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High-harmonic generation in hydrogenic ions

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We have calculated the frequency-dependent nonlinear susceptibilities of hydrogenic ions up to the 70th order of nonlinearity, in the framework of lowest-order perturbation theory. In this approximation, the critical driving intensity, at which the radiated harmonic intensity of the $(n+2)$th order exceeds that of the nth order, is found to decrease rapidly with n. The computed values of critical intensity are comparable to those at which "plateau" behavior is observed in recent experiments.

Generation of low harmonics of laser radiation in gases is a well-studied problem,[1] which to the present has been successfully described in terms of the atomic nonlinear susceptibilities computed by lowest-order perturbation theory (LOPT).

Recent experiments[2,3] on harmonic generation by noble gases irradiated at intensities of $\sim 10^{13}$ W/cm^2 have shown the presence of harmonic radiation up to $\sim$33rd order. Although the quantitative calculations of nonlinear susceptibilities at such high order have not previously been reported, the general expectation is that if perturbation theory provides a correct description of the process, then the observed harmonic intensity should decrease with increasing order, in the absence of resonances. In fact, the experimental data shows that, independent of the specific species, the radiated harmonic intensity shows no monotonic decrease over a range of high orders (roughly $7 < n < 19$), beyond which it falls off rapidly.

In this paper we present results of calculations of nth-order susceptibilities of hydrogenic ions, for n up to $\sim$45, within the framework of LOPT. This means that only the lowest-order nonvanishing terms in the perturbation expansion are taken into account, i.e., nth-harmonic generation is described by the absorption of exactly n photons of the fundamental frequency (higher-order processes involve additional absorption and emission). To the best of our knowledge, these computations provide the first concrete LOPT predictions of very-high-order harmonic-generation processes. With these results, we address the following questions: (1) What is the critical incident laser intensity beyond which LOPT is no longer a valid approximation? (2) What do these results imply about the convergence of higher-order perturbation theory?

The nth-order susceptibility (in a.u.) of an atom in the state $|g\rangle$ has the following general expression:

$$\chi_n(\omega)=\sum_{k=1}^{n+1}\sum_{i_1,i_2,\ldots,i_n}\frac{d_{gi_1}d_{i_1i_2}\cdots d_{i_{n-1}i_n}d_{i_ng}}{(\omega_{i_1g}-s_{k1}\omega)(\omega_{i_2g}-s_{k2}\omega)\cdots(\omega_{i_ng}-s_{kn}\omega)}, \tag{1a}$$

where d_{jk} is the dipole matrix element between atomic states j,k; ω_{jk} is their energy difference $\epsilon_j-\epsilon_k$, and

$$s_{k1}=\begin{cases}1, & \text{for } k\neq 1,\\ -n, & \text{for } k=1,\end{cases}\qquad s_{kj}=\begin{cases}s_{kj-1}+1, & \text{for } j\neq k,\\ s_{kj-1}-n, & \text{for } j=k.\end{cases} \tag{1b}$$

The first sum in Eq. (1a) runs over the $n+1$ "pathways," i.e., the $n+1$ distinguishable sequences of absorption of n photons of the fundamental frequency ω and emission of one photon at the harmonic frequency $n\omega$. The definition of parameter s_{kj} gives the appropriate energy denominators for each pathway. The internal sums in Eq. (1a) run over the (discrete and continuous) spectrum of the atom. The contribution from the kth pathway can be calculated implicitly by writing $\chi_n^{(k)} = \langle g | d | \phi_n^{(k)} \rangle$, where $\phi_n^{(k)}$ satisfies the inhomogeneous equation

$$(H - \epsilon_g - s_{kn}\omega) | \phi_n^{(k)} \rangle = d | \phi_{n-1}^{(k)} \rangle ,$$

and $| \phi_0 \rangle = | g \rangle$. These are the basic equations that we have solved.

Our calculations utilize a Sturmian expansion approach that is described elsewhere.[4] The essential idea is that the inhomogeneous differential equations of perturbation theory can be solved directly by expanding the perturbed atomic radial wave function in Sturmian functions $S_{nl}^{(\zeta)}(r)$. The expansion gives us a hierarchy of inhomogeneous linear equations with strongly banded coefficient matrices. These hierarchical equations can be solved accurately to very high order.

