Nonlinearity in the sequential absorption of multiple photons

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I classify multiphoton absorption into separable, linked, and simultaneous processes. The first and second types can be distinguished when the rate-equation approximation is valid whereas the third type refers to the case when the full description of multiphoton absorption is essential. For this purpose, rate equations are solved analytically without decay processes which shows that even if many photons are absorbed the interaction with the light field is linear and one has the case of separable multiphoton absorption. Next a short-pulse approximation is investigated in which I first solve the rate equations without decay processes and then solve only rate equations for the ensuing decay. Finally, the full rate equations are examined and a successive approximation of the underlying Volterra integral equation of the second kind is derived leading to linked multiphoton absorption by the involved decay widths. The three methods are applied to a nitrogen atom in intense and ultrafast x rays from free-electron lasers (FELs). The linearity theorem barely approximates the results in the presence of decay processes which is also not satisfactorily corrected for by the short-pulse approximation. The successive approximation gives excellent agreement with the numerically-exact solution of the rate equations.

Keywords: rate equations, system of linear first-order differential equations, multiphoton process, Volterra integral equation of the second kind, analytical solution, x rays, nitrogen atom

I. INTRODUCTION

Rate equations which are systems of linear first-order ordinary differential equations have recently come into focus in the study of the intense and ultrafast interaction of x rays with matter [e.g., Refs. 2–11] due to the development of x-ray lasers, especially the state-of-the-art x-ray FELs such as the the Linac Coherent Light Source (LCLS)12-13 in Menlo Park, California, USA, the SPring-8 Angstrom Compact free electron Laser (SACLA)14 in Sayo-cho, Sayo-gun, Hyogo, Japan, the SwissFEL15 in Villigen, Switzerland, and the European X-Ray Free-Electron Laser (XFEL)16 in Hamburg, Germany. Such rate equations have been used for a long time in the optical regime17–22 and, meanwhile, they have become frequently the basis for an understanding of the interaction with x rays2–5,10,11,23–25 even in the presence of resonances26–29 until coherent phenomena become important22.23 This approach is required as the x rays from FELs are so intense that multiple x rays can be absorbed in the course of the interaction unlike experiments at synchrotrons which are limited to one-x-ray-photon processes.11,14 Hence—although the interaction with the x rays remains well-described by few-photon absorption cross sections in the cases considered for this work15— a perturbative treatment of the interaction of the x-ray pulse with matter is typically no longer a viable approach as there is a substantial ground-state depletion.

In x-ray science the term “multiphoton absorption” is frequently used to refer to the case of the sequential absorption of several photons [e.g., Refs. 2, 5, 10, 11, 23–25, and 35] whereas for optical light predominantly the simultaneous absorption of several photons is meant22. The attribute simultaneous, thereby, refers to the fact that a few-photon absorption cannot be meaningfully broken up into isolated photon absorption events with a smaller number of photons. X-ray absorption may occur either non-resonantly2, 4, 10, 11, 24, 25 or resonantly-enhanced5, 9, 26. The latter refers to a form of resonance-enhanced multiphoton ionization (REMPI)22, which is termed in this context resonance-enabled x-ray multiple ionization (REXMI).22 Unlike optical photons, x rays typically have enough energy to eject electrons from atoms until maybe the highest charge states where simultaneous absorption of multiple x rays plays only a diminishing role.36–37

In many applications, the x-ray energy is far above the ionization threshold of the involved atoms in all charge states such as in structure determination of biomolecules38 and condensed matter.38 This is the case I focus on in this study. It is also what was examined in the initial works on matter in FEL x rays, e.g., Refs. 23, 24, 39.11 There the population of charge states due to ionization by the sequential absorption of multiple x rays and ensuing electronic decay processes are investigated by numerically solving rate equations.2, 3, 5, 10, 11 The solutions are then used to compute experimentally accessible quantities such as ion yields. Yet a more formal treatment of the underlying systems of differential equations has not been pursued to date.

Here I would like to investigate the solution of such rate equations analytically. I formulate and prove the linearity theorem of multiphoton absorption,22 a short-pulse approximation that uses this theorem with decay equations, and I investigate the successive approx-
imination of the solution of the rate equations. This allows me to classify multiphoton absorption into simultaneous, linked, and separable processes. Namely, specialized to a two-photon process, there is the well-known simultaneous absorption of two photons for x-rays. This changes when the rate-equation approximation without simultaneous two-photon terms is applicable. Then linked two-x-ray-photon absorption can be discussed where decay widths establish the link between two distinct one-x-ray-photon absorptions. In this article, I also turn to the third case of separable multiphoton absorption hitherto not analyzed which is covered by the linearity theorem. The reader should always bear in mind that linked and separable multiphoton absorption are approximations to simultaneous absorption. The core results of this article can be found in Sec. III where the analytical solution of the rate equations with decay are determined; Sec. II serves as an introduction to the subject neglecting decay processes.

