# Higher-harmonic generation from a metal surface in a powerful laser field

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We investigate the generation of higher harmonics from a metal surface in a powerful laser field. The metal is described by the Sommerfeld free-electron model. Solving the Schrödinger equation of the problem perturbatively in the Kramers-Henneberger frame, a simple expression for the harmonic production can be derived and evaluated numerically. Good agreement for the calculated harmonic-generation rates for a gold surface is found if compared with recent experimental data of Farkas *et al.* [Phys. Rev. A **46**, R3605 (1992)].

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During the past few years many experimental and theoretical papers have appeared on the generation of higher harmonics by an atomic system in a powerful laser field. Summaries of this research can be found in the book by Gavrila [1] and in the reviews by Eberly, Javanainen, and Rzążewski [2], Mainfray and Manus [3], L'Huillier, Schafer, and Kulander [4], and Burnett, Reed, and Knight [5]. On the other hand, very little is known on the generation of higher harmonics by a metal surface irradiated by a powerful laser field. Earlier work has been mainly concerned with the production of the second harmonic at moderate field intensities where perturbation theory applies [6–9]. In these investigations the coherent multielectron effects on the metal surface have been properly taken into account and satisfactory agreement between theory and experiment concerning the absolute rate of second-harmonic production has been obtained. Moreover, it has been found that the maximum efficiency of harmonic generation has to be expected if the laser-light polarization is perpendicular to the metal surface, and a similar result holds for the polarization of the harmonic light. Hence grazing laser-field incidence on the polished metal surface and picosecond laser pulses should be chosen to have maximum harmonic-production efficiency on the one hand and suppression of plasma formation on the metal surface on the other [7,10].

Only a few years ago, theoretical work was reported by Sacks and Szöke [11] on the generation of harmonics during electron scattering from a piecewise-constant potential in an intense electromagnetic field, and Mishra and Gersten [12,13] investigated the multiharmonic generation and multiphoton electron emission at a metal surface. In this latter work the metal is described by the Sommerfeld free-electron model, in which the Fermi gas of free electrons is bound to a square-well potential [14].

In their work, Mishra and Gersten evaluated the rates of higher-harmonic production for arbitrary order of perturbation theory. Although the results of such single-electron calculations cannot be directly compared with the experimental data since they do not take into account the collective electron effects on the metal surface, they nevertheless can be used to get some information on the relative harmonic production rates.

In a recent paper by Farkas *et al.* [15], multiple-harmonic radiation from a gold surface has been observed, induced by picosecond Nd:YAG (neodymium-doped yttrium-aluminum-garnet) laser pulses. Under grazing incidence the laser pulses had a power of 2 $\mathrm{GW\,cm^{-2}}$ on the metal surface and for the first time generation of coherent beams of even and odd harmonics up to the fifth order in the reflected direction with efficiencies $10^{-10}$–$10^{-13}$ has been measured. In these measurements the decrease of the harmonic efficiencies with increasing harmonic order turned out to be much weaker than predicted by the theory of Mishra and Gersten [12,13]. The harmonic rates evaluated from their theory are much too low by many orders of magnitude.

Using an integral-equation approach, we have derived [16] a simple expression for the transition amplitudes of harmonic production in a laser field by any system describable by a potential $V(\mathbf{x})$. Here we shall apply this method to the generation of harmonics from a metal surface, approximating the metal by Sommerfeld's model of a free-electron gas in a potential well of depth $-V_0$ [14], which should apply reasonably well to the description of the electronic properties of gold. Using the laser and gold parameters of Farkas *et al.* [15], our theoretical predictions of the relative harmonic-generation rates are in good agreement with the experimental data.