We limit our attention to cases in which the highest virtual state attained in the absorption process lies in the discrete spectral region, i.e., $\epsilon_g + n\omega < 0$. This restriction comes from our use of a real scaling parameter ζ, so our basis behaves as $e^{-\zeta r}$ at large r. There are examples in which this restriction has been removed by using a complex value of ζ.[5]

Partial results of our calculation for the frequency-dependent nonlinear susceptibility of the $1s$ state of hydrogenic ions are presented in Fig. 1 and Table I. If we denote the nuclear charge by Z, it is evident from Eq. (1) that

$$\chi_n(Z,\omega) = Z^{-(3n+1)} \chi_n(1, \omega Z^{-2}) . \tag{2}$$

We are thus able to construct a plot of $\chi_n(Z,\omega)$ for all Z by utilizing a variable $\nu = 1/(1 - 2n\omega/Z^2)^{1/2}$, as shown in Fig. 1. The variable ν can be identified as the effective principal quantum number of the highest virtual state reached in the photon absorption process. The susceptibility diverges when ν assumes an integer value, indicating resonance with a real intermediate state. It can be shown[6] that in the limit $\nu \to \infty$, the susceptibility takes the form

$$\chi_n(Z,\omega) = a_n(\epsilon) + b_n(\epsilon) \cot(\pi\nu) , \tag{3}$$

where a_n and b_n are analytic functions of $\epsilon = -Z^2/2\nu^2$, provided that there is no isolated resonance at $\epsilon = 0$. Figure 1 shows our computed results for χ_3 along with a fit to Eq. (3), with a_3 and b_3 represented by quadratic functions of ϵ. Our results agree with those of previous investigators to all figures cited by them,[7,8] although to the best of our knowledge no previous published work has treated the region $\nu > 2$. Parametrization of the functions a_n and b_n in Eq. (3) enables one to extrapolate the susceptibility all the way to the ionization limit.

We have carried out similar calculations and fitting for higher-order susceptibilities, and will provide a detailed