This article is structured as follows. Section II treats rate equations without decay processes which are introduced in Sec. II A. The linearity theorem of multiphoton absorption is proven in Sec. II B. Rate equations with decay processes are treated in Sec. III; they are formulated in Sec. III A. In Sec. III B I examine rate equations with decay processes in a short-pulse approximation. Section III C contains the derivation of a Volterra integral equation from the rate equations with decay and its successive approximation. Results and discussions are in Sec. IV where the time evolution of the charge states of a nitrogen is predicted using the approximations derived before. Conclusions are drawn in Sec. V.

Equations are formulated in atomic units. All details of the calculations in this article are provided in the Supplementary Data.

II. RATE EQUATIONS WITHOUT DECAY PROCESSES

A. Closed system of rate equations

I set out from rate equations which describe x-ray nonlinear optical processes of atoms and molecules. The discussion is restricted to the case that the x-ray energy is sufficiently high to ionize all electrons of the atom by one-photon absorption. The systems are assumed to be initially neutral with \( N \) electrons and in a nondegenerate ground state. The electronic configurations of the system are enumerated by a double index of the electron number \( n \) and the number of configurations \( K(n) \in N \) in charge state \( n \). The configurations are arranged with decreasing energy of configurations in each charge state. In total there are \( K = \sum_{n=0}^{N} K(n) \) configurations. There is only one neutral state and one electron-bare state, i.e., \( K(0) = K(N) = 1 \). For ease of notation, I let \( K(N+1) = 0 \). With x-ray flux \( J \) I denote a continuous real function in time which is greater than zero only on a finite time interval and zero otherwise. With \( \sigma_{j→i}^{(n)} \geq 0 \) for \( i \in \{1, \ldots, K(n)\} \), \( j \in \{1, \ldots, K(n-1)\} \), and \( n \in \{0, \ldots, N\} \), I specify one-x-ray-photon absorption cross sections, partial and total cross sections, respectively.

Here \( \sigma_{j→i}^{(n)} \) is the cross section to transition from a configuration \( i \) with \( n \) electrons to a configuration \( j \) with \( n-1 \) electrons by one-x-ray-photon absorption. Typically not all configurations \( j \) can be reached from configuration \( i \) and \( \sigma_{j→i}^{(n)} \) is set to zero, if it is not possible. For notational convenience, I let \( \sigma_{j→i}^{(0)} = \sigma_{j→i}^{(N+1)} = 0 \) for any \( i, j \). The \( \sigma_{j→i}^{(n)} \) is the cross section to transition from configuration \( i \) with \( n \) electrons to any accessible configuration with \( n-1 \) electrons. As no x-rays can be absorbed by the electron-bare nucleus, I have for this configuration \( \sigma_{1}^{(0)} = 0 \).

Rate equations can be constructed as follows or be derived from the master equation in Lindblad form as a Pauli master equation which is discussed in Refs. Given probabilities \( p_{j}^{(n)}(t) \) at time \( t \in R \) which are differentiable, to find the system at time \( t \in R \) with \( n \) electrons in configuration \( j \). The initial condition is specified at the initial time \( \tau \in R \) as \( p_{j}^{(n)}(\tau) \). Here I assume further that the system is initially in the single neutral charge state, i.e., \( p_{1}^{(n)}(\tau) = \delta_{1,0} \delta_{N,n} \) with the Kronecker-\( \delta \). Then the first rate equation, for the system in its neutral charge state reads

\[
\frac{dp_{1}^{(n)}(t)}{dt} = -\sigma_{1}^{(n)} p_{1}^{(n)}(t) J(t) ;
\]

it describes the ionization of the neutral system by the x-rays. The rate equations of the singly-ionized system already have the full form of rate equations without decay processes

\[
\frac{dp_{j}^{(n-1)}(t)}{dt} = \left[ \sigma_{j→i}^{(n)} p_{i}^{(n)}(t) - \sigma_{j→i}^{(n-1)} p_{j}^{(n-1)}(t) \right] J(t) ;
\]

for \( j \in \{1, \ldots, K(N-1)\} \). This continues analogously until the last rate equation, for the electron-bare system, which is

\[
\frac{dp_{1}^{(0)}(t)}{dt} = \sum_{i=1}^{K^{(1)}} \sigma_{1→i}^{(1)} p_{i}^{(1)}(t) J(t) .
\]

The above said can be compactly summarized as follows. Inspecting the rate equations, I observe that there are \( K \) rate equations which form the \( K \times K \) system of linear first-order ordinary differential equations

\[
\frac{dp_{j}^{(n)}(t)}{dt} = \sum_{i=1}^{K^{(n+1)}} \sigma_{j→i}^{(n+1)} p_{i}^{(n+1)}(t) - \sigma_{j→i}^{(n)} p_{j}^{(n)}(t) J(t) .
\]

Then this constitutes a system of rate equations. If for such a system of rate equations the total cross sections...
are given by
\[ \sigma_j^{(n)} = \sum_{i=1}^{K(n-1)} \sigma_{ij}^{(n)} , \]
then it is termed a closed system of rate equations.

