q_\parallel'^2/2$. However, since $\mathbf{q}_\parallel=\mathbf{q}'_\parallel$ this transverse kinetic energy cancels out and we may take ε_q and ε_f as the kinetic energy associated with z motion.

We now need to calculate the matrix element for the sharp step potential case. The matrix element for multiphoton emission is

$$M^{(n)}=\left[\frac{A_0\hat{\mathbf{e}}_z}{2c}\right]^n\langle f|p_z|u_+^{(n-1)}\rangle(2\pi)^2\delta(\mathbf{q}'_\parallel-\mathbf{q}_\parallel)\ , \tag{2.99}$$

where

$$\langle z|f\rangle=\begin{cases}(1+\rho)\exp(-ik_nz) & \text{if } z<0\\ \exp(iq_nz)+\rho\exp(-iq_nz) & \text{if } z>0\ .\end{cases} \tag{2.100}$$

The final state is chosen to be an "out state," i.e., a state which has a unit amplitude wave emerging from the solid into vacuum. The reflection amplitude for the time reversed state is

$$\rho=\frac{q_n+k_n}{q_n-k_n}\ . \tag{2.101}$$

Substituting the formula for $|u_+^{(n-1)}\rangle$ and evaluating the integral gives

$$\langle f|p_z|u_+^{(n-1)}\rangle=-i(1+\rho^*)kd_{n-1}\left[\frac{1}{k+k_n^*}-\frac{(-1)^nr}{k-k_n^*}\right]+i(1+\rho^*)\sum_{j=1}^{n-1}B_j^{(n-1)}\frac{k_j}{k_n^*-k_j}+\frac{i\gamma c_{n-1}}{\gamma+iq_n^*}$$
$$+i\sum_{j=1}^{n-1}A_j^{n-1}\frac{q_j}{q_j-q_n^*}+\frac{i\gamma\rho^*c_{n-1}}{\gamma-iq_n^*}+i\rho^*\sum_{j=1}^{n-1}A_j^{n-1}\frac{q_j}{q_j+q_n^*}\ . \tag{2.102}$$

According to Fermi's golden rule, the rate per unit area for the process in which n photons are absorbed and an electron in state $|q\rangle$ and a hole in state $|k\rangle$ are created is given by

$$\Gamma=2\pi\sum_{\mathbf{k},\mathbf{q},s}|M|^2[(2\pi)^2\delta(\mathbf{k}_\parallel-\mathbf{q}_\parallel)]\delta(\varepsilon_k+n\omega-\varepsilon_q)f_k^{(-)}$$
$$\times f_q^{(+)}\Theta(q_z)\ . \tag{2.103}$$

Since we are interested in those states producing electrons which leave the solid, we have included the factor $\Theta(q_z)$. We have also factored out $(2\pi)^2\delta(\mathbf{k}_\parallel-\mathbf{q}_\parallel)$ from the square of the matrix element corresponding to the conservation of transverse momentum. If we average over the polarization of the incident photon then only half the states contribute so we will include an additional factor of $\frac{1}{2}$. A factor of 2 comes from the summation over spins. Note that the factor $\Theta(q_z)$ forces $f_q^{(+)}$ to be 1. We may carry out the integral over transverse momenta and find

$$\int d^2k_\parallel f_k^{(-)}f_q^{(+)}\Theta(q_z)=\Theta(q_z)\pi(k_F^2-k_z^2)\Theta(k_F^2-k_z^2)\ . \tag{2.104}$$

Using the relations $\varepsilon_z=k_z^2/2-V_0$ and $\varepsilon'_z=q_z^2/2=\varepsilon_z+n\omega$, we get

$$\langle\Gamma\rangle_{\text{pol}}=\frac{1}{8\pi^2}\int_{-\infty}^{\infty}dk_z\int_0^{\infty}dq_z\delta\left[\frac{k_z^2}{2}-V_0+n\omega-\frac{q_z^2}{2}\right]$$
$$\times|M|^2(2\varepsilon_F+2V_0-k_z^2)$$
$$\times\Theta(2\varepsilon_F+2V_0-k_z^2)\ . \tag{2.105}$$

