

Multiple Ionization of a Hartree Atom by Intense Laser Pulses

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It is shown that a good representation of recent experimental results on the relative production of multiply charged ionic states by intense laser pulses of various wavelengths may be obtained on the basis of Hartree's independent-electron shell model of the atom.

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In recent experiments Rhodes and Luk and co-workers¹⁻³ have detected the existence of several ionic charge states which result from the irradiation of a large variety of atomic species under collision-free conditions by uv laser radiation (193 nm, 6.42 eV) in 5-ps pulses and intensities in the range 10^{15} to 10^{17} W/cm². The general process may be represented as $X + N_q h\nu \rightarrow X^{q+} + qe$, where ions have been detected for N_q and q values as large as 99 and 10, respectively. These maximum values correspond to a U-atom target, but data have also been obtained for He, Ne, Ar, Kr, I, Xe, Eu, Yb, and Hg. These experiments measure the relative abundance of X^{q+} at a given laser intensity. The most striking aspect of these data is the relatively slow variation of the ratio between successive relative abundances compared with what one might expect on the basis of the minimum needed photon number N_q .

In another series of experiments by Lompré, Mainfray, and co-workers,^{4,5} multiply charged states of He, Ne, and Xe were studied as a function of laser intensity for the fundamental and first harmonic of the Nd-doped yttrium aluminum garnet laser (1064 nm, 1.17 eV and 532 nm, 2.33 eV). They used 50-ps pulses and an intensity range of 5×10^{11} to 10^{15} W/cm². At the lowest intensities for which the singly charged ions were detected, their relative abundance followed the I^{N_1} behavior expected from the lowest order of perturbation theory. However, it was not possible to obtain a correlation between the numbers of multiply charged ions produced and I^{N_q} (where $q > 1$). These values of N_q become very large (see Table I). Thus the maximum value for N_q in the Lompré-Mainfray measurements was $N_5 = 144$ for Xe^{5+} (and $h\nu = 1.17$ eV).

In both experiments the laser beam is focused inside

the target-gas volume and all ions produced are time-of-flight analyzed. There is ion production over a spread-out region surrounding the point of peak intensity, and the size of this region is believed to increase as the intensity is increased. This is given by Lompré and Mainfray as the reason for departure from I^{N_1} behavior at some intensity I_S where they believe single ionization occurs with almost unit probability within the focal volume of the laser beam. The growth of the number of singly charged ions for $I > I_S$ is then attributed to an effective enlargement of the interaction volume. One would expect similar effects to be taking place in the Rhodes-Luk experiment. The result of this uncertainty in interaction volume is that an error of unknown magnitude is introduced into the procedure of taking measured relative abundances of variously charged ions as equivalent to the relative ionization probabilities for these ions.

While perturbation theory has been reasonably successful in providing an understanding of the multiphoton production of singly charged ions, very little theoretical progress has been made in the treatment of multicharged-ion production. The reason for this is the vast increase in complexity of the perturbation theory involved when the appropriate multiple-electron intermediate states must include preceding continua. The outlook for theoretical progress by brute-force high-order perturbation treatments does not appear promising, particularly when one notes the high orders needed (the N_q 's of Table I). Hence, we would like to propose an alternate treatment for the problem of multicharged-ion photoproduction which is based on the model of the Hartree atom.⁶

In the Hartree atom each shell of identical electrons is characterized by an effective self-consistent central

TABLE I. Values of N_q , the minimum number of photons needed to reach the q th stage of ionization from the atomic ground state of Xe.

$h\nu$ (eV)	N_1	N_2	N_3	N_4	N_5	N_6
1.17	11	29	56	96	144	232
2.33	6	15	29	48	73	116
6.42	2	6	11	18	27	42

potential $V_{nl}(r)$. All noncentral $1/r_{ij}$ interactions have been averaged over, and all screening from inner charges have been incorporated into the V_{nl} 's. We can now ask how such an atom will ionize in response to an applied laser field. The important simplification which the Hartree atom introduces is that the problem including interaction with the field remains completely separable, as the full Hamiltonian is

$$H = \sum_{s,i} H_{s,i} = \sum_{s,i} \{T_i + V_s(r_i) + e \mathbf{r}_i \cdot \mathbf{E}(t)\}. \quad (1)$$