The system of rate equations (4) for all \( n, j \) can be rewritten compactly by letting \( p(t) \in \mathbb{R}^K \) stand for the vector with the entries \( p_i(t) \), i.e.,
\[ p(t) = (p_1^{(N)}(t), p_1^{(N-1)}(t), \ldots, p_N^{(0)}(t)) \]
The partial cross sections \( \sigma_{j-i}^{(n)} \) form a strictly lower triangular matrix and \( -\sigma_i^{(n)} \) are on the matrix diagonal. Together they are referred to as the cross section matrix \( \Sigma \). With this notation, I express (1) as
\[ \frac{dp(t)}{dt} = \Sigma p(t) J(t) . \]
The structure of \( \Sigma \) can be characterized by
**Definition 1.** A real \( K \times K \) matrix \( A \) that has the closure property:
\[ -A_{ii} = \sum_{j=1}^{K} A_{ji} , \]
for all \( i \in \{1, \ldots, K\} \) is referred to as a closed matrix.

**Remark 1.** If the matrix \( A \) from Definition 1 is also lower-triangular, then it has at least one zero diagonal element because \( A_{KK} = 0 \) must hold in order to fulfill (5).

So far I referred to the \( p_i(t) \) as probabilities thereby assuming them to lie in \([0; 1]\) for all times \( t \). This fact, however, needs to be established rigorously.

**Remark 2.** The \( \Sigma \) is essentially nonnegative, i.e., \( \Sigma_{ij} \geq 0 \) for \( i \neq j \), and thus a Metzler matrix. Therefore, Theorem 16.VII on page 183 in Ref. [3] ensures the nonnegativity of the \( p_i(t) \).

The word “closed” was chosen above to hint that
**Lemma 1.** Probability in a closed system of rate equations (4) is conserved.

**Proof.** As \( \Sigma \) is a closed matrix, I observe that the column sums of \( \Sigma \) vanish, i.e., \( \sum_{j=1}^{K} \Sigma_{ij} = 0 \) for all \( j \in \{1, \ldots, K\} \). Then it follows by summing the components of (7):
\[ \frac{d}{dt} \sum_{i=1}^{K} p_i(t) = \sum_{i=1}^{K} \left( \sum_{j=1}^{K} \Sigma_{ij} \right) p_i(t) J(t) = 0 , \]
that the probability is conserved for all times \( t \). q.e.d.

Thus I make the
**Remark 3.** With Remark 2 and Lemma 1 I can rightfully refer to the \( p_i(t) \) as probabilities provided that the initial values fulfill \( 0 \leq p_i(\tau) \leq 1 \) for \( i \in \{1, \ldots, K\} \) and \( \sum_{i=1}^{K} p_i(\tau) = 1 \) holds.

**B. Linearity theorem of multiphoton absorption**

The rate equations (4) constitute a matrix initial-value problem which satisfies the Lappo-Danilevskii condition 55:
\[ \Sigma J(t) \int_{\tau}^{t} \Sigma J(t') \, dt' = \int_{\tau}^{t} \Sigma J(t') \, dt' \Sigma J(t) . \]
Hence the fundamental matrix can be written as an exponential function \( e^{\tau \Sigma} \int_{\tau}^{t} \Sigma J(t') \, dt' \), which leads to the solution of the rate equations (4) on the last line of Eq. (10). But only some of the results in the following paragraphs are found this way.

To gain deeper insight into the physics described by the rate equations (4), I obtain the solution of (4) in an alternative way using the eigenbasis of \( \Sigma \). For this I notice that, as \( \Sigma \) is lower triangular, its eigenvalues are the diagonal elements \( -\sigma_i^{(n)} \) which are negative or zero such as the last one \( -\sigma_1^{(0)} = 0 \) because the electron-bare nucleus cannot be ionized further—and pairwise distinct as the total absorption cross sections \( \sigma_i^{(n)} \) refer to different configurations \( i \) of charge state \( n \) where, on configuration level, there are no degeneracies. Following Lemma 2, \( \Sigma \) is diagonalizable where the eigenvalues form the diagonal matrix \( \Lambda = \text{diag}(\lambda_1, \ldots, \lambda_K) \) and the eigenvectors are gathered in the matrix \( U \). As \( \Sigma \) is time independent, so are \( \Lambda \) and \( U \). Transforming (4) to the eigenbasis of \( \Sigma \) yields
\[ U^{-1} \frac{dp(t)}{dt} = \frac{dp(t)}{dt} = U^{-1} \Sigma U \, U^{-1} p(t) J(t) = \Lambda q(t) J(t) , \]
which is a decoupled system of linear first-order ordinary differential equations. The \( \ell \) th equation reads
\[ \frac{dq_{\ell}(t)}{dt} = \lambda_{\ell} q_{\ell}(t) J(t) , \]
which has the solution for time \( t \geq \tau \) with the integration starting at time \( \tau \):
\[ q_{\ell}(t) = q_{\ell}(\tau) e^{\lambda_{\ell} \tau} , \]
where the initial value is \( q_{\ell}(\tau) \equiv (U^{-1} p(t))_{\ell} \) and the x-ray fluence is
\[ \Phi(t) = \int_{\tau}^{t} J(t') \, dt' . \]
As the system is initially in its ground state, I have $p(\tau) = (1, 0, \ldots, 0)^T \in \mathbb{R}^K$ and thus $q_0(\tau) = (U^{-1})_{11}$. From the solution $q(t)$, the probabilities follow via $p(t) = U q(t)$, hence

$$p_i(t) = \sum_{\ell=1}^K U_{i \ell} q_\ell(t) = \sum_{\ell=1}^K U_{i \ell} q_\ell(t) e^{-|\lambda_i| t} \Phi(t),$$

which is the unique solution of the system of rate equations (13).