This can be rewritten as

$$\Gamma=\frac{1}{8\pi^2}\int_0^{k_F}dk_z\frac{|M|^2}{(k_z^2-2V_0+2n\omega)^{1/2}}(k_F^2-k_z^2)\ . \tag{2.106}$$

It has been assumed that the incident radiation is unpolarized so that only the part that is perpendicular to the surface contributes. Here we take for M the expression obtained previously,

$$M=\left[\frac{A_0}{2c}\sin\theta\right]^n\langle f|p_z|u_+^{(n-1)}\rangle\ . \tag{2.107}$$

Dividing the rate per unit area by the incident photon flux gives the yield. Restoring the units results in the

final formula

$$Y=\frac{me^6}{4\hbar^4\pi\omega c}\left[\frac{eE_0\hbar}{2m\omega e^2}\right]^{2n-2}\sin^{2n}\theta \times\int_0^{k_F}dk_z\frac{|\langle f|p_z|u_+^{(n-1)}\rangle|^2}{(k_z^2-2V_0+2n\omega)^{1/2}}(k_F^2-k_z^2)\ . \quad (2.108)$$

III. RESULTS AND DISCUSSION

In this paper we considered two nonlinear processes that occur at the surface of an idealized metal. One process is multiharmonic generation and the other is multiphoton electron emission. Expressions were derived for the yields of these processes when the metal is illuminated by an intense laser field. In this section we present the results of the calculation.

In Figs. 6 and 7 we show the yield Y, defined in the previous section, for first-, second-, third-, and fourth-harmonic generation as a function of laser frequency for the free-electron metals Na and K. We start with frequency $\omega=0.05$ a.u. and go up to $\omega=0.5$ a.u. Note that as the laser frequency is increased the yield decreases rapidly and monotonically. In these calculations we took the work functions for Na and K to be 2.35 and 2.22 eV, respectively, and the corresponding Fermi energies to be 3.24 and 2.12 eV, respectively. The magnitude of the yield is sensitive to the size of both of these parameters. Also in Figs. 6 and 7 we show the yield versus frequency for two different laser intensities. These intensities are related to a nonlinear parameter x which is defined by $x=eE_0\hbar/(2m\omega e^2)$. We see that when the nonlinear parameter x is smaller perturbation theory works well.

Let us estimate the numerical size of the expected MHG yield for the case in which the parameter $x=1.0$. For a 1.17-eV photon (YAG laser, 1.06 μm) which corresponds to an intensity of 2.62×10^{14} W/cm^2 this gives 8.868×10^{-12} for the second harmonic generation for Na. The third-harmonic and fourth-harmonic yields are found to be 1.247×10^{-11} and 6.316×10^{-10}, respectively. At these field strengths perturbation theory has probably already broken down, because the third-harmonic yield is larger than the second-harmonic yield and the fourth-harmonic yield is larger than the third-harmonic yield. At weaker field strengths, however, the third-harmonic signal will, of course fall more rapidly than the second harmonic. We can see this for $x=0.1$ (which corresponds to an intensity of 2.62×10^{12} W/cm^2) where the second-harmonic yield is 8.868×10^{-14} and the third-harmonic yield is 1.247×10^{-15} for Na.

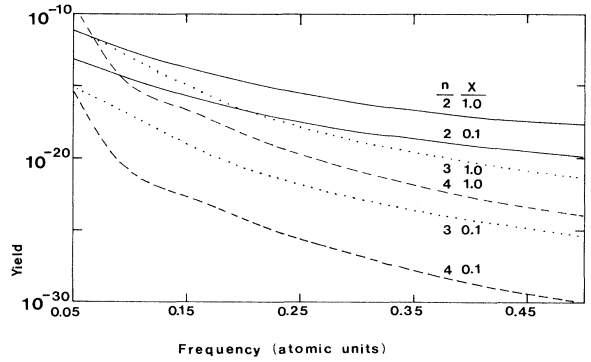

FIG. 6. Multiharmonic yield vs photon frequency from Na surface. Results are presented for two different laser intensities labeled by $x=0$ and $x=1$ (see text) and for the cases $n=2$, 3, and 4.