First we shall present a simple derivation of the transition matrix elements of harmonic production. Neglecting effects which only contribute to the scattering of the fundamental laser frequency from the metal surface, the Schrödinger equation of our problem reads in the Kramers-Henneberger frame [17,18]

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$$[\hat{H}_0+V_{\alpha,\alpha'}]|\Psi(t)\rangle=i\hbar\partial_t|\Psi(t)\rangle\ , \tag{1}$$

where $\hat{H}_0=\hat{\mathbf{p}}^2/2m+V(\mathbf{x})$ is the Hamiltonian in the absence of the laser field and $V_{\alpha,\alpha'}=V[\mathbf{x}+\boldsymbol{\alpha}(t)+\boldsymbol{\alpha}'(t)]-V(\mathbf{x})$ describes the interaction with the laser field $\boldsymbol{\alpha}(t)$ and the spontaneously emitted field $\boldsymbol{\alpha}'(t)$ (the latter in quasiclassical terms). Since we are only interested in the spontaneous emission of a single photon, we may use the approximation [16]

$$V_{\alpha,\alpha'}\approx\boldsymbol{\alpha}'(t)\cdot\nabla V[\mathbf{x}+\boldsymbol{\alpha}(t)] \tag{2}$$

with

$$\boldsymbol{\alpha}'(t)=\alpha_0'\boldsymbol{\varepsilon}'\sin\omega' t\ ,\quad \alpha_0'=eF_0'/m(\omega')^2\ ,\quad F_0'=2(2\pi\hbar\omega'/L^3)^{1/2}\ , \tag{3a}$$

$$\boldsymbol{\alpha}(t)=\alpha_0\boldsymbol{\varepsilon}\sin\omega t\ ,\quad \alpha_0=eF_0/m\omega^2\ . \tag{3b}$$

Expanding $|\Psi(t)\rangle$ in (1) into eigenstates of $\hat{H}_0$,

$$|\Psi(t)\rangle=\sum_\nu c_\nu(t)|\nu\rangle\exp(-iE_\nu t/\hbar)\ , \tag{4a}$$

we obtained by inserting this into (1) and by projecting on $\langle\mu|\exp(iE_\mu t/\hbar)$ and by denoting $E_\mu-E_\nu=\hbar\omega_{\mu\nu}$,

$$\dot{c}_\mu(t)=-(i/\hbar)\sum_\nu c_\nu(t)\langle\mu|\boldsymbol{\alpha}'(t)\cdot\nabla V[\mathbf{x}+\boldsymbol{\alpha}(t)]|\nu\rangle\times\exp(i\omega_{\mu\nu}t)\ . \tag{4b}$$

In lowest order of perturbation theory we take $c_\nu^{(0)}(t\to-\infty)=\delta_{\nu,i}$, where $|i\rangle$ is the initial state of the system. Hence we find from (4b) for transitions to the final state $\langle f|$,

$$c_{\rm fi}^{(1)}(t\to+\infty)=-(i/\hbar)\int_{-\infty}^{+\infty}\langle f|\boldsymbol{\alpha}'(t)\cdot\nabla V[\mathbf{x}+\boldsymbol{\alpha}(t)]|i\rangle\times\exp(i\omega_{\rm fi}t)dt\ . \tag{5}$$

Expanding here the laser-dressed potential into a Fourier series,

$$V[\mathbf{x}+\boldsymbol{\alpha}(t)]=\sum_n V_n(\mathbf{x})\exp(-in\omega t)\ , \tag{6}$$

we obtain from (5) by means of (3a) the transition matrix elements

$$T_{\rm fi}=\sum_n T_n\ ,\quad T_n=-2\pi i\delta(E_f+\hbar\omega'-E_i-n\hbar\omega)(\alpha_0'/2i)\times\langle f|\boldsymbol{\varepsilon}'\cdot\nabla V_n(\mathbf{x})|i\rangle\ . \tag{7}$$

In our particular problem $|i\rangle$ and $|f\rangle$ will essentially be free-electron states $|\mathbf{k}\rangle$ and $|\mathbf{k}'\rangle$, denoted by their wave vectors $\mathbf{k}$ and $\mathbf{k}'$, respectively. Their corresponding energies will be $E=(\hbar k)^2/2m$ and $E'=(\hbar k')^2/2m$. Farkas *et al.* [15] have chosen in their experiment grazing incidence of the laser beam and the polarization $\boldsymbol{\varepsilon}$ was essentially perpendicular to the metal surface. Hence we take the metal surface located in the $(x,y)$ plane and $\boldsymbol{\varepsilon}=\mathbf{e}_z$. With this choice the potential step near the metal surface can be described by

$$V(z)=V_0[\theta(z)-1]\ ,\quad \nabla_z V(z)=V_0\delta(z)\ ,\quad \nabla_z V_n(z)=(-i)^n(V_0/\pi\alpha_0)\times[1-(z/\alpha_0)^2]^{-1/2}T_n(z/\alpha_0)\ , \tag{8}$$