I observe that $p_i(t)$ depends only on the x-ray fluence $\Phi(t)$ as it is the case for one-photon absorption. The sign of $\lambda_i$ in (13) was made explicit in (15): it implies that the exponential functions in (15) decay quickly to zero with increasing fluence meaning that the probability of the system at time $t$ to be in the configuration $i$ with electrons decays to zero such that for $\Phi(t) \to \infty$, eventually, only the last configuration $K$ of the system which is stripped bare of electrons, i.e., $\lambda_K = 0$, has unit probability [see (10)]. Conversely, the limit $\Phi(t) \to 0$ lets all exponential functions in (15) become unity and thus $p(t) = p(\tau)$, i.e., the system remains in the initial state for all times $t$.

The solution (15) of the rate equations (7) is recast, by expanding the exponential function into a series using $q(t) = U^{-1} p(\tau)$, yielding

$$p_i(t) = \sum_{m=0}^{\infty} \frac{\Phi^m(t)}{m!} \sum_{j=1}^K (U)_{i j} \lambda_j^m (U^{-1})_{j i} p_j(\tau)$$

$$= \sum_{j=1}^K p_j(\tau) \sum_{m=0}^{\infty} \frac{\Phi^m(t)}{m!} \sum_{j}^m$$

$$= \sum_{j=1}^K \left[ e^{\Sigma \Phi(t)} \right]_{i j} p_j(\tau).$$

The middle expression in (16) exhibits the perturbative nature of the problem. Namely, the probability $p(t)$ is composed of the summands with increasing powers of $\Sigma \Phi(t)$, i.e., zero-photon absorption gives 1, one-photon absorption adds $\Sigma \Phi(t)$, two-photon absorption adds $\frac{1}{2} (\Sigma \Phi(t))^2$, etc. The above said proves

**Theorem 1** (Linearity theorem of multiphoton absorption). Given a system of rate equations (4), then there is no nonlinearity in the interaction of $x$ rays with the system and all multiphoton processes can be decomposed in terms of subsequent (chained) one-x-ray-photon absorptions (10).

The situation that is described by Theorem 1 is termed separable multiphoton absorption. The dependence of $p(t)$ on $t$ is nonlinear due to the exponential functions in (13) that become constants which depend only on the x-ray fluence after the x-ray pulse has passed for $t \to \infty$. In the case of separable multiphoton processes, no nonlinearity in the interaction is present. The fact that the exponential series always converges ought not to mislead the reader: this convergence does not imply that the physical problem of multiphoton absorption actually is amenable to a perturbative treatment which leads to the cross sections that enter (4). This fact needs to be established independently.35-37

### III. RATE EQUATIONS WITH DECAY PROCESSES

#### A. **Closed system of rate equations**

In many cases the formulation of the rate equations (4) from Sec. II A represent an idealization because there are decay processes occurring. First, there is electronic decay in which an electron drops from a higher shell to a lower shell releasing the excess energy by ejecting another electron from a higher shell. Second, there is radiative decay where an electron drops from a higher shell to a lower shell emitting a photon with an energy corresponding to the energy difference between the two shells involved in the transition. For electronic decay, the final state has one electron less compared with the initial state whereas in radiative decay the number of electrons is left unchanged.

With decay widths, the rate equations (4) become

$$\frac{d\sigma_j}{dt}(t) = \left[ \sum_{i=1}^{K^{(n+1)}} \sigma_j^{(n+1)} p_i^{(n+1)}(t) - \sigma_j^{(n)} p_j^{(n)}(t) \right] J(t)$$

$$+ \sum_{i=1}^{K^{(n)}} \gamma_{i \to j}^{(n)} p_i^{(n)}(t) - \gamma_j^{(n)} p_j^{(n)}(t),$$

where the partial decay widths for electronic decay are $\gamma_{i \to j}^{(n)} \geq 0$ and for radiative decay are $\gamma_{i \to j}^{(n)} \geq 0$.

Note that $\gamma_{i \to j}^{(n)} = 0$ for $j > i$. The total decay width of a system in configuration $j$ with $n$ electrons to make a transition to any in this way accessible other configuration is $\gamma_j^{(n)} = \gamma_{E,j}^{(n)} + \gamma_{R,j}^{(n)}$ in analogy to (10) given by

$$\gamma_{E,j}^{(n)} = \sum_{i=1}^{K^{(n-1)}} \gamma_{E,i}^{(n-1)} \gamma_{E,j}^{(n-1)}$$

and $\gamma_{R,j}^{(n)} = \sum_{i=1}^{K^{(n)}} \gamma_{R,i}^{(n)} \gamma_{R,j}^{(n)}$.