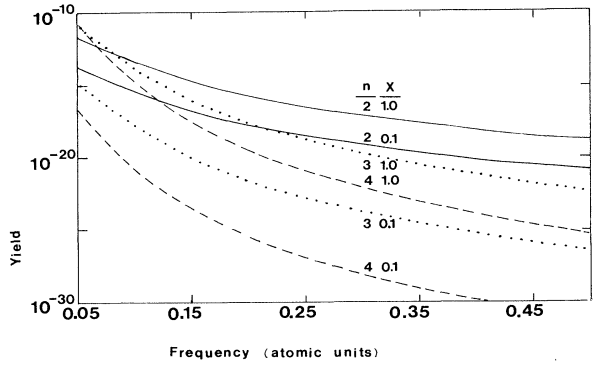

FIG. 7. Same as Fig. 6 but for K instead of Na.

In Figs. 8 and 9 we plot the nonlinear photoelectric yield versus photon frequency for Na and K for two different fields. Data are presented for several orders of MPEE. The curves plotted have an extra factor of 4π for the yield. One notes that the yield decreases with increasing frequency. We start with frequency $\omega=0.25$ a.u.and go up to 2.5 a.u. Estimated yield for K for the two photon case is 6.816×10^{-4} when the electric field is 1.63×10^{15} W/cm^2 (corresponding to $x=0.5$) and the incident frequency is 0.215 a.u. which is 5.848 eV. Frequency is in the ultraviolet region. When the intensity is 1.63×10^{13} W/cm^2 (corresponding to $x=0.05$) the yield is 6.816×10^{-6}.

In all these calculations we have taken the angle of incidence to be $\pi/2$. We notice that the MPEE yield is much greater (of the order of 10^9) than the MHG yield.

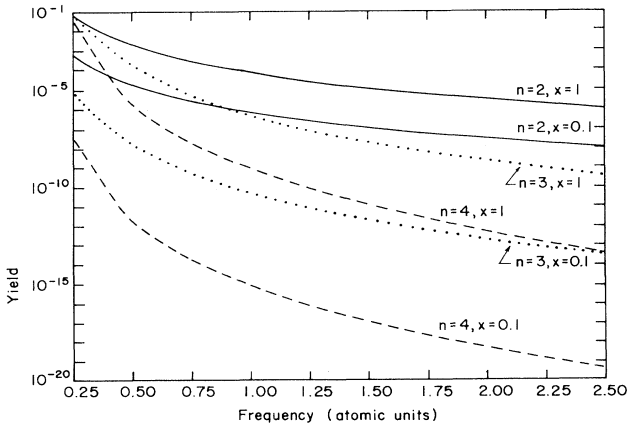

FIG. 8. Multiphoton electron emission yield vs photon frequency from a Na surface for two different laser intensities (see text). Results are presented for the cases $n=2$, 3, and 4.

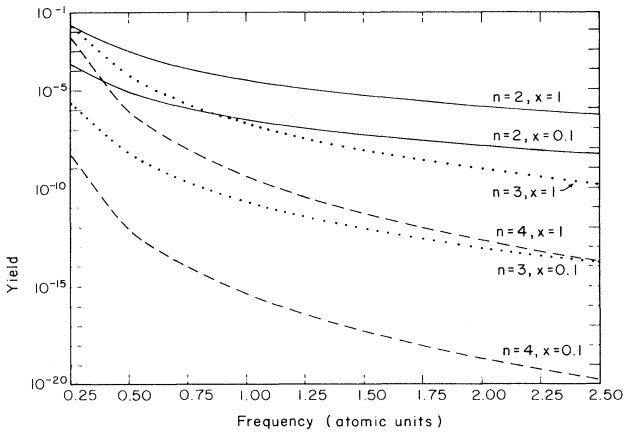

FIG. 9. Same as Fig. 8 but for K instead of Na.

This may be attributed to the greater availability of states for MPEE than that available for MHG.

We have also studied the dependence of the MHG yield and the MPEE yield as a function of the Fermi energy and the work function parameters. We notice that the MHG yield is essentially a function of the Fermi energy and not the work function and it decreases as the Fermi energy decreases. The reasons for this behavior is simple. As the Fermi energy is increased, the number of electrons that contribute to the nonlinear response of the system increases and so the yield also increases. Since it is not necessary for the electron to leave the solid in the case of MHG the work function plays only a minor role in determining the size of the yield.