where $\theta(z)$ and $\delta(z)$ are the step function and $\delta$ function, respectively, and the $T_n(z/\alpha_0)$ are Chebyshev polynomials of the first kind [19] yielding essential contributions for $|z|<\alpha_0$, consequently only for a thin layer along the metal surface. Moreover, the properly matched solutions of the Schrödinger equation $\hat{H}_0|\mathbf{k}\rangle=E_\mathbf{k}|\mathbf{k}\rangle$ near the metal boundary, which is assumed to be infinitely extended in the $(x,y)$ plane, are found to be

$$\Psi_\mathbf{k}(\mathbf{x})=\langle\mathbf{x}|\mathbf{k}\rangle=L^{-3/2}\exp(i\mathbf{k}_\parallel\cdot\mathbf{x}_\parallel)\times\begin{cases}\exp(ik_zz)+\dfrac{k_z-i(2mV_0/\hbar^2-k_z^2)^{1/2}}{k_z+i(2mV_0/\hbar^2-k_z^2)^{1/2}}\exp(-ik_zz)\ , & z<0\\ 2k_z[k_z+i(2mV_0/\hbar^2-k_z^2)^{1/2}]^{-1/2}\exp[-(2mV_0/\hbar^2-k_z^2)^{1/2}z]\ , & z>0\ .\end{cases} \tag{9}$$

By means of (8) and (9) the transition probabilities per unit time obtained from (7) will read

$$W_n/\tau=(2\pi/\hbar)\delta(E'+\hbar\omega'-E-n\hbar\omega)\times(\alpha_0'\varepsilon_z')^2|\langle\mathbf{k}'|\nabla_zV_n|\mathbf{k}\rangle|^2\ , \tag{10}$$

where $\varepsilon_z'=\boldsymbol{\varepsilon}'\cdot\boldsymbol{\varepsilon}=\boldsymbol{\varepsilon}'\cdot\mathbf{e}_z$ is the $\mathbf{z}$ component of the polarization of the emitted harmonics. Moreover, it is convenient to write $E=E_z+E_\parallel$ and $E'=E_z'+E_\parallel'$ by decomposing $\mathbf{k}=\mathbf{k}_z+\mathbf{k}_\parallel$ and $\mathbf{k}'=\mathbf{k}_z'+\mathbf{k}_\parallel'$.

For evaluating the total transition probability per unit time it is first of all necessary to sum $W_n/\tau$ over the initial and final wave vectors $\mathbf{k}$ and $\mathbf{k}'$ of the electron, respectively, after having multiplied (10) with the appropriate statistical weight factors $2f(\mathbf{k})$ and $2[1-f(\mathbf{k}')]$, where

$$f(\mathbf{k})=\{\exp[(\hbar^2k^2/2m-E_F)/k_BT]-1\}^{-1}$$

is the Fermi distribution at temperature $T$. The factor 2 stands for the two degenerate spin states of the electron. We thus take care of the fact that in the Fermi gas the initial state of the electron has to be occupied and the final state must be free. Moreover, we have to sum $W_n/\tau$ over the wave vectors $\boldsymbol{\kappa}$ of the outgoing harmonic photons. In this way we can evaluate from (10) the total transition probabilities $w_n$ per unit time and unit surface element of the metal

$$w_n = L^{-2} \sum_{\kappa} \sum_{\mathbf{k}'} \sum_{\mathbf{k}} 2[1-f(\mathbf{k}')]2f(\mathbf{k}) W_n / \tau \ . \tag{11}$$