The decay widths $\gamma_{R,j}^{(n)}$ and $\gamma_j^{(n)}$ make their first appearance in the rate equations for $n = N-1$, i.e., Eq. (2), and the $\gamma_{E,j}^{(n)}$ start to appear in the rate equations for $n = N-2$. There is no decay in the first rate equation, for the system in its neutral charge state which has the same form as (10). The last rate equation, for the electron-bare system, similar to (3), also does not contain a decay width.
Introducing the notation of \( \mathbf{i} \) and \( \mathbf{j} \), I express (17) compactly as

\[
\frac{d\mathbf{p}(t)}{dt} = \mathbf{\Sigma} \mathbf{p}(t) J(t) + \Gamma \mathbf{p}(t).
\]  

(19)

I have, additionally, the matrix of decay widths \( \Gamma \). Because of the radiative decay widths, for this matrix to be lower triangular with the negative of the total decay widths on the diagonal, the electron configurations need to be sorted with decreasing energy. Further the first and last rows and column of \( \Gamma \) are filled with zeros; the inner part shall be referred to by \( \Gamma' \), i.e., \( \Gamma \) can be written as the direct sum \( \Gamma = \mathbf{0} \oplus \Gamma' \oplus \mathbf{0} \). Due to the closure property \( \mathbf{\Sigma} \Gamma \) is a closed matrix and the probability \( \mathbf{\Sigma} \Gamma \) in the system of rate equations (17) is conserved in analogy to Remarks 2 and 3 and Lemma 1.

B. Decay equation

Inspecting (19), I find that, with decay widths present, one cannot proceed any longer as for the case without decay widths. Namely, as \( \mathbf{\Sigma} \) and \( \Gamma \), in general, do not commute, the Lapo-Danilevskii condition (10) is not fulfilled for \( \mathbf{\Sigma} J(t) + \Gamma \). For the same reason, the two matrices do not share a common eigenbasis, i.e., the matrix on the right-hand side of (19) cannot be diagonalized by a time-independent matrix as in (10). Certainly, Equation (19) can be integrated numerically as in Ref. 4 or solved using the analytical solutions of Sec. III C but here I would like to determine an approximate solution of it. I obtain the solution (15) of the rate equations without decay processes (19), then its solution is

\[
p(t) = e^{\mathbf{\Sigma} \Phi(t)} p(\tau) = e^{\mathbf{\Gamma} (t-\tau)} e^{\mathbf{\Sigma} \Phi(T)} p(\tau),
\]  

(24)

for times \( t \geq \tau \). Photoionization lasts till time \( T \) and decay processes start at time \( \tau \).

Theorem 2 does not reduce to Theorem 1 upon letting \( \Gamma = \mathbf{0} \) as the photoionization of the system is assumed to be completed at time \( T \), i.e., the temporal progression of photoionization does not enter (24). This apparent weakness of Theorem 2, however, can be used judiciously by replacing the solution of the nondecaying system \( e^{\mathbf{\Sigma} \Phi(T)} p(\tau) \) by a (numerical) solution of (19) in the time interval \( [\tau; T] \). In this case, the solution of Eq. (20), \( e^{\mathbf{\Gamma} (t-\tau)} p(\tau) \) for \( \mathbf{\Sigma} = \mathbf{0} \) and \( t \geq \tau \), is the (numerically-exact solution of (19). This procedure has been used to treat slow radiative decay to calculate photon yields in Ref. 11.

C. Successive approximation

A simple analytic solution of the interacting and decaying system (19) in terms of the Peano-Baker series is well known, it is stated in

Theorem 3. Given a system of rate equations with decay (19), then its solution is

\[
p(t) = X(t) \mathbf{p}(\tau),
\]  

(25)
for times \( t \geq \tau \) with the fundamental matrix:\footnote{25}

\[
X(t) = 1 + \int_{\tau}^{t} (\Sigma J(t') + \Gamma) \, dt'
\]  
(26)

\[
+ \int_{\tau}^{t} (\Sigma J(t') + \Gamma) \int_{\tau}^{t'} (\Sigma J(t'') + \Gamma) \, dt'' \, dt'
+ \ldots .
\]

Proof. The fundamental matrix \( X(t) \) solves the initial-value problem \( \frac{dX(t)}{dt} = (\Sigma J(t) + \Gamma) X(t) \), \( X(\tau) = 1 \).\footnote{26} This equation can be integrated leading to \( X(t) = 1 + \int_{\tau}^{t} (\Sigma J(t') + \Gamma) X(t') \, dt' \); it is a linear Volterra integral equation of the second kind. Its kernel \( \Sigma J(t') + \Gamma \) is continuous because \( J \) is assumed to be continuous. Therefore, it can be solved uniquely by successive approximations yielding a continuous solution, i.e., by inserting the equation on the right-hand side for \( X(t') \). This leads to (26) and the solution of (19) is (25). q.e.d.

Clearly, the analytical solution (25) of the coupled system of differential equations (19), despite its exactness, is of limited value. This is because the exponential functions that emerge in Theorems 1 and 2 are, thereby, expanded into a series. Thus the solution (25) can be expected to converge slowly with the time ordered into account in (26). Yet, despite its limited use, Theorem 3 reveals the emergence of nonlinearity due to decay in the sequential absorption of multiple x rays. This case is referred to as linked multiphoton absorption.