Here s designates a given nl shell, and the sum on i is over the electrons in that shell. The consequence of this is that the full time-dependent wave function has the product form $\Psi(\mathbf{r},t) = \prod_{s,i} \psi_s(\mathbf{r}_i,t)$, where $\psi_s(\mathbf{r}_i,0)$ are the initial free-atom Hartree orbitals. The $\psi_s(\mathbf{r}_i,t)$ satisfy the time-dependent Schrödinger equation, $i\hbar(\partial\psi_s/\partial t) = H_{s,i}\psi_s$, which describes the time evolution of an electron interacting with a central atomic potential and the external light wave, in the dipole approximation. The exact solution of the one-electron problem leads to a one-electron ionization probability $p_s(t;I)$, where the laser intensity I is included as a parameter. In principle, this one-electron problem is solvable for arbitrary laser pulse fields $E(t)$, but of course in practice many simplifying assumptions are needed. Typical of these are a monochromatic, rectangular laser pulse and the use of perturbation theory of minimum order equal to the number of photons needed to raise the bound electron to the ionization continuum. These approximations lead to the form for ionization probability $p_s(t;I) = \sigma_s F^N t$, where σ_s is the generalized cross section for N -photon absorption and F is the photon flux. If s is the outer shell of the atom, then $N = N_1$ by Koopmans' theorem. One expects this form for p_s to be generally valid when $p_s \ll 1$, but as p_s approaches its maximum value of 1 as a result of increasing F and/or t , there will be departures from this form, and a better one is $p_s = 1 - \exp(-\sigma_s F^N t)$.

The important property of the separability of the Hartree-atom model is that the probability for the ejection of q electrons from shell s (containing n_s electrons) is simply the product

$$P_s^{(q)} = \binom{n_s}{q} (p_s)^q (1-p_s)^{n_s-q}. \quad (2)$$

If one is considering such high laser intensities that electrons are being ejected with appreciable probability from more than one shell (as is the case in the Rhodes-Luk experiments), this is simply generalized to

$$P_{s,s'}^{(q+q')} = \binom{n_s}{q} (p_s)^q (1-p_s)^{n_s-q} \binom{n_{s'}}{q'} (p_{s'})^{q'} (1-p_{s'})^{n_{s'}-q'},$$

and so on. Note that this definition provides for unitarized probabilities, i.e.,

$$\sum_{q=0}^{n_s} \sum_{q'=0}^{n_{s'}} P_{s,s'}^{(q+q')} = 1,$$

where $P_{s,s'}^{(0)}$ is the probability that the atom remains un-ionized.

For comparison with the data we define the ratio of probabilities for the production of X^{q+} to X^+ ,

$$R_s^{(q)} = \frac{P_s^{(q)}}{P_s^{(1)}} = \frac{1}{n_s} \binom{n_s}{q} \left(\frac{p_s}{1-p_s} \right)^{q-1}. \quad (3)$$

In Fig. 1 we illustrate the behavior of $P_s^{(q)}$ for an $l=1$ shell with $n_s=6$. For $p_s \geq 0.3$ a reversal starts in the magnitudes of $P_s^{(q)}$ and the higher states of ionization are seen to become more probable.

We can now attempt a qualitative interpretation of the experimental data in terms of this model. In Fig. 2 the Rhodes-Luk results³ are shown for the ion-charge spectra of Xe at three laser intensities. First let us note how completely incompatible these results are with the conventional ideas of multiphoton ionization, where one expects a probability $P_s^{(q)} = \sigma_s^{(q)} F^{N_q} t$, or ratio of multiple to single ionization, $R_s^{(q)}(I) = (\sigma_s^{(q)}/\sigma_s^{(1)}) F^{N_q - N_1}$. This would lead to the ratio for two dif-