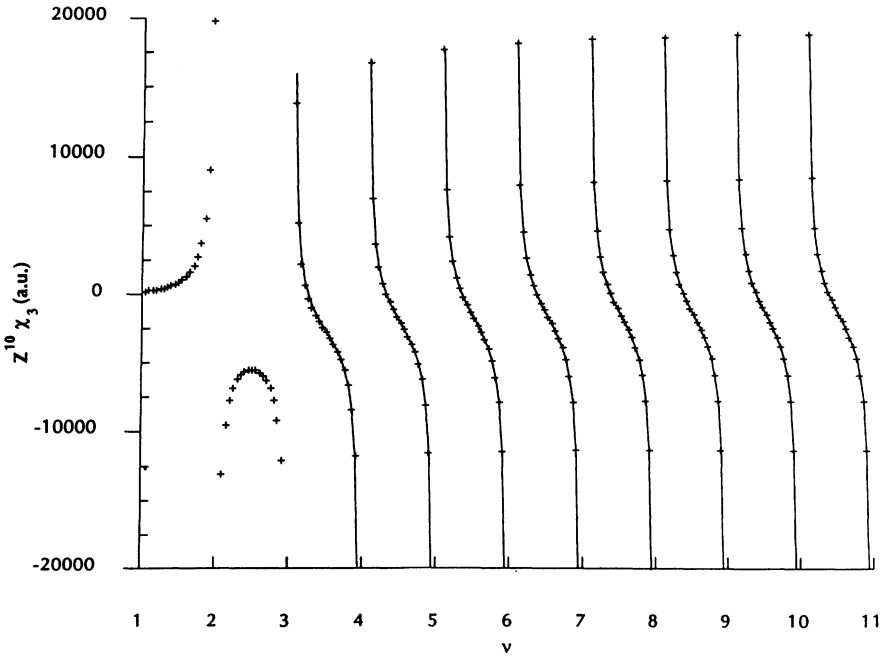

FIG. 1. Third-order frequency-dependent susceptibility of the $1s$ state of hydrogenic ions as a function of $\nu = 1/(1 - 6\omega/Z^2)^{1/2}$. Crosses are computed values; solid line is the result of a fit of the data for $\nu > 6$ to the form [see Eq. (3)]: $Z^{10}\chi_3 = a_0 + a_1\epsilon + a_2\epsilon^2 + \cot(\pi\nu)(b_0 + b_1\epsilon + b_2\epsilon^2)$, where $a_0 = -1324$, $a_1 = 26789$, $a_2 = 234442$, $b_0 = 3259$, $b_1 = 10751$, and $b_2 = 132908$. Note the reversal of phase between $\nu = 2$ and $\nu = 3$, which can be attributed to the sign difference of the matrix elements $(2s | r | 2p)$ and $(2s | r | 3p)$.

TABLE I. Nonlinear susceptibilities in a.u. of H and He^+ at the Nd:YAG laser frequency $\omega=0.0428$ a.u., as computed by lowest-order perturbation theory. The numbers in brackets give the power of ten by which these values must be multiplied. The range of order covers the discrete atomic spectrum in both instances.

n	χ_n (H)	χ_n (He^+)
3	2.7800[2]	2.1991[−1]
5	9.0293[4]	4.7872[−1]
7	2.0957[8]	1.8192[0]
9	−2.2704[13]	1.0923[1]
11	−2.9803[18]	1.0154[2]
13		1.4660[3]
15		3.3110[4]
17		1.1760[6]
19		6.5961[7]
21		5.8797[9]
23		8.4295[11]
25		1.9845[14]
27		7.9390[16]
29		5.7121[19]
31		8.2011[22]
33		3.0307[26]
35		6.4061[31]
37		3.4947[34]
39		−1.1072[38]
41		−2.7619[43]
43		4.6073[38]
45		1.3371[56]

report in a subsequent publication. Table I presents a few results of immediate interest: the susceptibilities of H and He^+ in Nd:YAG radiation ($\omega=0.0428$ a.u.), for orders up to 11 and 45, respectively. These should provide a rough facsimile of the qualitative behavior of the corresponding quantities for the noble gases.

In order to determine the range of intensities for which LOPT is valid, we introduce a parameter $I_c(n)$, the critical intensity of the incident field, at which the radiated intensity of the $(n+2)$th harmonic predicted by LOPT becomes equal to that of the nth harmonic. In the idealized case of plane-wave incident radiation with perfect phase matching, this critical intensity has the following simple expression:[1]

$$I_c(n)=\frac{c}{2\pi}\frac{n}{n+2}\left|\frac{\chi_n}{\chi_{n+2}}\right|. \tag{4}$$

Note that only the absolute value of χ_n appears in the expression.

Figure 2 shows $I_c(n)$ as a function of n, as computed from the values of χ_n displayed in Table I. Although some deviations from the obvious general behavior occur in resonance regions, it is evident that $I_c(n)$ decreases rapidly with n. We have carried out calculations at lower frequencies (i.e., the CO_2 laser at $\omega=0.0043$ a.u.) in which this trend can be seen up to ~70th order. LOPT therefore predicts that, for intensities greater than $I_c(n)$, the harmonic yield will increase without limit with respect to order.

We expect that in some isolated cases, e.g., in the presence of resonances, harmonic yield may indeed increase with order. However, it would be unphysical for a monotonic increase of the type revealed here to be maintained to arbitrarily high order. Our results thus provide upper bounds on the laser intensity at which these LOPT results are valid. More specifically, the upper bound of predicting nth harmonic intensity by LOPT is $I_c(n)$, and the highest upper bound of using LOPT for any order is $I_c(3)$. Note that for Nd:YAG radiation incident upon hydrogen, this highest upper bound is $I_c\sim 3\times 10^{14}$ W cm^{-2}, an intensity readily accessible in current experiments.