To incorporate more of the physics of the problem into the analytical expression for the solution, I change to the eigenbasis of \( \Sigma \) as for (11) which produces

\[
\frac{dq(t)}{dt} = \Delta q(t) J(t) + \Delta q(t),
\]

with \( \Delta = U^{-1} \Gamma U \). Next I express (27) componentwise by

\[
\frac{dq_i(t)}{dt} = \lambda_i q_i(t) J(t) + \sum_{j=1}^{K} \Delta_{ij} q_j(t),
\]

for \( i \in \{1, \ldots, K\} \). Letting \( q_i(t) = e^{\lambda_i \Phi(t)} r_i(t) \), I have

\[
\frac{dr_i(t)}{dt} = \sum_{j=1}^{K} e^{-\lambda_j \Phi(t)} \Delta_{ij} e^{\lambda_j \Phi(t)} r_j(t) = \sum_{j=1}^{K} \Xi_{ij} r_j(t),
\]

or in vector notation

\[
\frac{dr(t)}{dt} = \Xi(t) r(t).
\]

The time-dependent matrix \( \Xi(t) \) can be expressed succinctly by

\[
\Xi(t) = e^{-\Delta \Phi(t)} \Delta e^{\Delta \Phi(t)} = U^{-1} e^{-\Sigma \Phi(t)} \Gamma e^{\Sigma \Phi(t)} U.
\]

Equation (30) can be integrated on both sides leading to

\[
r(t) = r(\tau) + \int_{\tau}^{t} \Xi(t') r(t') \, dt'.
\]

(32)

This is a linear Volterra integral equation of the second kind. Its kernel \( \Xi(t') \) is continuous because the x-ray fluence \( U \) is a continuous function with time. Then the unique solution of Eq. (32) is continuous as well. Using Eq. (31), I rewrite Eq. (32) in the original basis

\[
p(t) = e^{\Sigma \Phi(t)} p(\tau) + e^{\Sigma \Phi(t)} \int_{\tau}^{t} e^{-\Sigma \Phi(t')} \Gamma p(t') \, dt'.
\]

(33)

where I realize that

\[
q(t) = e^{\Lambda \Phi(t)} r(t) = U^{-1} p(t),
\]

holds with the initial condition \( q(\tau) = r(\tau) = U^{-1} p(\tau) \).

Volterra equations such as Eq. (32) with a continuous kernel can be solved uniquely by successive approximation—i.e., inserting (32) for \( r(t') \) in (32)—reading

\[
r(t) = U(t, \tau) r(\tau),
\]

(35)

introducing the time-evolution matrix via

\[
U(t, \tau) = 1 + \int_{\tau}^{t} \Xi(t') \, dt' + \int_{\tau}^{t} \Xi(t') \int_{\tau}^{t'} \Xi(t'') \, dt'' \, dt' + \ldots ,
\]

(36)

which transforms the initial condition \( r(\tau) \) at time \( \tau \) into the solution \( r(t) \) at time \( t \geq \tau \). This is the matrix that needs to be evaluated in order to solve (35). Expressing (35) and (36) in the original basis, I prove that the solution of the Volterra integral equation (35) can be written concisely as stated in

**Theorem 4.** Given a system of rate equations with decay (19), then its solution is

\[
p(t) = e^{\Sigma \Phi(t)} U U(t, \tau) U^{-1} p(\tau),
\]

(37)

for times \( t \geq \tau \) with the time-evolution matrix \( U \) which can be expressed via (36) as

\[
U U(t, \tau) U^{-1} = 1 + \int_{\tau}^{t} e^{-\Sigma \Phi(t')} \Gamma e^{\Sigma \Phi(t')} \, dt' + \int_{\tau}^{t} e^{-\Sigma \Phi(t')} \Gamma e^{\Sigma \Phi(t')} \int_{\tau}^{t'} e^{-\Sigma \Phi(t'')} \Gamma e^{\Sigma \Phi(t'')} \, dt'' \, dt' + \ldots.
\]

(38)
The final result (38) clearly exhibits the role of decay processes for turning the interaction with x rays nonlinear in contrast to the case without decay in Theorem 1.

The line of arguments that constitutes the proof of Theorem 5 can be applied also to the complementary case that one transforms [19] to the eigenbasis of \( \Gamma \) [see Eq. (20) and the ensuing discussion] instead of using Eq. (27). Then a Volterra equation analogous to Eq. (33) is derived reading

\[
p(t) = e^{\Gamma(t-\tau)}p(\tau) + \int_{\tau}^{t} e^{-\Gamma(t'-\tau)} \sum J(t') p(t') \, dt',
\]

which is solved by successive approximation \(1,60,61,63\) proving

**Theorem 5.** Given a system of rate equations with decay (19), then its solution is

\[
p(t) = e^{\Gamma(t-\tau)} \mathbf{U}(t, \tau) \mathbf{U}^{-1} p(\tau)
\]

for times \( t \geq \tau \) with the time-evolution matrix \( \mathbf{U}(t, \tau) \) [analogous to Eq. (27)] which can be expressed as

\[
\mathbf{U}(t, \tau) \mathbf{U}^{-1} = \mathbf{1} + \int_{\tau}^{t} e^{-\Gamma(t'-\tau)} \sum J(t') e^{\Gamma(t'-\tau)} \, dt'
\]

\[
+ \int_{\tau}^{t} e^{-\Gamma(t'-\tau)} \sum J(t') e^{\Gamma(t'-\tau)} \, dt
\]

\[
\times \int_{\tau}^{t'} e^{-\Gamma(t''-\tau)} \sum J(t'') e^{\Gamma(t''-\tau)} \, dt'' \, dt'
\]

\[
+ \ldots
\]