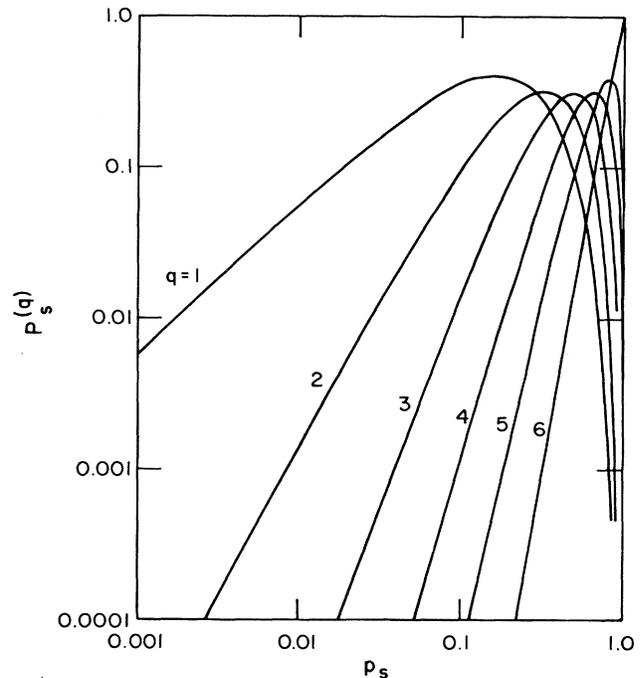


FIG. 1. Ionization probabilities for the q th charge state, $P_s^{(q)}$, for a six-electron atomic shell as a function of the one-electron ionization probability, p_s .

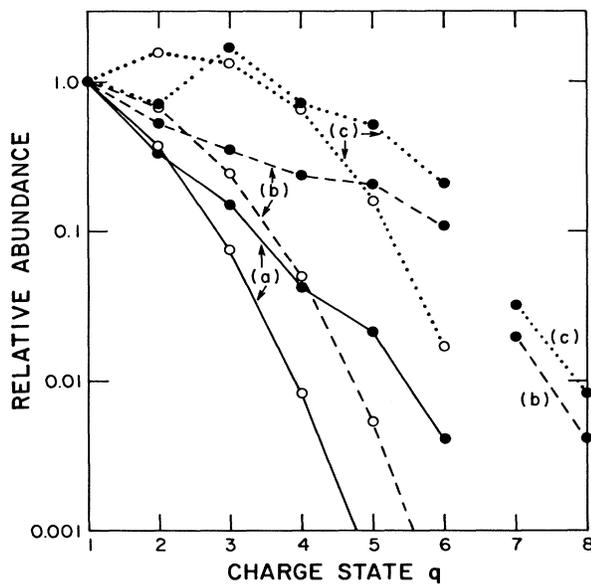


FIG. 2. The Rhodes-Luk data (solid points) for the relative abundance of charge states Xe^{q+} produced by laser intensities (a) $\sim 10^{15}$, (b) $\sim 10^{16}$, and (c) $\sim 10^{17}$ W/cm². The open points are the least-squares fit of form (3) to the $1 \leq q \leq 6$ data points, taking $n_s = 6$.

ferent intensities

$$\frac{R_s^{(q)}(I)}{R_s^{(q)}(I')} = \left(\frac{I}{I'} \right)^{N_q - N_1} \quad (4)$$

If we take $I \sim 10^{16}$ and $I' \sim 10^{15}$ W/cm², the measured values for $R_s^{(q)}(I)/R_s^{(q)}(I')$ for $q = 2, 3, 4,$ and 5 are 1.6, 2.3, 1.8, 2.7, respectively. The values expected for these ratios, from (4) and use of the N_q in Table I, are $\sim 10^4, 10^9, 10^{16},$ and 10^{25} , respectively. So it becomes quite clear that the use of a simple perturbative expression for $P_s^{(q)}$ based only on the number of photons needed to reach the particular stage of ionization (i.e., N_q) cannot represent the data to within many orders of magnitude, well outside any expected errors arising from the question of the uncertain interaction volume in the experiments.