If we replace the summations in (11) by integrations in the usual manner, all these integrations can be performed analytically, in particular, if we assume that $E_{\parallel}/kT \ll 1$, so that electrons moving almost perpendicular to the metal surface couple most effectively to the laser field. In this case the integrations over $E_{\parallel}$ and $E_z$ can be carried out separately and the integration over $E_z$ can be simplified by using the approximation

$$[1-f(E_z+\Delta E_n)]f(E_z) \simeq 4k_B T \delta(E_z - E_F) \frac{\exp(\Delta E_n / k_B T)}{[\exp(\Delta E_n / k_B T)+1]^2} \ , \tag{12}$$

where $\Delta E_n = n\hbar\omega - \hbar\omega'$. Thus we finally obtain from (9)–(12) for the differential probability densities for the $n$th-order harmonic production

$$\frac{d^2 w_n}{d\omega' \, d\Omega'} = (\varepsilon' \cdot \varepsilon)^2 (e^2/\hbar c)(V_0^2 / 2mc^2 \hbar\omega') \pi^{-6} (m/\hbar) \times [(k_B T)^2 / E_F] \times \{\exp(\Delta E_n / k_B T)[\exp(\Delta E_n / k_B T)+1]^{-2}\} \times |t_n(k_F)|^2 \ , \tag{13a}$$

where $k_F = (2mE_F)^{1/2}/\hbar$ is the Fermi wave number and

$$t_n(k_F) = \alpha_0^{-1} \int_{-\alpha_0}^{\alpha_0} dz \, \Psi^*_{\mathbf{k}'_z}(z) T_n(z/\alpha_0) \times [1-(z/\alpha_0)^2]^{-1/2} \Psi_{\mathbf{k}_F}(z) \ , \tag{13b}$$

with $\Psi^*_{\mathbf{k}'_z}(z)$ being the unrenormalized, $z$-dependent part of $\langle \mathbf{x} | \mathbf{k}' \rangle$ in (9) and $\mathbf{k}'_z$ follows from $E'_z = E_F + \Delta E_n$. Finally, the total spectral density of the production rate of higher harmonics is then given by the sum

$$\frac{d^2 w}{d\omega' \, d\Omega'} = \sum_n \frac{d^2 w_n}{d\omega' \, d\Omega'} \tag{14}$$

which, owing to the exponential factors in (13b), yields a sequence of peaks centered at the values $\omega' = n\omega$ with the maximum values proportional to $|t_n(k_F)|^2$. The widths of these harmonic peaks will be of the order of magnitude $4k_B T \simeq 0.1$ eV at room temperature ($T \simeq 300$ °K).

For the gold target considered by Farkas *et al.* [15], the Fermi energy $E_F = 5.51$ eV, the work function $W = 4.6792$ eV, and hence the potential depth $V_0 = 10.1892$ eV. Furthermore, the Nd:YAG laser ($\hbar\omega = 1.17$ eV) had a peak intensity of $2 \times 10^9$ W cm$^{-2}$ at the metal surface. For these parameters we evaluated from (13a), (13b), and (14) the relative peak spectral densities $I(n)/I(2)$ as a function of the harmonic order $n = 2, 3, \ldots, 6$ on a logarithmic scale and the normalized spectral densities $I(\omega'/\omega)/I(2)$ for $n = 2, 3$. Both results are depicted in Figs. 1(a) and 1(b), respectively. Despite the simplicity of our model, surprisingly good agreement between theory and experiment is found, where the squares in Fig. 1(a) represent the experimental data taken from Table I of Ref. [15]. The remaining discrepancies between the theoretical and experimental data, in particular for $n = 4$, are very likely due to the fact that our model only describes direct transitions whereas the possible contributions of near-resonance interband transitions are ignored. If the rule, found by Krause, Schafer, and Kulander [20], according to which the maximum harmonic frequency should be determined by $\hbar\omega'_{\max} \simeq I + 3U_p$ ($I$ is ionization energy, $U_p$ is ponderomotive energy), also applies to our present problem, then for the above parameters of laser intensity and work function we would expect no harmonics above the fifth, as seems to be confirmed by the experiment of Farkas *et al.*