As before, the analytical solution of the rate equations (11) showcases the impact of decay for rendering the absorption of x rays nonlinear. Theorem 5 becomes Theorem 2 by approximatively neglecting decay in the course of the interaction with the x rays, i.e., by letting \( \Gamma = 0 \) in \( \mathbf{U}(T, \tau) \) for a fixed time \( T \) and letting \( \tau = T \).

The derivation that has lead to Theorems 4 and 5 of this subsection resembles in many aspects the derivation of the time-dependent perturbation series in quantum field theory on pages 56–58 of Ref. 64. Thereby, Eq. (27) is structurally similar to the time-dependent Schrödinger equation for an interacting quantum system, however, with the crucial difference that in our case the time derivative is not multiplied by the imaginary unit. Then \( \Xi(t) \) [51] stands for the time-dependent perturbation in the interaction picture and \( \mathbf{U}(t, \tau) \) corresponds to the time-evolution operator. Note that for Theorem 4 in contrast to time-dependent perturbation theory, the exactly solvable part [first term on the right-hand side of Eq. (27)] is time dependent via \( J(t) \). In time-dependent perturbation theory, one proceeds by introducing time-ordered products and expressing the series (55) in terms of an exponential function \(44\).

**IV. RESULTS AND DISCUSSION**

I illustrate the theory of the previous Secs. II and III by applying it to the rate equations of a nitrogen atom, which has \( N = 7 \) electrons, in LCLS radiation. All details on the atomic electronic structure and the rate equations can be found in Ref. 4. I assume an x-ray photon energy of 840 eV and a fluence of \( 8 \times 10^{11} \text{ photons m}^{-2} \). The temporal pulse shape of the x-ray flux is Gaussian (see Eq. (7) in Ref. 4) and the spatial dependence is assumed to be constant. Unless stated otherwise, the x-ray pulse has a full width at half maximum (FWHM) duration of 2 fs. I calculate the probability to find the atomic cationic state with charge \( j \in \{0, \ldots, N\} \) via

\[
W_j(t) = \sum_{i=1}^{\min(N-j,0)} P_i^{(N-j)}(t).
\]

This quantity allows one to calculate the experimentally measurable ion yields from which follows the average charge state that is an indicator of the amount of charge found on the ions \(4,10,11\).

In Fig. 1 I plot the numerically-exact solution of the rate equations for a nitrogen atom together with the result from the linearity theorem (16). Both curves are indistinguishable which is not surprising as the rate-equation for ground-state depletion (11) does not contain any decay terms.

Single ionization is investigated in Fig. 2 and, again, a good agreement with the reference curve is found. However, this time, there is a decay term in the rate equations (17) which leads to a easily discernible deviation between both curves at the peak. The fact that the long-term behavior of both curves agrees so well can only be ascribed to the fact that further ionization of the atom leads to the observed decay and not Auger or radiative decay as they are not described by the linearity theorem (16).
FIG. 2. (Color) Single ionization $W_1(t)$ at time $t$ of a nitrogen atom. Line styles as in Fig. 1.

FIG. 3. (Color) Double ionization $W_2(t)$ at time $t$ of a nitrogen atom with the numerically-exact solution (solid-black lines), the linearity theorem (16) (dashed-red lines), and the successive approximation (37) in first (dash-dotted-green) and eighth order (dotted-blue).

FIG. 4. (Color) Double ionization $W_2(t)$ as in Fig. 3 but for an x-ray pulse with a FWHM duration of 200 as.

The decay equations (20) are used in Fig. 3 and Fig. 4 for x-ray pulses with a FWHM duration of 2 fs and 200 as, respectively, to examine double ionization. Thereby, I choose the time when the decay processes start $T$ to be the FWHM duration but the time $T$ at which the linearity theorem (16) is evaluated is chosen larger than $T$. Clearly, the curve from the decay equations in Fig. 3 shows a significant improvement over the result from the linearity theorem but does not approximate the numerically-exact solution acceptably. This changes dramatically if the FWHM pulse duration is decreased by an order of magnitude to 200 as in Fig. 4 where a good agreement is achieved. After the pulse is over the double ionization probability rises on the time scale of Auger decay of core holes of 6.7 fs which turns singly ionized nitrogen atoms into doubly ionized ones. Noteworthy is that this good agreement seen for double ionization does not remain so for charge states of N$^{4+}$ and higher. For them, to be accurately described by the decay equation, one needs to shorten the pulse duration even further in order to reduce the interplay between photoionization and decay processes. However, I need to stress that even assuming a 200 as pulse is stretching the validity of the rate-equation approximation too much. For such short pulses, coherence effects become important. The upshot of the analysis of the decay equations (20) in this paragraph is that they are of limited use in the x-ray regime.