On the other hand, the data in Fig. 2 are much more consistent with the predictions of the present theory. A least-squares fit of form (3) to the data of $1 \leq q \leq 6$, which is also shown in Fig. 2, gives $p_{5p} = 0.13, 0.21,$ and 0.39 for $I \sim 10^{15}, 10^{16},$ and 10^{17} W/cm², respectively. Since only two data points at each intensity exist for the 5s shell, we determine the corresponding p_{5s} directly from $P_{6p,5s}^{(8)}/P_{6p,5s}^{(7)} = \frac{1}{2} p_{5s}/(1 - p_{5s})$, to be $p_{5s} = 0.30$ and 0.35 for $I \sim 10^{16}$ and 10^{17} W/cm². The corresponding values of $R_s^{(q)}(I)/R_s^{(q)}(I')$ for $q = 2, 3, 4,$ and 5 are 1.8, 3.3, 5.9, and 11, a considerable improvement over the ratios given by (4).

The p_s 's increase with increasing intensity as one would expect. The fact that at $I \sim 10^{16}$ W/cm², $p_{5p} < p_{5s}$, while at $I \sim 10^{17}$ W/cm², $p_{5p} > p_{5s}$, is somewhat anomalous. It should also be noted that the least-squares fit when plotted on the logarithmic ordinate scale of Fig. 2 shows large departures from the data points at the high q values. Although no error bars are given for the measured points, we would expect systematically larger error bars (on the logarithmic scale) for the lower relative abundances. This together with the uncertainty in interaction volume could be responsible for the poor fit at high q values and the above anomalous inversion of p_{5s} and p_{5p} values. Additional measurements of increased accuracy and at higher intensities (particularly for the high q values) would be very desirable further to test this model, and the predicted inversions in relative abundance which are indicated in Fig. 1.

In trying to fit the Lompré-Mainfray Xe data with the present model we note that there is only a very small intensity range at which Xe^{5+} is observed and Xe^{6+} is not seen at all at their lower photon frequencies and intensities (than are used by Rhodes and Luk). In making a least-squares fit to their data at their maximum intensities we find $p_{5p} = 0.085$ for $h\nu = 1.17$ eV and $I \cong 10^{14}$ W/cm², and $p_{5p} = 0.047$ for $h\nu = 2.33$ eV and $I \cong 6 \times 10^{12}$ W/cm². These values of p_{5p} imply from Fig. 1 that $P_{5p}^{(1)}$, the probability for single ionization of Xe, should have a value of about 0.33 and 0.22, respectively. Our model would attribute the departure of $P_{5p}^{(1)}$ as a function of I from its original I^{N_1} form (beyond that occurring from changes in the effective interaction volume) to the redistribution of probability among the ionic states as indicated in Fig. 1. Lompré and Mainfray adopt a picture of a *sequential* production of $X^{(q+1)+}$ from X^{q+} while our model has all the probabilities being generated *simultaneously*. In the limit of low I our result is consistent with their observation since

$$P_{5p}^{(1)} \sim p_{5p} (1 - p_{5p})^5 \xrightarrow{I \rightarrow 0} p_{5p} \sim \sigma F^{N_1} t.$$

Our prediction for the intensity variation of Xe^{2+} would be

$$P_{5p}^{(2)} \sim p_{5p}^2 (1 - p_{5p})^4 \xrightarrow{I \rightarrow 0} p_{5p}^2 \sim (\sigma F^{N_1} t)^2,$$

or as the $2N_1$ power of the intensity, rather than the conventional perturbation result of I^{N_2} . The present limiting pulse-length dependence in $P_s^{(q)}$ is t^q , rather than the conventional linear form which corresponds to a constant ionization rate. Here we expect the power of the intensity to be qN_1 rather than N_q , and thus accurate measurements of the limiting I and t dependences for the production of multiply charged ions would be additional interesting tests of the present model.

The occurrence of intensity dependences in multiphoton ionization which vary as *lower* powers of the intensity than the minimum photon number required by energy absorption is a common feature when intermediate-state resonances play a significant role. In the present situation we may regard all the preceding continua as a form of intermediate-state resonances, which leads to the lowering of the effective exponent of the intensity. The higher the q value, the more such intermediate resonances participate and the greater is the *decrease* in effective exponent, $N_q - qN_1$, as can be immediately verified from Table I. Related behavior has also been suggested by Crance.⁷