In the MPEE case we have found that the yield is a function of both the fermi energy and the work function. It decreases when the Fermi energy decreases and increases when the work function decreases. This is reasonable because in the case of MPEE, the electron gets excited before leaving the surface. Again a decrease in the Fermi energy implies a reduced number of active electrons and hence an increased yield. On the other hand, a decreased work function means both that more electrons from the Fermi sea may be photoionized as well as a weakening of the binding to the solid.

The frequency of the laser beam also plays a major role in determining the magnitude of the yield. Notice that for lower frequencies there is no MPEE yield because the frequency is simply not large enough for the electron to cross the photoemission threshold. At high frequencies, the matrix elements become small due to the presence of the energy denominators.

In principle it should be possible to get multiphoton electron emission from a thermal process as well as from the direct quantum process considered here. For example, in the theory of thermionic emission it is the tail of the Fermi distribution that extends above the vacuum level that is responsible for the emitted electrons. The energy distribution is approximately Maxwellian since it is the high-energy tail of a Fermi distribution. If an intense radiation field impinges on a solid the temperature of the surface could become very high and this could broaden the tail of the distribution considerably. One would expect the temperature to be related to the energy fluence of the pulse. One may distinguish the thermal process from the quantum process discussed here by shortening the duration of the pulse while maintaining the same fluence. This will drive the peak strength of the electron field up and thereby accentuate the higher-order nonlinear processes. Electrons would be emitted after having absorbed two, three, or more photons. Thus we should find that the electrons would start to be emitted with a nonthermal distribution.

In this analysis we have completely disregarded the effect of surface roughness in determining the yields. For rough surfaces enhancement of the local fields can have an extraordinarily large effect on higher-order multiphoton process. However, our results for the smooth step derived in this paper may be combined with a knowledge of surface field enhancement factors to allow one to extend the present theory to such problems.

[1]J. G. Fujimoto, E. P. Ippen, J. M. Liu, N. Bloembergen, in *Ultrafast Phenomena IV,* Vol. 38 of *Springer Series in Chemical Physics,* edited by D. H. Auston and K. B. Eisenthal (Springer-Verlag, Berlin, 1984), p. 13.

[2]K. L. Vodopyanov, L. A. Kulevskii, C. Toth, Gyozo Farkas, and Gyorgy Zoltan Horvath, Izv. Akad. Nauk SSSR, Ser. Fiz. **53** (3), 557 (1989).

[3]Gail A. Massey, Michael D. Jones, and Joel C. Johnson, IEEE J. Quantum Electron. **QE-17** (6) 1035 (1981).

[4]M. Bensoussan and J. M. Moison, Physica B+C **118** (1), 117 (1983).

[5]A. M. Weiner, P. S. D. Lin, and R. B. Markus, Appl. Phys. Lett. **51** (5), 368 (1987).

[6]H. B. Nielsen, J. Reif, E. Mathias, E. Westin, in *Laser Spectroscopy,* Vol. 55 of *Springer Series in Optical Science,* edited by S. Svanberg and W. Persson (Springer-Verlag, Berlin, 1987).

[7]E. Mathias, H. B. Nielsen, J. Reif, A. Rosen, and E. Westin, J. Vac. Sci. Technol. B **5** (5), 1415 (1987).

[8]J. Reif, H. B. Nielsen, O. Semmler, E. Mathias, E. Westlin, and A. Rosen, Phys. Scr. **35** (4), 532 (1987).

[9]Gail A. Massey, Steven H. Bowersox, Saeid Ghamaty, and Ali Rahbar, IEEE J. Quantum Electron. **QE-23** (12), 2054 (1987).

[10]Gy. Farkas (unpublished).

[11]E. S. Friedkin and V. A. Kovarskii, Phys. Status Solidi B **60** (2), 605 (1973).

[12]V. A. Arutyunyan, S. L. Arutyunyan, and Kh. D. Topchyan, Izv. Akad. Nauk Arm. SSR, Fiz. **18** (2), 97 (1983).

[13]K. Giesen, F. Hage, H. J. Reiss, W. Steinmann, R. Haight, R. Beigang, R. Dreyfus, P. Avouris, and F. J. Himpsel, Phys. Scr. **35** (4), 578 (1987).