 Triple ionization of a nitrogen atom is displayed in Fig. 5 for the results from the linearity theorem, the successive approximation, and the numerically-exact solution. The linearity theorem produces a curve which only very crudely follows the behavior of the numerically-exact solution. Clearly, the absence of decay processes in the approximation leads to the overpopulation of the triple-ionization channels for $t > 0$. Furthermore, after the pulse is over, the probability remains constant whereas the numerically-exact solution slopes downward.
due to decay processes. Taking decay into account in terms of the successive approximation (37) in first order leads to a good agreement up to $\approx 0.5\,\text{fs}$. Afterwards the approximation quickly deteriorates. However, going to eighth order in the approximation of the Volterra integral equation improves the result dramatically such that it agrees with the numerically-exact solution up to $\approx 4.5\,\text{fs}$. Still higher orders in the successive approximation are required to approximate the numerically-exact result beyond this time.

One needs to consider several terms in the successive approximation to reach converged solutions of the Volterra integral equation. As can be seen in Fig. 5, the first-order produces already good agreement for short times. However, to approximate the numerically-exact solution for longer times, higher orders are required. This can be understood by considering very short pulses for which the solution of the decay equation (20) is acceptable. Then the iteration of the Volterra integral equation needs to reproduce the terms of the series of the exponential function with the decay matrix in (20) up to sufficiently high order to obtain good agreement. The larger the time, the higher orders in the series need to be included.

V. CONCLUSION

I carry out a formal analysis of multiphoton absorption which is called simultaneous, if it cannot be split into individual one- or few-photon absorptions but has to be described by the full expressions for the few-photon cross section. If a rate equation approximation turns out to be satisfactory, I can also distinguish linked multiphoton absorption—which are rendered nonlinear by the decay of intermediate states—and separable multiphoton absorption which depends only on the fluence the atom or molecule was subjected to—just like one-photon absorption. I turn to decay processes and analyze the situation under the assumption that the x-ray pulse is so short that the integral needs to be evaluated only for the duration of the x-ray pulse. Specifically, the systems of rate equations involving random numbers is changed by placing by matrix methods, i.e., the repeated solution of matrix times vector products for sparse matrices. Decisions whether to compute certain atomic quantities need to be made based on their relevance to these products where suitable criteria need to be devised.

The rate equations in this work are restricted to non-resonant one-x-ray-absorption for simplicity and because it is the most important case for practical applications which rely frequently on x-ray diffraction. This limita-
tion, however, can be lifted straightforwardly. One can include also REXMI terms \( \frac{\beta}{b} \) if the rate-equation approximation remains valid for these cases. The solution of the rate equations with decay, Theorems 4 and 5, can be extended, e.g., to include simultaneous two-photon absorption \( e^{2\alpha t} \) by augmenting the decay part in (19) by appropriate terms. The other way round is the case if there is no one-photon absorption, e.g., due to a too low photon energy. Then the analysis of Theorems 1, 2, 3, 4, and 5 can be done analogously starting with the lowest order of simultaneous multiphoton absorption instead. So far mostly configurations have been used in the literature to write down the rate equations. There is, however, no restriction that prevents one to use fine-structure-resolved states instead. This becomes relevant when heavier atoms are considered where relativistic effects are prominent.

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Appendix A: Diagonalizability of a closed, lower triangular matrix

Lemma 2. Given a real, lower triangular \( K \times K \) matrix \( A \) whose nonzero eigenvalues—the nonzero diagonal elements—are pairwise distinct; the eigenvalue 0 may occur multiple times. Furthermore, \( A \) is a closed essentially nonnegative matrix. Then \( A \) is diagonalizable and the eigenvectors corresponding to eigenvalues 0 are given by Cartesian eigenvectors \( e_i \), where \( i \in \{1, \ldots, K\} \) and the value 1 in these vectors is at the row index \( i \) of the eigenvalue 0 of \( A \).

Proof. As \( A \) is closed \( \mathbb{S} \) and essentially nonnegative, for \( A_{ii} = 0 \) follows that \( A_{ij} = 0 \) for all \( j \), i.e., the entire column of \( A \) is filled with zeros. Consequently, I have

\[
A e_i = A_{ii} e_i = 0. \tag{A1}
\]

Thus for all eigenvalues 0 of \( A \) I have found eigenvectors, i.e., the algebraic multiplicity in the characteristic polynomial due to eigenvalue 0 corresponds to its geometric multiplicity. All other eigenvalues are pairwise distinct. Hence the characteristic polynomial contains only linear factors with respect to these eigenvalues. Thus \( A \) is diagonalizable. \( \Box\)

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A fixed photon energy is assumed which needs to be high enough such that all electrons can be ionized; the dependence of the quantities on the photon energy is omitted throughout. If the x-ray photon energy is lower than the energy that is necessary to strip the system of all electrons, then the total absorption cross section of this last configuration—I assume that there is a single last configuration—is zero, although there are still electrons in lower lying shells. Increasing the x-ray photon energy renders the total absorption cross section nonzero. Please see figure 2 in and its explanation.

Only cationic configurations are included without regarding shake-off or shake-up processes and other multielectron effects such as double Auger decay.

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