In some very recent work Chin, Yergeau, and Lavigne⁸ have measured the relative ion production in Xe for $q \leq 3$ with 1.1-ns CO₂ laser pulses having intensities $\leq 2 \times 10^{14}$ W/cm². Their results as a function of intensity (for the 9.55- μ m line) show a remarkable resemblance to our respective curves in Fig. 1, including well-defined maxima for Xe⁺ and Xe²⁺. The present model allows us to extract the values at these maxima as $p_{5p} \cong 0.17$ and 0.33 at $I \cong 5.0 \times 10^{13}$ and 1.2×10^{14} W/cm², for these laser parameters. We would expect this one-electron-ejection process to be governed by some type of tunneling behavior rather than a multiphoton ionization cross section (since $N_1 = 104$ at this wavelength).

While the above discussion applies to the Xe^{q+} case, Lompré and Mainfray and co-workers⁵ have also made measurements on charge-state ratios for the other rare gases using Nd-doped yttrium aluminium garnet laser radiation, and these results correspond to the following maximum values p_s :

$h\nu = 1.17$ eV.—He⁺, He²⁺, $p_{1s} = 0.0010$ at $I = 1.2 \times 10^{15}$ W/cm²; Ne⁺, Ne²⁺, $p_{2p} = 0.00099$ at $I = 1.2 \times 10^{15}$ W/cm²; Ar⁺, Ar²⁺, Ar³⁺, $p_{3p} = 0.021$ at $I = 2.2 \times 10^{14}$ W/cm²; Kr⁺, Kr²⁺, Kr³⁺, Kr⁴⁺, $p_{4p} = 0.019$ at $I = 1.2 \times 10^{14}$ W/cm².

$h\nu = 2.33$ eV.—Ne⁺, Ne²⁺, $p_{2p} = 0.016$, $I = 5.0 \times 10^{13}$ W/cm².

Note that p_{2p} for Ne increases by a factor of 16 when $h\nu$ is doubled and the intensity is decreased by a factor of 20. This behavior could be the result of resonant variations in σ_{5p} depending on photon frequency and the atomic spectrum. The failure to detect any He²⁺ or Ne⁺ by Rhodes and Luk would be consistent with $p_s < 0.01$ (for He) and $p_s < 0.003$ (for Ne) for their laser pulses, since their system could not detect any ions produced with a probability of $< 10^{-4}$. Another interesting finding of Lompré and Mainfray was that for Cs atoms, no ions of higher charge than Cs⁺ were detected for $I < 10^{13}$ W/cm². This may be interpreted under the present model as a result of there being only one electron in the outer 6s shell, while for the deeper lying 5p shell, the probability $P_{6s,5p}^{(2)} = 6p_{6s}p_{5p}(1 - p_{5p})^5$ is too small to be detectable

because of the smallness of p_{5p} . The detection of a low level of Xe⁺ at 8×10^{12} W/cm² is consistent with the absence of a detectable level of Cs²⁺ at the same intensity, since the binding energies of a 5p electron in the Xe and Cs⁺ cores are 12.1 and 25.1 eV, respectively.

To the extent that p_s can be characterized by a specific functional form such as $\sigma_s F^N t$, or its generalization $\sigma_s \int_0^t dt' [F(t')]^N$, in the present model, we can extract *absolute* multiphoton cross sections σ_s from a measurement of the ratio of successive ionic charge-state probabilities arising from a given atomic shell. The electron-energy distribution expected in this model is just that which is associated with the one-electron problem. This distribution depends on I and t , and might be a single energy peak at $\epsilon = N_1 h\nu - V_I$ (V_I is the ionization potential) at low values of I and/or t , but may evolve into many peaks separated by $h\nu$ (the so-called above-threshold ionization) for high values of I and/or t , when p_s approaches 1.

In summary, we see that the use of a Hartree atom model, which in general gives a good quantitative picture of atomic structure, leads to a great simplification in the description of laser multiple ionization. The essential quantum mechanical multiphoton ionization problem is reduced from an n_s -electron problem to a one-electron problem, and the maximum number of photons one needs to deal with explicitly is N_1 rather than all the N_q 's. Comparison with the existing measurements shows that the model is a considerable improvement over the conventional picture of multiple ionization by multiphoton absorption.

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