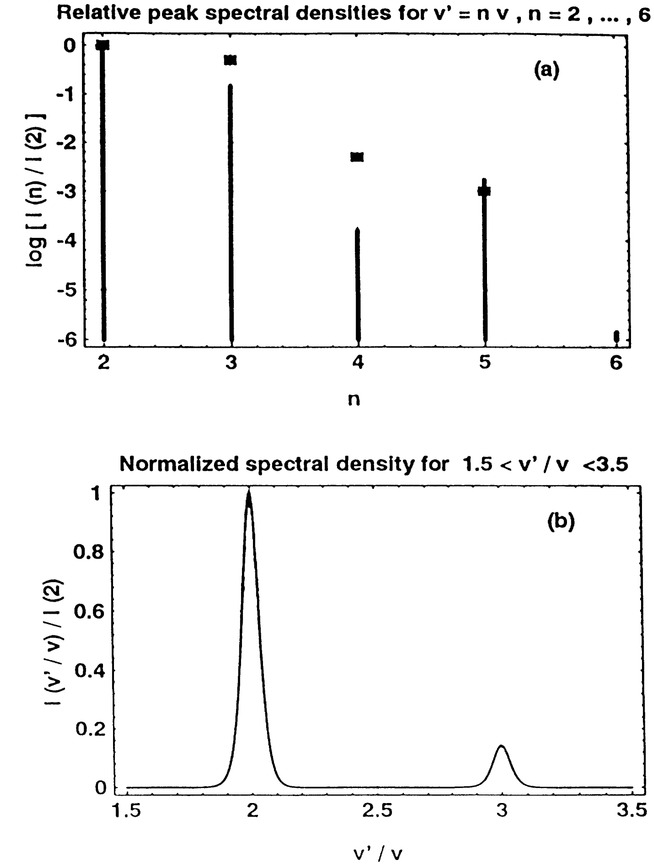


FIG. 1. In (a) we show the relative peak spectral densities $I(n)/I(2)$ on a logarithmic scale ($\log_{10}$) for $\omega' = n\omega$, $n = 2, \ldots, 6$, evaluated from (13a), (13b), and (14) for the parameters of the experiment by Farkas *et al.* [15]. The small squares indicate the corresponding values of the above experiment. (b) represents the normalized spectral density $I(\omega'/\omega)/I(2)$ in the parameter range $1.5 < \omega'/\omega < 3.5$. The width of these spectral lines is of the order of magnitude $4k_B T \simeq 0.1$ eV for $T \simeq 300$ K.

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[1] *Atoms in Intense Laser Fields,* edited by M. Gavrila (Academic, New York, 1992).

[2] J. H. Eberly, J. Javanainen, and K. Rzążewski, Phys. Rep. **204**, 331 (1991).

[3] G. Mainfray and C. Manus, Rep. Prog. Phys. **54**, 1333 (1991).

[4] A. L'Huillier, K. S. Schafer, and K. C. Kulander, J. Phys. B **24**, 3315 (1991).

[5] K. Burnett, V. C. Reed, and P. L. Knight, J. Phys. B **26**, 561 (1993).

[6] N. Bloembergen, R. K. Chang, S. S. Jha, and C. H. Lee, Phys. Rev. **174**, 813 (1968).

[7] S. S. Jha, Phys. Rev. **145**, 500 (1966); Phys. Rev. A **140**, 2020 (1965).

[8] Y. R. Shen, *The Principles of Nonlinear Optics* (Wiley, New York, 1984), p. 479 and references therein.

[9] L. E. Urbach, K. L. Percival, J. M. Hicks, E. W. Plummer, and H. L. Dai, Phys. Rev. B **45**, 3769 (1992).

[10] Gy. Farkas, S. L. Chin, P. Galarneau, and F. Yergeau, Opt. Commun. **48**, 275 (1983).

[11] R. A. Sacks and A. Szöke, J. Opt. Soc. Am. B **8**, 1987 (1991).

[12] A. Mishra and J. I. Gersten, Phys. Rev. B **43**, 1883 (1991).

[13] A. Mishra and J. I. Gersten, Phys. Rev. B **45**, 8665 (1992).

[14] A. Sommerfeld, Z. Phys. **47**, 1 (1928).

[15] Gy. Farkas, Cs. Tóth, S. D. Moustaizis, N. A. Papadogiannis, and C. Fotakis, Phys. Rev. A **46**, R3605 (1992).

[16] S. Varró and F. Ehlotzky, Can. J. Phys. **71**, 340 (1993).

[17] H. A. Kramers, *Collected Scientific Papers* (North-Holland, Amsterdam, 1956).

[18] W. C. Henneberger, Phys. Rev. Lett. **21**, 838 (1968).

[19] I. S. Gradshteyn and I. M. Ryzhik, *Tables of Integrals, Series and Products* (Academic, New York, 1980).

[20] J. L. Krause, K. J. Schafer, and K. C. Kulander, Phys. Rev. Lett. **68**, 3535 (1993).