[14]He Kexiang, Ph.D. thesis, Rensselaer Polytechnic Institute, 1987, available from University Microfilms.

[15]R. Murphy, M. Yeganeh, K. J. Song, and E. W. Plummer, Phys. Rev. Lett. **63** (3), 318 (1989).

[16]E. A. Stern, Report No. 717761 (unpublished).

[17]G. Berkovic, Y. R. Shen, and P. N. Prasad, J. Chem. Phys. **87** (3), 1897 (1987).

[18]E. Adler, Phys. Rev. **134**, A728 (1964).

[19]S. S. Jha, Phys. Rev. Lett. **15**, 412 (1965); Phys. Rev. **140**, A2020 (1965); **145**, 500 (1966).
[20]N. Bloembergen, R. K. Chang, S. S. Jha, and C. H. Lee, Phys. Rev. **174**, 813 (1968).
[21]J. Rudnick and E. A. Stern, Phys. Rev. B **4**, 4272 (1971).
[22]J. E. Sipe and G. I. Stegeman, *Surface Polaritons,* edited by V. M. Agranovich and D. J. Mills (North-Holland, New York, 1982).
[23]M. Corvi and W. L. Schaich, Phys. Rev. B **33**, 3688 (1986).
[24]G. S. Agarwal and S. S. Jha, Solid State Commun. **41**, 499 (1982).
[25]J. C. Quail and H. J. Simon, Phys. Rev. B **31**, 4900 (1985).
[26]H. Sonnenberg, Can. J. Phys. **45** (12), 4122 (1967).
[27]J. M. Chen, J. R. Bower, and C. S. Wang, in Proceedings of the 2nd International Conference on Solid Surfaces, edited by Hiroo Kumagai and Tomiyuki Toya [Jpn. J. Appl. Phys. Suppl. **13**, 711 (1974)].
[28]J. E. Sipe, V. C. Y. So, M. Fukui, and G. I. Stegeman, Phys. Rev. B **21**, 4389 (1980).
[29]J. E. Sipe, V. C. Y. So, M. Fukui, and G. I. Stegeman, Solid State Commun. **34** (7), 523 (1980).
[30]H. J. Simon, D. E. Mitchell, and J. G. Watson, Opt. Commun. **13** (3), 294 (1975).
[31]D. L. Mills, Solid State Commun. **24** (9), 669 (1977).
[32]C. K. Chen, Report No. LBL-12084 (unpublished).
[33]G. S. Agarwal and S. S. Jha, Phys. Rev. B **26**, 482 (1982).
[34]C. K. Chen, T. F. Heinz, D. Richard, and Y. R. Shen, Phys. Rev. B **27**, 1965 (1983).
[35]K. Arya, Phys. Rev. B **29**, 4451 (1984).
[36]G. T. Boyd, Th. Rasing, J. R. R. Leite, and Y. R. Shen, Phys. Rev. B **30**, 519 (1984).
[37]O. Keller, Phys. Rev. B **31**, 5028 (1985).
[38]Y. R. Shen, J. Vac. Sci. Technol. B **3**, 1464 (1985).
[39]H. W. K. Tom, C. M. Mate, X. D. Zhu, J. E. Crowell, Y. R. Shen, and G. Somorjai, Surf. Sci. **172**, 466 (1986).
[40]T. F. Heinz, M. M. Loy, and W. A. Thompson, Phys. Rev. Lett. **54**, 63 (1985).
[41]D. Heskett, K. J. Song, A. Burns, E. W. Plummer, and H. L. Dai, J. Chem. Phys. **85**, 7490 (1986).
[42]J. C. Hamilton and R. J. Anderson, Thin Solid Films, **166**, 345 (1988).
[43]John R. Bower, Phy. Rev. B **14**, 2427 (1976).
[44]B. N. J. Persson and L. H. Dubois, Phys. Rev. B **39**, 8220 (1989).
[45]A. Leibsch, Phy. Rev. Lett. **61**, 1233 (1988).
[46]K. J. Song, S. Heskett, H. L. Dai, A. Leibsch, and E. W. Plummer, Phys. Rev. Lett. **61**, 1380 (1988).