In comparing these critical intensities to the intensities of current experimental work,[3] we see an extremely suggestive correspondence. In the experiments, which were

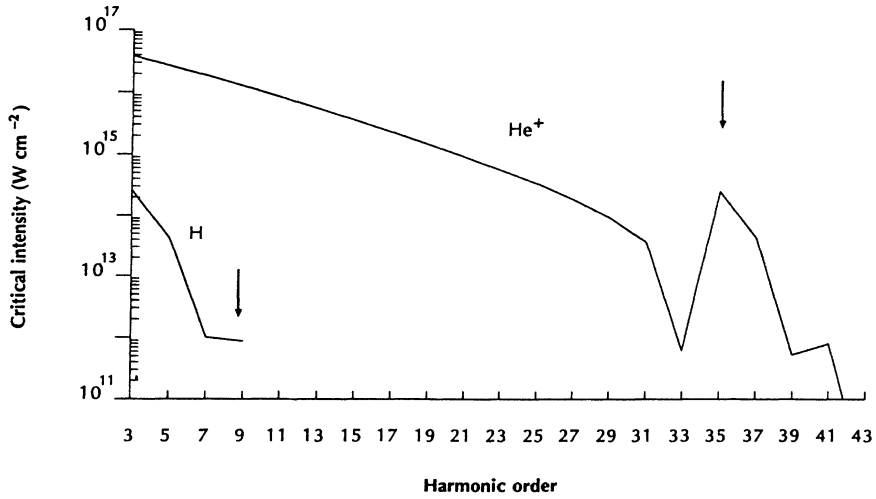

FIG. 2. Critical intensities $I_c(n)$ vs order n for H and He^+ at $\omega=0.0428$ a.u., as determined from Table I and Eq. (4). Arrows indicate the energy of the $2p$ resonance in each case.

carried out at a fixed intensity of about 10^{13} W cm^{-2}, the onset of a "plateau" region was found to occur in Xe, Kr, and Ar between the 5th and 7th orders. These orders are in reasonable correspondence with those for which we find $I_c \sim 10^{13}$ W cm^{-2} in hydrogen. Considering this qualitative comparison of our results and the experiment, we may conjecture that LOPT fails to describe the experimental results in the plateau region and beyond.

It thus appears that at high intensities, nth-order harmonic generation is not dominated by the nth-order frequency-conversion processes described by LOPT. We have not yet calculated higher-order contributions within the framework of perturbation theory. However, we can estimate their qualitative behavior as follows. Figure 3 is a symbolic representation of the $(n+2)$th-order contributions to the $(n+2)$th- and nth-harmonic generation. Each photon absorption or emission contributes an energy-weighted dipole matrix element to a transition amplitude of the form (1a). Since the number of total absorption and emission events is the same in both cases, the transition amplitudes for the two cases are different only in the denominators. In the case where all the absorptions and emissions are far off resonance, we expect the $(n+2)$th-order contribution to χ_n to be comparable to the $(n+2)$th-order (lowest-order) contribution to χ_{n+2}. This implies that the relative size of the $(n+2)$th-order corrections to χ_n will show the same divergence with respect to order as the ratio χ_{n+2}/χ_n calculated to lowest order. If this view is correct, it implies that when LOPT fails to be a good approximation, higher-order perturbation theory is also no longer a convergent calculation scheme. These conclusions can be drawn with better confidence after more calculations of higher-order χ_n, with the highest virtual state in the continuous region of the spectrum.

In conclusion, we have computed high-order nonlinear susceptibilities for hydrogenic ions. Our results suggest that the intensity upper bound for using LOPT is $\sim 10^{14}$ W cm^{-2} in the case of Nd:YAG radiation. Good correspondence is found between these results and experimental observations.

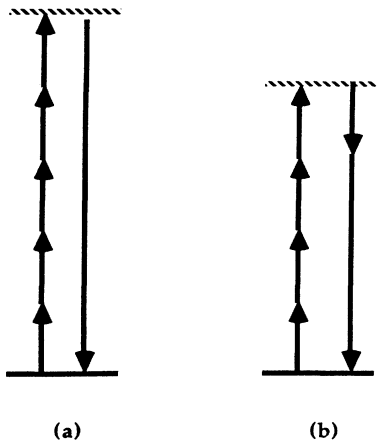

FIG. 3. Symbolic representation of partial 5th-order contributions to (a) χ_5 and (b) χ_3. Each upward-pointing arrow represents a photon absorption and each downward-pointing arrow represents a photon emission. The complete contribution to the transition amplitude is the summation of all distinguishable permutations of absorptions and emissions.

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